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# Ternary Ag/MgO-SiO<sub>2</sub> Catalysts for the Conversion of Ethanol into Butadiene

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Ternary Ag/Magnesia-silica catalysts were tested in the direct synthesis of 1,3-butadiene from ethanol. The influence of the silver content and the type of silica source on catalytic performance has been studied. Prepared catalysts were characterized by <sup>29</sup>Si NMR, N<sub>2</sub> sorption, small-angle X-ray scattering measurements, XRD, environmental scanning electron microscopy with energy dispersive X-ray analysis (ESEM/EDX), FTIR spectroscopy of adsorbed pyridine and CO<sub>2</sub>, temperature-programmed desorption of CO<sub>2</sub> and UV/Vis diffuse reflectance spectroscopy. Based on these characterization results, the cata-

Introduction

1,3-Butadiene (hereon referred to as butadiene) is an important petrochemical that recently gained renewed interest with a search for new production methods.<sup>[1]</sup> This chemical is mainly used for the production of polymers. Styrene-butadiene rubber (SBR) and polybutadiene, mainly used in the production of car tires, account for more than 50% of the available butadiene. Other important polymers consuming significant amounts of butadiene are acrylonitrile–butadiene–styrene (ABS), styrene–butadiene latex (co-polymer) and chloroprene rubber. Butadiene is also used as starting material for adiponitrile synthesis, a precursor for nylon production.<sup>[2]</sup>

Currently, butadiene is predominantly obtained via extractive distillation of the C4 fraction from naphtha steam crackers used for the production of ethylene, making the butadiene supply very dependent on the ethylene production. This dependence could become problematic because recent trends in shifting to lighter feedstock for the steam crackers will decrease butadiene yields, because of lower costs and the larger availability of ethane from shale gas. This can potentially lead to a shortage in butadiene production in the near future.<sup>[3]</sup>

This butadiene production gap can be overcome by direct production routes. A number of on-purpose technologies have

lytic performance of the catalysts in the 1,3-butadiene formation process was interpreted and a tentative model explaining the role of the different catalytically active sites was elaborated. The balance of the active sites is crucial to obtain an active and selective catalyst to form 1,3-butadiene from ethanol. The optimal silver loading is 1–2 wt% on a MgO-silica support with a molar Mg/Si ratio of 2. The silver species and basic sites (Mg–O pairs and basic OH groups) are of prime importance in the 1,3-butadiene production, catalyzing mainly the ethanol dehydrogenation and the aldol condensation, respectively.

the potential to become economic viable routes for the direct production of butadiene such as (bio)ethanol conversion to butadiene, dehydrogenation of butane and butenes, and dehydration of butanediols.<sup>[1a,4]</sup>

The direct production of butadiene from ethanol is an onpurpose method, starting with bioethanol, a new and renewable feedstock, produced via the fermentation of sugars and starch.<sup>[5]</sup> The production of bioethanol is growing to an industrial scale mainly for fuel use. The intensive investigations in the use of second generation feedstock like cellulose, for example, will help to further develop the bioethanol economy. The production of ethanol from syngas (chemical and fermentation) is another route that has been investigated in recent years.<sup>[6]</sup> When these technologies become industrially relevant, they will further increase the ethanol supply. A recent sustainability assessment demonstrated beneficial aspects of the biobased production of butadiene, mainly in terms of process costs, environmental impact and potential hazard of the ethanol route, when compared to the traditional naphtha cracking process.<sup>[7]</sup> A research partnership between Axens, IFP Energies Nouvelles and Michelin to develop bio-based butadiene, illustrates the industrial relevance of this butadiene from ethanol process.<sup>[8]</sup> It should be emphasized that this process has already been used in the chemical industry from 1920 to 1960. In Russia, the Lebedev one-step process used a variety of (mixed) oxide catalysts.<sup>[9]</sup> In the USA a two-step process has been implemented in which ethanol was partially dehydrogenated to acetaldehyde in a first reactor; then the ethanol-acetaldehyde mixture was transformed into butadiene in a second reactor with a tantalum oxide on silica catalyst.<sup>[11]</sup>

The formation of butadiene from ethanol is complex and the mechanism is still subject to debate. The reaction scheme

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 $\mbox{Scheme 1.} Reaction sequence for the conversion of ethanol into butadiene.$  $<math display="inline">^{(4,\,10,\,12)}$ 

illustrated in Scheme 1 is generally accepted today.<sup>[4, 10, 12]</sup> It involves multiple consecutive reaction steps such as: 1) Ethanol dehydrogenation to acetaldehyde. 2) Aldol condensation of two acetaldehyde molecules yielding acetaldol. 3) Dehydration of acetaldol to crotonaldehyde. 4) Meerwein-Ponndorf-Verley (MPV) reaction between crotonaldehyde and ethanol to form crotyl alcohol and acetaldehyde. 5) Dehydration of crotyl alcohol into butadiene. Active catalysts should be multifunctional containing different sets of active sites, that is, acid, base and redox sites, catalyzing dehydrogenation, aldol condensation, MPV reaction and dehydration. The strength, balance, and proximity of the different sites is crucial to obtain active and selective catalysts. The ethanol dehydrogenation step<sup>[10a]</sup> as well as the aldol condensation step,<sup>[10b]</sup> have been proposed in the literature as the rate-determining step in this reaction network.

Magnesia-silica catalysts are very intensively studied materials in the one-step process of ethanol to butadiene. Different procedures have been used for catalyst synthesis, the optimal Mg/Si ratio of the two oxides appearing as an important parameter. Niiyama et al. observed the highest acidity on samples with a Mg/Si ratio of 1, while the basicity increased with increasing MgO content.<sup>[10a]</sup> However, contradictory results have been reported on the optimal Mg/Si ratio. Niiyama et al. reported an optimal ratio of 5.7,<sup>[10a]</sup> while other authors reported other optimal ratios, amounting to 2<sup>[4,13]</sup> or 1.<sup>[10b,14]</sup> The MgO- $SiO_2$  catalysts showed butadiene yields ranging from 9 to  $42\,\%$ and selectivities between 30 and 84%.<sup>[4,10,13-15]</sup> Despite the different preparation methods and catalyst compositions, the productivities remain very low for these catalysts. The most active catalysts obtained productivities below  $0.1 \ g_{\text{BD}} \ g_{\text{catalyst}}^{-1} \ h^{-1} .^{[1a,4]}$ 

The activity of magnesia-silica-based catalysts can be further improved by post-synthetic modifications. The addition of dopants such as chromium, zinc, silver, manganese, copper, and nickel,<sup>[4, 12, 15-16]</sup> improved the dehydrogenation activity, resulting in an increased ethanol conversion and butadiene yield. In our recent article, we presented the influence of various transition metal (oxide) modifiers on the catalytic activity and butadiene selectivity of magnesia-silica catalysts.<sup>[4]</sup> A successive impregnation of the binary system proved to be most effective. The catalysts showed improved butadiene selectivity and yield for all transition metals and a reduced dehydration activity, resulting in reduced formation of the thermodynamically favorable ethylene and diethyl ether. Silver and copper were the most effective promoters showing almost complete ethanol conversion, and butadiene yields higher than 50%. These materials showed the highest productivities of all magnesia-silica-based materials at almost 0.2 g<sub>BD</sub> g<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>.

The hitherto published data on ternary MO<sub>x</sub>-MgO-SiO<sub>2</sub> catalysts focus on the catalytic performance of these systems using a "black box approach", rather than presenting an in-depth physicochemical characterization of these solids. In this work, the MgO-SiO<sub>2</sub> system doped with silver was studied in an attempt to understand this catalytic system, thus allowing the correlation of structural and catalytic properties. Therefore, a detailed characterization of the Ag/MgO-SiO<sub>2</sub> materials is compared with their catalytic performance. The redox dopant concentration and the silica properties, that is, morphology and pore size, are varied to obtain insight in the effect of acidity, basicity, location and dispersion of MgO in this catalytic system.

#### Results

#### **Catalytic results**

Three series of catalysts were prepared with a different silica source: commercial silica gel (further labeled as SiO<sub>2</sub>), MCM-41, and COK-12 materials. Catalysts were prepared according to the procedure described in Makshina et al.<sup>[4]</sup> and included the preparation of the magnesia-silica support followed by an impregnation with a silver containing solution (see details in the Experimental Section). The results of the tested catalysts are reported in Table 1 and Figures 1 and 2. The results of the individual oxides indicate that the presence of both MgO and silica is necessary to obtain active and selective catalysts for the butadiene synthesis (Table 1, entries 1–4, 6, 12 and 18). The



**Figure 1.** Catalytic results for the ethanol to butadiene reaction at 673 K (after time-on-stream (TOS) of 200 min and space velocity (WHSV) of 1.2 h<sup>-1</sup>) against the silver loading of xAg/MgO-SiO<sub>2</sub> catalysts.  $\blacksquare$  = ethanol conversion;  $\bullet$  = butadiene yield;  $\blacktriangle$  = acetaldehyde yield;  $\blacklozenge$  = ethylene yield;  $\Box$  = butadiene selectivity.

