Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Green Chemistry

Cutting-edge research for a greener sustainable future

www.rsc.org/greenchem

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Journal Name

ARTICLE

An analysis of the chemical, physical and reactivity features of MgO-SiO2 catalysts for butadiene synthesis with the Lebedev process

Juliana Velasquez Ochoa[a], Claudia Bandinelli[a], Olena Vozniuk[a], Alessandro Chieregato[a], Andrea Malmusi[a], Carlo Recchi[a], Fabrizio Cavani[a,b,†]

New insights on the transformation of ethanol into butadiene over MgO-SiO2 catalysts, prepared by means of the sol-gel technique, have been gained via characterization, catalytic tests, and in-situ infrared diffuse reflectance spectroscopy. Catalysts with low-Si-content, i.e., with a Mg/Si atomic ratio in the interval between 9 and 15, gave superior yield to butadiene, because of the proper combination of strong basic sites, required for ethanol activation, and a moderate number of medium-strength acid sites, needed for the dehydration of intermediately formed alkenols to butadiene. A model for the medium-strength, Lewis-type acid sites, consisting of Mg^{2+} cations with neighbouring Si^{4+} atoms, has been proposed; these sites are converted into Brønsted sites in the presence of water, a co-product of the multistep transformation of ethanol into C_4 molecules.

Introduction

Due to the harmful effects of oil use and the increased emission of greenhouse gases, the industry has been focusing on research into sustainable types of raw materials for the production of chemicals. Bio-ethanol obtained by the fermentation of sugars is one of the most interesting renewable materials, and has considerable potential as a building block for the chemical industry.[1] There are numerous applications for the conversion of ethanol into commodity chemicals (Scheme 1). In particular, the production of 1,3-butadiene is attractive since it is one of the most-used monomers in the production of tires, engineering polymers, and latex products.[2] With 25% of world rubber manufacturers using butadiene, there is an exigent need for its sustainable production.

According to literature, the mechanisms which have been suggested to explain how ethanol transforms into butadiene require catalysts with both acid and basic sites. It is generally accepted that ethanol is first dehydrogenated to acetaldehyde, which then undergoes an aldol condensation with ethanol, thus forming acetaldol.[3] But recently it has been stated that aldol condensation does not play a key role in this mechanism. Instead, the direct formation of crotyl alcohol by the reaction

a. "Toso Montanari" Department of Industrial Chemistry, Viale Risorgimento 4, 40136 Bologna, Italy.
b. INSTM, Research Unit of Bologna, Via G. Giusti 9, Florence, Italy
† e-mail: fabrizio.cavani@unibo.it

of acetaldehyde with an activated form of ethanol may lead afterwards to the formation of the diolefin by dehydration.[4]
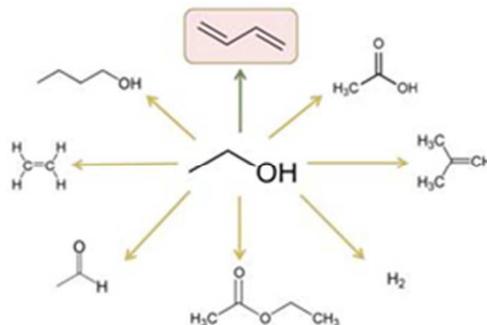
Scheme 1. Ethanol conversion into chemicals.

The industrial catalysts used for this reaction – which were used in the former Soviet Union mainly during the 1930s and later on until the 1950s in other countries as well – are based on MgO and SiO_2, but their preparation method and composition are considered to be crucial factors for their performance. In their review, Sels and co-workers observed that for several authors a Mg/Si ratio *equal to or higher* than unity was essential to achieve high butadiene selectivity.[5,6] However, catalysts with a very low Si content were not explored, and thus the activity was studied for materials with a higher acidic component. Nevertheless, in a previous work[4], we suggested that the Lebedev reaction can be carried out (with low efficiency) even with a purely basic catalyst. In the present study, sol-gel was chosen as the most suitable synthesis method to obtain a material where synergic effects between the two metal cations are promoted while the

influence of Mg-to-Si ratio was studied. Here we show that a very small amount of Si (much lower than that reported in literature as the optimal one) can significantly improve performance. This was explained in terms of acid/basic catalyst requirements, thus suggesting a new catalyst model for these complex materials.

