

Faculté des bioingénieurs

Preparation of bifunctional catalysts by aerosol-assisted sol-gel process for butadiene synthesis

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Abstract

For several years, butadiene production is experiencing a decrease and an urge to find a solution has risen. Ethanol conversion to butadiene is a sustainable alternative to petrol-based processes, which is in line with the current trend to find ecological solutions to produce polymers. Because of the mechanism, catalysts to enhance this reaction need to be bifunctional and to present features both acidic and redox. This master thesis has explored if peculiar textural properties, brought by an innovative synthesis process, such as aerosol-assisted sol-gel, would create catalysts with high performances. To position the results with more typical preparation method, benchmarks catalysts synthesized by dry impregnation on commercial or aerosol-made supports, have been studied too.

In that scope, Ag-TaO_x-SiO₂ ternary catalysts have been synthesized. Mesoporous ternary catalyst or binary TaO_x-SiO₂ supports have been prepared by aerosol-assisted sol-gel process (AASG). On the other hand, silver was either incorporated in one-pot or by dry impregnation. Different effects on the catalysts have been investigated; two different calcination furnaces (under static air or flowing air), three calcination temperatures (500°C, 600°C and 700°C) and a screening on the loadings. The catalysts have been characterized by N₂ physisorption, O₂ chemisorption, NH₃-TPD, XRD, XPS and infrared spectroscopy. The catalysts were then tested, after in-situ reduction, between 325°C and 415°C, to assess of their performances in the Lebedev one-step process.

From the results, it appears that calcination temperature influences the migration of silver from the bulk towards the surface and 500°C brought the best silver dispersion at the surface of the materials. Higher temperatures favored more sintering. Calcination under air highlighted itself by the ability to improve the migration of silver nanoparticles towards the surface. AASG catalysts presented a high tantalum oxide dispersion, acid sites were taking over the redox sites. Best results were then obtained with rather low tantalum oxide loading. AASG catalysts displayed an equivalent dispersion to silver impregnated sample for the same silver loading but with less silver at the surface since all of it did not migrate from the bulk. Best results were obtained with 5 wt. % Ag.

This work presents the advantages of the aerosol-assisted sol-gel process and the potential of the method.

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I. Introduction

1.1 Context

For the last twenty years, butadiene prices experience a general increase that has varied from a few percent to, sometimes, almost 900 % (1). This trend can be seen in Figure 1.1. The reason of this trend is the demand that is always increasing while on the other hand, the offer cannot keep up with this increase (2). Indeed, the traditional process used to synthesize butadiene is to obtain it as a byproduct of the steam cracking performed to create ethylene (95 % of the global production) (3). However, the feedstock used for the steam cracking is becoming lighter and lighter, resulting in lighter byproduct as well and so less butadiene is produced (2,3). Instead of using naphtha, industries are now using more and more butane or propane to form ethylene, thanks to a range of new technologies (2).

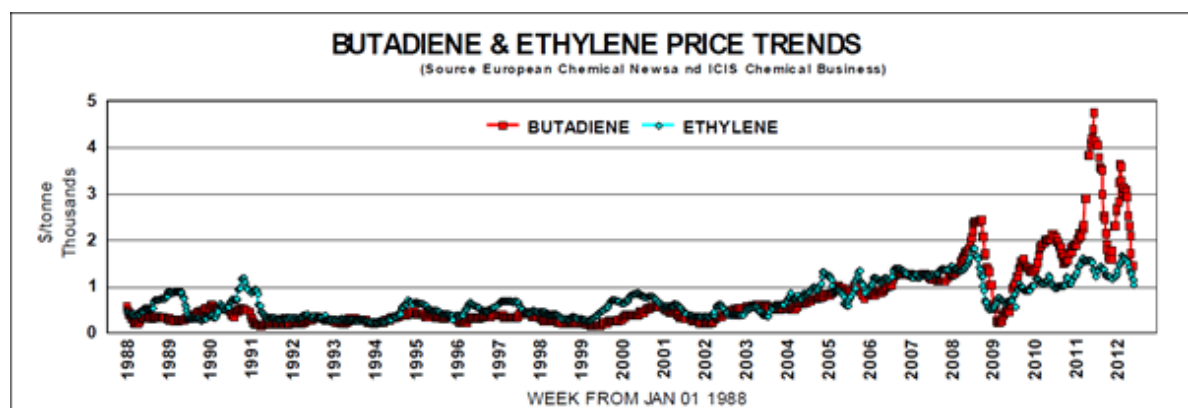


Figure 1.1 : Evolution of butadiene and ethylene prices from 1988 to 2012 (1).

When butadiene is obtained as a byproduct of ethylene steam crackers, the yield is depending on the feedstock used: the lighter the feedstock, the lower the production (3). Table 1.1 shows the evolution in yield of products according to the feedstock.

Table 1.1: Steam cracking yields (wt. %) (3)

	Light hydrocarbons			Naphthas and heavier		
	Ethane	Propane	n-Butane	Medium range naphthas	Atm. gas oil	Light vacuum gas oil
Hydrogen & methane	15.1	29.7	23.8	17.7	12.1	9.5
Ethylene	77.7	42.0	40.0	34.0	25.9	20.5
Propylene	2.8	16.	17.2	15.7	16.2	14.1
Butadiene	1.9	3.0	3.5	4.7	4.6	5.4

The current trend that is moving towards lighter feedstock, is creating a drop in the butadiene global production. An alternative is needed and might be brought by ethanol conversion to butadiene.

In 2015, almost 12 million tons of butadiene have been used worldwide and the global demand growth at an average of 32 % per year (4). Butadiene is mostly used in the polymer industry to obtain various products. Amongst those products, some more important than others, such as: polybutadiene rubber (elastomer found in the tires (5)), styrene – butadiene rubber and latex (tires vs. paper and textile coating (6,7)) or acrylonitrile – butadiene – styrene thermoplastic (material used in home appliance devices, automobile industry... (8)), etc (3) . Figure 1.2 shows an overview of the repartition of the demand in butadiene according to the final product.

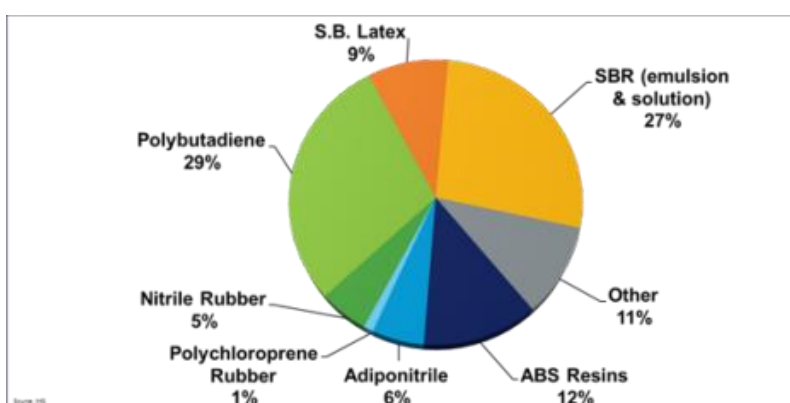


Figure 1.2 : Repartition of the global butadiene demand per product in 2015 (2)

To mitigate the tensions on the butadiene market, alternatives production methods can be implemented. However, none of them are both fully sustainable and independent from oil. These alternatives are the dehydrogenation of n-butane using the Houdry catadiene process and the oxidative dehydrogenation of n-butene. The first pathway involves treating butane over alumina mixed with chromia (20%) at high temperatures (600-700°C) and low pressure (3). The disadvantage of this process is high operating temperature, which leads to the formation of C₁ – C₃ byproducts, hydrogen and coke for an average butadiene yield of only 55% (3). The oxidative dehydrogenation of n-butenes takes place at high temperature on iron oxide/ bauxite or iron oxide/ chromia catalysts. A part of the heat required is provided by the exothermic oxidation of hydrogen and the oxygen used, acts with the steam to mitigate the coking (3).

Considering the growing price and the market volatility, and with the objective to find more sustainable ways to produce important chemicals like butadiene, new bio-based processes emerge to divert from the traditional fossil fuel-based methods mostly used today. For butadiene, bioethanol might be used as a starting bio-based chemical. Ethanol would be the perfect candidate to fulfill this task since it is easy to manufacture, at low price, by fermentation of cellulose or starch. Ethanol is already being investigated as a bio-based chemical to be part of several reactions of industrial relevance. It could replace petrochemical reactants in a broad range of applications (9,10). Among the various ways to upgrade ethanol, shown in Figure 1.3, the production of butadiene is currently the focus of intense research efforts (4,11,12).

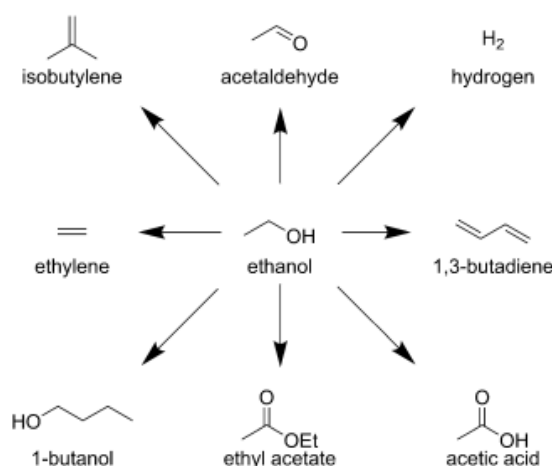
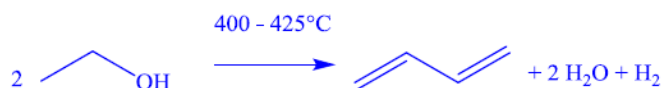


Figure 1.3: Most important chemicals obtainable from ethanol (9).

Fortunately, the transformation of ethanol to butadiene is well known since the beginning of the 20th century. Indeed, the process was discovered in 1903 by Ipatiev and Ostromislensky in Russia and then improved by Lebedev in 1928. The reaction took place initially between 370 and 390°C on MgO – SiO₂ or Al₂O₃ – SiO₂ catalysts (3). The process has been even already industrialized in the past. Both the United States and the USSR used it during WWII to make up to the oil and natural rubber shortages (4,13,14). After the 1960s, however, the process became economically unfavorable compare to the petrochemical route (15).

Two production pathways are possible for the conversion of ethanol into butadiene. They are simply called the “one step” (Lebedev), or the “two-steps” (Ostromislensky) processes (Figure 1.4). The first is performing the transformation directly from ethanol and need only one reactor whilst the other firstly requires the formation of acetaldehyde from ethanol and then the introduction of both ethanol and acetaldehyde in another reactor where butadiene is produced (11). In the present study, we will focus on the development of catalyst formulations that would be active in the one step process.

Lebedev pathway - direct conversion



Ostromislensky pathway - two-step process

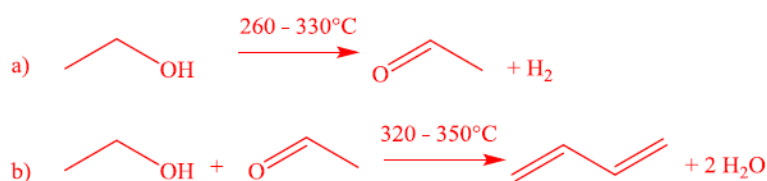


Figure 1.4: The two possible pathways for the production of butadiene from ethanol (4).

1.2 Ethanol to butadiene: mechanism & catalysts

1.2.1 Mechanisms

To this day, there is no agreement on one specific mechanism for the transformation of ethanol to butadiene, but two main mechanisms seem to be the most likely. They have been proposed by Cavani et al. and by Kagan et al. No matter the mechanism, the required properties of the catalyst are the same. The catalyst must be bifunctional to catalyze both dehydration and dehydrogenation reaction steps.

1.2.1.1 Mechanism proposed by Kagan

In this reaction mechanism, five consecutive reaction steps are involved before finally obtain butadiene. First, ethanol undergoes a non-oxidative dehydrogenation to acetaldehyde which then condenses with another equivalent to produce 3-hydroxybutanal. Afterwards, the product is dehydrated into crotonaldehyde that is reduced by ethanol (Meerwein – Ponndorf – Verley – Oppenauer reduction) to give crotyl alcohol and acetaldehyde again. Finally, butadiene is produced by dehydration of crotyl alcohol (9). Figure 1.5 displays the different steps of this mechanism. This mechanism has been verified for acidic and basic catalysts (12). The rate-limiting step seems to vary, governed by the properties of the catalyst. Indeed, over an acid catalyst, the limiting step is the MPVO reduction whilst over a basic sample, it is the dehydrogenation that is limiting (12).

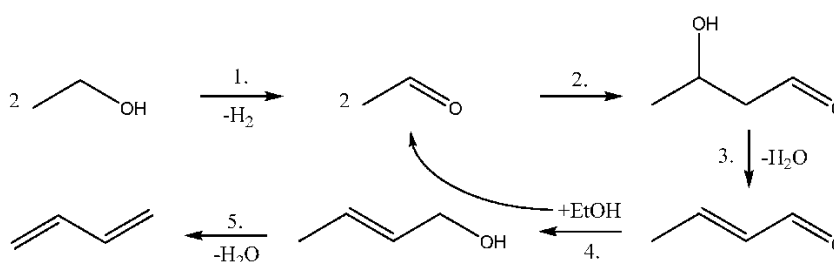


Figure 1.5: Butadiene formation mechanism according to Kagan et al. (9)

1.2.1.2 Mechanism proposed by Cavani

After noticing that the product of the aldolization of acetaldehyde (step 2 of Kagan's mechanism) was seldom detected with every type of catalysts and based on previous work from Corson et al. with $\text{Ta}_2\text{O}_5/\text{SiO}_2$ catalysts (16), Cavani et al. have proposed another possible

mechanism for this reaction (Figure 1.6) (11,17). This pathway has been investigated when using a MgO-based catalyst (11,17).

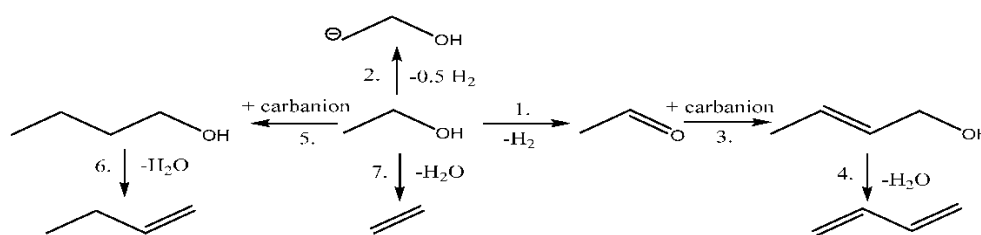


Figure 1.6: Butadiene formation mechanism with a MgO catalyst according to Cavani et al.(11)

According to Cavani et al., ethanol may be dissociated in hydrogen and acetaldehyde or be deprotonated to produce carbanionic species that would be stabilized by surface Mg cations. This species can then either react with acetaldehyde to produce crotyl alcohol that can be dehydrated and finally be transformed into butadiene or react with ethanol to form 1-butanol which can be dehydrated into 1-butene. Also, ethanol can be simply dehydrated to form ethylene (11).

Despite the existing differences between those two mechanisms, it is impossible at this moment to exclude one pathway or the other but in all cases, the crucial role of ethanol and acetaldehyde is highlighted. In this thesis, we focus on tantalum oxide mixed with silica catalysts, which should follow the Kagan mechanism since Cavani's mechanism has only been verified on magnesium-based catalyst. As Kagan's pathway implies the need for redox sites and acids sites, our work will consider bifunctional catalysts.

1.2.1.3 By – products

Unfortunately, side reactions can take place during the transformation of ethanol into butadiene. Figure 1.7 illustrates the reaction network including all the possible side reactions in the mechanism proposed by Kagan. The production of undesired compounds represents an additional purification costs (15). To maximize butadiene yield, one can optimize processing factors such as the properties of the catalyst, the space-velocity, the reaction temperature (18).

In particular, it can be seen from Figure 1.7 that the properties of the catalyst should dictate the selectivity profiles. For example, a catalyst with excessive acidity would form high amounts of diethyl ether and ethylene. At the same time, the acidity should be sufficient to allow catalyzing the desired dehydration reactions. This network perfectly demonstrates the importance of having properties well balanced in a bifunctional catalyst.

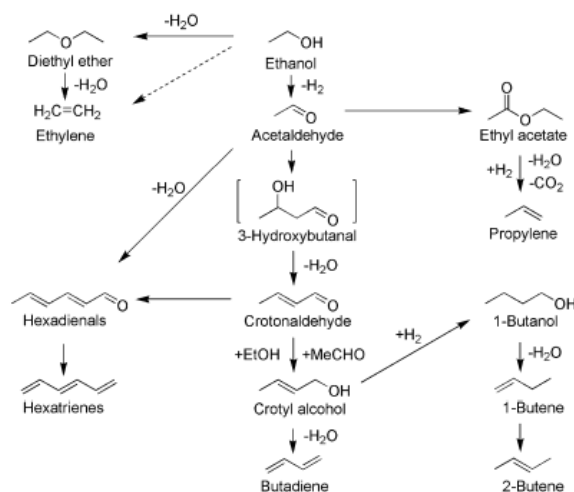


Figure 1.7: Reaction network and side reaction of the transformation of ethanol to butadiene (15)

1.2.2 Catalysts

Considering Kagan's mechanism and the synthesis of acids catalysts, it became clear that to have an efficient catalyst, it is necessary to have a bifunctional catalyst. Indeed, acidic sites are needed to perform the dehydration whilst redox active sites are required to complete the dehydrogenation. To complete this task, tantalum oxide and metallic silver have been chosen as active species, supported on silica. The following section develops the reasons of this choice.