Entry	Catalyst	Conversion [C%]		Selectivity [C%]				Productivity $[q_{BD} q_{cat}^{-1} h^{-1}]$	
			Butadiene	Acetaldehyde	Ethylene	Diethyl ether	Crotyl alcohol + butanol	Other <sup>[b]</sup>	
1	MgO	11	6	9	5	11	34	35	0.00
2	SiO <sub>2</sub>	6	2	51	20	11	0	16	0.00
3	COK-12	4	0	68	19	2	1	10	0.00
4	MCM-41	4	1	69	17	2	1	10	0.00
5	1.0Ag/SiO₂	38	4	66	7	11	1	15	0.01
6	MgO-SiO <sub>2</sub>	10	36	8	12	9	8	24	0.02
7	0Ag/MgO-SiO <sub>2</sub> <sup>[a]</sup>	9	39	4	23	18	2	14	0.02
8	0.5Ag/MgO-SiO <sub>2</sub>	26	47	16	4	7	6	20	0.08
9	1.0Ag/MgO-SiO <sub>2</sub>	44	46	19	3	4	5	23	0.14
10	2.0Ag/MgO-SiO <sub>2</sub>	50	41	24	2	3	4	26	0.15
11	4.0Ag/MgO-SiO <sub>2</sub>	50	38	23	3	3	4	29	0.12
12	MgO-COK-12	9	33	8	29	14	2	14	0.02
13	0Ag/MgO-COK-12 <sup>[a]</sup>	6	35	5	21	22	5	12	0.02
14	0.5Ag/MgO-COK-12	31	44	12	5	5	8	26	0.09
15	1.0Ag/MgO-COK-12	42	42	20	3	4	7	24	0.12
16	2.0Ag/MgO-COK-12	39	42	23	6	3	5	21	0.11
17	4.0Ag/MgO-COK-12	48	33	26	3	2	6	30	0.11
18	MgO-MCM-41	9	36	6	25	12	3	18	0.02
19	0Ag/MgO-MCM-41 <sup>[a]</sup>	11	28	4	27	25	3	13	0.02
20	1.0Ag/MgO-MCM-41	24	47	14	7	7	5	20	0.08
21	2.0Ag/MgO-MCM-41	24	47	13	9	6	5	20	0.08

[a] Catalysts wetted with water (conditions of Ag-free impregnation). [b] Other includes other by-products detected in minor amounts such as methane, COx, ethane, propylene, methanol, other C4 and C6 hydrocarbons, C3, C4, and C6 oxygenated compounds.



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**Figure 2.** Catalytic results of 1.0Ag/MgO-silica catalysts with different silica sources in the formation of butadiene from ethanol at 673 K (after TOS of 200 min and WHSV =  $1.2 h^{-1}$ ).  $\blacksquare$  = ethanol conversion;  $\bullet$  = butadiene yield;  $\blacktriangle$  = acetaldehyde yield;  $\blacklozenge$  = ethylene yield;  $\square$  = butadiene selectivity.

addition of Ag increases the ethanol conversion and butadiene yield significantly, while wetting solely with water ("impregnation" solution devoid of Ag, 0Ag/MgO-silica) does not affect the catalytic results (compare entries 6–8 in Table 1). The promotional effect of silver in the butadiene synthesis has previously been described in the literature.<sup>[4, 16e, 17]</sup> It was assumed that the first step in the reaction network (Scheme 1), that is, the dehydrogenation of ethanol, is catalyzed by silver. Selectivity to other intermediate products, for example, crotonaldehyde, was very low, that his, less than 5%. The main byproducts are ethylene, diethyl ether, and 1-butanol. The first two products are the result of a dehydration of ethanol and are mainly present on catalysts without Ag and their selectivity decreases significantly after the addition of Ag. Ethanol dehydration may be reduced due to blocking of dehydration sites after addition of Ag or due to a competition for ethanol with the dehydrogenating activity of the Ag species. The catalytic behavior of a magnesia-free 1.0 Ag/SiO<sub>2</sub> material proves this assumption (compare entries 2 and 5 in Table 1). The presence of silver clearly leads to substantial increase in conversion, acetal-dehyde becoming a major product, while ethylene selectivity decreases.

The amount of Ag on the MgO-silica support has a significant influence on the catalytic results of the final catalysts (Table 1 and illustrated in Figure 1 for SiO<sub>2</sub> as silica source). The conversion and acetaldehyde yield both increase with increasing silver content, until 2 wt%. The butadiene selectivity, however, decreases with increasing silver loadings. Both observations indicate that 1 wt% of silver is the optimal loading for all tested xAg/MgO-silica catalysts, independently of the silica source used (Table 1). A low silver content (0.5 wt%) gave high butadiene selectivity but low ethanol conversions, while the better conversions with higher silver loadings ( $\geq 2$  wt%) are mainly the result of an increased amount of acetaldehyde and did not result in higher butadiene yields.

Different silica sources were used to investigate their influence on the catalytic activity. Figure 2 compares the results of the catalysts prepared from different silica sources (a commercial silica (SiO<sub>2</sub>), COK-12, and MCM-41) and impregnated with 1 wt% Ag. The catalyst prepared with commercial silica shows slightly better behavior compared to COK-12. MCM-41-based catalysts show lower ethanol conversion, as well as reduced butadiene and acetaldehyde yield.

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### Influence of the reaction conditions on the catalytic performance

The activity of the most active catalysts can be further increased by increasing the reaction temperature (Figure 3). Both conversion and butadiene yield increase with increasing temperature. A significant increase of the butadiene productivity from 0.14 to 0.29  $g_{BD}g_{catalyst}^{-1}h^{-1}$  was obtained by increasing the temperature from 673 to 753 K. The acetaldehyde yield significantly decreases with increasing reaction temperature, while the selectivity to the other intermediate products remains very low.



**Figure 3.** Catalytic activity of  $1.0Ag/MgO-SiO_2$  at different temperatures (WHSV =  $1.2 h^{-1}$  after TOS of 200 min).  $\blacksquare$  =ethanol conversion;  $\bullet$  = butadiene yield;  $\blacktriangle$  =acetaldehyde yield;  $\blacklozenge$  =ethylene yield;  $\bigcirc$  =butadiene productivity.

The increased conversion and butadiene yield, together with decreased acetaldehyde yield indicate that the rate of the ratedetermining aldol condensation increases with increasing temperature. The higher temperatures also enhanced the dehydration activity of the catalyst, resulting in an increased ethylene yield up to 8% at 753 K. According to thermodynamic calculations in literature, the acetaldol formation becomes thermodynamically less favorable at higher temperatures.<sup>[1]</sup> But despite the thermodynamic considerations, the rate of the aldol condensation increases, showing higher butadiene yield, which is probably due to the increased dehydration activity of the catalyst at higher temperatures, for example, dehydration of acetaldol and eventually crotyl alcohol.

Lowering the contact time, by increasing the carrier gas flow rate, is detrimental for the butadiene formation (illustrated in Figure S1 in the Supporting Information). The effect of ethanol concentration in the gaseous stream at constant carrier gas flow rate (constant contact time) is shown in Figure S2. The level of conversion decreases with increasing ethanol amounts in the feed stream while butadiene selectivity is almost constant. This behavior indicates that the dehydrogenation capacity of the silver particles is not sufficient to convert the extra amount of ethanol. However, use of higher ethanol concentrations leads to higher butadiene productivities up to 0.28  $g_{BD}g_{catalyst}^{-1}h^{-1}$  at space velocity (WHSV) of 2.4  $h^{-1}$ .

## Characterization

SEM images show the morphologies of the parent silicas used in the preparation of the Ag-on-magnesia-silica catalysts (Figure S3A, C and E). MCM-41 appears as spherical particles with a regular surface. COK-12 has thin particles with a hexagonal shape. Both the MCM-41 and COK-12 particles are smaller than 1 µm. Their morphology corresponds to that shown in earlier publications.<sup>[18]</sup> The commercial silica shows a gel-type structure with less discrete particles. After mixing with Mg(OH)<sub>2</sub> powder and impregnation with aqueous Ag<sup>+</sup> solution, MCM-41 particles are covered by sheets (flakes) of MgO, some peeling off from the silica surface (Figure S3A and B). Also in the case of the commercial silica gel (Figure S3E and F), the silica surface is covered with multiple crystal layers of MgO. With the COK-12 silica (Figure S3C and D), the coverage with MgO is incomplete and evidence is present for the existence of separated MgO flakes. The fate of the small Ag species clearly cannot be revealed by SEM.

Environmental scanning electron microscopy with energy dispersive X-ray analysis (ESEM/EDX) was used to analyze the chemical composition of the catalysts at specific locations inside the catalyst particles. Figure 4A and B show ESEM pictures of a 4.0Ag/MgO-COK-12 catalyst with different magnification. In line with the SEM pictures (Figure S3C and D), two discrete phases are observed in these pictures, a darker one with few white dots (Figure 4B, area 2) and a lighter one with many small white dots (Figure 4B, area 1). The white dots correspond to Ag particles, because metal particles light up in the backscattering mode. Elemental analysis of the two phases (Figure 4B and C) confirms the chemical difference between the two phases. The lighter phase represents  $SiO_2$  with some Mg<sup>2+</sup>, while the darker phase indicates MgO with few Si atoms. The Ag atoms are clearly concentrated in the SiO<sub>2</sub> phase. The same behavior is also seen in the ESEM/EDX mapping experiment (Figure 4D, E and F).

Small-angle X-ray scattering (SAXS) measurements was used to determine whether the silica mesoporous ordering of MCM-41 and COK-12 survives the synthesis procedure. Figure 5 represents the SAXS patterns of the catalysts in different stages of the catalyst preparation. The parent COK-12 and MCM-41 support exhibit a well-resolved intense diffraction peak at q = 0.7and 1.6 nm<sup>-1</sup>, respectively, and a second smaller though broader peak at q = 1.2 and  $3.0 \text{ nm}^{-1}$ , respectively. Both are typical for ordered mesoporous silica with hexagonal pore structure.<sup>[18a, 19]</sup> The diffraction peaks at smaller angles in the SAXS pattern of COK-12 indicate an ordering over a larger distance in COK-12 compared to MCM-41. This corresponds with a larger unit cell for COK-12 (unit cell parameter a = 10.4 nm) compared to MCM-41 (a = 4.5 nm), in agreement with the larger pores and thicker pore walls in COK-12. Mixing of the COK-12 and MCM-41 silicas with magnesium oxide results in lower peak intensities due to the reduced amount of silica present in the sample (43 wt % SiO<sub>2</sub>). Wetting of the MgO-silica materials with water (without silver) leads to the disappearance of the diffraction peaks for both COK-12 and MCM-41, which indicates a serious loss of ordering of the porous network. Alternatively, due to

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**Figure 4.** ESEM/EDX measurements of 4.0Ag/MgO-COK-12. A) ESEM photo in backscattering mode; B) Magnification of the rectangle of photo A; C) Results of the elemental analysis (in wt%) of areas 1 and 2 from photo B; D– F) Determination of the specific location and concentration of different atoms (color intensity being a measure for the relative concentration): D) Ag L $\alpha$ , E) Si K $\alpha$ , F) Mg K $\alpha$ .