Experimental

Synthesis of catalysts

A series of materials with a Mg-to-Si atomic ratio from 1 to 30 were prepared by the sol-gel method. For example, in order to prepare the catalyst with Mg/Si = 15, 17.07 g $Mg(NO_3)_2 \cdot 6H_2O$ (99% Sigma Aldrich) and 1.0 mL tetraethylorthosilicate (TEOS, 98% Sigma Aldrich) were dissolved in 16.5 mL ethanol (>99,9% Merck) and 15 mL distilled water, maintained at 50°C using a water bath. The pH was held below 2 by adding drop by drop HNO_3 (68% VWR Chemicals). When the gel started to form, the stirring was discontinued and the remaining liquid was left to evaporate in the oven at 65°C. The obtained gel was dried at 120°C overnight and calcined at 600°C for 5h (heating rate 10 °C min^{-1}) in static air.

Characterization of catalysts

X-ray diffraction (XRD) patterns were recorded in the range $10° < 2\theta < 80°$ with a Philips PW 1050/81 apparatus controlled by a PW1710 unit (λ=0.15418nm (Cu), 40kV, 40mA). The scanning rate was 0.05°2θ.s^{-1} and step time 1s.

The specific surface area was measured by applying the single-point BET method. The instrument used was a Carlo Erba Sorpty 1700. Around 0.5g of the sample was placed inside the sample holder and then heated at 150°C under vacuum in order to release water, air, or other molecules adsorbed.

Attenuated Total Reflectance spectra of the materials were taken at room temperature with an ALPHA-FTIR instrument at a resolution of 2 cm^{-1}.

NH_3-Temperature-programmed desorption (TPD) measurements were obtained with a TPD/TPR/TPO Micromeritics instrument. 50-100 mg of catalysts were pre-treated at the calcination temperature for 1 h under He flow. After cooling down to 80°C, NH_3 was adsorbed by flowing the catalysts under 10% NH_3-He gas mixture for 30 min (30 mL min^{-1}, NTP), with subsequent He treatment at 80°C for 15 min to remove physisorbed molecules. Catalysts were then heated under He flow (50 mL min^{-1}, NTP) with a heating rate of 10°C min^{-1} up to the calcination temperature.

Reactivity tests

Reactivity experiments were performed using a continuous flow reactor, under atmospheric pressure. A catalyst amount ranging from 0.10 to 1 g was loaded in pellets (30-60 mesh). The residence time (calculated as the ratio between catalyst volume (mL) and total gas flow (mL s^{-1}) at the reaction temperature), was changed. Inlet feed molar ratios were always constant and set at 2 mol% ethanol + 98% nitrogen.

Downstream products were fed to an automatic sampling system for gas-chromatography. The latter was performed using an Agilent-6890 instrument equipped with FID and TCD detectors. Agilent chromatographic columns HP-5 (50 m, 0.20 mm) and HP-plot Al_2O_3-KCl (30 m, 0.50 mm) were used for product separation. Mass balances were accurately determined; values are reported in SI (Table S1).

In-Situ DRIFTS studies

In all the cases, samples were pre-treated at 450°C in a He flow (10 mL min^{-1}) for 45 min, in order to remove any molecules adsorbed on the material. Then the sample was cooled down to room temperature and ethanol was fed at 0.6 µL min^{-1} and vaporized. Subsequently, He was left to flow until weakly adsorbed ethanol was evacuated. The temperature was raised to 400°C and held for 1 min, then lowered to 85°C in order to record the spectrum again. In another set of experiments, after the pre-treatment and feeding of ethanol, the temperature was raised up to 450°C at 10°C min^{-1} without stopping the ethanol flow. The following selected mass spectroscopy signals (m/z) were monitored continuously with time (and temperature): 2, 16, 25, 28, 29, 30, 31, 40, 41, 43, 44, 45, 56, 58, 59, 60, and 61. By combining the information obtained from several different m/z signals, it was possible to obtain unambiguous information on the various products formed.

