

Article

Ag- and Cu-Promoted Mesoporous Ta-SiO₂ Catalysts Prepared by Non-Hydrolytic Sol-Gel for the Conversion of Ethanol to Butadiene

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Abstract: The direct catalytic conversion of bioethanol to butadiene, also known as the Lebedev process, is one of the most promising solution to replace the petro-based production of this important bulk chemical. Considering the intricate reaction mechanism—where a combination of acid-catalyzed dehydration reactions and metal-catalyzed dehydrogenation have to take place simultaneously—tailor-made bifunctional catalysts are required. We propose to use non-hydrolytic sol-gel (NHSG) chemistry to prepare mesoporous Ta-SiO₂ materials which are further promoted by Ag via impregnation. An acetamide elimination route is presented, starting from silicon tetraacetate and pentakis(dimethylamido)tantalum(V), in the presence of a Pluronic surfactant. The catalysts display advantageous texture, with specific surface area in the 600–1000 m² g^{−1} range, large pore volume (0.6–1.0 mL g^{−1}), an average pore diameter of 4 nm and only a small contribution from micropores. Using an array of characterization techniques, we show that NHSG allows achieving a high degree of dispersion of tantalum, mainly incorporated as single sites in the silica matrix. The presence of these monomeric TaO_x active sites is responsible for the much higher dehydration ability, as compared to the corresponding catalyst prepared by impregnation of Ta onto a pristine silica support. We attempt to optimize the butadiene yield by changing the relative proportion of Ta and Ag and by tuning the space velocity. We also demonstrate that Ag or Cu can be introduced directly in one step, during the NHSG process. Copper doping is shown to be much more efficient than silver doping to guide the reaction towards the production of butadiene.

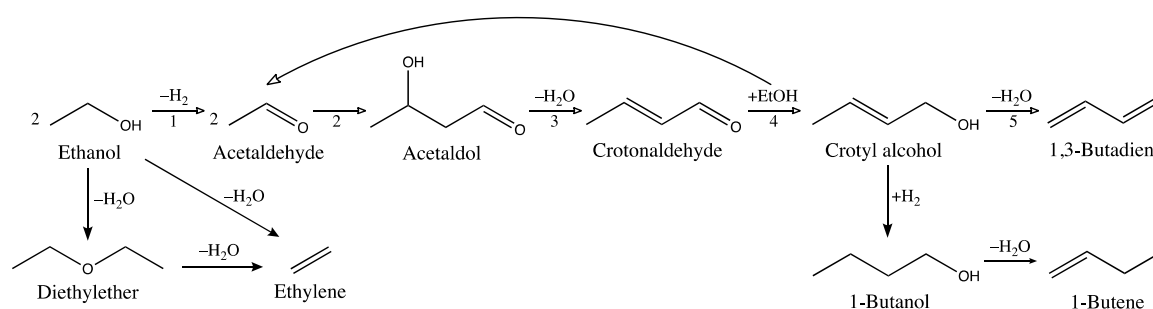
Keywords: Mesoporous metallosilicate; tantalum oxide; bioethanol; bifunctional catalysts; dehydration; dehydrogenation

1. Introduction

1,3-butadiene (BD) is one of the main monomers used in polymer production, mainly for styrene-butadiene rubber and polybutadiene [1,2]. Industrially, the steam cracking of naphta represents a vast majority (ca. 95%) of the butadiene production, as a by-product of ethylene manufacturing [1–4]. The global production of butadiene is rising steadily, and is currently sat at around 12,000 kT, as of 2015 [1]. Currently, however, butadiene supply tends to decrease with the advent of lighter feedstocks exploitation like shale gas [1]. It should also be mentioned that steam cracking is responsible for 8% of the global energy consumption and for the release of 180–200 million tons of CO₂ worldwide [1,5]. Thus, there is a striking tension on the butadiene market and an urgent need for a more sustainable alternative for the production of butadiene.

Bio-based processes as alternatives to petroleum-based production processes are under intense research in the last years [1,6–9]. A wide range of raw biomass streams can be upgraded, for example, by biotechnological processes towards bioethanol. The global production of bioethanol reached 120 billion liters in 2017 and is expected to reach 130 billion liters by 2024 [1]. Being recognized as a major platform chemical for the future bio-based chemical industry [10], bioethanol has a broad scope of applications [6,7]. In particular, the catalytic conversion of ethanol to butadiene is currently attracting great attention [1–3,11–13].

While it is long known that butadiene can be obtained from ethanol [14,15], an intense research effort is currently being paid to understand the working behavior of bifunctional catalysts being able to catalyze this reaction. In fact, two processes are known to convert ethanol into butadiene: The Lebedev process (i.e., the direct conversion of ethanol to butadiene with one catalyst in one reactor), and the Ostromislensky process (i.e., the conversion of a mixture ethanol/acetaldehyde to butadiene, where acetaldehyde is produced in a separate step; two distinct reactors with two different catalyst) [1,3,16,17]. The Lebedev process is considered more attractive on an environmental and economic point of view [1]. The so-called “Kagan mechanism” is generally reported as the most likely reaction pathway for the ethanol to butadiene (ETB) reaction when considering acidic catalysts [3,17,18]. Scheme 1 shows the complete pathway to obtain butadiene directly from ethanol: The reaction involves an intricate network of dehydrogenation, hydrogen transfer and dehydration steps [17]. This complex mechanism shows the importance of having a multifunctional catalyst possessing correctly balanced redox and acid/base properties to reach high butadiene yield, so as to restrain the formation of by-products, such as ethylene, diethylether and unconverted acetaldehyde [18]. In practice, bi-functional catalysts featuring acid sites for dehydration and metallic nanoparticles for dehydrogenation are needed to complete the direct conversion of ethanol to butadiene.