Figure 5. SAXS patterns of i) COK-12, ii) MgO-COK-12, iii) 0Ag/MgO-COK-12, iv) MCM-41, v) MgO-MCM-41, and vi) 0Ag/MgO-MCM-41.

the random coverage of MgO throughout the silica material, a modified scattering contrast could also be possible.

The textural properties of the materials at different stages of the preparation are summarized in Table S1. The isotherms and the samples and changes the isotherms, while the pore size distribution curves indicate the loss of the mesoporous structure, probably due to the interaction with MgO. This is in line with the picture drawn from the SAXS experiments.

pore size distribution curves of

the catalysts prepared from COK-12 are illustrated in Figure 6 and Figure S4. The starting silica materials all have high surface areas and their adsorption isotherms are typical for mesoporous materials. MCM-41 and COK-12 materials show a steep condensation step on both the and adsorption desorption branches, pointing to the existence of a narrow pore size distribution. In case of commercial silica the shape of the hysteresis loop suggests a broad pore size distribution. Also the average pore size of commercial silica is higher (6.3 nm) compared to the ordered mesoporous supports, amounting to 5.4 and 1.9 nm for COK-12 and MCM-41, respectively. Although addition of MgO to the silicas leads to a decrease of the surface area, the shapes of the isotherms and the pore size distribution curves are similar to those of the starting silicas, except for the additional hysteresis loop at high partial pressures in the isotherms, resulting from the porosity of the MgO phase. The surface area of MgO-SiO<sub>2</sub> is higher than could be derived from that of the individual oxides. This points to a better dispersion of MgO in presence of commercial silica compared to bulk MgO. Conversely, the surface areas of MgO-COK-12 and MgO-MCM-41 are slightly reduced, while the decrease upon MgO addition is more pronounced in case of MCM-41. This observation is explained by a partial covering of the external silica surface by MgO particles resulting in a partial pore blockage. Such changes confirm the results obtained by SEM. The wetting and impregnation step followed by calcination both further decrease the surface area of

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**Figure 6.** Nitrogen adsorption/desorption isotherms (A) and pore-size distribution curves (based on the BJH model for adsorption) (B) of COK-12-based catalysts at different stages of the synthesis: COK-12 (-----); MgO-COK-12 (------); 0Ag/MgO-COK-12 (------).

XRD patterns of the MgO-SiO<sub>2</sub> support and the catalysts with the highest Ag loading (4 wt%) are shown in Figure 7. All catalysts show the presence of a crystalline MgO phase. The diffraction peaks observed at  $2\theta$ =36.9, 42.8, 62.2, 74.6, and 78.6° correspond to the face-centered cubic form of MgO [per-iclase, PDF 01-071-1176 (ICDD, PDF-2, 2008)]. The MgO diffrac-



**Figure 7.** XRD patterns of i) MgO-SiO<sub>2</sub>, ii) 4.0Ag/MgO-SiO<sub>2</sub> and iii) 4.0Ag/MgO-COK-12. The diffraction peaks are identified as diffractions of periclase MgO (M) and metallic Ag (A).

tion peaks in the spectrum of 4.0Ag/MgO-SiO<sub>2</sub> are broader and less intense compared to the diffraction peaks in the diffractogram of the MgO-SiO<sub>2</sub> support. Similar effects have been reported when comparing a MgO/SiO<sub>2</sub> catalyst prepared by wetkneading with a mechanically mixed sample.<sup>[10b]</sup> It was assumed that the decrease in crystallinity is due to a decrease in the size of the MgO crystals or to an increase in the crystal defects (creating more corners, edges, and steps on the MgO surface), both caused by the interaction with SiO<sub>2</sub>. The broad and low intensity band at  $2\theta = 20-30^{\circ}$  is due to the presence of amorphous silica. Reflections corresponding to crystalline magnesium silicates were not observed. Presence of crystalline silver [PDF 03-065-2871 (ICDD, PDF-2, 2008)] was detected only for samples with a loading higher than 2 wt%, as is evident from diffraction peaks at  $2\theta =$  38.0, 44.3, 64.4, and 77.2°. In case of the materials with lower silver loading (0.5–1 wt%), no diffraction peaks of Ag have been observed in XRD patterns. This indicates that on catalysts with low silver loadings, crystal-line silver (Ag<sup>®</sup>) is absent or present as small silver nanoparticles undetectable with XRD.

Another possibility is that the amount of crystalline silver is too low to be detected with the XRD setup. The presence of a diffraction pattern of metallic silver on

catalysts with 4 wt% Ag indicates the presence of much more and/or bigger silver nanoparticles compared to the lower silver loadings (0.5–1 wt%). Peaks of Ag particles were more intense and had a slightly larger FWHM (full with at half maximum) for commercial silica gel containing samples in comparison to COK-12, indicative of slightly bigger silver particles on the ordered silica support.

UV/Vis diffuse reflectance spectra are presented in Figure 8. The spectra of starting calcined MgO-silicas reveal two major bands at 230 and 290 nm, which are similar to those of bulk MgO, as well as a shoulder at 210 nm. The first band is attributed to a charge-transfer transition involving Mg-O pairs located on the edges and terraces of MgO crystallites, while the second one could be associated with tri-coordinated O<sup>2-</sup> ions on corners.<sup>[10b, 20]</sup> Charge-transfer transitions involving OH groups may also have an impact on the band at 290 nm, if the MgO powder is pretreated below 973 K.<sup>[20a]</sup> The presence of the band at 210 nm was not observed on spectra of pure MgO, and is likely due to charge-transfer transitions involving Mg<sup>2+</sup> atoms bound to a silica surface.<sup>[20a]</sup> The ratio between the two major bands is different for commercial silica gel and ordered COK-12 and MCM-41, suggesting that the ordered silicas contain more isolated O<sup>2-</sup> ions and OH groups on the MgO surface than the MgO-SiO<sub>2</sub> sample. After wetting the MgO-silica supports (Figure 8A), a change in the intensity of the two bands at 230 and 290 nm is observed in favor of the second band. The changes in the UV-spectra of the ordered silicas after wetting are so pronounced that the formation of a new band near 260 nm has to be taken into account. Kvisle et al. already described such a band on magnesia-silica materials and assigned it to a Mg–O–Si species.<sup>[10b]</sup> The wetting might therefore induce changes in the support material: modifications of the MgO surface, creating more O<sup>2-</sup> ions on corners, and the formation of new Mg-O-Si species. Addition of silver also leads to changes in the UV spectra (Figure 8B). Important bands characteristic for different Ag species are expected at 190-250 nm for charged Ag atoms (Ag<sup>+</sup>), at 260-330 nm for charged silver clusters (Ag $_n^{\delta+}$ ) and at 350 nm and higher wavelengths for metallic clusters and nanoparticles

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**Figure 8.** Diffuse-reflectance UV-vis spectra of different catalysts after different steps in the synthesis. A) Mixed supports (solid lines) and supports after wetting with water (dotted lines), curves were shifted vertically for clarity; B) Different silver loadings of xAg/MgO-SiO<sub>2</sub> catalysts.

(>400 nm).<sup>[21]</sup> The presence of metallic Ag nanoparticles is observed on the DRS spectra for all silver-containing catalysts. The contribution of charged Ag clusters  $(Ag_n^{\delta^+})$  and  $Ag^+$  ions appears to be small, but it should be noted that the presence of these bands below 300 nm is not easily distinguishable from the strong absorption of MgO. The intensities of the absorption bands corresponding to metallic silver are lower in case of the samples prepared with COK-12 and MCM-41 (Figure S5 A and B), pointing to a lower amount of the metallic nanoparticles in these catalysts.

<sup>29</sup>Si Magic Angle Spinning (MAS) NMR spectroscopy was used to evaluate the state of the silicon atoms during the different catalyst synthesis steps. NMR spectra of parent and MgO-modified silica supports (Figure 9A, Figure S6 black and red spectra) show three signals with chemical shifts typical for amorphous silica materials as previously described in literature: -110 ppm for a Si atom with four siloxane bonds (Si\*(OSi)<sub>4</sub>); -100 ppm for a Si atom with three siloxane bonds and a hygroup (Si\*(OSi)<sub>3</sub>(OH)); droxyl -90 ppm for a Si atom with two siloxane bonds and two hydroxyl groups (Si\*(OSi)<sub>2</sub>(OH)<sub>2</sub>).<sup>[22]</sup> This means that MgO and silica interact only very weakly in the mixed MgO-silica materials, confirming the adsorption and SAXS results. However, significant changes are present in the spectra of the samples after the wetting and silver impregnation steps. The signals at -110 and -101 ppm drastically decrease and new signals appear at -92, -85, and -75 ppm (Figure S7). Since the spectra of the impregnated materials containing silver

are similar to those without silver (0Ag/MgO-silica) irrespective of the silica source, it can be concluded that appearance of the new signals is not related to the interaction of Ag atoms with surface silanols, but rather to an interaction of the silica surface with magnesium oxide.