For pyridine adsorption experiments, samples were pre-treated and the pyridine pulse (0,01 mL) was injected at 50°C, then raising the temperature up to 400°C. CO_2 adsorption was performed directly by feeding CO_2 at 400°C. The IR apparatus used was a Bruker Vertex 70 with a Pike DiffusIR cell attachment. Spectra were recorded using a MCT detector after 128 scans and 2 cm^{-1} resolution. The mass spectrometer was an EcoSys-P from European Spectrometry Systems.

Results

The synthesis of MgO-SiO$_2$ by the sol-gel method

In literature, the MgO-SiO$_2$ system for ethanol transformation into butadiene is conventionally prepared by means of mechanical mixing, co-precipitation, or wet kneading. The sol-gel method has also been used,[8-12] and found out to be suitable for obtaining an intimate mixing of components. However, the above-mentioned methods were used to prepare materials with a Mg/Si atomic ratio typically ranging from 1 to 5. In recent studies, for instance, it has been stated that the wet kneading method is best suited for obtaining active catalysts (with a max. 16% yield to butadiene), but this concerned the case of an equimolar Mg/Si ratio.[13,14] Conversely, we studied a wider ratio between the two cations using the sol-gel method, with the aim of investigating the role of Si^{4+} when used as a dopant for MgO, and how it affects performance in the Lebedev reaction.

Characterization of MgO-SiO$_2$ catalysts

The obtained materials were analysed by means of powder X-ray diffraction (XRD); patterns are presented in Figure 1. Clearly, the materials with higher Si content were mainly amorphous with just weak reflections corresponding to MgO. When the Mg/Si ratio increased, the intensity of lines attributable to the MgO phase increased as well. Some small reflections corresponding to another crystalline phase were detected in the intermediate range of Mg/Si ratio (2–9). Those peaks (whose relative maximum intensity was for MgSi-3) were identified as a forsterite-like phase (Mg_2SiO_4). On the other hand, a Mg/Si ratio higher than 9 made it possible to have the Si atoms (or silica domains) dispersed in the crystalline matrix of MgO. This interstitial dispersion was verified by the fact that the lines corresponding to MgO in the mixed samples were shifted toward lower 2θ values compared to pure MgO. This suggests an expansion of the cubic cell volume for MgO, which cannot be explained by a replacement of the Mg^{2+} cation (size 86 pm) for Si^{4+} (size 54 pm).

in a higher silicate stretching frequency. Especially the highest-frequency band appears predominantly shifted, due to the particular environment of this Si-O tetrahedra when surrounded mainly by Mg-O species. Those shifts and the fact that in the XRD pattern only MgO is visible, confirm that – in this case – Si atoms were well dispersed in MgO.
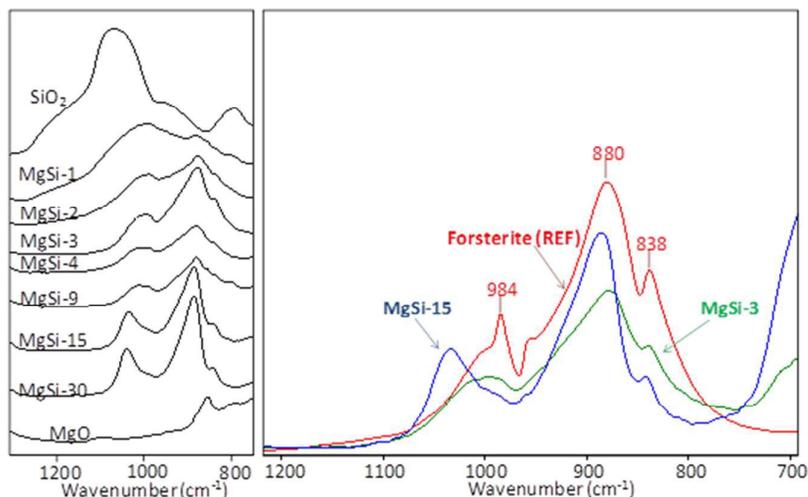