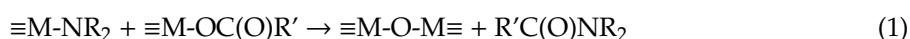
Scheme 1. Kagan mechanism for the direct conversion of ethanol to butadiene in the Lebedev process [17]: (1) Non-oxidative dehydrogenation of ethanol (EtOH) to acetaldehyde (AA); (2) condensation of two AA molecules into 3-hydroxybutanal (acetaldol); (3) acetaldol dehydration to crotonaldehyde; (4) production of crotyl alcohol and AA after a Meerwein-Ponndorf-Verley (MPV) reduction involving ethanol; (5) dehydration of crotyl alcohol to butadiene [17].

The literature describes supported catalysts, such as $\text{ZrO}_2/\text{SiO}_2$ or $\text{Ta}_2\text{O}_5/\text{SiO}_2$, promoted with metals like Ag, Co, Cu, Fe or Zn as typical formulations for the Lebedev process [3,13,15,19–21]. In most cases, wet impregnation is used to incorporate the active elements onto a preformed support (e.g., silica). However, such preparation methods show some limitations, especially in terms of control on the speciation of the metal oxide and on the dispersion of metal nanoparticles [13,19]. Therefore, more advanced preparation techniques have also been proposed, in a search for improved performance. Recently, for example, Ta-based zeolites (Ta-SiBEA) promoted with Ag, Cu or Zn were reported to display high butadiene selectivity, owing to the presence of isolated Ta(V) species which give acidic properties to the catalyst [16,22]. This shows the importance of controlling the type of active sites during the synthesis process to obtain the required acidity.

Sol-gel processes have emerged as promising routes for the preparation of advanced heterogeneous catalysts [23,24]. In classical sol-gel methods, molecular precursors undergo hydrolysis and inorganic

polycondensation reactions to form, in a bottom-up fashion, a solid material with the desired properties. Importantly, wide ranges of composition can be envisaged, and the texture of the solid can be fine-tuned, for example, by using appropriate sacrificial templating agents. Nevertheless, classical hydrolytic sol-gel chemistry routes face two limitations: (i) Markedly different reactivity of different precursors often leads to inhomogeneous solids and (ii) water elimination during drying tends to cause pore collapse, due to high surface tension. One possible solution to avoid these issues is to work in non-aqueous conditions where oxo bridges are formed with the help of oxygen donors other than water [25–30]. In these “non-hydrolytic sol-gel” (NHSG) routes, the reactivity of different precursors tends to be levelled off, leading to highly homogeneous metallosilicate materials. Also, working in organic solvents with low surface tension prevents the pores collapse during drying, which leads to highly porous materials [25,30]. NHSG routes were reported to lead to various types of metallosilicate catalysts showing high performance in many different fields of applications, including olefin metathesis [31,32], olefin epoxidation [33,34], mild oxidation of sulphur compounds [35], aminolysis [27,36], aniline photocatalytic degradation [37], etc. To the best of our knowledge, Ta oxide-based materials prepared by NHSG have never been reported in the literature.

In this work, we use the non-hydrolytic acetamide elimination route (Equation (1)) [30] to obtain highly homogeneous and mesoporous Ta-silicate materials. The incorporation of tantalum into the silica matrix is described using X-ray photoelectron spectroscopy (XPS), infrared and diffuse reflectance UV spectroscopies. We use NH₃-TPD to quantify the acid sites in the catalysts. The new catalysts are systematically compared to a catalyst that was prepared by simple wet impregnation of tantalum ethoxide on a silica support also prepared by NHSG. Ta-based materials were impregnated with silver in order to obtain a bifunctional catalyst also exhibiting redox properties. The catalysts are tested in the ethanol to 1,3-butadiene reaction. Several effects influencing butadiene yield are discussed: (i) The degree of Ta incorporation into the silica matrix, (ii) the effect of Ta and Ag loadings and ratio, and (iii) the effect of contact time. By doing so, we identify the key parameters that dictate catalyst performance, and we propose guidelines for the preparation of more efficient catalysts. Finally, we propose a one-step NHSG method that allows to incorporate both Ta and Ag in the gel. We also show that replacing Ag by Cu leads to a much more active catalyst.



2. Results

2.1. Incorporation of Ta in the Silica Matrix and Impact on Catalysis

In this section, a catalyst obtained by direct incorporation of Ta into the silica matrix via NHSG followed by Ag impregnation (4TaSi_{NHSG}-2Ag) will be described in detail and compared to the corresponding catalyst obtained by the simultaneous impregnation of Ta and Ag (4Ta_{IMP}Si-2Ag). First, the textural properties are described, then tantalum dispersion in the materials is studied using ICP, XPS, IR and DRUV studies, and finally, these properties are confronted with the performance of both samples in the ethanol to butadiene reaction.

The binary metallosilicate was prepared by the NHSG acetamide route, starting from silicon tetraacetate and pentakis(dimethylamido)tantalum(V), in dichloromethane and in the presence of F127 (see details in the Experimental section). The catalyst is mainly mesoporous (type IV isotherms), with an evident hysteresis loop in the N₂-physisorption isotherms (Figure 1). It shows a specific surface area (SSA) close to 1000 m² g^{−1}, a high pore volume (0.96 mL g^{−1}, of which a large part is attributed to mesopores and only a small fraction arises from micropores) and an average pore size diameter of 3.9 nm (Table 1). The pristine silica synthesized by NHSG (Si_{NHSG}) has a lower SSA, possibly due to a smaller amount of Lewis species catalyzing the polycondensation reactions. This may result in lower levels of linking between silica chains, and thus, poorer texture. Upon subsequent impregnation of Ag (4TaSi_{NHSG}-2Ag), the catalyst tends to lose a fraction of both specific surface area (SSA, −30%) and pore volume (−32%), but remains mesoporous and maintains the same average pore size (indicating a

partial pore plugging). When the pristine Si_{NHSG} materials prepared by the NHSG acetamide route is simultaneously impregnated with Ta and Ag, a similar drop in SSA and pore volume is observed, and the average pore size diameter is also maintained at 4 nm. All in all, both bifunctional catalysts ($4\text{Ta}_{\text{IMP}}\text{Si}-2\text{Ag}$ and $4\text{TaSi}_{\text{NHSG}}-2\text{Ag}$) present a very similar texture.