A cross-polarization (CP) experiment (<sup>29</sup>Si CP MAS NMR spectra) was conducted to identify the nature of the new signals (Figure 9B). The signal intensity at -92 and -85 ppm is enhanced in this CP experiment, which means that these Si atoms are located at or very close to the silica surface.<sup>[22b]</sup> Similar signals with chemical shift at -85 and -92 ppm were already reported for MgO-silica systems in the literature and they were assigned to Si\*(OMg)(OSi)<sub>2</sub>(OH) and Si\*(OMg)(OSi)<sub>3</sub>, respectively.<sup>[23]</sup> These results indicate that the use of the aqueous solution during the impregnation with subsequent calcination leads to the formation of an amorphous surface magnesium silicate phase. Similar observations were made previously



**Figure 9.** A) <sup>29</sup>Si MAS NMR spectra of catalysts after different synthesis stages; the starting COK-12 (——); MgO-COK-12 after mechanical mixing and calcination (——); 0Ag/MgO-COK-12 after wetting/impregnation and calcination (——) and 1.0Ag/MgO-COK-12 after wetting/impregnation and calcination (——) and 1.0Ag/MgO-COK-12 after wetting/impregnation and calcination (——). B) Comparison of <sup>29</sup>Si CP MAS NMR (——) and <sup>29</sup>Si MAS NMR spectra (——) of 0Ag/MgO-COK-12 (the spectra were scaled differently for easier comparison). The NMR spectra of catalysts prepared with SiO<sub>2</sub> and MCM-41 are included in the Supporting Information (Figure S6).

phous and crystalline magnesium silicate formation) and Kvisle et al. (Mg-O-Si interactions) for MgO-silica catalysts prepared by wet-kneading.<sup>[10b, 13]</sup> The wetting during the impregnation step appears to have a stronger influence when the ordered mesoporous materials (COK-12 and MCM-41) are used as silica source. Their signals at -110 and -101 ppm are lower compared to the signals of the magnesium silicate phase (-92 and -85 ppm). Such behavior is not unexpected taking into account that the pore walls are thinner and thus more reactive in case of ordered COK-12 and MCM-41

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compared to the commercial silica gel and better accessible for an interaction with dissolved magnesium hydroxide during the impregnation. The previously cited groups did not observe chemical shifts higher than -80 ppm. Here, the signals are small but clearly observable. In the CP experiment, this signal was not enhanced as much as the other signals, meaning that this type of Si atom is not as close to protons as the other signals. Thus this species could be assigned to Si\*(OMg)<sub>2</sub>(OS)<sub>2</sub>.

Infrared spectroscopy is a popular technique to visualize the OH groups present on silica and other surfaces. Figure 10 represents the FTIR spectra in the OH vibration region of the catalysts at different stages of their synthesis. In the 3900–3200 cm<sup>-1</sup> region, the FTIR spectra of the parent silica materials exhibit one sharp and intense absorption band around 3740 cm<sup>-1</sup> attributed to isolated silanol groups ( $\equiv$  Si–OH).<sup>[24]</sup>



**Figure 10.** FTIR spectra in the OH vibration region of catalysts after different stages of the synthesis. The spectra were measured at 423 K after evacuation at 673 K to remove adsorbed water: i) COK-12, ii) MgO, iii) MgO-COK-12, iv) 0Ag/MgO-COK-12, v) 1.0Ag/MgO-COK-12. The IR spectra of catalysts prepared with SiO<sub>2</sub> and MCM-41 are included in the supporting information (Figure S8).

A shoulder around 3700 cm<sup>-1</sup> that can be assigned to hydrogen bound silanols, is clearly visible. The IR spectrum of bulk MgO has a band at 3750 cm<sup>-1</sup>, corresponding to isolated MgOH groups present on the MgO surface and a small, broad band at 3520 cm<sup>-1</sup> assigned to multi-coordinated hydroxyl groups (hydroxyls formed after protonation, by H<sub>2</sub>O dissociation, of low coordinated oxygen atoms on corners and steps).<sup>[25]</sup> Modification of the host silica matrices with magnesium oxide results in an intensity decrease of the OH band due to a decrease of the silica content of the magnesia-silica materials compared to the parent silica. Wetting and/or Ag impregnation of the premixed MgO-silica support shows the appearance of two new bands at 3705 and 3665  $cm^{-1}$  (Figure 10). Similarly to changes observed by NMR and UV/Vis spectroscopy, these new bands most probably originate from the interaction of the silica surface with magnesium (hydr)oxide. Kermarec et al. observed such a band near 3675 cm<sup>-1</sup> in the IR spectrum of magnesia-silica gels, relating it to the presence of magnesium atoms in tetrahedral coordination.<sup>[26]</sup> Moreover, various hydrous silicates, that is, talc, sepiolite, and serpentine group minerals (like chrysotile, lizardite, and picrolite) exhibit OH stretching vibrations in this region of 3660–3700 cm<sup>-1.[27]</sup> Thus both bands at 3665 and 3705 cm<sup>-1</sup> are most likely attributed to various surface species of an amorphous Mg-silicate phase, like silanol groups next to Mg atoms or Mg-OH groups bonded to the silica surface. For an exact identification of these new OH vibrations, further investigation is necessary. A comparison of the spectra of the xAg/MgO-silica samples prepared from different silica sources indicates that the silica surface of the ordered supports (COK-12 and MCM-41, spectra iv and v in Figure 10 and Figure S8B, respectively) is more affected by the interaction with magnesium atoms than the commercial silica (spectra iv and v in Figure S8A), confirming the results of the NMR analysis.

Temperature-programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) and infrared spectroscopy of preadsorbed CO<sub>2</sub> were used to characterize the properties of basic sites on the surface of the investigated catalysts. The basicity of the catalysts originates from the MgO phase, as almost no CO<sub>2</sub> is observed in the TPD of pure SiO<sub>2</sub> (Table 2, entry 2). CO<sub>2</sub> can adsorbs on the basic sites of MgO, forming three different species.<sup>[28]</sup> These species have different IR vibrations and can therefore be visualized by IR spectroscopy. Bicarbonates are formed on weakly basic OH groups and reveal a C–OH bending vibration near 1220 cm<sup>-1</sup> and a symmetric and asymmetric O-C-O stretching vibration at 1480–1420 and 1665–1650 cm<sup>-1</sup>, respectively. Bidentate carbonate species are generated by interaction of carbon dioxide with intermediate strength Mg–O pairs and have characteristic vibrations near 1630–1610 and 1340–1320 cm<sup>-1</sup> (asymmetric and symmetric stretching vibrations of O-C-O, respectively). Interaction of CO<sub>2</sub> with strongly basic O<sup>2-</sup> anions results in formation of unidentate carbonates, with asymmetric and symmetric stretching vibrations near 1560-1510 and 1420-1360 cm<sup>-1</sup>. Figure 11 represents the IR spectra of desorption behavior of preadsorbed CO<sub>2</sub> at different temperatures over 1.0Ag/MgO-COK-12 material. The IR spectrum of adsorbed CO<sub>2</sub> at room temperature shows broad and overlapping bands (Figure 11, black curve). Contributions of all three adsorbed species are observed in this spectrum at low temperature, with the unidentate carbonate species dominating the spectrum. Increasing the desorption temperature to 373 K resulted in the desorption of the bicarbonates; only uni- and bidentate carbonates were observed at this temperature. Both species were still present at 473 K but with significant decreased intensities. At higher desorption temperatures (573 and 673 K), very low intensities of adsorbed CO<sub>2</sub> were observed, indicating that most of the CO<sub>2</sub> was desorbed at these temperatures.

To access the strength and the amount of the basic sites, TPD experiments were conducted (Table 2 and Figure 12). The TPD profiles of the catalysts were deconvoluted into three desorption peaks: bicarbonate species on weakly basic OH groups, bidentate carbonate on Mg–O pairs with intermediate strength, and unidentate carbonate on strongly basic  $O^{2-}$ anions (in accordance with the three observed species in IR spectroscopy). These peaks had maxima around 358, 403, and

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Entry	Catalvst	Relative Lewis acidity <sup>[a]</sup>	Basicity <sup>(b)</sup> [ $\mu$ mol g <sub>cat</sub> <sup>-1</sup> ]			
,	,	$[cm^{-1}g_{cat}^{-1}]$	Total Peak 1		Peak 2	Peak 3
1	MgO	43	25	8	10	7
2	SiO <sub>2</sub>	11	1	1	0	0
3	COK-12	15	-	-	-	-
4	MCM-41	21	-	-	-	-
5	1.0Ag/SiO <sub>2</sub>	41	-	-	-	-
6	MgO-SiO <sub>2</sub>	66	32	10	13	10
7	0Ag/MgO-SiO <sub>2</sub>	363	42	12	14	16
8	0.5Ag/MgO-SiO <sub>2</sub>	196	17	6	5	6
9	1.0Ag/MgO-SiO <sub>2</sub>	235	27	9	7	11
10	2.0Ag/MgO-SiO <sub>2</sub>	236	11	5	2	4
11	4.0Ag/MgO-SiO <sub>2</sub>	296	17	6	6	5
12	MgO-COK-12	43	27	8	4	15
13	0Ag/MgO-COK-12	335	31	13	9	9
14	0.5Ag/MgO-COK-12	215	20	7	7	7
15	1.0Ag/MgO-COK-12	290	16	6	5	6
16	2.0Ag/MgO-COK-12	374	16	5	5	5
17	4.0Ag/MgO-COK-12	233	13	5	5	4
18	MgO-MCM-41	129	22	7	5	10
19	0Ag/MgO-MCM-41	185	30	9	10	11
20	1.0Ag/MgO-MCM-41	312	16	6	4	6
21	2.0Ag/MgO-MCM-41	348	16	6	4	5

[a] The relative Lewis acidity is represented by the peak area of the signal at 1450 cm<sup>-1</sup> of pyridine desorbed at 423 K corrected for the thickness of the wafer. [b] The basicity is obtained after CO<sub>2</sub>-TPD and signal deconvolution (see Figure 12).

face area of MgO or an increased roughening of the surface (more corners, terraces, and edges) leads to an increase in basicity.<sup>[29]</sup> The dispersion depends on textural properties of the silica used. Regarding the basic site distribution, it should be noted that the MgO-SiO<sub>2</sub> material contains more medium strength whereas the Ma-O pairs, number of basic OH groups and strong basic O<sup>2-</sup> sites is lower. The basic site distribution of MgO-SiO<sub>2</sub> is similar to the distribution on the surface of bulk MgO (Table 2, entries 1 and 6). Conversely, COK-12 and MCM-41 containing samples reveal a higher number of strongly basic isolated O<sup>2-</sup> ions and a reduced amount of Mg-O pairs, while the number of surface basic OH groups is comparable



**Figure 11.** FTIR spectra of preadsorbed CO<sub>2</sub> on 1.0Ag/MgO-COK-12. The different curves represent different desorption temperatures: 298 K (——), 373 K (——), 473 K (——), 573 K (——), 673 K (——). The presented IR spectra are after subtraction of the spectrum without CO<sub>2</sub> adsorption.