Figure 2. ATR spectra of MgSi-3 and MgSi-15 (Left) and comparison with Forsterite spectrum (Right).
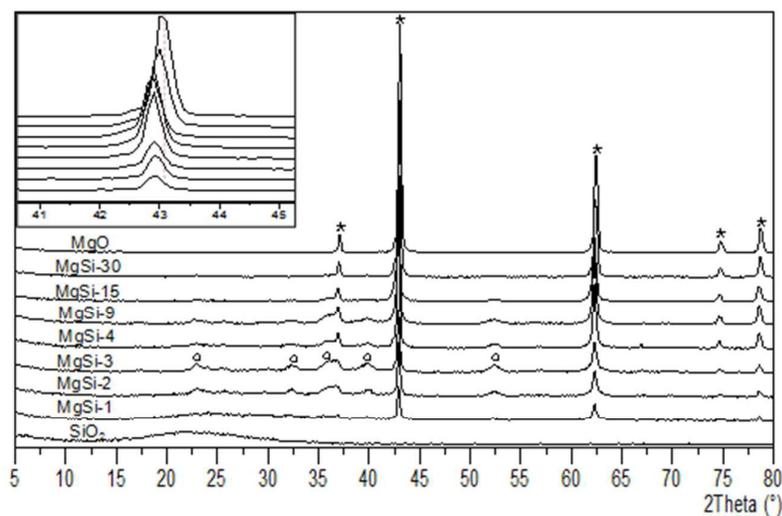

Figure 1. XRD patterns for the synthesized materials. (*) MgO diffraction lines (JCPDS 01-077-2364) (°) Mg_2SiO_4 (Forsterite) diffraction lines (JCPDS 01-085-1364).

Attenuated Total Reflectance (ATR, Figure 2) analysis showed that Si^{4+} was not segregated as amorphous SiO_2 but formed silicates (except, perhaps, for materials with Mg/Si ratio equal to 1 and 2). For samples with Mg/Si ratio from 3 to 9, spectra correspond well to a forsterite-like compound, which is in agreement with XRD results. On the other hand, materials with Mg/Si ratios 15 and 30 show more defined vibration bands. These bands in the region from 800 to 1100 cm^{-1} are related to the internal Si-O vibration modes of SiO_4 tetrahedra. The shift of bands could be due to the combination of Mg-O stretching force constants with that of the Si-O bond, which might result

BET results shown in Table 1 reveal that the chosen synthesis method led to relatively low surface area materials. In general, an increased Mg/Si atomic ratio led to a decreased surface area value, up to the lowest value shown by MgO. It is also important to notice, however, that the surface area of SiO_2 was lower than that shown by samples with the greatest Si content (Mg/Si ratio between 1 and 4): an effect which may be attributable to the formation of forsterite in these samples, but which is in any case indicative of a changed morphology in the mixed systems, when compared to SiO_2.

In Table 1 the results of NH_3-TPD experiments are also included, showing that the acidity was greatly affected by the Mg/Si ratio. The number of acid sites per unit surface area increased from SiO_2 up to sample MgSi-9, where the concentration of acid sites was almost 6 times that of silica. A further increase in the Mg/Si ratio led to a slight decrease in acid site density up to MgO, which showed no ammonia adsorption at all. It is worth noting that this was not due to its low surface area, since an analogous result was observed with a MgO sample prepared by the conventional precipitation method from a $Mg(NO_3)_2$ solution, showing a surface area of around 80 m^2/g after the calcination treatment.