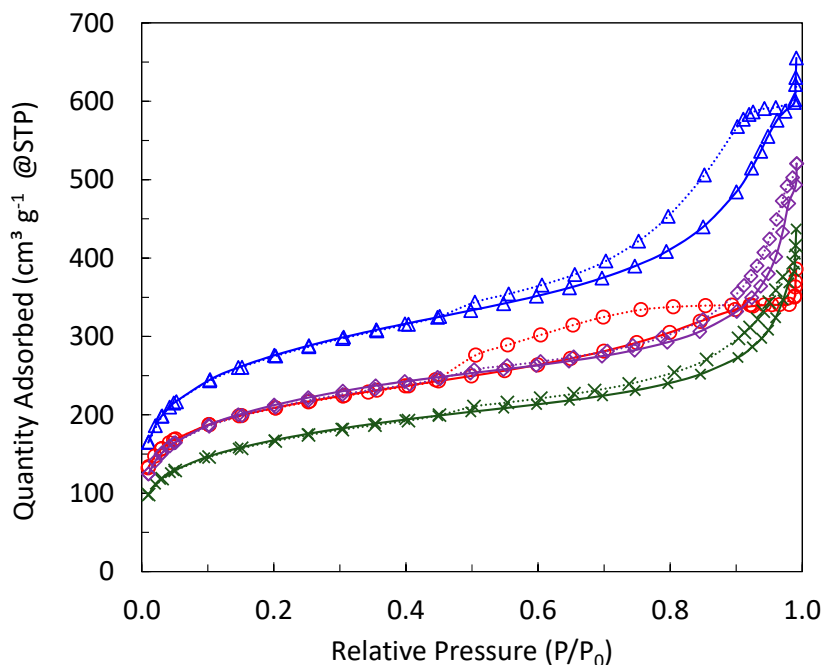


Figure 1. N_2 -physisorption isotherms of $4\text{TaSi}_{\text{NHSG}}$ (Δ), $4\text{TaSi}_{\text{NHSG}}-2\text{Ag}$ ($\circ$), Si_{NHSG} ($\diamond$), and $4\text{Ta}_{\text{IMP}}\text{Si}-2\text{Ag}$ ($\times$). Adsorption isotherms are plotted as solid lines, desorption isotherms are plotted as dotted lines. NHSG, non-hydrolytic sol-gel.

Table 1. Textural properties (N_2 -physisorption) and analysis of composition (ICP-OES), surface composition (XPS) and surface acidity (NH_3 -TPD) for the catalysts prepared with a 4 wt.% Ta loading either by NHSG or dry impregnation (IMP).

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p (mL g^{-1}) ^a	V_μ (mL g^{-1}) ^b	D_p (nm) ^c	% Ta (w/w) ^d	% Ag (w/w) ^d	Surface Si/Ta ^e	Acid Sites (mmol g^{-1}) ^f
$4\text{TaSi}_{\text{NHSG}}^g$	990	0.96	0.17	3.9	4.3	-	65	n.m.
$4\text{TaSi}_{\text{NHSG}}-2\text{Ag}$	690	0.65	0.11	3.8	4.8	1.7	61	$3.7 \cdot 10^{-2}$
Si_{NHSG}	760	0.76	0.13	4.0	-	-	-	n.m.
$4\text{Ta}_{\text{IMP}}\text{Si}-2\text{Ag}$	600	0.59	0.09	4.0	4.1	1.6	34	$1.5 \cdot 10^{-2}$

^a Pore volume at $P/P_0 = 0.98$; ^b via the t -Plot; ^c Calculated as $4V_p/S_{\text{BET}}$ (the mesopore size distribution shows the presence of large mesopores in the 10–20 nm range (Supplementary Material, Figures S1 and S2); ^d Determined by ICP; ^e Determined by XPS; ^f Determined by NH_3 -TPD (see thermograms in Figure S3); ^g if the same formulation is prepared in the absence of F127, a microporous mixed oxide is obtained with $V_p = V_\mu = 0.22 \text{ mL g}^{-1}$. Thus, for the synthesis with the acetamide route, the use of a texturing agent is mandatory to obtain a mesoporous sample [26].

For all catalysts, the experimental composition (ICP-OES) matched the nominal values closely (Table 1), showing that both the non-hydrolytic sol-gel and the impregnation steps were done with good control over composition.

To further assess the active sites dispersion, the molar surface composition was measured by XPS, and the Si/Ta ratio was calculated (Table 1). For the catalysts where the tantalum was incorporated through non-hydrolytic sol-gel ($4\text{TaSi}_{\text{NHSG}}$ and $4\text{TaSi}_{\text{NHSG}}-2\text{Ag}$), the experimental Si/Ta molar ratio was very close to the nominal value (60). This suggests a homogeneous dispersion of Ta throughout the metallosilicate materials, without preferential enrichment of the bulk or the surface. When tantalum

was incorporated by impregnation ($4\text{Ta}_{\text{IMP}}\text{Si-2Ag}$), the Si/Ta molar ratio reached 34 only, expectedly indicating a higher amount of tantalum on the surface.