503 K (denoted as peak 1, 2, and 3, respectively). This deconvolution is illustrated in Figure 12 for the 4.0Ag/MgO-SiO<sub>2</sub> catalyst. The TPD profiles of all catalysts have a similar shape. Mechanical mixing of Mg(OH)<sub>2</sub> with silica followed by calcination increases the basicity compared to the calcined bulk MgO. This can be explained by a better dispersion (less agglomeration of the MgO particles, see flakes of magnesia on silica in the SEM pictures of Figure S3) and/or a higher surface heterogeneity of the formed magnesia particles on the external surface of the silica particles. It has been shown that an increase of the sur-



**Figure 12.**  $CO_2$ -TPD on xAg/MgO-SiO<sub>2</sub> catalyst with different Ag loadings: 0Ag/MgO-SiO<sub>2</sub> (—); 1.0Ag/MgO-SiO<sub>2</sub> (—); 4.0Ag/MgO-SiO<sub>2</sub> (—). The dotted lines are the results of the deconvolution of the TPD signal with the 4.0Ag/MgO-SiO<sub>2</sub> catalyst. Peaks 1, 2, and 3 (Table 2) appear at increasing desorption temperature.

to that of MgO-SiO<sub>2</sub> (Table 2, entries 12 and 18). Wetting with water followed by calcination results in an increase of the basicity (Table 2, entries 7, 13 and 19). The reason for this could be an increase of the MgO surface area due to rehydration of MgO and a better dispersion of the formed magnesium hydroxide not only on the external but also on the intraporous silica surface. On one hand, this leads to the interaction of Mg(OH)<sub>2</sub> with the silica surface and the formation of surface silicate during calcination, thus decreasing the total amount of "free" MgO. On the other hand, the surface rearrangements on

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the MgO surface also result in changes in the basic strength distribution of the catalysts.

The presence of silver nitrate in the impregnation solution leads to decreasing amounts of basic sites (Table 2, entries 8-11, 14-17, and 20-21). All three desorption peaks decrease with increasing Ag loading. The decreasing basicity with increasing Ag loading can be explained by the presence of higher concentrations of NO<sub>3</sub><sup>-</sup> ions in the impregnation solution, which may interact with the MgO phase during the drying step. According to Choudhary et al., the thermal decomposition of Mg(NO<sub>3</sub>)<sub>2</sub> results in bigger crystals with lower amounts of surface defects, a lower surface area and consequently a lower total basicity compared to MgO obtained via rehydration and thermal decomposition of a powdered commercial MgO.<sup>[29a]</sup> Thus, it can be assumed that the presence of nitrate ions might exert the same effect on the MgO phase formed after impregnation. Regarding the strength distribution of the basic sites, it was observed that the amount of all types of basic sites decrease with increasing silver loadings and that the amount of the weakly basic OH groups is similar to that of the strong basic isolated O<sup>2-</sup> sites, whereas the number of the basic sites of intermediate strength (Mg-O pairs) is always lower.

The acid properties of the catalysts were analyzed by IR spectroscopy of adsorbed pyridine (Table 2). The IR spectra of 1.0Ag/MgO-COK-12 after pyridine adsorption and desorption at different temperatures are shown in Figure 13 [the spectra of other COK-12 materials without Ag are given in Figure S9; the spectra of other catalysts (SiO<sub>2</sub> and MCM-41) showed similar vibration bands]. Characteristic vibrations of pyridine adsorbed on acid sites are 1450 cm<sup>-1</sup> for strong Lewis acid sites (SL), 1490 cm<sup>-1</sup> for a combination of Lewis and Brønsted acid sites (B+L), 1540 cm<sup>-1</sup> for Brønsted acid sites, 1578 cm<sup>-1</sup> for weak Lewis acid sites (WL), 1607 cm<sup>-1</sup> for strong Lewis acid sites reveal that there are only Lewis acid sites present on the catalysts surface, while the presence of an absorption band at



Figure 13. FTIR spectra of 1.0Ag/MgO-COK-12 after pyridine adsorption and evacuation at different temperatures: i) 323 K, ii) 423 K, iii) 523 K. The characteristic absorption peaks of pyridine on acidic sites are the following: Brønsted (B), weak Lewis (WL), strong Lewis (SL) and hydrogen bound pyridine (H).

1540 cm<sup>-1</sup> for Brønsted acid sites was not detected. The origin of the Lewis acidity is illustrated in Figure 14 and Figure S9. Silica surface adsorbs very low amounts of pyridine on its surface. Ag supported on SiO<sub>2</sub> adsorbs pyridine at 423 K. Higher amounts are obtained for the samples containing MgO. These results indicate that charged Ag species<sup>[31]</sup> and Mg atoms as



Figure 14. FTIR spectra of different SiO<sub>2</sub> materials after pyridine adsorption and evacuation at 423 K: i) 1.0Ag/MgO-SiO<sub>2</sub>, ii) 0Ag/MgO-SiO<sub>2</sub>, iii) MgO-SiO<sub>2</sub>, iv) 1.0Ag/SiO<sub>2</sub>, v) SiO<sub>2</sub>.

coordinatively unsaturated  $\rm Mg^{2+}$  atoms (in the MgO  $\rm phase^{[30c]}$ and Mg atoms in the SiO<sub>2</sub> phase<sup>[26]</sup>) create the Lewis acid sites in the catalysts. The Mg atoms have the largest contribution to the Lewis acidity of the final, impregnated catalysts. The Lewis acid sites on the catalysts were estimated using the absorbance of the vibration band near 1450 cm<sup>-1</sup> at a desorption temperature of 423 K. These results are included in Table 2. Whereas the starting materials and the mechanically mixed supports show low acidity, the catalysts after wetting with water and after impregnation with silver have much more Lewis acid sites on their surface. No clear correlation is observed between the Lewis acid strength and the Ag loading (Table 2, entries 7-11, 13-17 and 19-21). It may be assumed that presence of both  $Ag^+$  and  $NO_3^-$  ions in the impregnation solution influences the final acidity of the catalysts. The Ag ions will add Lewis acidic Ag species to the catalyst. The presence of NO<sub>3</sub><sup>-</sup> ions will result in lower MgO dispersion (bigger crystals with less defects in the surface, as discussed during the analysis of the CO<sub>2</sub>-TPD results), which results in less coordinatively unsaturated Mg<sup>2+</sup> atoms. Thus, both ions seem to counteract each other in creating Lewis acidity on the surface of the catalysts.

# Discussion

The synthesis of butadiene from ethanol is a process with multiple reaction steps (see Scheme 1). Different authors have suggested different reactions as the rate-determining step depending on the investigated catalyst. The current catalytic data give insights into the rate-determining step of the investigated

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magnesia-silica-based catalysts. The catalysts without silver (mechanically mixed supports and supports after a wetting treatment) show low conversions and very low selectivities to intermediate products such as acetaldehyde, crotonaldehyde, and crotyl alcohol, but a significant selectivity to the final product, that is, butadiene. This suggests that the first reaction step, that is, the dehydrogenation of ethanol, is the rate-determining step with magnesia-silica catalysts devoid of silver. The addition of Aq, with its ethanol dehydrogenating potential, results in a significant increase of the conversion and butadiene yield. The acetaldehyde yield also increases with increasing Ag loading while the selectivity to the other intermediate products remains very low. The significant promotional effect of silver as well as the presence of acetaldehyde in the product mixture, suggests that the aldol condensation becomes ratedetermining on the silver-containing catalysts. Calculation of the observed activation energy from the kinetics at different temperatures (see Figure 3) reveals a value of 35 kJ mol<sup>-1</sup>, in agreement with typical reported values for aldol condensation reactions.<sup>[32]</sup>

Next, the characterization results of the catalysts are used to interpret the catalytic results in the butadiene formation process. The starting magnesia-silica materials show similar low conversion levels, since the dehydrogenation of ethanol is the rate-determining step on these silver-free catalysts. On basic catalysts, the dehydrogenation is catalyzed by either basic OH groups or acid-base pair of sites (Mg–O pairs),<sup>[10a, 28d]</sup> which are both present on the surface of the MgO-silica catalysts (see CO<sub>2</sub>-TPD results). These basic sites are not effective; few products resulting from the ethanol dehydrogenation are present in the product stream (yield of acetaldehyde and C4 products combined is less than 5%, see Table 1). These mixed supports also show some dehydration activity (more than 20% selectivity for ethylene and diethyl ether combined). The catalytic results of the individual oxides (Table 1, entries 1-4) indicate that the dehydration activity of the mixed supports originates from the silica phase because all three silica sources have significantly higher selectivities to dehydration products compared to pure MgO. Surface silanols in the silica phase are most probably responsible for the dehydration activity according to E1 mechanism.<sup>[33]</sup> The mixed supports also contain basic sites on their surface indicating that an E1cB-like mechanism, suggested for basic catalysts as bulk MgO or Mg-rich Mg<sub>x</sub>AlO<sub>y</sub> mixed oxides, is also a possible route of ethylene formation.<sup>[34]</sup>