Figure 3, showing ammonia desorption profiles of samples, indicates that MgSi-1 showed a greater acidity than silica, not only in terms of acid sites density but also of strength, with a

broad desorption band that covered almost the whole temperature range, whereas the increase in Mg/Si ratio caused the desorption profile to narrow, while the temperature at which it reached its peak shifted to lower temperatures, indicating a weaker acidity. Sample MgSi-30 showed the weakest acid strength. These results are similar to Niiyamas' findings, in the sense that the most acid material (holding strongest sites) is the equimolar one (Mg/Si = 1).[7]

Table 1. Surface area results (BET method)

Catalyst	Mg/Si atomic ratio	Surface area (m^2/g)	Acid sites number*$(10^{-6}$ mol/g) (T_{max})	Acid sites density*$(10^{-6}$ mol/$m^2)$
MgO		2±1	--	--
MgSi-30	30	12±2	24 (204°C)	2.0
MgSi-15	15	21±2	45 (255°C)	2.1
MgSi-9	9	25±2	58 (232°C)	2.3
MgSi-4	4	38±2	56 (252°C)	1.5
MgSi-3	3	47±3	69 (281°C)	1.5
MgSi-2	2	63±3	52 (249°C)	0.8
MgSi-1	1	102±4	72 (256°C)	0.7
SiO$_2$	0	24±2	11 (190°C)	0.4

*As measured by NH$_3$-TPD desorption
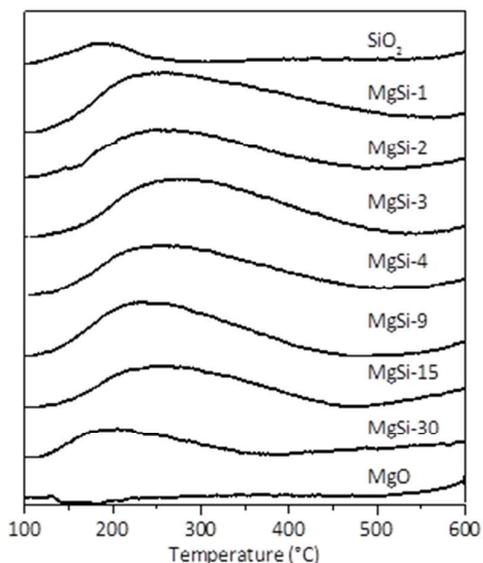
Figure 3. NH$_3$-TPD profiles for the Mg-Si materials

Studies on pyridine adsorption were also performed on selected samples. Figure 4 (top) shows the results during adsorption on MgSi-4; adsorption was carried out at 50°C. From these spectra it is clear that the dominant acid sites are Lewis type (strong): 1436 cm^{-1} and 1599 cm^{-1} for the 19b and 8a mode.[15] The bands rising at 1580 and 1484 cm^{-1} are due to the adsorption of pyridine on weaker Lewis sites.