The peak corresponding to the Si 2p orbital always has the expected position at 103.4 eV, which corresponds the expected position for SiO_2 [38,39]. The binding energies (BE) of the Ta $4f_{7/2}$ orbital falls around 26.9 eV for $4\text{Ta}_{\text{IMP}}\text{Si-2Ag}$, very close to the position found for pure Ta_2O_5 [40,41]. On the contrary, for catalysts where tantalum was incorporated by NHSG, a 0.3–0.4 eV shift was consistently observed (Figure 2). This shift can be explained by the difference in electronegativity between Si and Ta [39,42]: When incorporated into a silica matrix, Ta atoms have a lower electron density, and therefore, electrons have a higher BE. A similar effect was reported in the case of Ti incorporated in silica [43], or with V incorporated into titania [44]. Such significant shift in BE can be taken as a further indication of the dispersion of Ta into the silica matrix in the case of NHSG catalysts, as opposed to the case where Ta is brought to the support surface by impregnation.

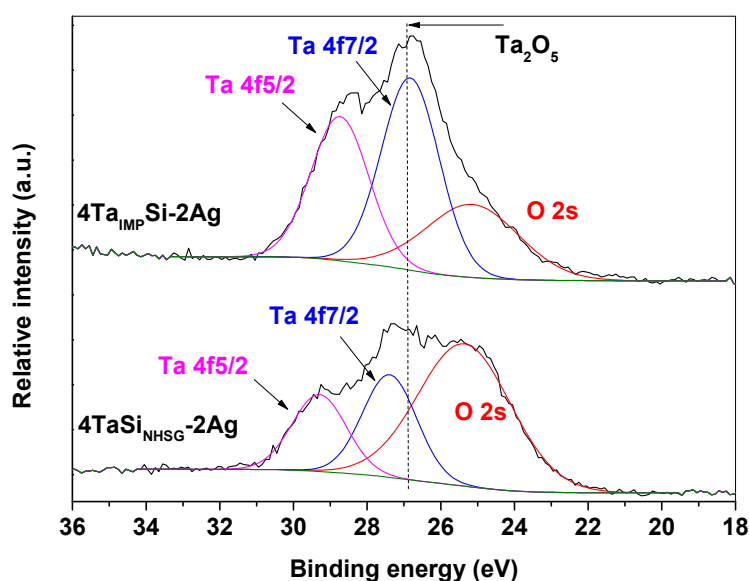


Figure 2. Binding energy shift of tantalum in XP spectroscopy spectra between Ta impregnated ($4\text{Ta}_{\text{IMP}}\text{-2Ag}$) and Ta one pot ($4\text{Ta}_{\text{NHSG}}\text{-2Ag}$).

Tantalum dispersion was also inspected by infrared spectroscopy. The band at 950 cm^{-1} corresponds to the Si–O–Ta bond stretching mode (Figure 3) and the intensity of this band is linked to the amount of Si–O–Ta bonds in the catalyst [45,46]. When Ta is incorporated through NHSG, the band at 950 cm^{-1} is better resolved and higher in intensity, as compared to the impregnated catalyst, consistently indicating a greater occurrence of Si–O–Ta bonds in the former case. This difference is another indication of the incorporation of Ta into the silica matrix by NHSG compared to the impregnation of Ta that tends to form TaO_x species on the catalyst surface.

In DRUVS (Figure 4), the narrow absorbance band found at around 210 nm for $4\text{TaSi}_{\text{NHSG}}\text{-2Ag}$ can be assigned to mononuclear Ta(V) species, similar to those found in Ta-BEA zeolite where Ta is incorporated in the zeolite structure as single sites [47]. For $4\text{Ta}_{\text{IMP}}\text{Si-2Ag}$, the broadening of the signal above 220 nm—with a distinct contribution around 260 nm—is indicative of the presence of polymeric Ta oxide species [46,48]. While the presence of such condensed species in $4\text{TaSi}_{\text{NHSG}}\text{-2Ag}$ cannot be excluded, their contribution is clearly more important in $4\text{Ta}_{\text{IMP}}\text{Si-2Ag}$. Thus, DRUVS confirms that NHSG allows the formation of a relatively high fraction of isolated Ta(V) sites incorporated in silica, while impregnation results in the formation of polymeric TaO_x species.

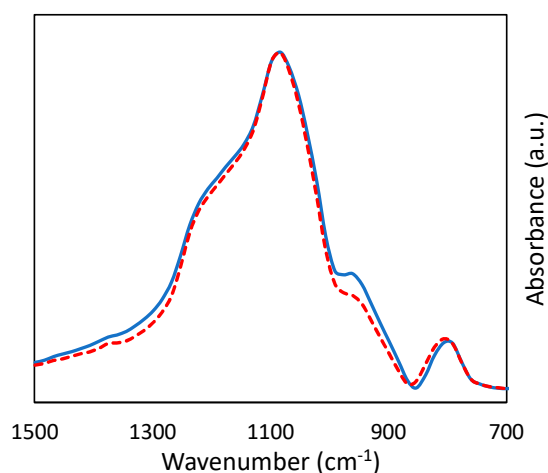


Figure 3. FTIR spectra obtained on 4TaSi_{NHSG}-2Ag (solid blue line), 4Ta_{IMP}Si-2Ag (dotted red line).

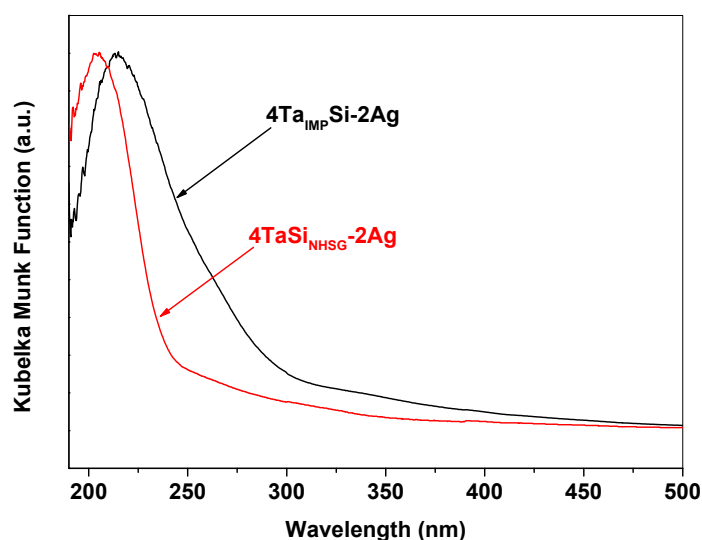


Figure 4. DRUV spectra obtained for 4TaSi_{NHSG}-2Ag and 4Ta_{IMP}Si-2Ag.