1.2.2.1 Tantalum oxide

Interests for the tantalum as metallic oxide for the reaction of ethanol to butadiene appears in the 1940's. Corson et al. were looking to improve the two steps process for the production of butadiene. Based on a large screening on impregnated catalysts containing magnesium oxide or transition metals oxide (Ti, Zr, Ta, V, Cr, ...) on silica or alumina, they reached the conclusion that tantalum oxide on silica was the most active catalyst. Continuing their work but focusing on the one step process, they showed that tantalum oxide on silica

alone was not effective but becomes effective when supplemented with magnesium oxide or copper oxide (19).

During the second half of the 20th century, research stopped because of the low cost of butadiene production from oil (15,20). However, recently, interest for the ethanol to butadiene reaction has risen again, in line with the objectives of the bio-economy (21). Surprisingly, tantalum oxide is no longer in the focus of the attention and only a few publications have explored the potential of the properties brought by tantalum oxide on silica.

Even if this study aims to find catalysts active in the one-step process, it is also interesting to look to the existing catalysts available for the two-step pathway because there is no significative difference for the acidic properties needed. Table 1.2 gathers some of the most active catalysts based on tantalum oxide on silica from the literature for the two-step process and Table 1.3 illustrates the equivalent for the one step process.

Table 1.2: Existing tantalum oxide on silica catalysts for the two-steps process

Catalysts	Temp. (°C)	LHSV ¹ (h ⁻¹)	Ethanol / Acetaldehyde	Butadiene yield (%)	TC ² (%)	Ref.
1.8 % Ta ₂ O ₅ /SiO ₂	350	0.4	2.75	67	/	(19)
2.3 % Ta ₂ O ₅ /SiO ₂	400	0.4	2.75	69	/	(19)
2 % Ta ₂ O ₅ / SiO ₂	350	1	2.5	23	31.5	(20)
3 % Ta/SiBEA	350	0.8	3.2	43.1	58.9	(11,22)

From Table 1.2, one can notice that the most active catalyst at 350°C, the typical reaction temperature, was synthesized by Corson et al. in 1950 with 1.8 wt. % loading in tantalum oxide. However, an increased temperature might increase by a few percent the performances.

Also, a lower liquid hourly space velocity seems to be preferable to a higher one given the fact that the best results have been obtained with a LHSV of 0.4 h⁻¹ and the least active catalyst had a LHSV of 1 h⁻¹.

¹ Liquid Hourly Space Velocity (volumetric flow rate of feed/ volume of catalyst)

² Total conversion

Table 1.3: Existing tantalum oxide on silica catalysts for the one-step process

Catalysts	Temp. (°C)	WHSV ³ (h ⁻¹)	Ethanol conv. (%)	Butadiene yield (%)	Activity (g.g _{cata} ⁻¹ .h ⁻¹)	Ref.
1 % CuO/ 2% Ta ₂ O ₅ / SiO ₂	425	0.5	83	25	0.06	(12,19)
21 % MgO/ 2% Ta ₂ O ₅ / SiO ₂	425	0.4	/	18	/	(19)
60 % MgO/ 2% Ta ₂ O ₅ / SiO ₂	420	0.4	68	34	0.08	(12,19)
1 % Zn/ 1 % Ta ₂ O ₅ / SiBEA	325	0.5	51.7	22.1	0.07	(23)
1 % Ag/ 1 % Ta ₂ O ₅ / SiBEA	325	0.5	82.9	51.9	0.15	(23)
1 % Cu/ 1 % Ta ₂ O ₅ / SiBEA	325	0.5	87.9	63.8	0.19	(23)
1 % Ag/SiBEA + 1 % Ta ₂ O ₅ /SiBEA	325	0.5	58.3	26.8	0.08	(23)

From Table 1.3, the highest yield was obtained with tantalum loadings of 1 wt. % on a zeolite with a transition metal added for the redox activity such as copper, zinc or silver. It can be noticed that when a transition metal is added, the most efficient temperature decreases by almost 100°C to settle at a temperature equivalent to the two-steps process.

In the case of the one-step process, the same observation can be made about the space velocity: the highest activity has been reached with a relatively small WHSV of 0.5 h⁻¹.

In addition to those activity results, Kim et al. have investigated the importance of the porosity and the size of the particles (Table 1.4 and 1.5). Tantalum oxide supported spherical silica catalysts prepared by impregnation have been studied. The silica supports were commercial spherical silica “CARiACT Q-n” from *Fuji Sylisia*, the “n” in the name stands for the pore size in nanometer of the support (20). Furthermore, to access data about the optimal particle size, different range of particle dimensions have been examined on a spherical silica support possessing a pore size of 6 nm (20).

³ Weight Hourly Space Velocity (mass flow rate of ethanol/ weight of catalyst)

Table 1.4: Investigation on the consequences of porosity on the activity of catalysts. $T = 350^{\circ}\text{C}$, $\text{LHSV} = 1.0 \text{ h}^{-1}$, $\text{EtOH}/\text{acetaldehyde} = 2.5$ (20).

Catalysts	S.S.A. ⁴ (m^2/g)	Pore volume (cm^3/g)	Avg. pore size (nm)	Ethanol/acetaldehyde conversion (%)	Butadiene yield (%)
2 % $\text{Ta}_2\text{O}_5/\text{Q-3}$	688	0.37	2.2	10.9	5.2
2 % $\text{Ta}_2\text{O}_5/\text{Q-6}$	530	0.58	5.9	31.5	22.7
2 % $\text{Ta}_2\text{O}_5/\text{Q-10}$	214	1.15	13.3	30.6	21.5

From Table 1.4, it can be noticed that an optimum of yield is reached when a compromise is found between large pores that favor mass transfer, and high specific surface area, maximize the active surface. It is essential that both properties are optimized to achieve a higher ethanol to butadiene activity.

Table 1.5: Effect of the particle size on the activity of 2 % Ta_2O_5 on a spherical silica support catalyst, pore size = 6 nm. $T = 350^{\circ}\text{C}$, $\text{LHSV} = 1.0 \text{ h}^{-1}$, $\text{EtOH}/\text{acetaldehyde} = 2.5$ (20).

Particle size (μm)	Ethanol/acetaldehyde conversion (%)	Butadiene selectivity (%)	Butadiene yield (%)
75-150	33.4	75.2	25.1
75-200	30.1	74.6	22.5
200-300	31.5	72.0	22.7
300-500	24.6	71.0	17.5

According to the results of Kim et al., the optimal particle size range is between 75 and 150 μm , yield decreasing with the larger particles because of the loss of active surface.

1.2.2.2 Silver

Tantalum oxide displays some redox properties, but on its own in the one-step process, it provides only low acetaldehyde yield (23,24). Some publications have reported the doping of ethanol-to-butadiene catalysts with redox species such as other oxides and transition metals. Among those catalysts, some samples composed of transition metal on silica or magnesium oxide on silica, show interesting results (Table 1.6).

⁴ Specific Surface Area

Table 1.6: Existing ethanol to butadiene catalysts doped with reducing agents.

Catalysts	Temp. (°C)	WHSV (h ⁻¹)	Ethanol conv. (%)	Butadiene yield (%)	Activity (g·g _{cata} ⁻¹ ·h ⁻¹)	Ref.
Effect of the formulation						
3 % CuO/ 56 % MgO/ SiO₂	400	0.7	86	44	0.20	(25)
4 % Ag/ 55 % MgO/ SiO₂	400	0.7	92	49	0.22	(25)
1.0 % Ag/ MgO/ SiO₂	400	1.2	44	20.2	0.14	(26)
0.3 % Ag/ 4 % ZrO₂/ SiO₂	325	0.31	30.0	22.1	0.04	(15)
0.3 % Cu/ 4 % ZrO₂/ SiO₂	325	0.31	26.8	19.7	0.04	(15)
0.3 % Ni/ 4 % ZrO₂/ SiO₂	325	0.31	10.3	7.0	0.01	(15)
1 % Ag/ TaSiBEA	325	0.5	82.9	51.9	0.15	(23)
1 % Cu/ TaSiBEA	325	0.5	87.9	63.8	0.19	(23)
1 % Zn/ TaSiBEA	325	0.5	51.7	22.1	0.07	(23)
Effect of the loadings						
0.5 % Ag/ MgO/ SiO₂	400	1.2	26	12.2	0.08	(26)
2.0 % Ag/ MgO/ SiO₂	400	1.2	50	20.5	0.15	(26)
1.0 % Ag/ 4 % ZrO₂/ SiO₂	325	0.31	48.0	34.6	0.06	(15)
2.0 % Ag/ 4 % ZrO₂/ SiO₂	325	0.31	55.2	39.4	0.07	(15)

From the literature, it can be observed that the highest performance has been obtained with silver or copper as doping agent. However, it has already been exposed that silver nanoparticles is highly active for the dehydrogenation of alcohols and therefore silver was chosen for this study (27). For the loadings, the most effectives were 1 or 2 wt. % in silver. It is also interesting to notice that the best activity result was achieved with tantalum oxide as acidic species.

1.3 Aerosol-assisted sol-gel process

Nowadays, more than 90 % of the industrial chemical processes involve catalysts (28). The need to improve them is then obvious and to achieve this goal, a possibility is to play on the textural properties of the material. There again, the options are numerous but one promising prospect is the sol-gel process which has already demonstrated to be a synthesis giving highly performing catalysts (29). Moreover, the capacity of adaptation of the process allows a broad range of variations, resulting in the production of catalytic formulations with different compositions and different properties.

Heterogeneous catalysis is governed by the surface phenomena. The activity of a catalyst depends on the textural properties such as the porosity or the specific surface area but also on the dispersion and the nature of active species. In that scope, aerosol-assisted sol-gel allows to obtain tailored textural properties in the materials while keeping control on the composition and homogeneity (29).

Processes based on aerosol methods are not new, they were already used to prepare several materials with defined properties, solid materials in the 1920's and divided siliceous materials or thermal decomposition of mixtures of salts the 1930's (30–32). At this day, aerosol processes are used in many different applications such as: drying of a broad range of materials or the production of nanomaterials, etc... (33,34). Thanks to the advancement made in sol-gel methods, a new concept binding the two has emerge, called "aerosol-assisted sol-gel" (AASG).

Aerosol processes involve the atomization of a liquid as a mist made of small droplets that are then processed to form solid particles. However, there are different types of processes, depending on the starting liquid sample or the procedure of the solid formation. In 2018, Debecker et al. proposed a classification of those different types of aerosol processes (Table 1.7) (35).

Table 1.7: Classification of the aerosol processes by Debecker et al. (35).

	Method		Starting liquid samples	Solid formation
Type I	Drying		Suspension of liquid particles	Drying of pre-formed particles
Type II	Precipitation		Solution containing molecular species	Drying and precipitation caused by the increasing concentration
Type III	a	Flame-aerosol synthesis	Solution containing reactive molecular precursors	Fast thermal decomposition and condensation
	b	High temperature thermal decomposition		Thermal decomposition (without flame)
	c	Aerosol-assisted sol-gel		Organic polycondensation at mild conditions
Type IV	Gas atomization of metals and alloys		Melted metal or alloy	Cooling and deposition

- Type I involves no reactions and creates solid particles of the same composition as the pre-formed ones in the suspension but brings different aggregation form, humidity content or size, etc (35). In heterogeneous catalysis, this method is used to obtain larger particles that can be more easily recovered in fixed beds or if additives were added to tune the aggregation, to improve attrition resistance (36).
- Type II creates solids by precipitation. Depending on the starting solution and the drying procedure, composition, size, crystallinity, humidity or texture of the final solid may be tuned. This kind of spray-drying is commonly used in the pharmaceutical and in the food industry (35,37,38).
- Type III is the most complex class and involves a solid formation by decomposition or inorganic polycondensation reactions. In this case, the molecular precursors contained in the starting solution react to give a new compound chemically different from the

original species. Type III may be divided in three sub-classes, from “a” to “c”, depending on the applied conditions during the spray-drying. Types IIIa and IIIb use heat and high temperature to decompose the precursors and the obtained solids are then non-porous. Type IIIc however, operates with mild conditions and the obtained materials are porous (35). The addition of templating agents like surfactants improves this porosity. Type IIIc is the one used in this study, Figure 1.8 illustrates the method.

- Type IV uses aerosol to cool down melted metals to obtain small spherical particles of metal or alloys useful in heterogeneous catalysis (35).

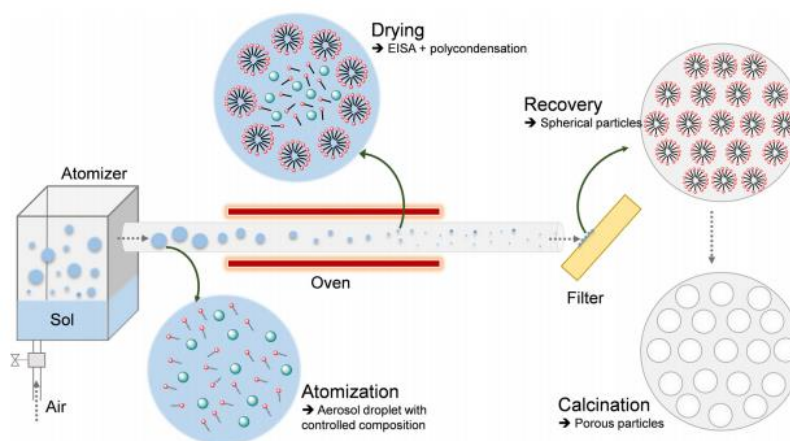
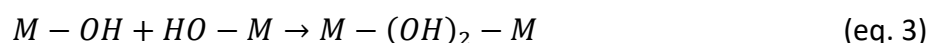
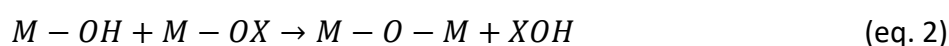


Figure 1.8 : Illustration of the Type IIIc aerosol process by Debecker et al. (29).

To fully understand the aerosol-assisted sol-gel process (Type IIIc aerosol process), it is necessary to investigate the sol-gel method. It is based on the polycondensation of metal organic precursors or metallic salts to produce inorganic metal oxides polymers. To do so, the precursors (usually an alkoxide) undergo two or three consecutive reactions. First, the organic metal precursors “M-OR” (M = Ti, Zr, Al, ... and OR = alkoxy group) are hydrolyzed to obtain reactive species “M-OH” (eq. 1). Then, these species may condense to form M-O-M products by oxolation (eq. 2, X = H or alkyl group) or M-OH-M products by ololation (eq. 3) (35). In the case of silica, only the two first equations must be considered but not for tantalum mixed oxide.



As mentioned above, this process allows to obtain tailored materials. Indeed, the structure of the oxo-polymers that will impact the structure of the final material can be controlled by changing the synthesis parameters such as pH, temperature, use of a complexing ligands or the nature of the solvent (35).

Aerosol-assisted sol-gel process (Type IIIc) can also be combined with the evaporation-induced self-assembly (EISA) of surfactant molecules, occurring during the condensation of molecular precursors. All happening in small aerosol droplets, in a very short time and in a continuous mode. Indeed, the method gradually increases the compounds concentration in the droplets until micelles are formed while polycondensation reactions take place. After the synthesis, a heat treatment is needed to remove the organic micelles and doing so, create porosity made of calibrated pores (29,35). Different ways to create a well calibrated porosity exists and it is not only limited to the use of surfactants. It can be achieved by using synthetic polymer beads (39) or natural biopolymers (40) but in this case the pores will be larger.

There are numerous advantages of AASG (35).

- The starting solution is homogeneous during the atomization. Therefore, every droplet has the same composition. Indeed, no new species is formed thanks to a dilution that allows a metastable state of the molecular precursors. The consequences of this are a good control of the composition and the homogeneity of the particles in the final material.
- The sol-gel reactions between the active species take place rapidly in the droplet. The remaining less active species are then trapped in the polymeric network (41). This kinetic characteristic allows to obtain solids in a metastable phase while keeping a homogeneous dispersion of the species. The metastable solids can exhibit specific molecular structures in which the angles between the atoms and/or the coordination are different than those obtained in the thermodynamically favored phase, resulting in different reactivity behavior.

- The surfactant micelles are captured by the organic structure and will help to create the desired porosity. However, the kinetic of the EISA can be tuned with the experimental conditions to make sure that it takes place at the same time as the formation of the organic network and therefore obtain controlled textural properties.

1.4 Goals

The purpose of this master thesis is to leverage on the specific features of the aerosol process to synthesize new types of bifunctional catalysts with advantageous textural properties and with a high dispersion of the active species. The catalysts will be tested in the transformation of ethanol into 1,3-butadiene, in a search for high performance. The idea is also to position these new catalysts in comparison with more classical formulations and to highlight the possible advantages of the aerosol process for the preparation of such bifunctional formulations. On the fundamental scientific level, we aim at demonstrating the impact of parameters such as texture (available active surface, pore size, etc.) and dispersion on the catalyst behavior.

1.5 Strategy

Base on the state of the art presented above, we chose to focus on catalysts based on Ta oxide and Ag on silica. Ag-TaO_x-SiO₂ catalysts are prepared in one pot using the aerosol-assisted sol-gel method (35). To control the texture, we use a sacrificial templating agent (pluronic F127) which undergoes evaporation induced self-assembly during the processing of the droplets (and thus during the inorganic polycondensation of the silica-based oxide) (35,42). In an attempt to bring Ag towards the surface of the catalyst – in the form of small metallic nanoparticles – we apply different types of thermal treatments, which are thought to provoke migration phenomena. Nevertheless, the drawback is that at high temperature, sintering is more favored, so the obtained particle size is larger. The objective was then to find the temperature that represents the best compromise between migration and sintering.

As benchmarks, we have prepared catalysts where Ag and Ta are incorporated into the formulation in a separate step, via a simple impregnation on a preformed support. Unlike the one-pot aerosol technique, impregnation brings all the active phase at the surface of the support (thus available for surface reactions) but is also expected to yield lower dispersion levels.