However, after the flush with He for several minutes, another spectrum was taken and only the bands for the strong Lewis sites remained (Figure 4 bottom). Moreover, the temperature was raised up to 400°C for 1 min and then brought down to 50°C to repeat the measurement, and the result was that pyridine did not desorb completely (red line in Figure 4 bottom). The adsorption of pyridine was repeated by first inducing a water pre-adsorption (see Figure S1), and it is shown that water generated Brφnsted acid sites (bands at 1542 and 1648 cm^{-1}) by interaction with Lewis sites.
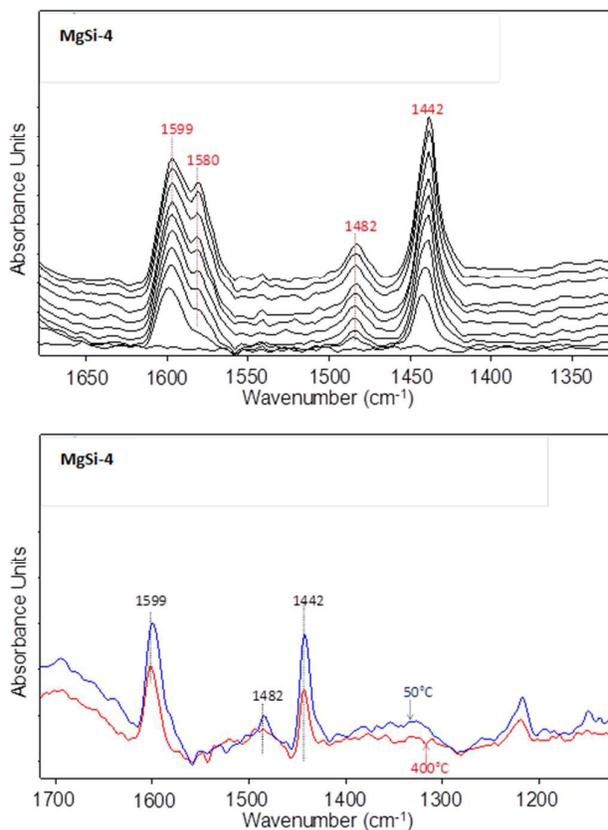

Figure 4. Continuous adsorption of pyridine on MgSi-4 at 50°C (top). Pyridine remaining on the surface after flushing under a He stream at 50°C and 400°C (bottom).

From these measurements it can be concluded that the Mg^{2+} ion, which is a very weak Lewis acid site, acts as a medium-strength Lewis acid site in the mixed catalyst due to the electronic withdrawal by Si^{4+} present in close proximity, because of the greater electronegativity of Si^{4+} compared to Mg^{2+}. However, the acidity-enhancement effect on Mg^{2+} increased when the Si content in catalysts increased; in fact, MgSi-30 showed the weakest acid strength. This may be due to the fact that the charge withdrawal on Mg^{2+} sites – due to the presence of neighboring Si^{4+} atoms – was more efficient when the number of Si atoms close to each Mg^{2+} site was increased compared to MgSi-30. Table 1 also shows that even though the number of acid sites clearly increased together with the

concentration of Si in catalysts, their number was not simply directly proportional to the latter value, as may be expected if the relative amount of the two cations in the structure (and on the surface) is taken into account.

Worth of note, when the same experiment was carried out with sample MgSi-1 (see Figure S2, comparing MgSi-1 and MgSi-4), a blue-shift of the band attributed to the interaction of pyridine with the Lewis site indicated a stronger acidity of that site.

We also performed some analyses via SEM-EDX, in order to check the homogeneity of samples. In general, with samples having the lower Mg/Si ratio, the presence of particles of different sizes was observed; larger particles, of more regular shapes, showed a Mg/Si atomic ratio close to the expected one, whereas other smaller particles were made of MgO alone, more rarely of SiO_2, or showed a Mg/Si ratio higher than the nominal one. This is shown, for example, in Figure S3, for sample MgSi-4. Conversely, samples with higher Mg/Si ratio were more homogeneous, with all spots analysed containing both Mg and Si.

The acid–base properties of MgO-SiO_2 catalysts prepared by kneading magnesium hydroxide with colloidal silica, in terms of Mg/Si ratio have been investigated previously by other authors. For example, Niiyama et al.[7] concluded that acidity reaches its peak for the equimolar Mg/Si ratio while, on the other hand, basicity increases continuously with the increase of MgO. However, they also observed a "limit" in the rate of butadiene formation, which reached its peak for a content of MgO of 85% mol (Mg/Si = 5.7; higher ratios were not explored). Weckhuysen and co-workers[13] studied the acidity of the equimolar MgO-SiO_2 catalysts prepared by different methods, and concluded that the wet kneaded ones were performing better due to the appropriate balance among a small amount of strong basic sites, combined with an intermediate amount of acidic sites and weak basic ones. Makshina et al[16] studied systems prepared by different methods in the Mg/Si range from 0 to 3. They observed that even large variations in dispersion and crystallinity of the basic component (MgO) had little impact on the butadiene yield, whereas a change in the acidic component (silica) could drastically modify the selectivity; in their case, when Grace silicagel 254 was used as the support, the optimal ratio was Mg/Si = 2.