Wetting with water of the MgO-silica mixed supports results in significant surface rearrangements in both phases. The contact with water changes the pore structures of the materials significantly (see nitrogen sorption and SAXS analysis) and results in the formation of an amorphous surface magnesium silicate phase, due to partial hydration of MgO surface followed by interaction of dissolved Mg<sup>2+</sup> ions with the silica surface.<sup>[10b, 13]</sup> These reactions also result in the creation of new Lewis acid sites and basic sites on the surface of the resulting catalysts. Despite the increased basicity, which was expected to increase the dehydrogenation activity, the wetting step does not affect the conversion level significantly and changes the product distribution only slightly. An increase in the Lewis acidity, observed by IR pyridine adsorption, results in an increase in the diethyl ether formation for all 0Ag/MgO-silica catalysts. The diethyl ether formation requires the adsorption of two ethanol molecules on neighboring Lewis acid and basic sites.<sup>[28d]</sup> Addition of silver results in a significant increase of the conversion and butadiene selectivity. The added silver species are much more active in the dehydrogenation of ethanol than the basic sites of the mechanical mixed and the wetted supports. These silver species on the active catalysts are mainly metallic nanoparticles, as observed by UV/Vis spectroscopy and XRD. The silver nanoparticles catalyze the C-H cleavage and the recombination and desorption of H<sub>2</sub> molecules much faster than the basic sites.<sup>[35]</sup> For all silica sources, the conversion increases with increasing Ag loading until around 2 wt% and higher loadings did not result in higher conversions anymore. Thus the optimal Ag loading for the first step in the reaction Scheme of the butadiene formation, the dehydrogenation, is 1-2 wt% Ag. This is explained here by a decrease of the dispersion of the silver particles, due to the formation of bigger nanoparticles with higher silver loadings, as observed in the XRD data. On the other hand, the selectivity towards butadiene reaches a maximum at a silver loading of 0.5-1% and then decreases due to higher amounts of unconverted acetaldehyde. The presence of unconverted acetaldehyde in the product stream indicates that the aldol condensation becomes rate-determining. The decrease of the butadiene selectivity, observed with increasing silver loading, could be due to a reduction of the basicity with increasing Ag content (observed by the TPD of CO<sub>2</sub>). Basic sites are known to catalyze the aldol condensation on oxides and mixed oxides. Weak, medium and strong basic sites are present on the surface of the investigated catalysts. Identification of the most active basic site was not possible as changes in the basicity were similar for all types of basic sites. In literature, all strengths of basic sites have been reported to catalyze this reaction. The weakly basic OH groups and Lewis acid-weak base pair sites (Mg-O) are the most efficient catalytic sites because the strong basic O2- sites are quickly deactivated by polycondensation products.<sup>[34a, 36]</sup> Moreover, a slightly lower catalytic performance of COK-12 (based on the series of catalysts for both conversion and BD selectivity) is also explained by a lower amount of "free" MgO left due to the interaction with the silica surface and the silicate formation, which is confirmed by the NMR data and IR spectra of the OH groups.

The MPV reduction of formed crotonaldehyde by ethanol can be catalyzed by Lewis acid sites on acidic catalysts or Lewis acid-base pair sites (Mg–O pairs) on basic catalysts.<sup>[37]</sup> Both types of sites are observed on all the tested catalysts; Lewis acid sites via IR spectroscopy of adsorbed pyridine and Lewis acid-base pair sites with TPD of CO<sub>2</sub>. Very little crotonal-dehyde is observed in the reaction products, indicating that these sites are sufficiently active to catalyze the formation of crotyl alcohol.

The dehydration of crotyl alcohol to butadiene is also efficiently catalyzed by the silver-promoted magnesia-silica catalysts; the combined selectivity of crotyl alcohol with 1-butanol is less than 10%. The dehydration of crotyl alcohol to buta-

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diene is assumed to be catalyzed by the surface silanols in the silica phase. However, the pyridine probe IR experiments did not show the presence of Brønsted acid sites, indicating that residual silanols on silica can only be mildly acidic. The double bond in the crotyl alcohol molecule will aid the dehydration reaction by stabilizing the cationic intermediate after the abstraction of the protonated hydroxyl group according to the E1 mechanism.

The commercial silica  $(SiO_2)$  resulted in the most active catalysts of the three silica materials, followed by COK-12. The MCM-41-based catalysts showed the lowest levels of conversion, indicating indirectly that some part of the Ag particles is not accessible for the reactants due to the collapse of the MCM-41 pore structure (see SAXS and N<sub>2</sub> sorption experiments). However, the butadiene selectivity is similar to that of 0.5–1.0Ag/MgO-SiO<sub>2</sub> catalysts, indicating that the amount of "free" MgO is enough to perform the aldol condensation.

The above results and discussion created clear insights on the activity of the Ag/MgO-silica catalysts. These findings and insights were used to construct a model of the ternary catalyst system to explain the catalytic activity of these materials. This model is illustrated in Figure 15. The yellow phase illustrates



**Figure 15.** Illustration of the proposed model to explain the catalytic activity of the ternary Ag/MgO-Silica catalysts in the conversion of ethanol into butadiene.

the silica phase. This phase is loaded with metallic silver particles (red) and an amorphous surface magnesium silicate layer (represented by "Mg<sup>2+</sup>"). A magnesium-rich phase is located on top of the silica phase and is illustrated by the grey particles. The different reaction steps for the conversion of ethanol into butadiene are also included in the Figure. Each active site catalyzing the individual reaction steps is included with a reference to its location on the catalyst.

The activity of the ternary Ag/MgO-silica system is the result of an interplay of different active sites on different locations in the catalyst. The dehydrogenation of ethanol is catalyzed by the metallic silver nanoparticles located on the SiO<sub>2</sub> phase of the catalyst. Next, the formed acetaldehyde reacts via an aldol condensation reaction to crotonaldehyde, catalyzed by basic sites (like Mg–OH, Mg–O arrays and O<sup>2–</sup> on corners) present on the MgO rich phase. Crotonaldehyde is reduced to crotyl alcohol through a MPV reaction in which ethanol acts as the hydrogen donor. This reaction is catalyzed by coordinatively unsaturated, Lewis acidic Mg<sup>2+</sup> atoms (at corners on the MgO phase and in the SiO<sub>2</sub> phase). The final step is the dehydration of crotyl alcohol to form butadiene. This step is catalyzed by silanol groups located on the SiO<sub>2</sub> phase. The model of our catalyst illustrates the importance of the three different components in our catalyst and explains the lower activity of catalysts lacking one of these components.

# Conclusions

The MgO-SiO<sub>2</sub> system doped with silver is an active catalyst for the production of butadiene from ethanol. It was shown that the impregnation method, apart from introducing silver, also resulted in the formation of an amorphous magnesium silicate layer on the silica phase. The best catalytic results were obtained with commercial silica (SiO<sub>2</sub>), which had the most stable pore architecture and silica structure, and had an optimal silver loading near 1-2 wt%. Higher temperatures had a beneficial effect on the activity of the ternary catalysts. The highest butadiene productivity reached, was 0.29  $g_{BD} {g_{Catalyst}}^{-1} h^{-1}$  with 1.0Ag/MgO-SiO<sub>2</sub> at 753 K and a WHSV of 1.2 h<sup>-1</sup>, corresponding to a BD yield and selectivity of 42 and 50%, respectively. The catalytic results were explained by combining the characterization results of the investigated catalysts. In an optimal catalyst composition, a high amount of accessible silver nanoparticles and a high amount of basic sites (Mg-O pairs and basic OH groups) were present. Both species are critical in butadiene production as they catalyze very efficiently the dehydrogenation of ethanol and the aldol condensation, respectively. Both steps appear as rate-determining steps in the butadiene formation on different magnesia-silica catalysts. The dehydrogenation of ethanol is rate-determining on silver-free catalysts, while, on the most active, silver-containing catalysts, the aldol condensation becomes the rate-determining step. The consecutive aqueous impregnation of silver is a very effective procedure as it introduces dehydrogenation activity in the form of silver species, and, at the same time, increases the Lewis acidity and retains sufficient basicity to catalyze the gas-phase conversion of ethanol into butadiene. All this new information about the catalytic performance of the silver-promoted MgOsilica catalysts was combined into a model to explain the different active sites of the different reaction steps in the butadiene formation and the location of these active sites on the surface of the active catalysts.

# **Experimental Section**

#### **Catalyst preparation**

Grace silica 254 was used as the commercially available amorphous mesoporous silica (further referred to as SiO<sub>2</sub>).

COK-12, an ordered mesoporous silica, was prepared according to the method of Jammaer et al.  $^{[18a]}$  The starting surfactant solution

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was prepared by dissolving of the triblock copolymer Pluronic P123 (BASF, 4 g) in deionized water (107.5 g) before adding citric acid monohydrate (Riedel-De Haen, 3.684 g) and trisodium citrate (UCB, 2.540 g). The resulting solution was stirred for 24 h. A sodium silicate solution (10% NaOH, 27% SiO<sub>2</sub>, Merck, 10.4 g) was diluted in deionized water (30 g) and added to the surfactant solution. The solution was stirred for 5 min and aged at RT for 24 h. The material was filtered, washed, and dried at 333 K overnight. Finally, it was calcined in air first at 573 K for 8 h, and then at 773 K (1 Kmin<sup>-1</sup>) for 8 h.

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The method of Grün et al. was used to synthesize spherical MCM-41 particles.<sup>[18b]</sup> The starting surfactant solution was prepared by dissolving *n*-hexadecyltrimethylammonium bromide (C<sub>16</sub>TMABr, Fluka, 2.5 g) in deionized water (50 g) before adding aqueous ammonia (32 wt%, Merck, 13.2 g) and absolute ethanol (VWR, 60.0 g). The solution was stirred for 15 min, before tetraethyl orthosilicate (TEOS, Aldrich, 4.7 g) was added. The resulting gel was stirred for 2 h, filtered and washed with deionized water (100 mL) and methanol (Aldrich, 100 mL). The washed sample was dried overnight at 363 K and calcined at 823 K for 5 h (1 Kmin<sup>-1</sup>).

 $Mg(OH)_2$  was obtained from the rehydration of commercial MgO according to the method of Di Cosimo et al.,<sup>[38]</sup> involving dilution of commercial MgO (Aldrich, 25 g) in deionized water (250 mL). The mixture was then stirred and heated to 353 K for 4 h, and finally dried at 358 K.

The MgO-silica catalysts were prepared by dry milling of  $Mg(OH)_2$  with each of the silicas followed by calcination at 673 K for 3 h (2.5 Kmin<sup>-1</sup>). Commercial silica gel (SiO<sub>2</sub>), COK-12, and MCM-41 were used as silica sources. All the mixed systems had a molar Mg/ Si ratio of 2. Pure MgO was obtained by calcining Mg(OH)<sub>2</sub> in the same manner as the mixed catalysts.