Several characterizations have been executed on the catalysts to explore the physicochemical properties (TPD, XRD, XPS, O₂ chemisorption, IR) and to determine the textural properties (BET).

Finally, the samples have been tested in a fixed bed reactor to assess their performances in the one step process of converting ethanol to butadiene. Various reaction temperatures were investigated. Catalytic data were used to identify the parameters of the catalyst formulations that dictate the performance level and to iteratively adjust the preparation method.

II. Experimental

2.1. Catalyst synthesis

The catalysts synthesized in this study consists of a mixed oxide support with a metal active phase on the surface. Every support was synthesized by aerosol-assisted sol-gel whilst the active phase was incorporated by two different processes. Nevertheless, two benchmark samples were prepared, one by impregnation on commercial silica and the other by impregnation on aerosol-made silica.

2.1.1. Synthesis

2.1.1.1. Aerosol-assisted sol-gel process

The aerosol-assisted sol-gel process was used to prepare both the final Ag-TaO_x-SiO₂ catalysts and the materials which serve as benchmark catalysts (binary Ag-SiO₂ and TaO_x-SiO₂ formulation) or as supports for further impregnation of Ag and/or Ta.

The synthesis protocol has been adapted from Debecker et al. from 2012 (43).

For 100 ml of final solution:

1. Preparation of the starting solutions:

- Solution A: 12 g of tetraethyl orthosilicate (TCI Chemicals, > 97.0 %)

20 g of aqueous solution of nitric acid (Merck, 65 %) 0.01 M

- Solution B: 3.88 g of Pluronic F127 (Sigma-Aldrich)

45 g of ethanol absolute (VWR, > 99.8 %)

8 g of distilled water

2. Solutions A and B are left under magnetic stirring overnight and then put together.
3. If the desired catalyst contains tantalum oxide, addition of acetyl acetone (Sigma-Aldrich, >99 %) to the tantalum precursor salt, tantalum ethoxide (Ta(OEt)₅) (Abcr, 99.99 %), with equivalent molar amount to avoid precipitation of tantalum oxide.

Stirring until total dissolution. Amount of tantalum ethoxide added to have the desired wt. % of tantalum oxide in the catalyst.

4. Addition of the tantalum solution to the starting solution.
5. If the desired catalyst contains silver, addition of silver precursor salt, silver nitrate (Merck, > 99 %). Stirring until total dissolution. Amount to have the desired wt. % of Ag in the catalyst.
6. Addition of the whole homogeneous sol into the atomizer (TSI, Six-jet atomizer 9306).
7. Nebulization of the sol by a compressed air flow of 30 psi. The aerosol is processed by passing through a tubular furnace set at 450°C (residence time ~1 sec).
8. Recovery of the powder on a nitrocellulose filter with a pore size of 0.45 µm (Sartorius Stedim).
9. The powder is then calcined at a temperature of either: 500°C, 600°C, 700°C under air for 5 hours (Stanton Redcroft tubular furnace or Carbolite AAF 1100 furnace).

2.1.1.2 Dry impregnation

In order to compare the characteristics given by aerosol with the ones given by impregnation, either silver, tantalum or both were impregnated on silica. Whether it was only silica, or a binary catalyst made of tantalum oxide and silica, the supports were synthesized by aerosol.

The tantalum or silver loading added varied from 1 to 10 wt. % for tantalum oxide and from 1 to 5 wt. % for silver. The volume of solvent added to dilute the salts has been calculated to fill the pore volume of the support. Ethanol absolute was used as solvent in the impregnations where tantalum ethoxide was involved. If only silver nitrate was impregnated, water was used as solvent. It was important to avoid the addition of water to tantalum ethoxide because of the risk of precipitation of tantalum oxide.

The protocol was as follow:

1. Dissolution of AgNO₃ in ethanol (resp. distilled water). The solution is left in an ultrasound bath for 30 minutes.
2. Grinding of the support.
3. Addition of the impregnation solution to the support.

4. Stirring, mixing and grinding to obtain a homogeneous paste. The paste is left to stand for 2 hours.
5. The paste is then dried overnight in an oven.
6. Calcination under air at 500°C for 5 hours with 5°C/min as ramp in either a static air furnace (Carbolite AAF 1100 furnace) or a tubular furnace (Tubular furnace Stanton Redcroft) with flowing dry air.

2.1.2. Summary of the synthesis

The samples are denoted according to their process of synthesis:

- The composition of the sample always precedes its calcination temperature. And the weight percentage is added before each supported element.
- If the supported element was impregnated rather than spray-dried with the aerosol setup, this element is put between brackets.

For instance, a one pot ternary sample, synthesized by aerosol, with a composition of 1 wt. % Ag and 5 wt. % Ta and calcined at 600°C, is called: 1.Ag/5.Ta/SiO₂.600. A silver impregnated sample on a tantalum – silica support with the same loadings as the one pot catalyst mentioned before, calcined at 500°C, is called: (1.Ag)/5.Ta/SiO₂.500.

2.2 Catalytic tests

2.2.1 Reactor

The setup used for the catalytic tests includes the gas inlet system, the reactor, the oven, the gas chromatograph and the system of command and analysis.



Figure 2.1: Photography of the catalytic setup used during this study. 1. Syringe pump, ethanol inlet. 2. Reactor. 3. Gas flow controller for H_2 and N_2 . 4. Gas chromatograph.

- The gas inlet system is also made of different parts. The gas exit flow, out of the bottle, is controlled by an electronically-operated mass flow rate controller (EL-FLOW Bronkhorst hi-tec). In order to calibrate the setup, a soap bubble flow meter was used.
- The catalytic fixed bed reactor is a 28 cm long tube with a 0.8 cm diameter installed in an oven (Minicor 42 Coreci). The temperature of the oven is controlled thanks to a thermocouple installed in the oven.
- The gas chromatograph (Varian CP-3800) is equipped with a polar column (Restek Rt-U-Bond (30 m x 0.32 mm x 10 μ m)). During a test, the gas is injected by a split injector (split ratio = 50) whose temperature is set at 150°C. During an injection, at the start of the column, the pressure is 15 psi and the temperature is set at 110°C. The temperature stays at 110°C for 5 minutes and then increased to 150°C at a rate of 10°C/min to finally settle for 5 minutes at this temperature.

The overseeing of the injections during a test and the data treatment of the outflowing gases is managed by a single computer with the *Varian Star Workstation* software.

2.2.2 Detection

The detector used in the chromatograph is a flame ionization detector (FID). The detector operates on the ionization of the organic compounds. The column effluents are mixed with H_2 and then burned with air with a negative voltage. The formed cations are captured by a cathode which leads to some variation in the voltage. These variations are recorded after amplification. The voltage variation is proportional to the concentration of the charged compound in the gas.

2.2.3 Reaction conditions

To perform a test, 192 mg of catalyst with a particle size between 200 μm and 400 μm are put inside the reactor, on a fixed bed. The remaining volume is filled with glass beads with a diameter of 500 μm . During the test, the temperature program is as shown in Figure 2.2.

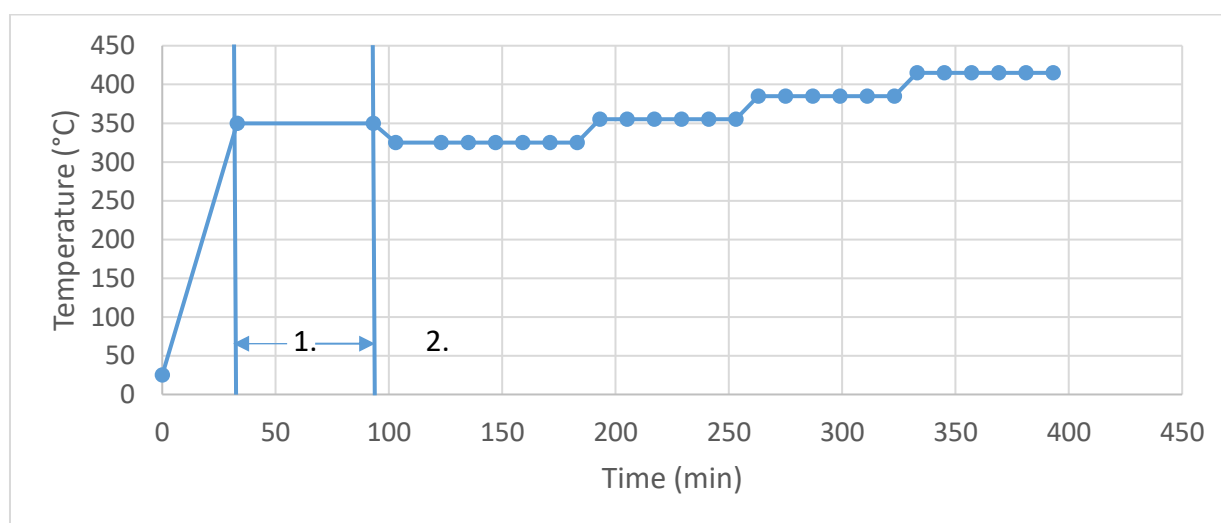


Figure 2.2: Catalytic reactor temperature program during a test. 1. Reduction under H_2 . 2. Catalytic tests under N_2 .

The first step of the test is to reduce the catalyst at 350 °C during an hour with a continuous flow of 15 ml/min of H_2 (mixed with 37.3 ml/min N_2). This step is important to have metallic Ag particles on the catalyst instead of the oxide.

Once the temperature is stabilized at 325°C and all the hydrogen has been flushed out of the reactor using a nitrogen flow (37.3 ml/min), the ethanol feed is connected to the setup

and the reactor is fed with ethanol with a volumetric flow rate of 0.27 ml/h. The flow rate is insured by n-300 syringe pump from QiS. The ethanol feed is mixed with nitrogen to the proportion 95:5 nitrogen/ethanol (molar).

The reaction is done at atmospheric pressure, on a range of temperature from 325°C to 415°C with an increment of 30°C by step. Every GC injection lasts 12 minutes; each temperature step is maintained for 60 minutes to allow five injections per temperature.

2.2.4 Data processing

To evaluate the molar fraction of the different compounds coming out of the column of the chromatograph, some calibration curve had to be done. Therefore, every inlet and outlet compounds have been calibrated one by one. Doing so, the molar fraction of every outlet compound during a test is easy to quantify.

2.2.4.1 Catalytic performance indicators

Thanks to the catalytic tests, some indicators of the catalytic performance of the samples can be obtained. They are useful to assess if a catalyst is good or not.

The first one is the conversion of the reactant. For a reactant i , the conversion is by definition:

$$Conversion = \frac{Quantity\ of\ reactant\ transformed}{Quantity\ of\ reactant\ introduced} \cdot 100\ (\%) \quad (1)$$

Another useful indicator is the selectivity. It allows to determine if the catalyst is active on the desired reaction or on some others and at what scale. This indicator is defined as:

$$Selectivity = \frac{Quantity\ of\ the\ desired\ product\ formed}{Quantity\ of\ reactant\ transformed} \cdot 100\ (\%) \quad (2)$$

Yield can also be obtained, it is defined as:

$$Yield = \frac{Quantity\ of\ the\ desired\ product\ formed}{Quantity\ of\ reactant\ transformed} \cdot 100\ (\%) = \frac{Conversion \cdot Selectivity}{100} (\%) \quad (3)$$

Finally, specific activity gives the number of moles of product we can obtain per time and per mass of catalyst:

$$Specific\ activity = \frac{Quantity\ of\ product\ formed}{time \cdot mass\ of\ catalyst} \left(\frac{mol}{s.g_{cata}} \right) \quad (4)$$

2.3 Characterization

To characterize the catalysts, different methods have been used: thermogravimetric analysis, BET N₂ physisorption, X-Ray photoelectron spectroscopy, O₂ chemisorption, X-Ray diffraction, NH₃ Temperature programmed desorption, Transmission electron microscopy and Inductively coupled plasma – atomic emission spectroscopy.

2.3.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis has been used to evaluate the range of temperature required to calcine the catalysts after synthesis with the aerosol to remove the surfactant of the powder.

Through the temperature program, heat induces physical changes and reactions. Because of these changes, mass varies, and it is this variation in mass that is measured precisely. The analyzer used in the apparatus is simply a high precision weighing machine supporting a sample pan. This weighing machine is inside a furnace which follows the temperature program previously set.

20 mg of catalyst is put in a 70 µl alumina crucible and put in a *TGA/DSC 3+ STAR System* from *Mettler Toledo*, the temperature then increases until 700°C and the mass of the samples is monitored by the apparatus to determine the mass loss of the sample by function of time or temperature.

2.3.2 BET N₂ physisorption

To determine the textural properties of the materials, N₂ physisorption was used. Before the test, the sample is degassed to flush every already adsorbed compound from the surface. During the analysis, the pore size distribution is measured by the quantity of gas adsorbed at the surface, at a specific pressure and temperature. A known volume of N₂ is introduced and the adsorbed quantity is calculated by measuring the remaining nitrogen after adsorption and because of the adsorption, a pressure drop is obtained.

Then, it also estimates a relation between the calculated amount of adsorbed molecules and the relative pressure P/P_0 . This relation can be plotted to obtain isotherm linear plot which gives information about the type of porosity in the material. Thanks to the BET

model (Brunauer, Emmett and Teller) applied on the adsorption isotherm, on relative pressure between 0.05 and 0.3, surface areas can be calculated.

The range of pore sizes that can be measured by N₂ physisorption is between 2 and 50 nm. BJH (Barret, Joyner and Halenda) is the most current method to derive the pore size distribution from a specific isotherm.

150 mg of sample are degassed at 150°C until the pressure in the tube decreases under 80 mTorr with a *Vacprep 061* degasser from *Micromeritics*. The analysis is done at - 196°C, the boiling point of nitrogen on a *Micromeritics TriStar 3000* device.

2.3.3 X-Ray photoelectron spectroscopy (XPS)

X-Ray photoelectron spectroscopy is a standard method to analyze the surface of materials on a thickness up to ten nanometers. This analysis is useful for the identification and the quantification of the species dispersed on the surface of the catalyst.

The spectrometer used is a *Surface Science instruments SSX 100/206* equipped with AlK_α X-Ray beam, micro-focused and monochromatized, powered with 20 mA and 10 kV. The samples are deposited on double-sided tape on the conductive sample holder carousel in aluminum.

During the analysis, pressure may reach 10⁻⁶ Pa in the analysis chamber. The screening zone equals 1.4 mm² and the energy emitted by the spectrometer is set at 150 eV. The angle between the normal vector coming out the surface and the axis of the input lens of the analyzer is 55°. At these settings, the width at half height of the peak at 4f_{7/2} of a standard gold sample is 1.6 eV. A nickel grid put at 3 mm over the sample surface and an electron gun set at 8 eV are installed to stabilize the charge (44).

In order to insure the stability of the compensation of charges with time and the absence of degradation of the sample, some spectra are registered (general spectrum, C 1s, O 1s and C 1s again).

To set the binding energy scale, the C-(C, H) component of the peak C 1s is set at 284.48 eV. The data treatment is then performed by the software *CasaXPS* from *Casa Software Ltd*. With this software, after the subtraction of a non-linear baseline, the spectra of interest are decomposed following a model of Gaussian function and Cauchy distribution (fitting by least

square method). Finally, the molar fraction is given by integrating the surface area under the peaks, normalized with the acquisition parameters and the sensitivity factors given by the manufacturers.

2.3.4 O₂ chemisorption

To assess the dispersion of metallic silver on the surface of the samples, the chosen technique was O₂ chemisorption. To carry out this characterization, a *PulseChemiSorb 2075* from Micromeritics was used.

Approximately 200 mg of sample is introduced in a U-shaped glass tube furnished with the setup and is then reduced at 350°C for one hour with hydrogen. This pretreatment insured the elimination of any previously adsorbed species and the reduction of silver to its metallic state. The samples were heated in a *Micromeritics Furnace controller*. After this pretreatment, the hydrogen flow is stopped, and the temperature decrease to 170°C under helium.

The adsorption of oxygen is measure at 170°C under pulse flow of O₂ by a thermal conductivity detector (TCD) until every adsorption sites are occupied (45).

2.3.5 X-Ray diffraction (XRD)

X-Ray diffraction allows to determine the crystallographic structure of the catalysts. The diffractometer used is a Bruker D8 Advance, set in Bragg-Brentano geometry.

During the analysis, the sample is put on a single crystal of silicon. The X-Ray source operates with a power of 1200 W (30 mA, 40 kV). The diffractometer is equipped of a Lynxeye XE-T detector from *Bruker*. The analyses are done through the copper K $\alpha_{1,2}$ ray ($\lambda = 0.15418$ nm) following a range of 2θ angles from 5° to 80°, adding 0.02° every 0.15 seconds.

Above the sample, a divergence slit is moving accordingly to the analysis angle to keep the same studied surface area. The beam is conditioned on both sides of the sample by copper Soller slits. A blade is also put right above the sample to minimize the beam diffraction by the air and so, to increase the precision of the analysis.

To treat the data, two databases were used to find matches to the peaks: COD and PDF-2.

2.3.6 NH₃ Temperature programmed desorption (NH₃ - TPD)

Based on the chemisorption of certain components on the surface of a material, temperature programmed desorption is a characterization technique giving information about the reaction's sites available on the surface of a sample. The analysis is based on the adsorption of certain molecules on a surface which minimize their energy.

When increasing, the temperature disadvantages the adsorption, so the number of adsorbed molecules is dropping at high temperature. Focusing on this forced desorption, the device can determine the interactions between the surface and the desorbed species. Doing so, the adsorption sites on the surface of the material are characterized and data about the number and the strength of the acidic sites is obtained.