On the other hand, our acidity measurement experiments highlight that in samples prepared by means of sol-gel, the dispersion of Si^{4+} in MgO lattice occurring when the Mg/Si value is high, generates Lewis acid sites which are associated to Mg^{2+} cations in the proximity of Si^{4+}. Not only the number, but also the strength of these sites is affected by the Mg/Si atomic ratio used. In addition, in the presence of steam, these sites are transformed into Brønsted sites. In samples with the lowest Mg/Si ratio (lower than 9 but higher than 2), the formation of Mg silicate domains (Forsterite) leads to an even higher acid strength, with levelling in the number of acid sites and reduced density. Finally, samples showing the strongest acidity were those having the lower Mg/Si ratio (MgSi-1 and MgSi-2); for these samples no evidence for the formation of

Mg silicate was shown, and domains of SiO_2 and MgO were likely formed.

Reactivity of MgO-SiO_2 catalysts in the Lebedev reaction

Mixed Mg-Si oxides are the main components of industrial catalysts for the Lebedev process (butadiene from ethanol). However, their catalytic performance is highly dependent on the synthesis method, Mg/Si ratio, and experimental conditions. A recent review by Sels and co-workers[5] shows that the yields obtained (for undoped Mg-Si materials) cover a broad range between 9-37% with a 20-62% selectivity (not taking into account the values reported by Ohnishi et al., since their results were not reproducible and were obtained at the very beginning of the catalyst lifetime). These studies, however, are limited to materials with a Mg/Si molar ratio between 0.8 and 6, and higher values were not explored in literature, even when the best results were obtained with a Mg/Si>3.
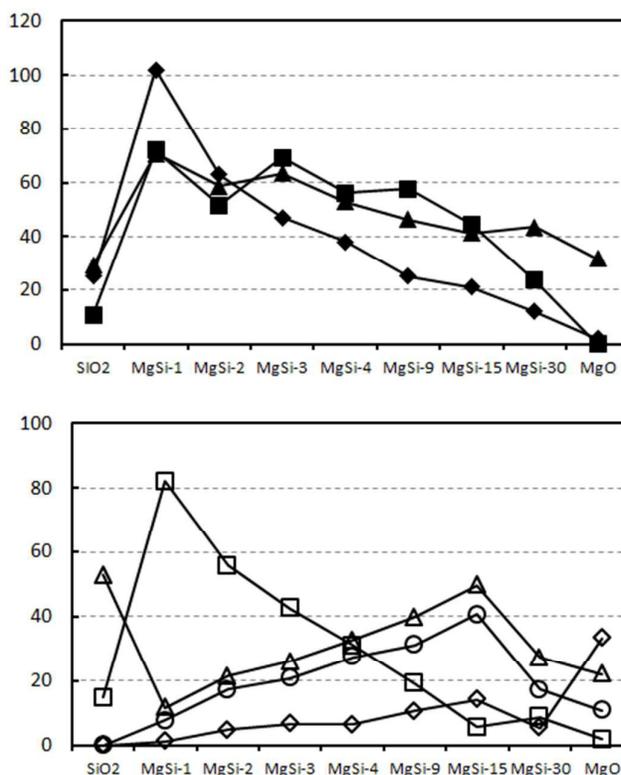
Figure 5. Top: % conversion of ethanol (▲) (reaction conditions: feed ethanol 2% in N_2, T=400°C contact time 0.41 s), surface area (m²/g) (◆), and overall number of acid sites (10^{-6}mol NH_3/g, see Table 1) (■) for the various MgSi samples. Bottom: selectivity to ethylene (□), acetaldehyde + alkenols + butadiene (△), 1-butanol + butenes (◇) and butadiene (○) at 400°C for various MgSi samples.