Silver-containing samples with different Ag loading were prepared by incipient wetness impregnation of the calcined MgO-silica support with the appropriate amount of an aqueous silver nitrate solution ranging from 30 mM to 260 mM.<sup>[4]</sup> After impregnation the samples were dried at 333 K and calcined at 673 K for 3 h (2.5 Kmin<sup>-1</sup>). The samples were denoted as xAg/MgO-silica, where x represents the silver loading in wt%. Blanco catalysts devoid of silver (0Ag/MgO-silica) were also prepared using the same preparation method, using deionized water as wetting solution. A Mg-free Ag-on-silica sample (1.0Ag/SiO<sub>2</sub>) was obtained by the same impregnation method.

#### Catalyst characterization

SEM images were recorded on an SEM Philips XL 30 FEG. The samples were fixed on a carbon tape and coated with a layer of gold. ESEM/EDX mapping was performed on a ESEM Philips XL 30 FEG equipped with an EXD detector (EDAX). The surface of the powdered catalysts, embedded in a resin, was grinded, polished and coated with carbon before the measurement.

SAXS measurements were recorded at RT with a SAXSSess mc<sup>2</sup> instrument (Anton Paar, Graz, Austria) equipped with a line-collimated CuK<sub>α</sub> X-ray source ( $\lambda$ =0.154056 nm) and a 2D imaging plate detector. The SAXS patterns were normalized to the incident beam intensity. Background subtraction (from an empty capillary) and correction for instrumental broadening were performed by using the SAXSquant software.

Powder XRD patterns were recorded on a STOE STADI P Combi diffractometer equipped with a Ge (111) monochromator (CuK<sub> $\alpha$ </sub> X-ray

The specific surface areas and porosities of the catalysts were determined by nitrogen adsorption at 77 K on a Micromeritics Tristar 3000 instrument. All samples were degassed under nitrogen flow at 673 K for 6 h before the measurements. The BJH model was applied on the adsorption branch of the nitrogen isotherm to obtain the pore size distributions.

<sup>29</sup>Si MAS NMR spectra were recorded on a Bruker AMX300 spectrometer (7.0 T). At this field, the resonance frequency of <sup>29</sup>Si is 59.6 MHz. 4,000 scans were accumulated with a recycle delay of 60 s, the pulse length being 5.0  $\mu$ s. The spinning frequency of the rotor was 5 kHz. The <sup>29</sup>Si CP MAS NMR spectrum was recorded on a Bruker Avance400 spectrometer (9.4 T). At this field, the resonance frequency of <sup>29</sup>Si is 79.5 MHz. 17,000 scans were accumulated with a recycle delay of 10 s. The CP contact time was 4.0 ms. The spinning frequency of the rotor was 10 kHz. For both measurements the samples were packed in 4 mm Zirconia rotors. Tetramethylsilane was used as chemical shift reference.

Basicity of the catalysts was determined by temperature-programmed desorption of  $CO_2$  ( $CO_2$ -TPD). A flow apparatus was equipped with a Pfeiffer Omnistar quadrupole mass spectrometer for the detection of the desorbed gases. Prior to adsorption, the sample (150 mg) was pretreated in a helium flow for 1 h at 673 K (5 Kmin<sup>-1</sup>). Saturation of the samples was performed in a  $CO_2$  flow at RT for 30 min. Weakly bound  $CO_2$  was removed by flushing with helium for 1 h. The TPD experiments were carried out in a helium flow of 20 mLmin<sup>-1</sup> in the temperature range of 298–693 K with a heating rate of 10 Kmin<sup>-1</sup>.

IR experiments were performed on a Nicolet 6700 spectrometer equipped with a DTGS detector (128 scans; resolution of 2 cm<sup>-1</sup>). Self-supporting wafers were pretreated in vacuum at 673 K for 1 h (5 Kmin<sup>-1</sup>) before measurements. Acidity of the catalysts was analyzed using pyridine as probe. After pretreatment at 673 K, the samples were saturated with about 25 mbar of pyridine vapor at 323 K for 20 min. The evacuated samples containing the sorbed pyridine were subjected to a temperature-programmed desorption at 323, 423, 523 K for 20 min, respectively, with a heating rate of 5 Kmin<sup>-1</sup> and the IR spectra were recorded in situ at these temperatures. CO<sub>2</sub> was also used as probe to analyze the basicity. After pretreatment at 673 K, the sample was saturated in a  $\rm CO_2$  flow at 298 K for 30 min. The saturated sample was subjected to a temperature-programmed desorption at 298, 373, 473, 573 and 673 K for 20 min, respectively, with a heating rate of 5 Kmin<sup>-1</sup> and cooling down to 298 K in between to record the IR spectra. For analysis, the spectrum of the sample without CO<sub>2</sub> is subtracted from the spectra with adsorbed CO<sub>2</sub>.

The nature of the silver and magnesium oxide species was examined by UV/Vis DRS. Spectra were recorded on an Agilent Carry 5000 spectrophotometer using Halon white standard as reference. Prior to the measurements, the samples were pretreated under a nitrogen flow at 673 K for 1 h (5 Kmin<sup>-1</sup>).

#### **Catalytic reactions**

The catalytic conversion of ethanol to butadiene was carried out in the reactor system described previously.<sup>(4)</sup> Briefly, a downstream continuous-flow quadri-reactor containing four parallel alloy 600 reactor tubes with 3 mm internal diameter was used. Typically,

radiation,  $\lambda = 0.154056$  nm) in transmission geometry with a position sensitive image plate detector (IP PSD). Measurements at RT in Debye–Scherrer mode were carried out in capillaries with 0.7 mm internal diameter.

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300 mg of catalyst, pelletized to a 0.25-0.5 mm fraction, was placed in the middle part of the reactor between silicon carbide layers (SiC, 200-450 mesh particle size, Aldrich) to limit the contact time in the alloy reactor and avoid the thermal reaction of ethanol. Blank tests at reaction temperature without catalyst showed only trace conversions. Ethanol was introduced into the system using a StepDos 03S pump at a rate of 1.8 mL h<sup>-1</sup> and diluted with argon as the carrier gas (20  $mL\,min^{-1}$  per reactor), corresponding to a WHSV of 1.2 h<sup>-1</sup>. The reaction was performed at 673 K and atmospheric pressure. Products were analyzed with an on-line gas chromatograph equipped with a CP-Poraplot Q-HT column, a methanator, and a FID detector, avoiding the use of sensitivity coefficients. The carbon balance was always better than 90% and, with thermogravimetric analysis, (TGA Q500 TA instruments) of spent catalysts only a small amount of coking was observed (<2 wt% cokes relative to the amount of ethanol fed). Conversion (X) and selectivity (S) in %C, were calculated according to the formula [Equations (1), (2)]:

$$X = \frac{\sum_{n_i - n_{\text{EIOH}}}{\sum_{n_i}} \cdot 100 \tag{1}$$

$$S = \frac{n_i}{\sum n_i - n_{\text{ErOH}}} \cdot 100 \tag{2}$$

where  $n_i$  is the amount of C moles of product *i* in the stream of the reaction products.

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- a) E. V. Makshina, M. Dusselier, W. Janssens, J. Degreve, P. A. Jacobs, B. F. Sels, *Chem. Soc. Rev.* 2014, *43*, 7917–7953; b) C. Angelici, B. M. Weckhuysen, P. C. A. Bruijnincx, *ChemSusChem* 2013, *6*, 1595–1614.
- [2] a) H. N. Sun, J. P. Wristers in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc. DOI: 10.1002/0471238961.02212001192114.a01, 2000; b) J. Grub, E. Löser in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2000.
- [3] a) K. Laird, Bio-Based Chemicals Receive Boost From Shale Gas Boom in North America, 2014, http://www.plasticstoday.com/articles/bio-basedchemicals-receive-boost-from-shale-gas-boom-in-north-america-140523;
   b) M. Hackett, Chemical Building Blocks from Renewables, 2014, http:// www.ihs.com/products/chemical/planning/special-reports/chemical-renewables.aspx.
- [4] E. V. Makshina, W. Janssens, B. F. Sels, P. A. Jacobs, Catal. Today 2012, 198, 338-344.
- [5] S. Pariente, N. Tanchoux, F. Fajula, G. Centi, S. Perathoner in *Catalysis for Renewables* (Eds.: G. Centi, R. A. Van Santen), Wiley-VCH, Weinheim, 2007, pp. 183–207.
- [6] a) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 2006, 106, 4044–4098;
   b) Y. Liu, K. Murata, M. Inaba, I. Takahara, K. Okabe, *Catal. Today* 2011,

164, 308–314; c) J. J. Spivey, A. Egbebi, *Chem. Soc. Rev.* **2007**, *36*, 1514–1528; d) V. Subramani, S. K. Gangwal, *Energy Fuels* **2008**, *22*, 814–839.