During an analysis, roughly 60 mg of samples was introduced in a quartz tube between two layers of quartz wool and then put into a *Hiden Isoschema Catlab* microreactor module coupled to a *Hiden Analytical QGA* quantitative gas analysis system. Figure 2.3 shows the temperature program during a characterization. After degassing at 300°C, to remove any previously adsorbed compounds, ammonia is adsorbed on the sample at 150°C for 40 minutes (20 ml/min Ar; 5% vol. NH₃). Then, there is a purge for 80 minutes followed by the desorption program with the increase of the temperature to 600°C. Every ramp of temperature was the same and was 10°C/min. Except during the adsorption, the flow consisted in 40 ml/min of Argon.

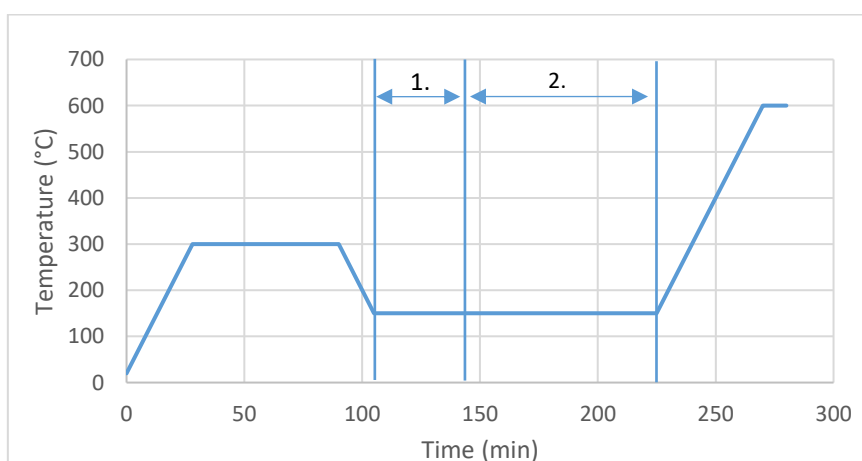


Figure 2.3: NH₃ - TPD temperature program. 1. NH₃ adsorption. 2. Purge.

2.3.7 Infrared spectroscopy (IR)

Infrared spectroscopy is used to measure the variation in the vibration state of molecule bonds. Every bond has different vibrational energy and will absorb different wavelength depending of the atoms linked. The molecular vibrations can be induced by wavelength between 750 nm and 0.1 mm corresponding to the infrared range of energy. During an analysis, the variation of the infrared beam is monitored in function of the wavelength. In the case of this study, 150 mg of potassium bromide (Roth) is grinded and homogenized with approximately 1 % of its mass of sample. After homogenization, the powder is transformed into a pellet in a *SPECAC* mechanical press and analyzed with a *Bruker spectrometer* (128 Scans between 4000 and 500 cm^{-1}). The collected data is processed with the software *OPUS* where the spectra is corrected to a baseline and the intensity normalized.

III. Results

3.1 Catalysts characterizations

3.1.1 One-pot aerosol-assisted sol-gel samples

For the preparation of the catalysts, three different effects have been investigated during this study; two different types of furnaces, calcination temperature and the loadings of active phase.

3.1.1.1 Effect of the calcination furnace

A major key point of this study being the establishment of the optimal calcination temperature to improve the migration of silver to the surface while minimizing the sintering of the particles. In this perspective, two different furnaces with different performances have been compared: A static air furnace (*Carbolite AAF1100*) and a tubular flowing air furnace (*Stanton Redcroft*).

Textural analysis

Samples with different silver or tantalum oxide loadings have been analyzed by N₂ physisorption to assess if the textural properties would vary depending on the furnace. The compared samples have been respectively synthesized in the same batch before calcination. Table 3.1 display the results of this analysis. The external surface area, detailed in the Table below, equals the surface area not included in the microporosity.

Table 3.1: Comparison of textural properties brought by different furnaces.

Sample	Specific Surface Area (m ² /g)	External surface area (m ² /g)	Avg. pore size (BET) (nm)	Pore volume (cm ³ /g)
Calcination with static air furnace				
1.Ag/ 1.Ta/ SiO ₂ .500	450	250	4.7	0.53
1.Ag/ 5.Ta/ SiO ₂ .500	430	210	4.4	0.47
5.Ag/ 2.5.Ta/ SiO ₂ .500	420	220	4.5	0.48
Calcination with flowing air furnace (tubular)				
1.Ag/ 1.Ta/ SiO ₂ .500	420	240	4.9	0.52
1.Ag/ 5.Ta/ SiO ₂ .500	370	220	5.0	0.47
5.Ag/ 2.5.Ta/ SiO ₂ .500	400	230	4.7	0.47

It can be observed from Table 3.1 that the furnace used did not impact the textural properties of the samples. Indeed, every property seems to remain stable from one furnace to another. Also, it can be seen that the surfactant has burned at 500°C to let place to the desired texture.

O₂ chemisorption

Focusing more on silver on the surface, its dispersion has been evaluated by O₂ chemisorption on 5.Ag/2.5.Ta/SiO₂, calcined at 500°C with the two furnaces (Table 3.2). To obtain these results, like the other silver dispersion results below in this study, a reference is used to measure only the adsorbed oxygen on silver particles. In this case, the reference was 2.5.Ta/SiO₂, a catalyst containing no silver but with the same tantalum oxide loadings. The reference results are then subtracted to the sample of interest results.

Table 3.2: Silver dispersion on the surface of 5.Ag/2.5Ta/SiO₂ catalysts, depending on the calcination furnace

Furnace	Silver dispersion (%)	Average diameter (nm)
Static air	8	13.2
Flowing air	20	5.0

It appears that silver is less dispersed when the sample is calcined with a static air furnace than with a flowing air furnace (Table 3.2). The dispersion decreases by 60% when calcined under static air. From the dispersion data, the average diameter can be approximated. According to those results, silver particles tend to sinter more when calcined under static air, ending on particles 2.6 times bigger than under flowing air.

XRD

The same samples as examined by oxygen pulse chemisorption have been analyzed by XRD to evaluate also the dispersion of silver on the surface of the catalysts and to confirm the chemisorption data. The obtained diffractograms have revealed important differences (Figure 3.1). 5.Ag/2.5.Ta/SiO₂.500 calcined under flowing air is amorphous, suggesting a satisfying dispersion of active sites. However, a problem appears when the sample is calcined under static air. The corresponding diffractogram is presenting peaks matching to silver chloride.

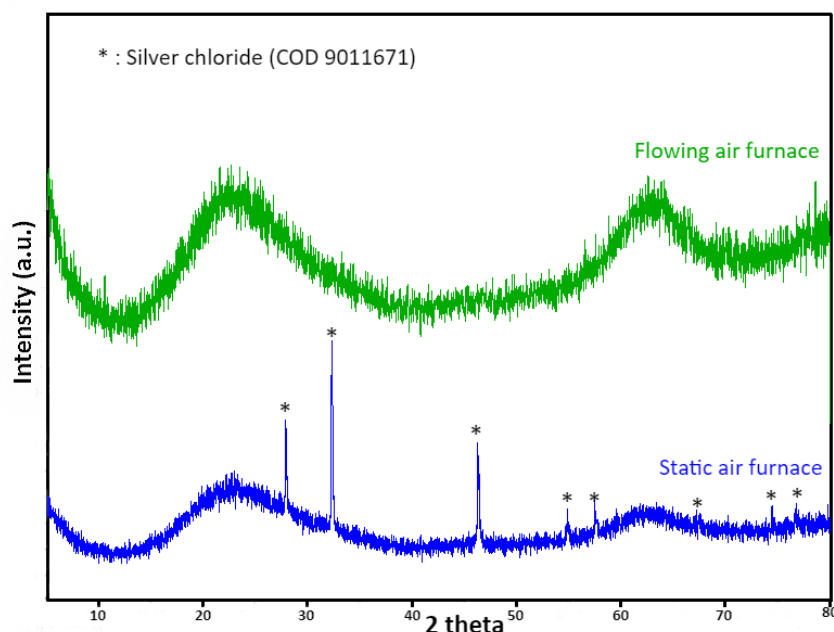


Figure 3.1: Diffractogram of 5Ag/2.5Ta/Si.500 calcined with the flowing air furnace or the static air furnace.

XPS

The presence of chloride was confirmed by checking on the 2p orbital of chlorine by XPS on the previously analyzed samples (Table 3.3). Nevertheless, results seem to suggest that chlorine is present in similar amount in both samples. Chloride presence is probably due to contamination during the calcination since no source of chloride were used during the synthesis. Also, it has to be noted that chloride is present in a really low amount in the samples.

Table 3.3: XPS analysis for 5Ag/2.5Ta/SiO₂ catalysts, calcined at 500 °C in different furnaces.

Furnace	Si (2p) conc. (%)	Ta (4f) conc. (%)	Ag (3d) conc. (%)	Cl (2p) conc. (%)	Si/Ta mol. ratio	Si/Ag mol. ratio
Static air	19.587	0.159	0.359	0.12	123.2	54.6
Flowing air	18.226	0.171	1.04	0.147	106.6	17.5

In addition to the chlorine presence in both samples, another important characteristic is brought to light by the XPS results. It can be seen on Table 3.3 that silver seems to migrate less towards the surface when the samples are calcined under static air. Indeed, silver is 3.12 times more concentrated at the surface when calcined under flowing air. These results can be added to the ones presenting that static air calcination was favoring sintering (Table 3.2).

3.1.1.2 Effect of calcination temperature

In the same scope of establishing the best calcination temperature to optimize the dispersion of silver particles on the surface, three different calcination temperature have been studied. The templating agent decomposing at 400°C (checked by TGA, not shown), the screening on the temperature has started at 500°C until 700°C.

Textural analysis

First, the textural properties were studied by N₂ physisorption on either silica, binary Ta-Si catalysts or ternary Ag-Ta-Si catalysts, all three calcined at the three temperatures (Table 3.4). The chosen composition to run this test on binary or ternary catalysts was 5 wt. % tantalum oxide and if required, 1 wt. % silver.

Table 3.4: Textural properties of supports and catalysts depending on the calcination temperature.

Calcination temp. (°C)	Specific Surface Area (m ² /g)	External surface area (m ² /g)	Avg. pore size (BET) (nm)	Pore volume (cm ³ /g)
Silica				
500	370	260	5.4	0.50
600	300	260	6.2	0.46
700	190	185	7.4	0.35
5.Ta/ SiO₂				
500	460	200	4.1	0.47
600	370	180	4.5	0.42
700	300	170	4.8	0.37
1.Ag/ 5.Ta/ SiO₂				
500	370	220	5.0	0.47
600	330	320	6.5	0.55
700	290	230	6.7	0.48

The main trend coming out of Table 3.4 is that even if the specific surface area is decreasing with the increasing temperature, the external surface area, experiences a softer decrease. This means that the surface area loss comes mostly from the microporous surface area which has a smaller impact on the surface available for active sites and reaction because the molecules diffuse less in smaller pores. Also, it can be seen that the average pore size is

increasing with the calcination temperature. Finally, the pore volume remains constant between 500 and 600°C before going down at 700°C.

XPS

The migration of silver towards the surface was monitored by XPS on the three different calcination temperature. Tantalum was also verified during XPS measurements and the results are showed in Table 3.5. The sample analyzed was 1.Ag/5.Ta/Si.

Table 3.5: XPS analysis of 1.Ag/5.Ta/SiO₂ calcined at different temperature.

Sample	Si (2p) conc. (%)	Ta (4f) conc. (%)	Ag (3d) conc. (%)	Si/Ta mol. ratio	Si/Ag mol. ratio
500	16.1	0.257	0.282	62.5	57.0
700	18.7	0.259	0.100	72.1	186.8

When observing the amount of silver on the surface, one can see that silver is either better dispersed or forms smaller particles when calcined at the lowest temperature since a higher temperature improves the migration (Table 3.5). According to the molar ratio between Si and Ag, silver is approximately three times more available when the sample is calcined at 500°C rather than 700°C.

NH₃ – TPD

Finally, the variation in the acidity of the samples after calcination has also been studied. Acidity was measured by NH₃–TPD on 1.Ag/5.Ta/Si catalysts calcined at 500 and 700°C and the results are reported in Table 3.6.

Table 3.6: Total acidity and surface acidity of 1.Ag/5.Ta/Si calcined at different temperature.

Calcination temperature (°C)	Acid sites (mmol/g)	Acid sites (mmol/m ²)
500	0.064	1.4×10^{-4}
700	0.050	1.7×10^{-4}

Table 3.6 shows that the number of acid sites is decreasing with an increased calcination temperature. However, this diminution is made up by the diminution of the specific surface area as well (Table 3.4), resulting in a rather stable number of acid sites per m².

3.1.1.3 Effect of the loadings

The last effect studied on the one-pot samples was a screening of both silver and tantalum oxide loadings. These loadings have been varied from 0 to 5 wt. % for silver and from 1 to 10 wt. % for tantalum oxide.

Textural analysis

The textural properties have been measured for every one-pot sample to investigate if either silver or tantalum oxide loadings could impact it. The data corresponding to these measurements can be seen in Table 3.7.

Table 3.7: Textural analysis of one-pot samples with varied loadings of silver and tantalum oxide.

Samples	Specific Surface Area (m ² /g)	External surface area (m ² /g)	Avg. pore size (BET) (nm)	Pore volume (cm ³ /g)
1 wt. % tantalum oxide				
1.Ag/ 1.Ta/ SiO₂.500	450	250	4.7	0.53
2.5 wt. % tantalum oxide				
2.5.Ta/ SiO₂.500	410	190	4.2	0.43
1.Ag/ 2.5.Ta/ SiO₂.500	400	210	4.6	0.44
5.Ag/ 2.5.Ta/ SiO₂.500	400	230	4.7	0.47
5 wt. % tantalum oxide				
5.Ta/ SiO₂.500	460	200	4.1	0.47
1.Ag/ 5.Ta/ SiO₂.500	370	220	5.0	0.47
2.Ag/ 5.Ta/ SiO₂.500	480	260	4.7	0.56
10 wt. % tantalum oxide				
10.Ta/ SiO₂.500	400	170	5.3	0.54
1.Ag/ 10.Ta/ SiO₂.500	390	170	4.2	0.40
2.Ag/ 10.Ta/ SiO₂.500	420	200	4.3	0.45

Although all the textural properties appear to remain stable with a screening of both active phases, a trend can be seen for the external surface area. It seems to increase with higher silver loadings.

Regardless of the Ta or Ag loading, the catalysts are mesoporous as evidenced by the shape of the nitrogen physisorption isotherms with a typical Type IV shape showing a hysteresis between p/p_0 0.45 and 0.80 (Figure 3.2).

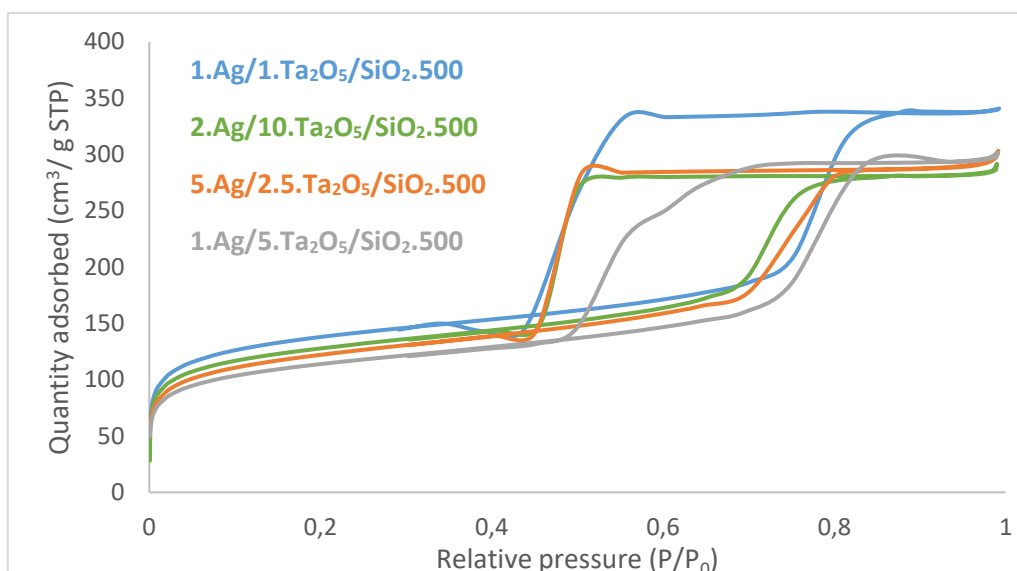


Figure 3.2: Isotherm plot of nitrogen adsorption for representative one-pot samples.

Moreover, the shape of H_2 hysteresis loops on the isotherm plots (Figure 3.2), means that the mesopores of the materials are interconnected and that the size distribution of the pores is narrow. The narrow distribution is confirmed when looking at Figure 3.3, representing the pore volume in function of the pore size of the same representative samples as in Figure 3.2.

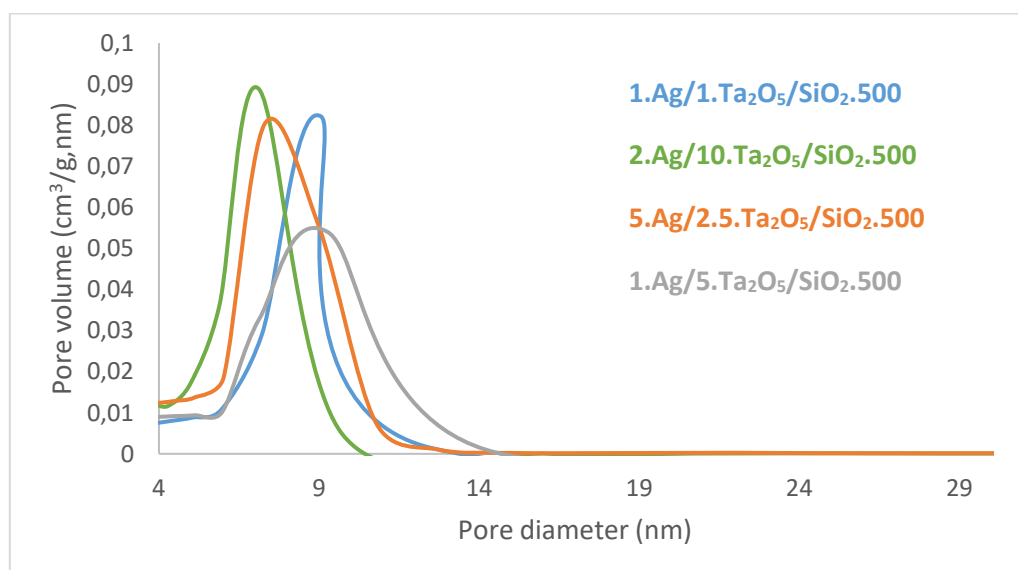


Figure 3.3: Pore volume in function of the pore diameter of representative one-pot samples. Deduced from the BJH adsorption plot.