The quality of the dispersion of Ta has a marked impact on the acidity of the catalysts. It has been reported that—unlike tantalum oxide—Ta incorporated as single sites within the crystalline structure of zeolites display high acidity [22,46]. Similarly, it can be expected that Ta incorporated as single sites in an amorphous silica matrix can be expected to exhibit high acidity. Indeed, despite having a much lower Ta surface concentration (XPS), 4TaSi_{NHSG}-2Ag shows a number of surface acid sites 2.5 times higher as compared to 4Ta_{IMP}Si-2Ag (Table 1). This corroborates again the formation of a true metallosilicate via NHSG, featuring a high dispersion of Ta.

In the ethanol-to-butadiene reaction, both catalysts exhibited a similar butadiene yield: Ten percent and twelve percent, respectively, for 4TaSi_{NHSG}-2Ag and 4Ta_{IMP}Si-2Ag (Table 2). In fact, the impregnated catalyst was less active, but more selective towards butadiene. Interestingly, the ethylene yield was much higher for the catalyst prepared by the direct incorporation of Ta via NHSG. Ethylene results from the direct dehydration of ethanol, which is catalyzed by acid sites [49–51]. As demonstrated above, when Ta is incorporated through NHSG, a high Ta dispersion is obtained, resulting in the formation of a much more acidic catalyst, owing to the presence of a larger fraction of Si–O–Ta bonds (isolated Ta sites). Thus, the modest butadiene yield obtained with 4TaSi_{NHSG}-2Ag can be attributed to an excessive dehydration activity: A large proportion of the ethanol feed is rapidly converted to ethylene instead of forming acetaldehyde or reacting with crotonaldehyde to continue the cascade

towards butadiene. Other by-products (propylene, n-butenes and crotonaldehyde) are produced in similar amounts with both catalysts. It can be noted that both catalysts showed similar behavior in terms of stability with time on stream (Figures S4 and S5).

Table 2. Catalytic conversion of ethanol, yield and selectivity for butadiene and by-products; Reaction conditions: T = 355 °C, WHSV = 1.10 h^{−1}.

Catalyst	Ethanol Conversion (%)	Butadiene (%)		Acetaldehyde (%)		Ethylene (%)		Diethylether (%)		Others (%)	
		Yield	Sel	Yield	Sel	Yield	Sel	Yield	Sel	Yield	Sel
4Ta _{IMP} Si-2Ag	53.7	12.1	22.5	13.3	24.8	7.7	14.3	10.3	19.2	10.3	19.2
4TaSi _{NHSG} -2Ag	78.1	10.4	13.3	17.0	21.8	28.9	37.0	8.1	10.4	13.8	17.7
4TaSi _{NHSG} -5Ag	90.4	15.4	17.0	17.1	18.9	31.5	34.8	5.3	5.9	21.1	23.3
2TaSi _{NHSG} -2Ag	64.8	4.6	7.1	17.3	26.7	23.6	36.4	7.2	11.1	12.1	18.7
2TaSi _{NHSG} -5Ag	84.5	16.6	19.6	28.5	33.8	13.0	15.4	3.5	4.1	22.9	27.1
2Ta _{IMP} Si-5Ag	64.5	14.6	22.6	34.5	53.5	6.1	9.4	3.5	5.4	5.9	9.1
2TaSi5Ag _{NHSG}	65.2	8.9	13.7	19.9	30.5	22.2	34.0	4.9	7.5	9.5	14.6
2TaSi5Cu _{NHSG}	75.3	23.3	30.9	29.8	39.6	1.4	1.9	0.8	1.1	20.0	26.6

2.2. Influence of Tantalum and Silver Loading on Butadiene Yield

In a search for a better balance between the acid (dehydration) and the redox (dehydrogenation) functions of the catalyst prepared by NHSG, the silver and tantalum loadings have been modified. It can be noted that all catalysts mentioned here have similar textural properties as those described in Table 1 (see Supplementary Materials, Table S1).

When keeping a 4% Ta loading, but increasing the silver loading to 5% to increase the dehydrogenation activity, both the ethanol conversion and the butadiene yield increase (4TaSi_{NHSG}-5Ag). Ethylene and diethylether yields remain at the same level as well, showing that the dehydration power of the catalyst is similar, regardless of the silver loading. Indeed, surface acid site density determined by NH₃-TPD was found to be the same as for 4TaSi_{NHSG}-2Ag (3.7 10^{−2} mmol g^{−1}). The production of acetaldehyde remains fairly constant, suggesting that a higher proportion of the acetaldehyde that is obtained through dehydrogenation further undergoes self-condensation that allows proceeding towards butadiene formation.

When keeping a 2 wt.% silver loading, but decreasing the Ta loading to 2 wt.% to mitigate the dehydration activity (2TaSi_{NHSG}-2Ag), the ethanol conversion decreases and the butadiene yield drops dramatically. In fact, the selectivity to dehydration products (ethene and diethyl ether) remains fairly constant, but the catalyst is simply less active probably because there is a lower density of strong acid sites, which accounts for a lower conversion and lower yields in dehydration products. Dehydrogenation towards acetaldehyde still occurs in appreciable amounts; yet the further conversion toward butadiene remains modest, possibly because the next steps of the mechanism also require acid sites in substantial amounts.