- [7] A. D. Patel, K. Meesters, H. den Uil, E. de Jong, K. Blok, M. K. Patel, Energy Environ. Sci. 2012, 5, 8430–8444.
- [8] IFP Energies Nouvelles, Axens, IFPEN and Michelin Join Forces to Create a Synthetic Rubber Production Channel Using Biomass, 2013, http:// www.ifpenergiesnouvelles.com/actualites/communiques-de-presse/creation-d-une-filiere-de-production-de-caoutchoucs-synthetiques-a-partirde-biomasse-axens-ifpen-et-michelin-unissent-leurs-forces.
- [9] a) S. V. Lebedev, **1929**, FR 665,917; b) S. V. Lebedev, **1930**, GB331,482;
   c) H.-J. Arpe, S. Hawkins, *Industrial Organic Chemistry, 5th Edition*, John Wiley & Sons, Inc., **2010**.
- [10] a) H. Niiyama, S. Morii, E. Echigoya, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 655–659; b) S. Kvisle, A. Aguero, R. P. A. Sneeden, *Appl. Catal.* **1988**, *43*, 117–131.
- [11] a) W. J. Toussaint, J. T. Dunn, D. R. Jachson, *Ind. Eng. Chem.* 1947, *39*, 120–125; b) W. J. Toussaint, J. T. Dunn, 1947, US 2,421,361.
- [12] V. L. Sushkevich, I. I. Ivanova, V. V. Ordomsky, E. Taarning, *ChemSusChem* 2014, 7, 2527–2536.
- [13] G. Natta, R. Rigamonti, Chim. Ind. (Milan). 1947, 29, 239-243.
- [14] R. Ohnishi, T. Akimoto, K. Tanabe, J. Chem. Soc. Chem. Commun. 1985, 1613–1614.
- [15] a) B. B. Corson, H. E. Jones, C. E. Welling, J. A. Hinckley, E. E. Stahly, Ind. Eng. Chem. 1950, 42, 359–373; b) C. Angelici, M. E. Z. Velthoen, B. M. Weckhuysen, P. C. A. Bruijnincx, ChemSusChem 2014, 7, 2505–2515.
- [16] a) J. M. Berak, R. Guczalski, J. Wojcik, Acta Chim. Acad. Sci. Hung. 1966, 50, 163–166; b) Y. Kitayama, A. Michishita, J. Chem. Soc. Chem. Commun. 1981, 401–402; c) Y. Kitayama, M. Satoh, T. Kodama, Catal. Lett. 1996, 36, 95–97; d) Y. Kitayama, K. Shimizu, T. Kodama, S. Murai, T. Mizusima, M. Hayakawa, M. Muraoka in Stud. Surf. Sci. Catal., Vol. 142 (Eds.: G. G. R. Aiello, F. Testa), Elsevier, 2002, pp. 675–682; e) V. Gruver, A. Sun, J. J. Fripiat, Catal. Lett. 1995, 34, 359–364.
- [17] V. V. Ordomskiy, V. L. Sushkevich, I. I. Ivanova, 2012, WO 2012/015340A1.
- [18] a) J. Jammaer, A. Aerts, J. D'Haen, J. W. Seo, J. A. Martens, J. Mater. Chem. 2009, 19, 8290–8293; b) M. Grün, K. K. Unger, A. Matsumoto, K. Tsutsumi, Microporous Mesoporous Mater. 1999, 27, 207–216.
- [19] a) J. Jammaer, T. S. van Erp, A. Aerts, C. E. A. Kirschhock, J. A. Martens, J. Am. Chem. Soc. 2011, 133, 13737–13745; b) B. Pauwels, G. Van Tendeloo, C. Thoelen, W. Van Rhijn, P. A. Jacobs, Adv. Mater. 2001, 13, 1317–1320.
- [20] a) G. Martra, H. Yoshida, V. Dellarocca, C. Murata, T. Hattori, S. Coluccia, L. Marchese in *Stud. Surf. Sci. Catal., Vol. 140* (Eds.: C. C. A. Gamba, S. Coluccia), Elsevier, **2001**, pp. 331–340; b) S. Coluccia, A. J. Tench, R. L. Segall, *J. Chem. Soc. Faraday Trans. 1* **1979**, *75*, 1769–1779.
- [21] a) A. N. Pestryakov, A. A. Davydov, J. Electron Spectrosc. Relat. Phenom. 1995, 74, 195–199; b) J. Lu, J. J. Bravo-Suárez, A. Takahashi, M. Haruta, S. T. Oyama, J. Catal. 2005, 232, 85–95; c) L. Jin, K. Qian, Z. Jiang, W. Huang, J. Mol. Catal. A 2007, 274, 95–100; d) R. Yamamoto, Y.-s. Sawayama, H. Shibahara, Y. Ichihashi, S. Nishiyama, S. Tsuruya, J. Catal. 2005, 234, 308–317; e) Y.-s. Sawayama, H. Shibahara, Y. Ichihashi, S. Nishiyama, S. Tsuruya, Ind. Eng. Chem. Res. 2006, 45, 8837–8845; f) N. Bogdanchikova, F. C. Meunier, M. Avalos-Borja, J. P. Breen, A. Pestryakov, Appl. Catal. B 2002, 36, 287–297; g) L. Zhang, C. Zhang, H. He, J. Catal. 2009, 261, 101–109.
- [22] a) D. W. Sindorf, G. E. Maciel, J. Am. Chem. Soc. 1983, 105, 3767–3776;
   b) G. E. Maciel, D. W. Sindorf, J. Am. Chem. Soc. 1980, 102, 7606–7607.
- [23] a) J. S. Hartman, R. Millard, *Phys. Chem. Miner.* **1990**, *17*, 1–8; b) J.-B. d'Espinose de La Caillerie, M. Kermarec, O. Clause, *J. Phys. Chem.* **1995**, *99*, 17273–17281.
- [24] a) A. Jentys, N. H. Pham, H. Vinek, J. Chem. Soc. Faraday Trans. 1996, 92, 3287–3291; b) G. Mestl, H. Knözinger in Handbook of Heterogeneous Catalysis (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH Verlag, Weinheim, 2008, pp. 932–971.
- [25] a) E. Knözinger, K.-H. Jacob, S. Singh, P. Hofmann, Surf. Sci. 1993, 290, 388–402; b) C. Chizallet, G. Costentin, M. Che, F. Delbecq, P. Sautet, J. Am. Chem. Soc. 2007, 129, 6442–6452.
- [26] M. Kermarec, M. Briend-Faure, D. Delafosse, J. Chem. Soc. Faraday Trans. 1 1974, 70, 2180–2188.
- [27] a) J. Bishop, E. Murad, M. D. Dyar, *Clay Miner.* 2002, *37*, 617–628; b) J. Madejová, *Vib. Spectrosc.* 2003, *31*, 1–10; c) N. N. Herrera, J.-M. Letoffe, J.-P. Reymond, E. Bourgeat-Lami, *J. Mater. Chem.* 2005, *15*, 863–871;

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d) R. L. Frost, O. B. Locos, H. Ruan, J. T. Kloprogge, *Vib. Spectrosc.* **2001**, *27*, 1–13; e) J. B. d'Espinose de La Caillerie, J. J. Fripiat, *Catal. Today* **1992**, *14*, 125–140.

- [28] a) R. Philipp, K. Fujimoto, J. Phys. Chem. 1992, 96, 9035–9038; b) Y.
   Fukuda, K. Tanabe, Bull. Chem. Soc. Jpn. 1973, 46, 1616–1619; c) T.
   Kanno, M. Kobayashi in Stud. Surf. Sci. Catal., Vol 90 (Eds.: M. M. Hideshi Hattori, O. Yoshio), Elsevier, 1994, pp. 207–212; d) J. I. Di Cosimo, V. K.
   Díez, M. Xu, E. Iglesia, C. R. Apesteguía, J. Catal. 1998, 178, 499–510.
- [29] a) V. R. Choudhary, V. H. Rane, R. V. Gadre, J. Catal. 1994, 145, 300-311;
   b) S. Ardizzone, C. L. Bianchi, B. Vercelli, *Colloids Surf.* 1998, 144, 9-17;
   c) A. O. Menezes, P. S. Silva, E. Padrón Hernández, L. E. P. Borges, M. A. Fraga, *Langmuir* 2010, 26, 3382-3387.
- [30] a) F. de Clippel, M. Dusselier, R. Van Rompaey, P. Vanelderen, J. Dijkmans, E. Makshina, L. Giebeler, S. Oswald, G. V. Baron, J. F. M. Denayer, P. P. Pescarmona, P. A. Jacobs, B. F. Sels, *J. Am. Chem. Soc.* **2012**, *134*, 10089– 10101; b) O. M. Busch, W. Brijoux, S. Thomson, F. Schüth, *J. Catal.* **2004**, *222*, 174–179; c) G. Connell, J. A. Dumesic, *J. Catal.* **1987**, *105*, 285–298.
- [31] F. Benaliouche, Y. Boucheffa, P. Ayrault, S. Mignard, P. Magnoux, *Microporous Mesoporous Mater.* 2008, 111, 80–88.
- [32] a) Y.-C. Chang, A.-N. Ko, Appl. Catal. A 2000, 190, 149–155; b) J. Venselaar, Gas-Phase Aldol Condensation over Tin on Silica Catalysts. doctoral thesis, Delft University of Technology (Delft), 1980.

- [33] K. Tanabe, M. Misono, Y. Ono, H. Hattori, New Solid Acids and Bases Their Catalytic Properties, Vol. 51, Elsevier, Amsterdam, 1989.
- [34] a) V. K. Díez, C. R. Apesteguía, J. I. Di Cosimo, *Catal. Today* 2000, *63*, 53–62; b) A. Gervasini, J. Fenyvesi, A. Auroux, *Catal. Lett.* 1997, *43*, 219–228.
- [35] a) K.-i. Shimizu, K. Sugino, K. Sawabe, A. Satsuma, *Chem. Eur. J.* 2009, *15*, 2341–2351; b) V. L. Sushkevich, I. I. Ivanova, E. Taarning, *ChemCatChem* 2013, *5*, 2367–2373.
- [36] a) G. Zhang, H. Hattori, K. Tanabe, *Appl. Catal.* 1988, *36*, 189–197;
   b) V. V. Ordomsky, V. L. Sushkevich, I. I. Ivanova, *J. Mol. Catal. A* 2010, 333, 85–93.
- [37] a) V. A. Ivanov, J. Bachelier, F. Audry, J. C. Lavalley, J. Mol. Catal. 1994, 91, 45–59; b) G. K. Chuah, S. Jaenicke, Y. Z. Zhu, S. H. Liu, Curr. Org. Chem. 2006, 10, 1639–1654; c) J. R. Ruiz, C. Jimenez-Sanchidrian, Curr. Org. Chem. 2007, 11, 1113–1125.
- [38] J. I. Di Cosimo, V. K. Díez, C. R. Apesteguía, Appl. Catal. A 1996, 137, 149–166.

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# **FULL PAPERS**

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**Ternary Ag/MgO-SiO<sub>2</sub> Catalysts for the** Conversion of Ethanol into Butadiene



**Renewable route to butadiene:** A silver-loaded MgO-SiO<sub>2</sub> catalyst is active in the direct formation of butadiene from ethanol. Preparation steps have significant impact on internal organization of the final catalyst in terms of redox-acid/base properties. Based on extensive characterizations, a model is constructed to describe the catalytic activity of this system.