XRD

To verify that silver is well dispersed on the surface of ternary Ag-Ta-Si catalysts and not forming large clusters that would reduce its effect, XRD analysis was run on every sample. The diffractogram of two representative samples with varied silver and tantalum oxide loadings are displayed in Figure 3.4. The diffractograms presented on Figure 3.4 confirms that silver is well dispersed on the catalysts surface or at least not forming large particles on every spray-dried catalyst and that the materials are amorphous.

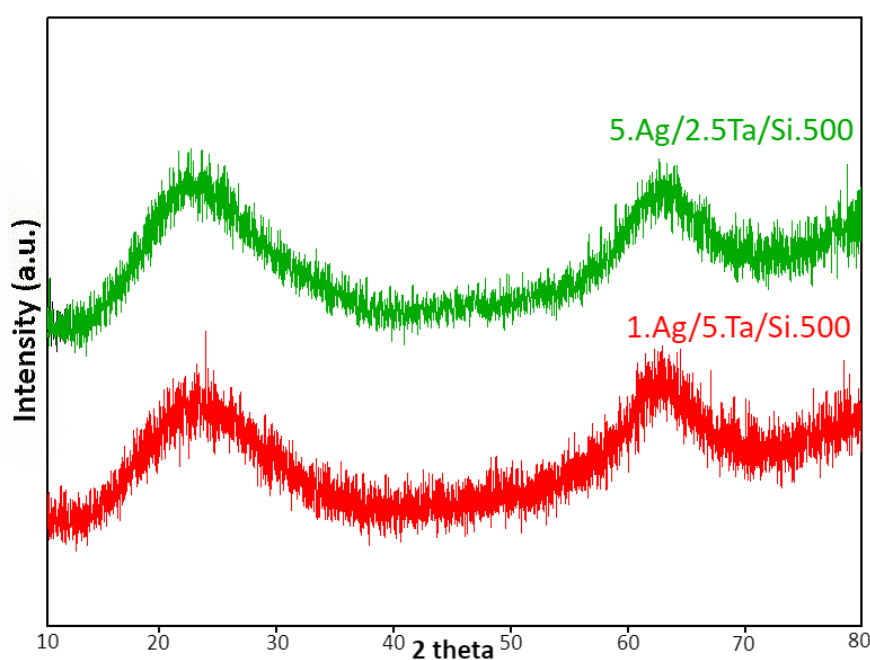


Figure 3.4: Diffractogram of representative one-pot catalysts with varying loadings.

Infrared spectroscopy

To determine if the tantalum is well incorporated into the silica matrix, the signature of Si-O-Ta bonds in infrared spectroscopy can be compared between the samples. Indeed, the studied bonds have a characteristic band at 950 cm^{-1} , corresponding to Si-O-M stretching mode (M= metal) (46). The band at 1100 cm^{-1} corresponds to Si-O-Si stretching mode. IR spectra of samples containing 2.5 and 5 wt. % of tantalum oxide loadings with varying silver loadings are displayed on Figure 3.5.

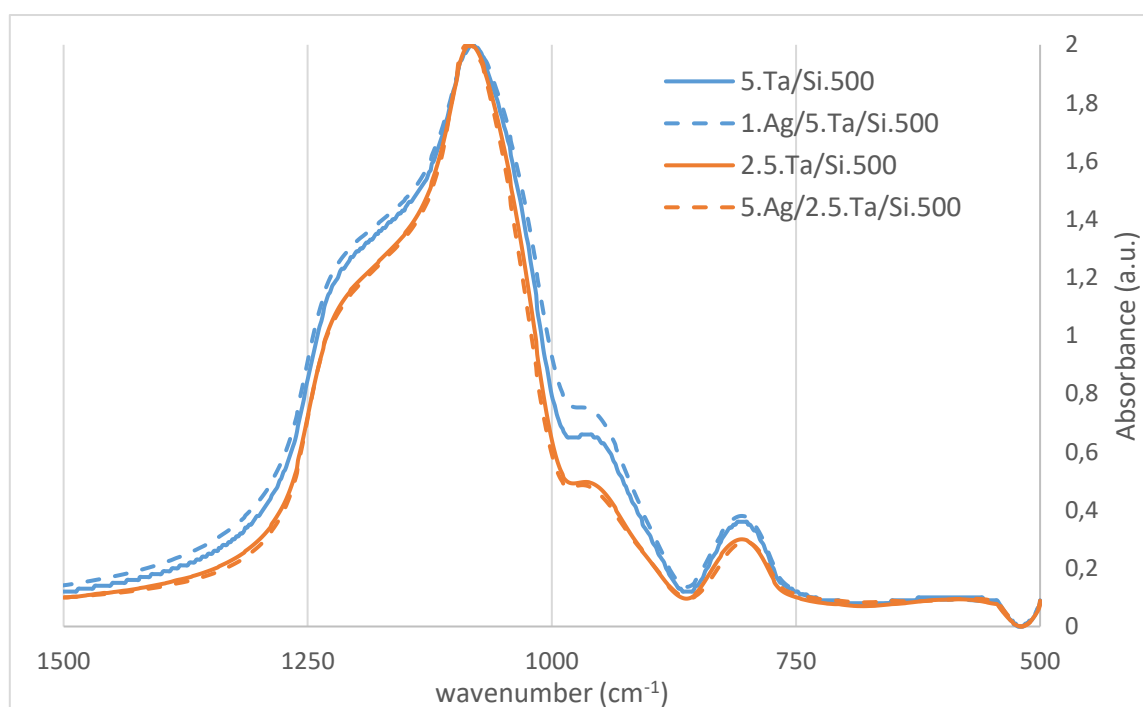


Figure 3.5: Impact of the silver and tantalum oxide loadings on the infrared spectra of one-pot samples.

From the spectra on figure 3.5, it can be observed that the intensity of the 950 cm^{-1} band is lower at lower tantalum loadings. This result confirms that incorporation of tantalum into the matrix can be followed by infrared. Also, the silver loading does not appear to influence the incorporation of tantalum.

NH_3 – TPD

The availability of acid sites was also investigated on one-pot catalysts by ammonia temperature programmed desorption (Table 3.8).

Table 3.8: Total and surface acidity measured by NH_3 -TPD for one-pot catalysts.

Sample	Acid sites (mmol/g)	Acid sites (mmol/m ²)
5 wt. % of tantalum oxide		
5.Ta/ SiO₂.500	0.061	1.65×10^{-4}
1.Ag/ 5.Ta/ SiO₂.500	0.064	1.4×10^{-4}
2.Ag/ 5.Ta/ SiO₂.500	0.059	1.2×10^{-4}
10 wt. % of tantalum oxide		
1.Ag/ 10.Ta/ SiO₂.500	0.086	2.2×10^{-4}
2.Ag/ 10.Ta/ SiO₂.500	0.081	2.0×10^{-4}

Expectedly, the number of acid sites increases for higher tantalum loadings (Table 3.8). However, the introduction of silver seems to slightly affect negatively the acidity of the materials since the number of acid sites on the surface of the catalyst is dropping with increased silver loadings.

3.1.2 Impregnated samples

Concerning the benchmarks samples, prepared by impregnation, only the impact of the loadings was considered. Indeed, the calcination temperature was no more investigated because every support has been calcined at 500°C to optimize the specific surface area and the observations about the calcination furnace are the same than for one-pot samples. However, the silver and tantalum incorporation method were studied here also.

3.1.2.1 Effect of the loadings

Like for the one-pot synthesized samples, a screening of both silver and tantalum oxide loadings have been applied to impregnated samples, in the same range of weight percentages. In this section, we present the results obtained on samples prepared by impregnation of silver on top of a Ta-SiO₂ catalyst prepared by aerosol. Also, two benchmark catalysts are presented with both tantalum and silver incorporated by impregnation, (1 wt. % Ag and 5 wt. % Ta₂O₅) on either a commercial silica (*Aldrich*) or on an aerosol-made silica support.

Textural analysis

Textural properties have been measured for every silver impregnated samples and benchmarks, to assess if the impregnation process influenced it. In Table 3.9, obtained results are compared with the corresponding support, used for the impregnation.

Table 3.9: Textural analysis for impregnated samples and comparison with the support.

Samples	Specific surface area (m ² /g)	External surface area (m ² /g)	Avg. pore size (BET) (nm)	Pore volume (cm ³ /g)
SiO ₂ _aer.500	370	260	5.4	0.50
SiO ₂ _com.500	190	170	14.3	0.61
(1.Ag/ 5.Ta)/ SiO ₂ _aer.500	340	250	6.0	0.51
(1.Ag/ 5.Ta)/ SiO ₂ _com.500	140	130	16.2	0.57
2.5 wt. % tantalum oxide				
2.5.Ta/ SiO ₂ .500	410	190	4.2	0.43
(2.Ag)/ 2.5.Ta/ SiO ₂ .500	290	190	5.2	0.37
(5.Ag)/ 2.5.Ta/ SiO ₂ .500	250	180	5.5	0.34
5 wt. % tantalum oxide				
5.Ta/ SiO ₂ .500	460	200	4.1	0.47
(1.Ag)/ 5.Ta/ SiO ₂ .500	310	220	4.5	0.35
(2.Ag)/ 5.Ta/ SiO ₂ .500	330	180	4.8	0.39
(5.Ag)/ 5.Ta/ SiO ₂ .500	250	160	5.2	0.33
10 wt. % tantalum oxide				
10.Ta/ SiO ₂ .500	400	170	5.3	0.54
(2.Ag)/ 10.Ta/ SiO ₂ .500	290	140	4.5	0.33

The specific surface area is decreasing with the impregnation of silver and the impact becomes more important at higher silver loadings (Table 3.9). Nevertheless, this negative influence seems to be counterbalanced by a rather stable external surface area, meaning that the loss concerns mainly the microporous surface area. On the other hand, the average pore size is increasing at higher impregnated silver loadings, this could be caused by silver particles plugging the smallest pores, thus shifting the pore size distribution to higher size. Moreover, the pore volume of the samples is decreasing at higher silver loadings, which is in line with previous observations.

Regarding the catalysts prepared on a commercial silica, the specific surface area is lower than for the silver impregnated catalysts on aerosol-made silica. Its pore size distribution is broader than the other catalysts (plot not shown) but its pore volume is similar to the rest of the samples.

N₂ physisorption isotherms silver impregnated samples can also be observed for the impregnated materials to draw conclusion about the evolution of the porosity of the materials. Figure 3.6 shows that conclusion about the mesoporosity for impregnated samples

on aerosol-made supports are the same than for one-pot silver incorporated samples (Figure 3.2).

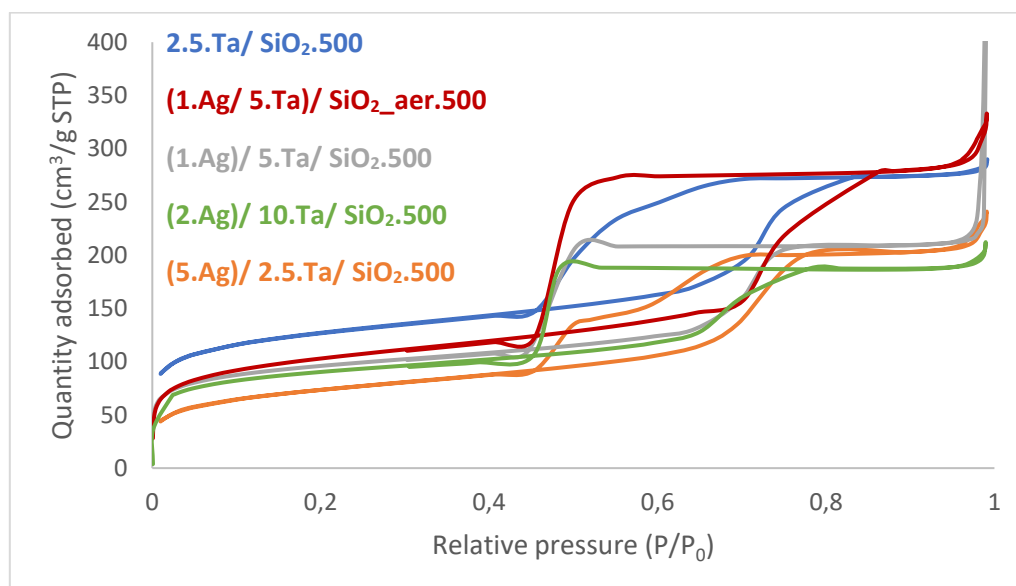


Figure 3.6: Isotherm plot of nitrogen adsorption for representative impregnated samples and comparison with a support.

Concerning the pore size distribution, it is narrow, as suggested by the H_2 hysteresis loop on Figure 3.6 and confirmed by the plot of pore volume in function of the pore width (Figure 3.7).

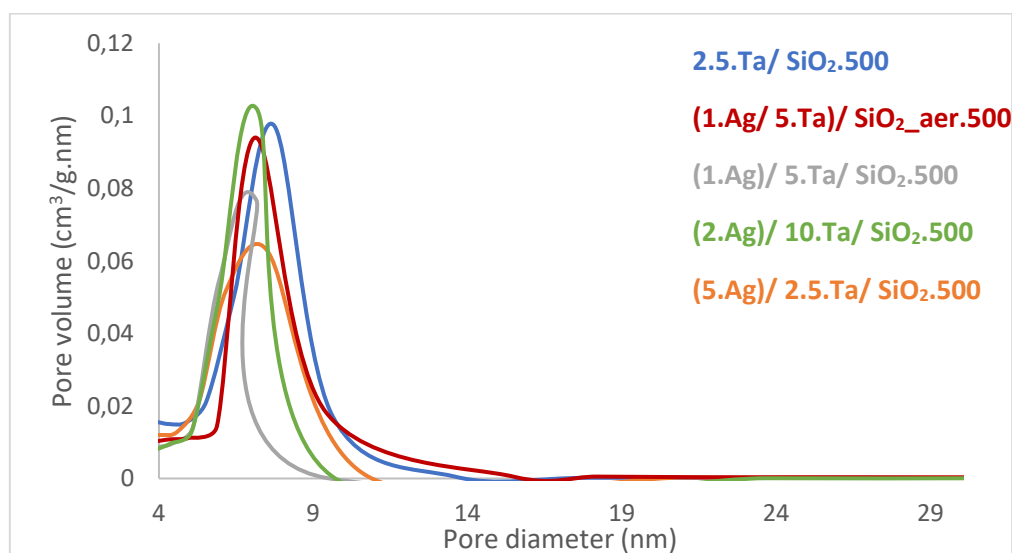


Figure 3.7: Pore volume in function of the pore diameter of representative impregnated samples and comparison with a support. Deduced from BJH adsorption plot.

XPS

To compare the different preparation process, the quantity of active compounds at the surface was measured by XPS. To do so, catalysts with the same loadings but prepared by one-pot, silver impregnation or both impregnation of silver and tantalum have been analyzed (Table 3.10). As expected, the amount of both tantalum and silver at the surface is higher for impregnated materials (Table 3.10).

Table 3.10 : XPS analysis of 1.Ag/5.Ta/SiO₂, prepared by different impregnations and comparison with the one-pot sample.

Sample	Si (2p) conc. (%)	Ta (4f) conc. (%)	Ag (3d) conc. (%)	Si/Ta mol. ratio	Si/Ag mol. ratio
1.Ag/5.Ta/SiO₂.500	16.1	0.257	0.282	62.5	57.0
(1.Ag)/5.Ta/SiO₂.500	17.6	0.242	0.513	72.5	34.2
(1.Ag/5.Ta)/SiO₂.500	15.9	1.82	1.12	8.7	14.2

XRD

XRD was used to compare the dispersion of silver brought by the different preparation method but also brought by different loadings of silver impregnated at the surface of materials. From Figure 3.8, it can be seen that no matter the preparation process, the materials remain amorphous with no peaks matching to silver, meaning that the metal is either well dispersed or at least do not forms big crystals at the surface. The same observation can be made for silver (Figure 3.9): it seems that the impregnated loading of silver does not influence a good dispersion at the surface of the catalysts.

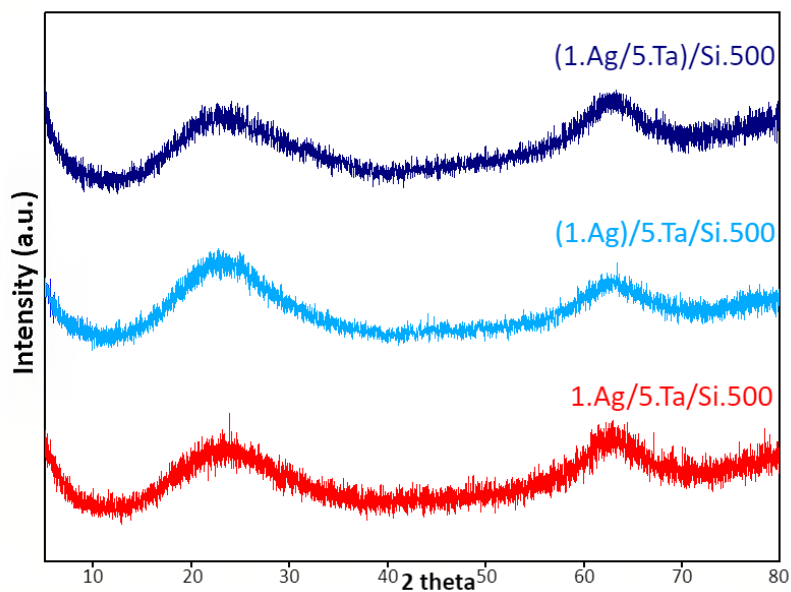


Figure 3.8: Impact on diffractograms of the incorporation of active phase in the support.