The combination of a high Ag loading (5%) and a lower Ta loading (2%) leads to the highest butadiene yield (16.6% with 2TaSi_{NHSG}-5Ag). This is slightly higher than with 4TaSi_{NHSG}-5Ag. Such increase indicates a more favorable combination of (i) an efficient dehydrogenation ability toward acetaldehyde and (ii) a moderate dehydration ability leading to fewer dehydration by-products. The catalyst with the same composition, but prepared by impregnation (2Ta_{IMP}Si-5Ag) reached a slightly lower butadiene yield. The production of ethylene is clearly lower, due to the different state of Ta in the impregnated catalyst compared to NHSG incorporation, resulting in a catalyst with lower dehydration activity. While the best performance was obtained with the 2TaSi_{NHSG}-5Ag, we suggest that further research is required to determine the optimal Ta and Ag loadings in these bifunctional catalysts, so as to guide the intricate reaction scheme towards the production of butadiene.

Instead of tuning the catalyst composition, playing on the operational parameters is also a relevant approach to enhance the butadiene yields. Figure 5 shows how the butadiene and acetaldehyde yields are affected by space velocity. When the weight hourly space velocity (WHSV) is decreased, the yield to acetaldehyde drops and the yield to butadiene is boosted. By decreasing the WHSV,

the contact time between the reagents and the active sites is increased. Consequently, a higher fraction of the acetaldehyde that is produced through dehydrogenation has the opportunity to undergo self-condensation, leading to acetaldol, which is further converted to crotonaldehyde and then butadiene. This increase in yield, however, comes at the cost of lower butadiene productivity.

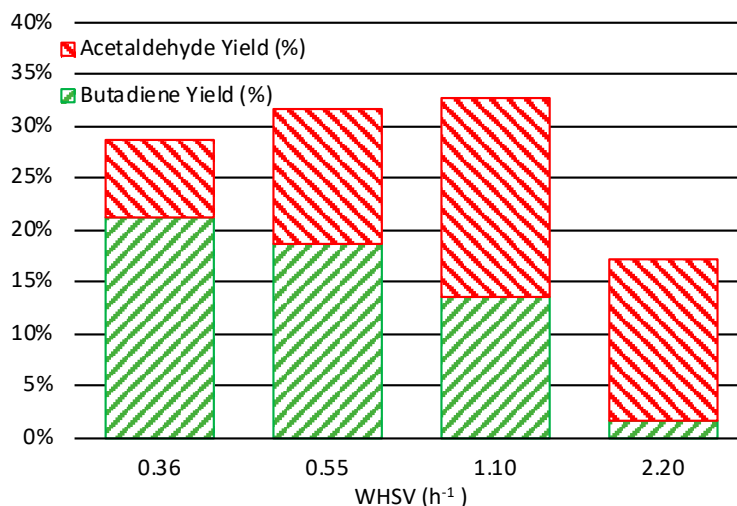


Figure 5. Butadiene and acetaldehyde yields as a function of the contact time for 4TaSiNHSG-5Ag at 355 °C.

2.3. One-pot NHSG Preparation of Ag-TaSiO₂ Bifunctional Catalyst

To further leverage on the versatility of the NHSG process, a one-step preparation of bifunctional catalysts was developed. The idea is to incorporate Ag directly in the NHSG protocol, thereby circumventing the need for a subsequent impregnation step. In this case, a precise amount of (bis)dodecylamine-silver—corresponding to a 5 wt.% nominal loading—was added in the precursor solution right before placing the autoclave in the oven for polycondensation. Also, the solvent was changed to toluene (instead of dichloromethane that was inducing the formation of AgCl), and Brij58 was used as the templating agent (instead of F127 which has relatively low solubility in toluene). The catalyst prepared via this one-pot approach (2TaSi5Ag_{NHSG}) also exhibited a favorable texture: $S_{\text{BET}} = 710 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.89 \text{ mL g}^{-1}$, $D_p = 5.0 \text{ nm}$. Ag nanoparticles could be observed in TEM, dispersed throughout the highly porous Ta-SiO₂ matrix, with a relatively large size distribution (1–30 nm) (Figure 6). This catalyst was also able to catalyze the dehydration and dehydrogenation reactions, yet the butadiene yield remained modest as compared to the best catalysts discussed previously (prepared in two steps). We suggest that further improvements could be obtained by optimizing the catalyst composition and the calcination procedure to better control the formation of well-dispersed silver nanoparticles.

2.4. Copper as an Effective Alternative to Silver

The same strategy was adopted to prepare a 2TaSi5Cu_{NHSG} catalyst, using copper(II) acetylacetonate as a source of Cu. The texture was again very similar ($S_{\text{BET}} = 640 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.60 \text{ mL g}^{-1}$, $D_p = 3.8 \text{ nm}$). The butadiene yield, however, was almost three times higher as compared to the corresponding Ag-based catalyst, reaching 23% (Table 2). The higher performance of Cu-promoted catalysts as compared to Ag-promoted catalysts was already reported by Kyriienko et al. [16], and attributed to a higher dehydrogenation activity. It was also suggested that the metal doping could modify the acid-base properties of the support, thereby affecting the dehydration activity as well. Indeed, with the Cu-based catalysts, we observe a very low yield in dehydration products. This suggests that a better balance was found, with an efficient dehydrogenation activity and a moderate dehydration activity. In the next steps of this research, we plan to further study the impact of the Ta and Cu loadings, in a search for higher butadiene yields.