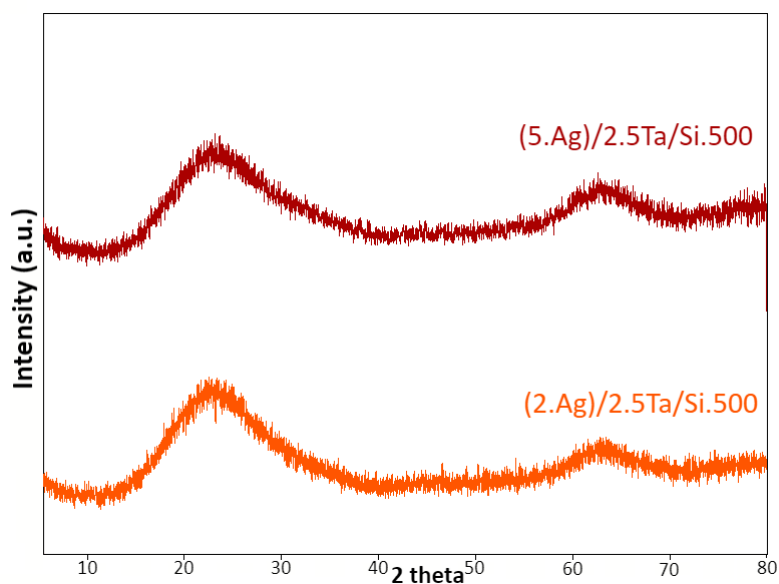


Figure 3.9: Impact on diffractogram of the silver loadings

Infrared spectroscopy

Tantalum incorporation was investigated by infrared to compare the preparation method but also to evaluate if the impregnation of silver impacts it. In this context, three samples containing the same loadings but prepared by three different method are compared (Figure 3.10) and samples with varying impregnated silver loadings are compared to their respective support (Figure 3.11).

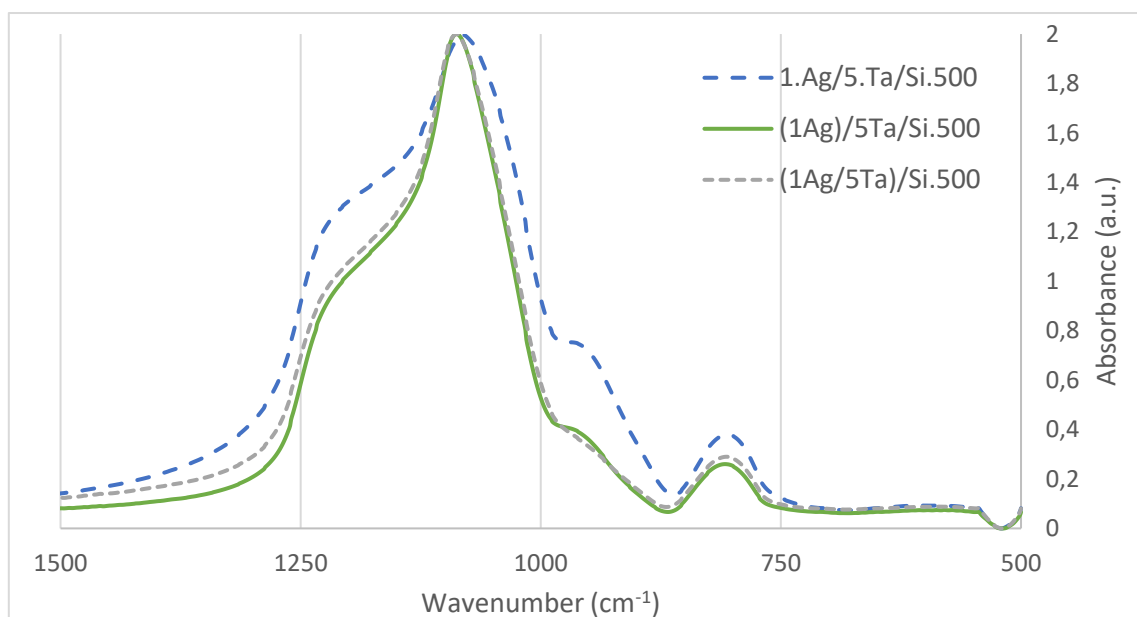


Figure 3.10: Impact of the incorporation of silver method on the infrared spectra.

It can be seen from Figure 3.10 that the 950 cm^{-1} band can be correlated to the presence of mixed oxide (Si-O-Ta bonds). Indeed, the band does not appear clearly for the sample where tantalum was impregnated, which is expected because by impregnation, the probability to form such mixed oxide bonds is lower than to form Ta_xO_y clusters at the surface of the catalyst. However, the band at 950 cm^{-1} is also lower for the silver impregnated sample (where Ta was incorporated by aerosol) than for the one-pot sample, which is surprising.

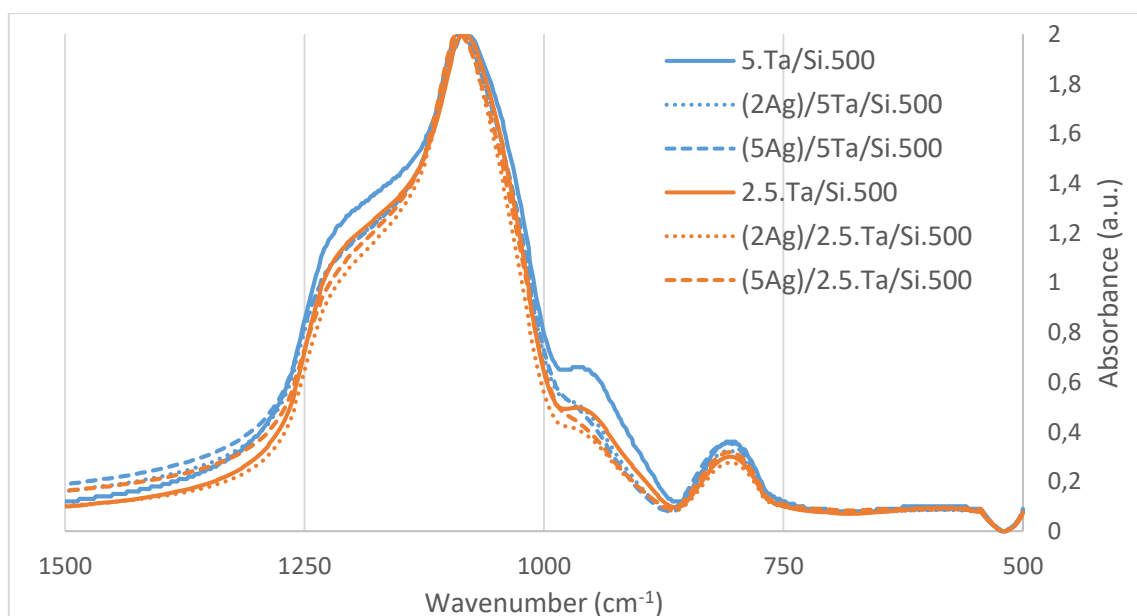


Figure 3.11: Impact of the silver loadings on the infrared spectra of silver impregnated samples.

The impregnation of different loadings of silver do not have any effect on the incorporation of tantalum into the silica matrix (Figure 3.11). However, it seems that the impregnation itself has an impact on it which is unlikely since the impregnation impacts only the surface of the material while IR spectroscopy is a bulk analysis.

O₂ chemisorption

Dispersion of silver particles on the surface of silver impregnated catalysts has been measured by oxygen pulse chemisorption to determine the impact of the silver loading on its dispersion (Table 3.11).

Table 3.11: Silver dispersion and average diameter of silver particle on the surface of catalyst with 2.5 wt. % of tantalum oxide.

Sample	Silver dispersion (%)	Average diameter (nm)
(2.Ag)/ 2.5.Ta₂O₅/ SiO₂.500	12	8.7
(5.Ag)/ 2.5.Ta₂O₅/ SiO₂.500	20	5.0

It appears that dispersion is improved with higher silver loading, forming smaller particles at the surface (Table 3.11). It can also be noticed that for samples with the same loadings, the dispersion is equivalent between silver impregnation and one-pot synthesis (Table 3.2).

NH₃ – TPD

Finally, to put in light a last time the differences brought by the different preparation processes, the availability of acid sites has been measured for the different methods. The influence of silver loadings was also investigated (Table 3.12).

Table 3.12: Total acidity and surface acidity of catalysts depending of the silver loadings and the incorporation method.

Sample	Acid sites (mmol/g)	Acid sites (mmol/m ²)
1.Ag/ 5.Ta/ SiO₂.500	0.064	1.4×10^{-4}
(1.Ag/5.Ta)/SiO₂.500	0.024	7.1×10^{-5}
(1.Ag)/5.Ta/SiO₂.500	0.061	2.0×10^{-4}
(2.Ag)/5.Ta/SiO₂.500	0.041	1.3×10^{-4}

The main observation from Table 3.12 is that incorporating Ta via one-pot AASG method results in the formation of approximately 3 time more acid sites as compared to the case when Ta is brought onto the support by impregnation.

Also, there are no big differences in the number of acid sites between one-pot and silver impregnated samples but the specific surface area being lower by impregnation, the number of acids sites per m^2 is therefore higher. The silver loading seems to have the same negative impact as for one-pot samples.

3.2 Catalytic results

3.2.1 Benchmarks

Before focusing on the performances of the one-pot and silver impregnated samples, the benchmarks must be set. A comparison between the catalytic results of samples with tantalum and silver impregnated on a silica support (commercial or spray-dried) has been done. The yields obtained for the different products is displayed on Figure 3.12 and 3.13, the summation or the individual yields, gives the total conversion of ethanol. It is important to note that the results obtained for (1.Ag/5.Ta)/SiO₂_aer.500 have been found at an early stage of the project with a different GC column than the rest of the samples (*Agilent DB-5ms Ultra Inert*) which was not able to quantify acetaldehyde nor ethanol. The acetaldehyde yield, and the ethanol conversion are therefore unavailable for this sample.

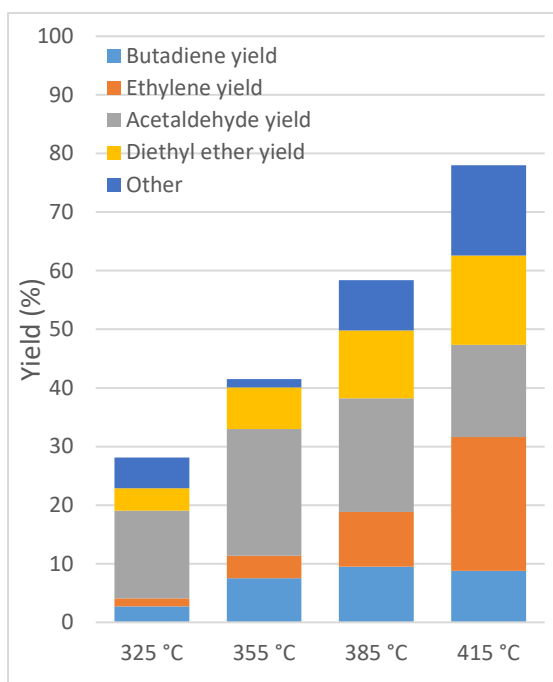


Figure 3.12: Products yields for (1.Ag/5.Ta)/Si_{com}.500; WHSV = 1.10 h⁻¹

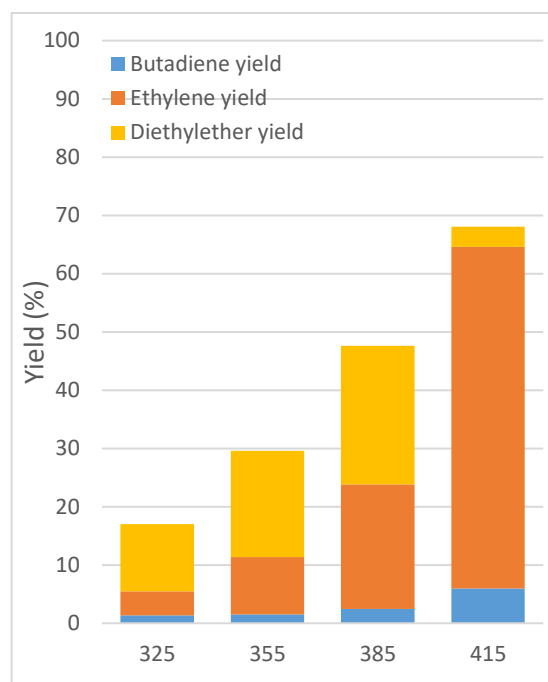


Figure 3.13: Products yields for (1.Ag/5.Ta)/Si_{aer}.500; WHSV = 1.10 h⁻¹

It appears that both catalysts are yielding butadiene, but the double impregnated on commercial silica is yielding more butadiene than the double impregnated on aerosol silica. Indeed, the butadiene yield of the first one is reaching 9.5 % at 385°C against only 2.5 % for the second. The maximum yield obtained with impregnation on aerosol silica was at 415°C, giving a butadiene of 5.2 %. Furthermore, the impregnated on aerosol silica sample is producing more ethylene and diethyl ether, meaning that the acid sites are more active in this sample than on the other one. However, a common point can be observed, both catalysts are yielding more ethylene when the temperature is increased. Also, from Figure 3.12, it can be seen that silver is active for the dehydrogenation of ethanol to acetaldehyde.

3.2.2 One-pot catalysts

The same effects as for the characterization have been investigated by catalytic tests for the catalysts synthesized by AASG in one-pot (calcination temperature, furnace and loading).

3.2.2.1 Calcination temperature

Very poor results were obtained for samples calcined at 600 and 700°C (butadiene yield of 0.23 % for the sample at 600°C and 0.65 % for the one calcined at 700°C, at 385°C). Although

the selectivity for the different products was comparable, the low conversion of ethanol with these two catalysts was the reason of the poor results.

The calcination temperature presenting the best catalytic performances (Butadiene yield of 2.0 %) with the 1.Ag/5.Ta/SiO₂ sample, 500°C, was chosen to continue the study.

3.2.2.2 Effect of the furnace

The catalyst with the formulation; 5.Ag/2.5.Ta/SiO₂, was calcined with the two different furnaces and then tested in the catalytic setup. The main observation that comes out of Figure 3.14 is that the sample calcined under flowing air produces butadiene with at a relatively high yield (17.5% at 355°C) whilst the other do not or barely (maximum yield of 1.3 % at 355°C).

Catalyst calcined under static produced more ethylene and less acetaldehyde than the catalyst calcined under flowing air. Also, it can be noticed that production of ethylene increased with the temperature for both sample, which is in line with the observation made with the benchmark catalysts. Finally, ethanol conversion was generally higher for the sample calcined in the flowing air furnace. The detailed results of these tests are available in Table 3.13. For the next steps of this project, only the flowing air furnace was used.

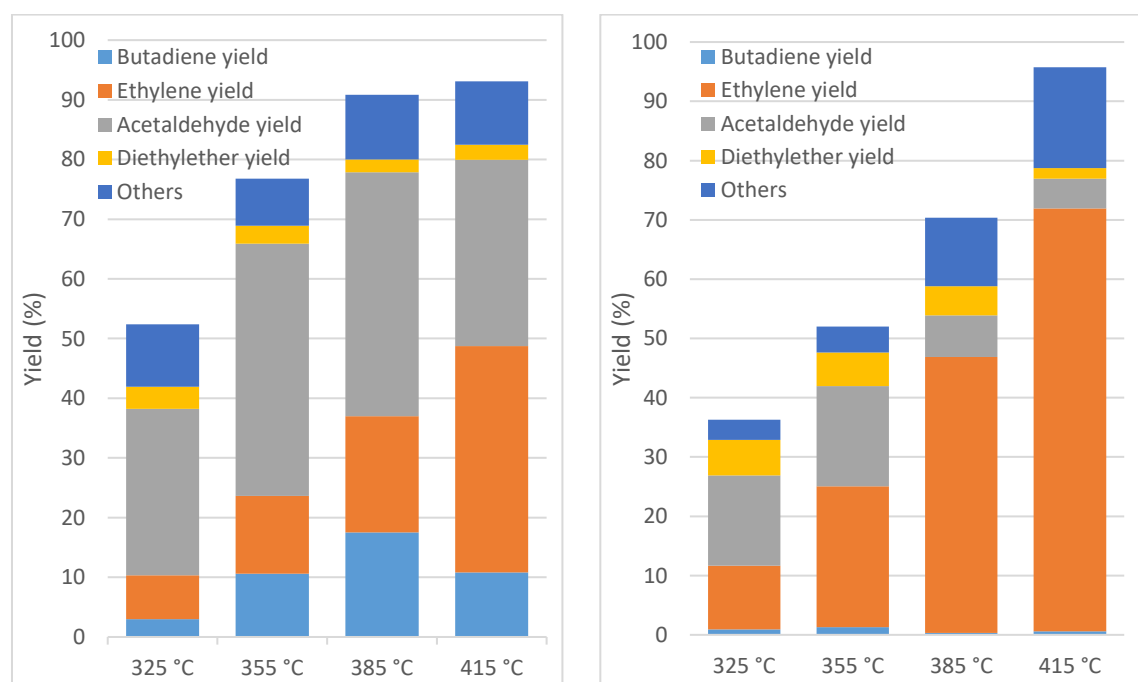


Figure 3.14: Comparison between the products yields obtain with 5.Ag/2.5.Ta/SiO₂.500, calcined under flowing air (left) or static air (right); WHSV = 1.10 h⁻¹.