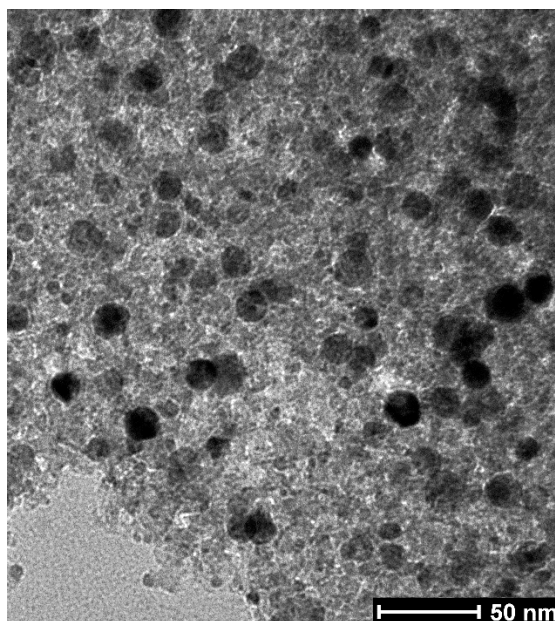


Figure 6. TEM micrograph of the 2TaSi5Ag_{NHSG} catalyst.

3. Conclusions

Non-hydrolytic sol-gel (NHSG) and more specifically the acetamide elimination route is shown to be an effective method to incorporate tantalum in a silica matrix, resulting in a highly homogeneous acidic mixed oxide. With the addition of a templating agent (Pluronic F127), the catalysts display a mesoporous texture with relatively large pore volumes and high specific surface area. Importantly, several characterization tools, allowed us to demonstrate that Ta is mainly incorporated as highly dispersed species into the silica. As a result, even if the surface concentration is lower than in a catalyst prepared by simple impregnation, the density of acid sites is significantly higher in the NHSG-made catalyst. Upon promotion with Ag, the catalyst becomes active in the ethanol to butadiene reaction, even if butadiene yields remain modest. In fact, the selectivity toward ethylene is high, which indicates that the catalyst dehydration power is too high as compared to its dehydrogenation power. Tuning down the acidity by decreasing the Ta loading from 4 to 2 wt.% does not allow reaching higher performance, presumably because acid sites are also needed for the further steps of the reaction mechanism. Increasing the Ag loading results in a higher butadiene yield, showing that the key for further improvement is probably to enhance the dehydrogenation activity. The contact time is also shown to have a great impact on the butadiene yields. Interestingly, we show that bifunctional catalysts can be prepared in one step using NHSG. Ag/Ta-SiO₂ and Cu/Ta-SiO₂ catalysts were prepared in this way, and we show that Cu doping results in much higher butadiene yield as compared to the corresponding Ag-doped catalysts.

4. Experimental

4.1. Catalyst Preparation

General. NHSG processes were performed under Ar atmosphere or high vacuum by using the Schlenk line and a dry box with H₂O and O₂ levels below 1 ppm. CH₂Cl₂ (Carl Roth GmbH, Karlsruhe, Germany, ≥99.8%) was dried with P₄O₁₀. Toluene (Carl Roth GmbH, Karlsruhe, Germany, ≥99.5%) was dried over Na metal. All solvents were distilled and stored in a glove box under molecular sieves. Silicon tetraacetate, pentakis(dimethylamido)tantalum(V) and silver bis(dodecylamine) nitrate were prepared according to the literature [52–54], and stored in a glove box. Silicon tetrachloride (Acros Organics, Geel, Belgium, 99.8%), ethanol absolute (AnalaR NORMAPUR, Leuven, Belgium,

99.95%), silver nitrate (VWR, Leuven, Belgium, 99.9%), dodecylamine (VWR, Leuven, Belgium $\geq 97.0\%$), copper(II) acetylacetonate (TCI, Tokyo, Japan 97%), tantalum(V) ethoxide (ABCR, Karlsruhe, Germany, 99.99%) and acetonitrile (VWR, Leuven, Belgium, isocratic grade) were used as received. Pluronic F127 and Brij 58 (Sigma-Aldrich, Overijse, Belgium) were dried under vacuum at 100 °C overnight and stored in a glove box.

Xerogel synthesis. For the synthesis of Ta-SiO₂ binary oxides, silicon tetraacetate and Pluronic F127 were loaded in a Teflon autoclave in a glove box and dissolved in 40 mL of dichloromethane (for the exact quantities involved in each preparation, see Supplementary Materials, Table S2). In a separate vial pentakis(dimethylamido)tantalum(V) was dissolved in dichloromethane. This solution was then added to the solution of Si(OAc)₄ and Pluronic F127, while stirring. The autoclave was sealed and kept in an oven at 160 °C for 72 h for the gelation. Afterwards, the autoclave was cooled down and put back into the glove box, opened, and the gel was transferred into a Schlenk flask. The gel was dried under vacuum at 60 °C overnight to remove solvent and volatile condensation products (dimethylacetamide and acetic acid anhydride). Finally, the resulting powder was calcined at 500 °C (flowing air, 5 °C min⁻¹, 5 h) to remove organics. Samples are denoted XTaSi_{NHSG} where “X” is the nominal Ta wt.% in the metallosilicate (either 2 or 4 wt.%). A silica sample was synthesized as a reference pristine support, using the same protocol, but with only a very small amount of Ta (small amount of Lewis acid is necessary to induce the polycondensation reactions). The sample is denoted Si_{NHSG} and actually contains a nominal loading of 0.1 wt.% Ta.

Dry impregnation. After calcination, TaSi_{NHSG} materials were impregnated with 2 or 5 % silver. The appropriate amount of silver nitrate was weighted (see Table S3) and dissolved in a volume of water corresponding to the pore volume of the catalyst to impregnate. The solution was put in an ultrasonic bath for 15 minutes to allow the dissolution of silver nitrate and then added to 1 g of TaSi_{NHSG} catalyst. The mixture was stirred until a thick paste was obtained. The paste was put to rest for 1 hour at RT and then dried in an oven at 100 °C to evaporate the water. Finally, the powder was calcined again at 500 °C (flowing air, 5 °C min⁻¹, 5 h). For comparison, a sample was prepared by impregnation of both Ta and Ag on the Si_{NHSG} support (4Ta_{IMP}-2Ag). 47.5 mg of Ta(OEt)₅ and 16.7 mg of AgNO₃ were dissolved in ethanol and added to 0.5 g of Si_{NHSG} using the same impregnation protocol.

4.2. Characterization

Textural properties (surface area, pore volume, pore size) were determined by nitrogen physisorption at 77.4 K on a Tristar 3000 instrument from Micromeritics, Norcross, GA, USA. Prior to measurement, samples were degassed at 150 °C for 8 h minimum. The specific surface area was determined by the BET method with at least five data points with relative pressure between 0.05 and 0.3. The total pore volume (V_P) is measured at $p/p_0 = 0.98$, and the microporous volume is determined via the t -Plot. The mesoporous volume can be obtained by subtracting the latter to the former. Silicon, tantalum and silver content were determined on an ICP optical emission spectrometer iCAP 6500 Duo from Thermo, Waltham, MA, USA equipped with a solid-state generator with a frequency of 27.12 MHz and a maximum power input of 1350 W. X-ray photoelectron spectroscopy measurements were carried out on an SSI X probe spectrometer (model SSI 100, Surface Science Laboratories, Mountain View, CA, USA) equipped with a monochromatized Al-K α radiation (1486 eV). The catalyst powders previously pressed in small stainless troughs of 4 mm diameter, were placed on an insulating home-made ceramic carousel. The pressure in the analysis chamber was set at around 10⁻⁶ Pa. The analyzed area was approximately 1.4 mm², and the pass energy was set at 150 eV. The C1s peak of carbon has been fixed to 284.8 eV to set the binding energy scale [39]. Data treatment was performed with the CasaXPS program (Version 2.3.17PR1.1, Casa Software Ltd, Nottingham, UK) and spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after baseline subtraction. Temperature programmed desorption of ammonia (NH₃-TPD) was performed on a Hiden CATLAB-PCS microreactor from Hiden Analytical Ltd., Warrington, UK connected to a mass spectrometer equipped with a quadrupole separator. Samples (400–800 μ m

particle size) were first dehydrated at 300 °C (10 °C min^{−1}) for 1 hr under Ar (40 mL min^{−1}). Ammonia adsorption took place at 150 °C for 40 minutes (20 mL min^{−1} of Ar, 5 %vol NH₃) before an 80 minutes purge under Ar (40 mL min^{−1}). The temperature was then increased to 600 °C (10 °C min^{−1}) to desorb ammonia. FTIR spectra (4000–400 cm^{−1}) were recorded on a Bruker Equinox 55 spectrometer from Bruker Belgium SA/NV, Kontich, Belgium (transmission mode, through KBr pellets). DRUV spectra (150–500 nm) were recorded on a Shimadzu UV-3600Plus from Shimadzu, Brussel, Belgium.

4.3. Ethanol to Butadiene Reaction

The reactor set-up is schematically described in Figure S6. Calcined catalysts (0.192 g, pressed and sieved in the 0.20–0.40 mm particle size range) were diluted with glass beads (0.5–1 mm) in order to keep the volume of the catalyst bed constant. The rest of the tubular reactor (stainless steel, 0.6 cm internal diameter) was filled with silica beads. Before reaction, the catalyst was pretreated in situ by feeding hydrogen (30 vol.% H₂ in N₂) for 1 h at 355 °C (silver/copper reduction). Catalytic testing was carried out by feeding 0.212 g h^{−1} of ethanol absolute (fed with a NE-300 syringe pump) and 40 mL min^{−1} of nitrogen (4.4 mol.% of ethanol in N₂), WHSV = 1.1 h^{−1} (unless stated otherwise). The tests were carried out at atmospheric pressure and between 325 and 415 °C (results at 355 °C are discussed in details here, but some data at different temperatures are available in Figures S4 and S5). After a stabilization of 10 minutes at the set temperature, effluent gas were analyzed on a VARIAN 3800 Gas Chromatograph from Varian Medical Systems, Machelen, Belgium (5 injections at each temperature, injector set at 150 °C) equipped with a flame ionization detector (FID) set at 190 °C and a Restek Rt-U-Bond column (30 m long, internal diameter of 0.32 mm, film thickness of 10 µm) and a programmed oven (110 °C for 5 minutes, increase to 150 °C by 5 °C/min, 150 °C for 5 minutes). Conversion and selectivity are defined as:

$$\text{Conversion (\%)} = \frac{\text{EtOH}_{\text{IN}} - \text{EtOH}_{\text{OUT}}}{\text{EtOH}_{\text{IN}}} \times 100\%,$$

$$\text{Selectivity (\%)} = N * \frac{X_{\text{Product}}}{\text{EtOH}_{\text{IN}} - \text{EtOH}_{\text{OUT}}} \times 100\%,$$

where EtOH_{IN} is the molar fraction of ethanol in the feed, EtOH_{OUT} is the molar fraction in the effluent (analyzed by GC). X_{Product} is the molar fraction of the considered product in the effluent (analyzed by GC), and N is the number of ethanol molecules needed to form 1 molecule of the product (N = 2 for butadiene). The yield for a given product is the conversion multiplied by the selectivity.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/11/920/s1>, **Table S1:** Textural properties (N₂-physisorption) for catalysts used in catalytic study, **Table S2:** Synthesis of Si-Ta binary oxides—amounts of precursors and surfactant, **Table S3:** Impregnation of silver—amounts of catalyst and Ag salt used, **Figure S1:** Pore size distribution in 4TaSi_{NHSG}-2Ag, **Figure S2:** Pore size distribution in 4Ta_{IMP}Si-2Ag, **Figure S3:** Ammonia desorption profiles of 4TaSi_{NHSG}-2Ag and 4Ta_{IMP}Si-2Ag, **Figure S4:** Evolution of activity over time for all tested temperatures for 4TaSi_{NHSG}-2Ag, **Figure S5:** Evolution of activity over time for all tested temperatures for 4Ta_{IMP}Si 2Ag, **Figure S6:** Schematic view of the catalytic setup.

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