Table 3.13: Detailed results for 5.Ag/2.5Ta/SiO₂.500, calcined in two different furnaces; WHSV = 1.10 h⁻¹.

Furnace	Temp. (°C)	Butadiene yield (%)	Ethylene yield (%)	Acetaldehyde yield (%)	Diethyl ether yield (%)	Others (%)
Flowing air	325	3.0	7.3	27.9	3.7	10.5
	355	10.6	13.1	42.2	3.0	7.9
	385	17.5	19.5	40.9	2.1	10.8
	415	10.8	37.9	31.2	2.5	10.6
Static air	325	0.9	10.8	15.3	6.0	3.4
	355	1.3	23.8	16.9	5.7	4.4
	385	0.3	46.6	7.0	4.9	11.6
	415	0.6	71.3	5.0	1.8	17.0

3.2.2.3 Effect of the loadings

Both the loadings of tantalum oxide and silver were screened for the samples prepared in one-step by AASG (Figure 3.15). Generally, the best butadiene yield was obtained at 385°C.

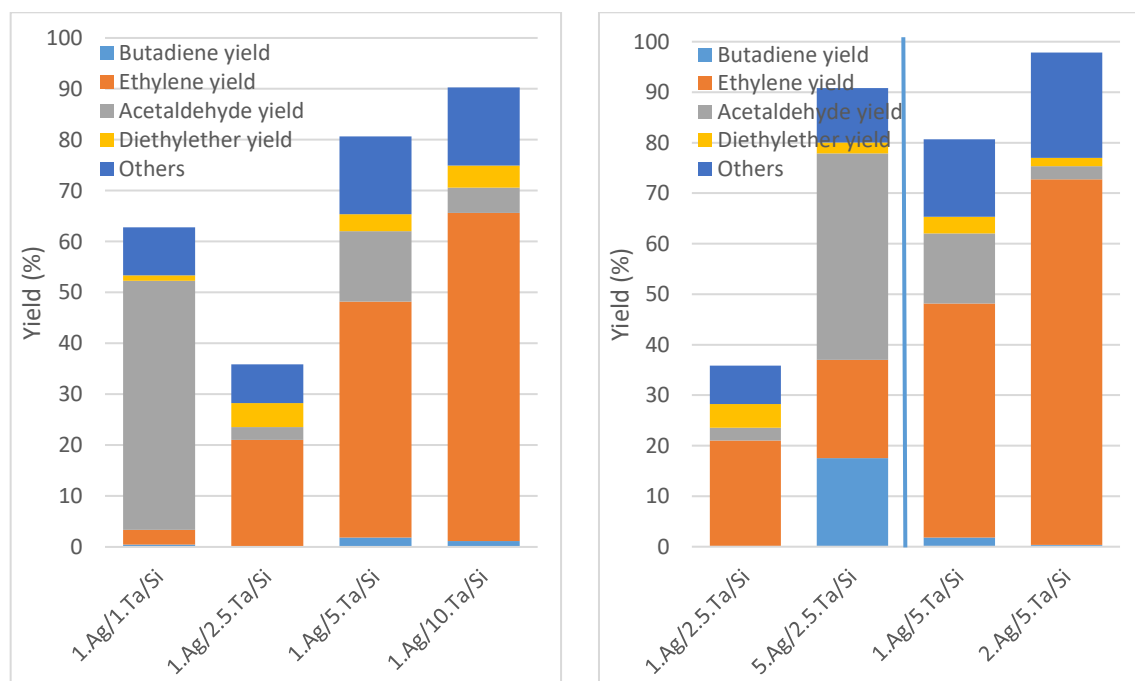


Figure 3.15: Evaluation of the impact of tantalum oxide (left) and silver (right) loadings of one-pot catalysts on the products yields; T = 385°C, WHSV = 1.10 h⁻¹. The blue line on the right separates catalysts with different Ta loadings.

Exception made for the 5.Ag/2.5.Ta/SiO₂ and 1.Ag/1.Ta/SiO₂ catalysts, every sample was yielding mostly ethylene, meaning too strongly acid properties or not enough redox properties brought by the silver particles. As expected, ethylene yield was increasing at higher tantalum oxide loadings. Redox properties were the most efficient when silver loading was either the same as tantalum oxide loading or higher. Ethanol conversion was optimized at high loadings of either silver or tantalum oxide. Detailed results about conversion and products yields are available in Table 3.14.

Table 3.14: Detailed catalytic results for one-pot catalysts calcined at 500°C; $T = 385^{\circ}\text{C}$, $\text{WHSV} = 1.10 \text{ h}^{-1}$.

Samples	Butadiene yield (%)	Ethylene yield (%)	Acetaldehyde yield (%)	Diethyl ether yield (%)	Others (%)
1.Ag/1.Ta/SiO ₂	0.4	2.9	48.9	1.1	9.4
1.Ag/2.5.Ta/SiO ₂	0.0	21.0	2.5	4.7	7.6
5.Ag/2.5.Ta/SiO ₂	17.5	19.5	40.9	2.1	10.8
1.Ag/5.Ta/SiO ₂	1.8	46.3	13.9	3.3	15.3
2.Ag/5.Ta/SiO ₂	0.4	72.3	2.7	1.6	20.9
1.Ag/10.Ta/SiO ₂	1.2	64.5	5.0	4.4	15.4
2.Ag/10.Ta/SiO ₂	1.0	71.4	2.7	1.4	22.2

3.2.3 Silver impregnated catalysts

Concerning silver impregnated catalyst, only a screening on the loadings was investigated, most of the silver impregnated samples have their equivalent catalyst, with the same loadings, in one-pot.

3.2.3.1 Effect of the loadings

Adding silver by impregnation should improve the redox properties of the catalysts since it is deposited entirely at the surface of the catalysts. The catalytic results confirm partially this hypothesis and the ones obtained at 385°C are displayed on Figure 3.16. As expected, the dehydrogenation of ethanol was more important when the silver loading was equal or higher than the tantalum oxide loading. In these cases, ethylene yields were much lower than for the other catalysts.

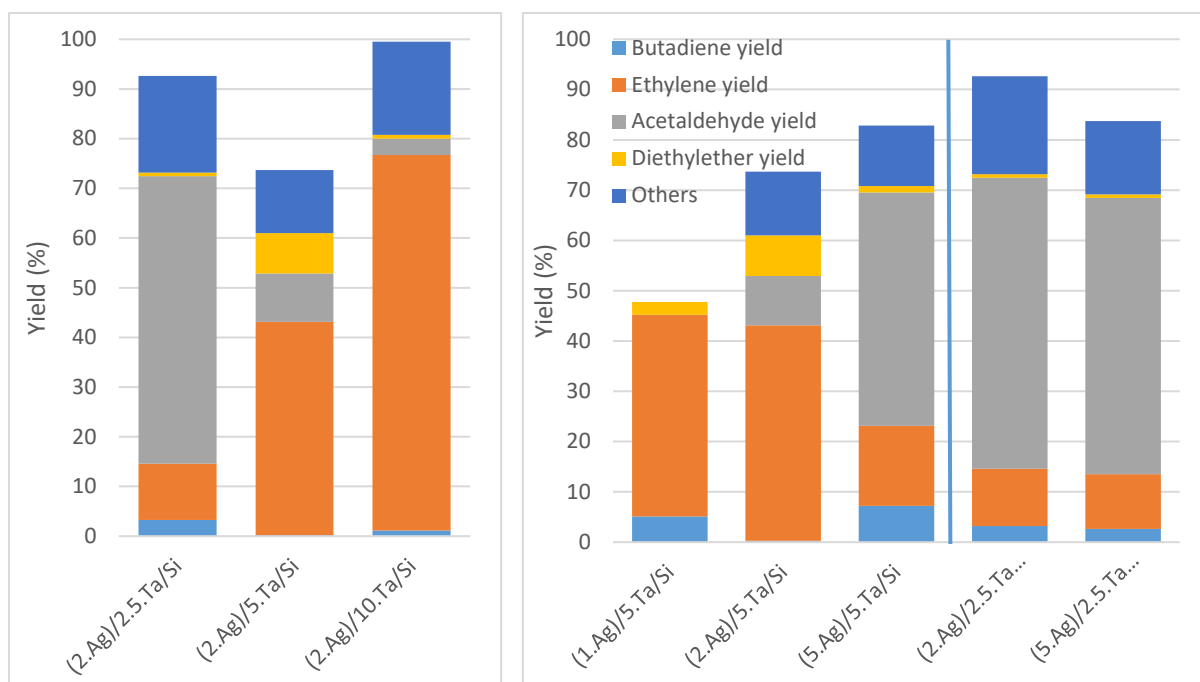


Figure 3.16: Evaluation of the impact of tantalum oxide (left) and silver (right) loadings of silver impregnated catalysts on the products yields; $T = 385^{\circ}\text{C}$, $\text{WHSV} = 1.10 \text{ h}^{-1}$. (Results for (1.Ag)/5.Ta/Si were obtained with Agilent DB – 5ms UI GC column, unable to quantify ethanol or acetaldehyde). The blue line on the right side of the figure separates catalysts with different tantalum loadings.

If the tantalum oxide loading was higher than the silver one, the products of the reaction was mainly ethylene. Nevertheless, an exception as to be made for (1.Ag)/5.Ta/SiO₂. Even if the acetaldehyde cannot be seen and ethylene yield reached 40 %, a noteworthy amount of butadiene was produced (yield = 5.1 %), at least higher than for the others catalyst with lower silver loading than tantalum oxide and higher than the yield reached with the corresponding one-pot catalyst. This means that redox properties were active for this sample.

The sample that reached the highest butadiene yield was (5.Ag)/5.Ta/SiO₂, obtaining a yield of 7.2 % of butadiene. The detailed data of the catalytic test of silver impregnated samples are available in Table 3.15.

Table 3.15: Detailed catalytic results for silver impregnated catalysts; $T = 385^{\circ}\text{C}$, $\text{WHSV} = 1.10 \text{ h}^{-1}$.

Samples	Butadiene yield (%)	Ethylene yield (%)	Acetaldehyde yield (%)	Diethyl ether yield (%)	Others (%)
(2.Ag)/2.5.Ta/SiO ₂	3.2	11.4	57.9	0.7	19.5
(5.Ag)/2.5.Ta/SiO ₂	2.6	10.9	54.9	0.7	14.6
(1.Ag)/5.Ta/SiO ₂	5.1	40.1	/	2.6	/
(2.Ag)/5.Ta/SiO ₂	0.3	42.9	9.8	8.1	12.7
(5.Ag)/5.Ta/SiO ₂	7.2	15.9	46.4	1.2	12.0
(2.Ag)/10.Ta/SiO ₂	1.2	75.6	3.2	0.8	18.7

3.3 Spent catalysts characterizations

Some representative one-pot samples were characterized again after catalytic test. They were analyzed again by N₂ physisorption, XRD and XPS. Furthermore, the catalyst that reached the best catalytic performance, 5.Ag/2.5.Ta/SiO₂.500, was tested again in the reactor after experiencing a new reducing treatment.

3.3.1 Textural analysis

The spent catalysts chosen to evaluate the evolution of the textural properties after catalysis were representative of the synthesized samples. Indeed, here again, silver and tantalum loadings are screened (Table 3.16).

Table 3.16: Textural properties of representative spent catalysts.

Spent samples	Specific surface area (m ² /g)	External surface area (m ² /g)	Avg. pore size (BET) (nm)	Pore volume (cm ³ /g)
5.Ta/ SiO₂.500	330	160	4.4	0.37
5.Ag/ 2.5.Ta/ SiO₂.500	320	180	4.7	0.38
1.Ag/ 5.Ta/ SiO₂.500	360	220	5.2	0.47
2.Ag/10.Ta/SiO₂.500	400	210	4.5	0.46

When comparing results of Table 3.16 with the ones of fresh catalysts in Table 3.7, some observations can be made. First, whilst the specific surface area decreases after catalytic test, the external surface area remains roughly stable, once again it means that the loss in surface area comes mainly from the loss of microporous surface area. Secondly, the average pore size increases after reaction, this could come from the fact that micropores have closed, shifting the size distribution towards higher diameter. Finally, the general decrease of pore volume could be attached to the same phenomenon.

3.3.2 XRD

The one-pot catalyst 5.Ag/2.5Ta/SiO₂.500 that was calcined by the two different types of furnace and already described by XRD on Figure 3.1 was analyzed again by XRD after catalytic test (Figure 3.17).

The peaks noticed on the fresh catalyst calcined under static air, corresponding to silver chloride have now shifted to match peaks corresponding to metallic silver (Figure 3.17).

Concerning the sample calcined under flowing air, the diffractogram is no longer the one of an amorphous material and is now displaying peaks matching to metallic silver as well (Figure 3.17). A possible reason of that change can be the sintering of the metallic silver particles during the reduction pretreatment and the following catalytic test.

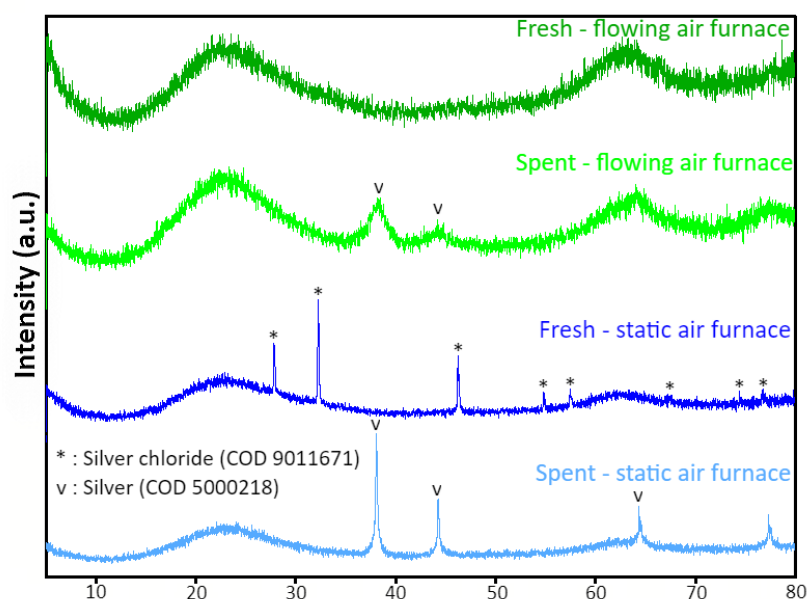


Figure 3.17: Comparison of Diffractograms between fresh and spent 5.Ag/2.5Ta/SiO₂.500 catalysts calcined under flowing air or static air.

3.3.3 XPS

The evolution of the properties at the surface were also monitored by XPS on 1.Ag/5.Ta/SiO₂.500 catalyst (Table 3.17).

Table 3.17: Comparison between 1.Ag/5.Ta/SiO₂.500 fresh and spent by XPS.

Sample	Si (2p) conc. (%)	Ta (4f) conc. (%)	Ag (3d) conc. (%)	Si/Ta mol. ratio	Si/Ag mol. ratio
1.Ag/5.Ta/SiO ₂ .500 fresh	16.064	0.257	0.282	62.5	57.0
1.Ag/5.Ta/SiO ₂ .500 spent	18.894	0.157	0.123	120.3	153.6

It can be observed from Table 3.17 that both amount of tantalum and silver have decreased during a catalytic test. By looking at the molar ration with silica, the tantalum amount has decreased by half whilst silver amount has been nearly divided by three.

This decline can have been caused by sintering of silver particles or sintering of the support.

3.3.4 Determination of catalytic deactivation source

An important remark that must be done concerning the catalytic tests is that the activity of most samples was not stable through time (Figure 3.18). The results displayed in the previous section were based on an average yield from 5 GC injections spread over one hour.

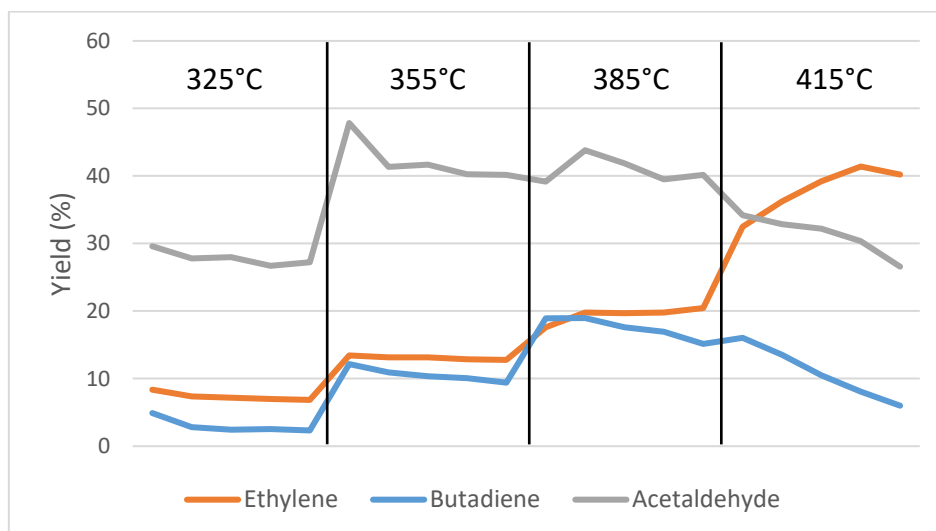


Figure 3.18: Evolution of the products yields through time for 5.Ag/2.5Ta/SiO₂.500

By looking at Figure 3.18, it appears that only ethylene yield was stable through time whilst butadiene yield followed the trend of acetaldehyde yield and decreased from one injection to another at a same temperature. The drop of dehydrogenation of ethanol to acetaldehyde is the consequence of the inactivation of the redox sites but on the other hand, acid sites seem to remain active since the dehydration of ethanol appears stable through time.

To explore if the source of deactivation of the catalysts could be a loss of activity of silver particles by oxidation, a spent catalyst (5.Ag/2.5Ta/SiO₂.500) was tested again in reaction conditions, after undergoing a new reducing treatment under hydrogen at 350°C for 1 hour (Figure 3.19). The complete results of these tests are available in Table 3.18.

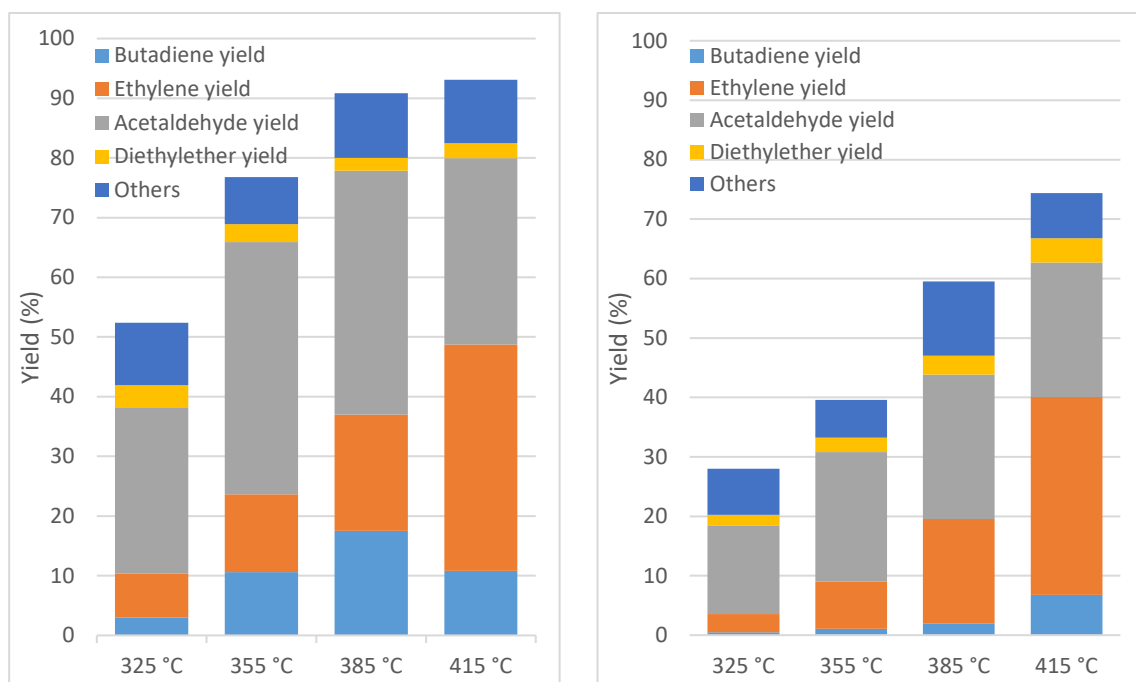


Figure 3.19: Comparison of catalytic activity between fresh (left) and spent (right) 5.Ag/2.5Ta/SiO₂.500 catalyst, calcined under flowing air; WHSV = 1.10

It appears from Figure 3.19 and Table 3.18 that every products yield has decreased for the spent catalyst. Butadiene yield is decreasing the most and is barely present except at the highest temperature. Acetaldehyde, the product of the reduction of ethanol, is divided by two for the two lowest temperature and by nearly 1.5 for the two-remaining temperature.

However, it can be observed that diethyl ether production remains stable even after catalytic test. A similar observation can be made about ethylene production. Although it decreased significantly at the lowest temperatures, it remains stable at 385 and 415°C. This observation implies that acid sites are still active at approximately the same level than for the fresh samples.

The consequence of these remarks is that deactivation comes indeed from a loss of activity of redox sites. However, the deactivation does not come from a possible oxidation of silver because the reducing treatment would have taken care of this problem. The source can be, as proposed with the XPS results (Table 3.17), the sintering of silver particles. Also, the source could be coking, produced by reaction at the acid sites and then that would have migrated on the catalyst.

Table 3.18: Detailed catalytic results of the comparison between fresh and spent 5.Ag/2.5Ta/SiO₂.500 catalysts; WHSV = 1.10 h⁻¹

	Temp. (°C)	Butadiene yield (%)	Ethylene yield (%)	Acetaldehyde yield (%)	Diethyl ether yield (%)	Others (%)
Fresh	325	3.0	7.3	27.9	3.7	10.5
	355	10.6	13.1	42.2	3.0	7.9
	385	17.5	19.5	40.9	2.1	10.8
	415	10.8	37.9	31.2	2.5	10.6
Spent	325	0.5	3.1	14.9	1.8	7.7
	355	1.1	9.0	21.7	2.4	6.3
	385	2.0	17.5	24.3	3.2	12.5
	415	6.8	33.3	22.7	4.1	7.6

IV. Discussion

From the results, several conclusions and answers to our hypothesis can be drawn for the different effects studied in this thesis.

4.1 Effect of the furnace

From the results comparing the two furnaces, it clearly appears that the furnace used impacts the silver particles. Also, noticing that no textural differences can be exposed between the two kinds of calcination, it can be established that there were no temperature differences.

The diffractograms from Figure 3.1 indicates that the sample calcined under static air contains AgCl. Therefore, one might think that this furnace brought some chlorine contamination, from a deposit on the walls, from a previous calcination of samples containing chlorine. However, XPS analysis indicates that there is a contamination by chlorine in both samples (Table 3.3), at the same scale, in a very small quantity. Since chlorine was not used at any moment during the synthesis, the reason of its presence remains unfortunately unclear at this moment. The formation of AgCl crystals on one sample rather than both is still a remaining question mark at the end of this study.

Concerning the difference in silver dispersion, exposed by O₂ chemisorption in Table 3.2, it is probably a consequence of the formation of silver chloride crystals on the sample calcined under static air. Nevertheless, XPS analysis exposed also that the calcination under flowing air improved the migration of silver towards the surface, the formation of AgCl crystals cannot be held responsible alone of the dispersion difference.

Regarding the catalytic performances, the determining difference explaining why a sample did produce butadiene whilst the other did not, relies also on the availability of silver particles to express their redox properties. Indeed, it can be noticed from the products yield graph (Figure 3.14) that when butadiene was produced in significant quantity, the production of acetaldehyde, and so the reduction of ethanol, was also higher. It can be thought then that the dispersion of silver did indeed play a key role in the conversion of ethanol into butadiene.

Yet, XRD on spent catalysts shows that silver chloride was reduced to silver after catalytic test (Table 3.17). If it was reduced, silver should have been active to perform the reduction of

ethanol and this explain why the sample did produce some acetaldehyde. However, the size of the peaks on the diffractogram highlights also the poor silver dispersion. It means that silver formed large particles, making the silver not accessible enough to yield butadiene.

Considering all those results, the calcination under flowing air was undeniably more effective than under static air. Therefore, the tubular furnace was used for the remaining of the calcinations.

4.2 Effect of the calcination temperature

The purpose of studying different calcination temperature was to find the optimal thermal treatment that would provoke the migration of silver towards the surface while limiting the sintering of the silver particles and keeping a high specific surface area.

Logically, the lowest temperature (500°C) is showing the highest specific surface area (Table 3.4). Fortunately, this temperature is also showing the highest amount of silver at the surface from the XPS measurement (Table 3.5). These results confirmed our assumptions about silver migration and that 500°C is already enough to optimize it. At higher temperature, sintering took over the migration, causing a drop in the amount of silver quantified by XPS. The dilemma was therefore no longer present, since 500°C answered all the requirements needed. This calcination temperature was then used for every one-pot synthesized sample and for every support.

4.3 Comparison one-pot catalysts and silver impregnated catalysts

It has been demonstrated through this thesis that preparation method influenced markedly the activity and properties of the samples. Depending on the tantalum incorporation or the method of addition of silver, features and performances varied.

Concerning the tantalum incorporation, it has been seen from the results that spray-dried tantalum-silica mixed oxide is more acidic than tantalum oxide deposited at the surface of silica (Table 3.12). In fact, the number of acid sites is multiplied by approximately 2.6 when the Tantalum is spray-dried with silica rather than impregnated. This is certainly due to its better incorporation inside the silica matrix, confirmed by infrared (Figure 3.10), resulting in the availability of acid sites as single sites at the surface rather than deposited larger clusters of Ta oxide. This is validated by looking at the XPS data (Table 3.10) and comparing it to the

NH₃ – TPD data mentioned above, even if tantalum is present in a higher concentration at the surface of the catalysts by impregnation, they are less acidic, meaning that the dispersion is poorer and/or that mixed oxide Si-O-Ta is more acid than Ta₂O₅.

The catalytic results of double impregnation on a commercial silica or on aerosol silica are in line with the characterization, showing a lower ethylene production. Also, diethyl ether production is higher for those samples, meaning that dehydration properties are weaker and cannot go until the ethylene.

Regarding the silver incorporation, one-pot aerosol synthesis allows to obtain an equivalent dispersion as the impregnation (Table 3.2 and 3.11). Nevertheless, by looking at the XPS data (Table 3.10), as expected there is much less silver at the surface in a one-pot sample than in an impregnated one. It means that aerosol synthesis manages to obtain an equivalent dispersion with less silver at the surface so with smaller nanoparticles.

Although a homogeneous dispersion of nanoparticles is important, the amount of silver must be sufficient so that the rate of dehydrogenation matches the high dehydration rate obtained thanks to the highly homogeneous dispersion of Ta. Indeed, as the catalytic tests results suggest, the acid sites are still taking the advantage on the redox sites even with a good dispersion and as soon as the silver dispersion is not high enough, the butadiene production drops and the ethylene yield increases.

Finally, focusing on the textural properties, the objectives are reached with success whether for one-pot aerosol catalysts or for silver impregnated on aerosol tantalum oxide-silica support. First, the specific surface area is greater than the one that can be obtained by double impregnation on commercial silica (Table 3.7 and 3.9). The average pore size is between 4 and 5.5 nm with a narrow size distribution (Figure 3.2 and 3.6). As expected, every material is mesoporous as the isotherm plot suggests (Figure 3.6 and 3.7). Secondly, the XRD confirms that silver, even impregnated, does not aggregate to form large clusters at the surface (Figure 3.8).

4.4 Effect of the loadings

No matter the synthesis method, it seems by looking at all the results that silver loading and tantalum oxide loading have, respectively, precise and rather stable effects on the properties of the catalysts. Silver impregnation on aerosol-made support and one-pot AASG synthesis will then be considered together to establish what would be the perfect balance between redox and acid sites to optimize the production of butadiene.

First, from results displayed in Figure 3.15 and 3.16, it is clear and that ethylene production, and so dehydration by acid sites, depend directly on tantalum oxide loadings. However, butadiene yield does not follow the same trend and does not improve at higher tantalum oxide loading. As a result of this observation, it seems that low tantalum oxide loadings, especially 2.5 wt. %, are preferable to draw the reaction towards butadiene. This is likely the consequence of the incorporation of tantalum into the silica matrix and doing so, its effective dispersion at the surface as single sites.

Secondly, it became already evident when studying the furnace effect that silver dispersion is determining to improve the conversion and butadiene yield. In addition to a good dispersion, enough redox sites are needed. From Figure 3.15 and 3.16, it appears that butadiene production is enhanced at higher silver loadings. Indeed, butadiene yield is strongly related to the dehydrogenation of ethanol to acetaldehyde. To allow the expression of the redox activity, the silver active sites must be enough to overcome the acidity brought by the Ta-Si mixed oxide. In that scope, it appears that silver loadings must be equal or higher the tantalum oxide loadings (in wt. %), as it was for the best sample synthesized in one pot which contained 5 wt. of silver against 2.5 wt. % of tantalum oxide and yielded 17.5 % of butadiene. This assumption is also supported by the results obtained with the best silver impregnated sample, which contained 5 wt.% Ag and 5 wt. % Ta₂O₅ and reached a butadiene yield of 7.2 %.

V. Conclusion

5.1 General conclusion

The aim of this master thesis was to synthesize performant catalyst by aerosol-assisted sol-gel process to produce butadiene from ethanol. The reaction mechanism needs both acid and redox sites to take place and these were brought respectively by tantalum oxide and silver. The method was supposed to give highly dispersed Ag-TaO_x-SiO₂ catalysts, mesoporous, with a homogeneity of the oxides in the matrix. These ternary catalysts were compared to samples prepared by dry-impregnation on commercial silica or on aerosol-made supports. The impregnated aerosol-made supports were composed of either only silica or TaO_x-SiO₂ mixed oxide, where obviously only silver was impregnated.

At the end of this thesis, it can be confirmed that aerosol-assisted sol-gel process allows to obtain mesoporous materials with high specific surface area. The addition in one-pot of active metal or oxides does not impact significantly the textural properties. Although, the dry impregnation of those active phase on aerosol-made supports influences these properties, it is counterbalanced by the features brought by the aerosol synthesized support.

The main difference between one-pot aerosol synthesis and dry impregnation was the dispersion of active sites. Aerosol-assisted sol-gel method gave materials with acids sites homogeneously dispersed in the silica matrix, available as single sites and redox sites finely dispersed as nanoparticles at the surface of the supports. On the other hand, dry impregnation gave materials where the active sites were more conducive to sintering and the formation of large clusters but still, with a satisfying dispersion of silver.

Heat treatment was also studied, to find out which calcination temperature was optimal to force silver to migrate towards the surface of the materials while minimizing sintering when it was incorporated in one-pot. Three different calcination temperatures were applied on the catalyst, to find a compromise between good textural properties and high silver dispersion. 500°C presented the most promising results with both better textural properties and the higher silver dispersion at the surface. Two different types of calcination furnaces were investigated too, either with static air or with flowing air. The flowing air furnace have displayed a better capacity to force silver to migrate towards the surface.

The catalytic performances were evaluated for the one-step transformation of ethanol to butadiene. Several reaction temperatures were investigated between 325°C and 415°C and the loadings of the active species of the catalysts were screened. The best result was obtained with a one-pot aerosol catalyst, with a composition containing 5 wt. % Ag and 2.5 wt. % Ta₂O₅ at 385°C, achieving a butadiene yield of 17.5 %.

Finally, spent catalysts analysis have showed that textural properties remained stable but as suggested by XRD analysis, silver nanoparticles sintered at the surface of the catalysts.

As a conclusion, aerosol-assisted sol-gel process have met the expectations concerning textural properties but still some parameters concerning the active species and the catalytic tests can be improved.

5.2 Perspectives

In the case of future studies on the same subject, different features can be enhanced or investigated to improve the performances of the catalysts.

Concerning the synthesis, a further investigation of composition with low loadings of tantalum oxide seems to be more promising since AASG catalysts shows a high dispersion of acid sites that takes over the activity of the redox sites.

Another templating agent than Pluronic F127 can be studied, to find out if greater pore size can be preferable to improve the conversion towards butadiene, as studied by Kim et al. (20).

Also, other transition metals as redox sites can be investigated. Indeed, Kyriienko et al. achieved higher butadiene yield using copper instead of silver (23).

On the other hand, reaction parameters can also be improved, especially the space velocity. A longer contact time between the catalyst and the reactants could increase the conversion and draw the selectivity towards butadiene. This assumption is based on the results of Sushkevich et al. and Kyriienko et al., who achieved their best results at a WHSV of respectively, 0.31 h⁻¹ and 0.5 h⁻¹ (15,23).

Finally, to go deeper in this same study, the regeneration and long-time reactions can be further explored

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Preparation of bifunctional catalysts by aerosol-assisted sol-gel process for butadiene synthesis

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Abstract

For several years, butadiene production is experiencing a decrease and an urge to find a solution has risen. Ethanol conversion to butadiene is a sustainable alternative to petrol-based processes, which is in line with the current trend to find ecological solutions to produce polymers. Because of the mechanism, catalysts to enhance this reaction need to be bifunctional and to present features both acidic and redox. This master thesis has explored if peculiar textural properties, brought by an innovative synthesis process, such as aerosol-assisted sol-gel, would create catalysts with high performances. To position the results with more typical preparation method, benchmarks catalysts synthesized by dry impregnation on commercial or aerosol-made supports, have been studied too.

In that scope, Ag-TaO_x-SiO₂ ternary catalysts have been synthesized. Mesoporous ternary catalyst or binary TaO_x-SiO₂ supports have been prepared by aerosol-assisted sol-gel process (AASG). On the other hand, silver was either incorporated in one-pot or by dry impregnation. Different effects on the catalysts have been investigated; two different calcination furnaces (under static air or flowing air), three calcination temperatures (500°C, 600°C and 700°C) and a screening on the loadings. The catalysts have been characterized by N₂ physisorption, O₂ chemisorption, NH₃-TPD, XRD, XPS and infrared spectroscopy. The catalysts were then tested, after in-situ reduction, between 325°C and 415°C, to assess of their performances in the Lebedev one-step process.

From the results, it appears that calcination temperature influences the migration of silver from the bulk towards the surface and 500°C brought the best silver dispersion at the surface of the materials. Higher temperatures favored more sintering. Calcination under air highlighted itself by the ability to improve the migration of silver nanoparticles towards the surface. AASG catalysts presented a high tantalum oxide dispersion, acid sites were taking over the redox sites. Best results were then obtained with rather low tantalum oxide loading. AASG catalysts displayed an equivalent dispersion to silver impregnated sample for the same silver loading but with less silver at the surface since all of it did not migrate from the bulk. Best results were achieved with 5 wt. % Ag.

This work presents the advantages of the aerosol-assisted sol-gel process and the potential of the method.

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