In the present study, in fact, the best results were obtained for the materials with a Mg/Si ratio between 4 and 15, higher than that reported in literature for this type of catalyst.[5] This can be seen in Figure 5, which shows the conversion of ethanol (top)

and the selectivity to (i) butadiene, (ii) ethylene, (iii) acetaldehyde + alkenols + butadiene, and (iv) 1-butanol + butenes (bottom), in function of the Mg/Si ratio, at fixed reaction conditions. Details on the yields of all products are shown in Table S1.

It is important to note that, as recently reported, with MgO the formation of ethylene and the main C_4 products (1-butanol and butadiene) occurs by means of kinetically parallel routes, where the alcohol is formed by the direct condensation of two ethanol molecules (Guerbet reaction), whereas the diolefin is formed by reaction between ethanol and acetaldehyde, leading to alkenols (mainly crotyl alcohol) via water elimination; the latter dehydrates in the end to butadiene. Therefore, if this is what happens for MgO-SiO$_2$ samples also, the selectivity to (i) ethylene, (ii) 1-butanol + butenes, and (iii) acetaldehyde + alkenols + butadiene, should be almost independent from ethanol conversion (Scheme 2).

In fact, tests carried out with MgSi-4 by varying contact time under isothermal conditions (see later, Figure 6) demonstrated that within a certain range of ethanol conversion (between 40 and 60%), the distribution of products was only marginally affected by conversion.
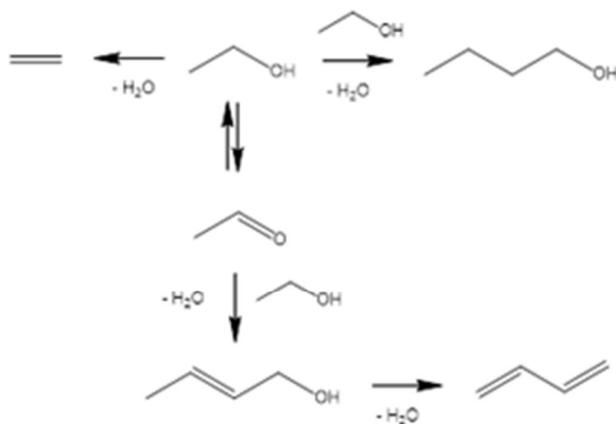
Scheme 2. The three main parallel reaction pathways by which ethanol is transformed over MgO-based catalysts.[4]

Ethanol conversion (Figure 5 top) with MgSi-1 was higher than that shown by SiO$_2$, and a further decrease of Si content led to a decreased conversion, until the lowest value shown by MgO. Conversion was not obviously correlated with the overall amount of acid sites, and also did not correspond to the acidity strength (see Figure 3). This agrees with our recent findings that with MgO key steps in ethanol activation are the formation of ethoxide species (which evolves to the formation of acetaldehyde), and the generation of a carbanion species on ethanol, which further evolves either by dehydration to ethylene, or by reaction with adsorbed ethanol and acetaldehyde; both events are obviously related to the catalyst basicity.[4] On the other hand, it may be expected that with MgO-SiO$_2$ acid sites are also involved in ethanol conversion, because of the primary reaction of ethanol dehydration, which provides an additional contribution to ethylene formation. A correlation between ethanol conversion and surface area was

shown (Figure 5 top), even though the relationship between the two was not that of a direct proportionality; in other words, the increase in conversion shown for samples at increasing Si content (until MgSi-1) was lower than the increase in surface area. This may be attributed to the fact that the basic strength of MgSi samples with higher Mg/Si ratio was greater than that of samples with lower ratio (see below). It may thus be concluded that a low Mg/Si ratio leads to a decrease in surface basicity (and an increase in acidity), with a concomitant increase in the surface area and activity.

With regard to the distribution of products (Figure 5, bottom), the maximum selectivity to butadiene was shown at Mg/Si = 15. An increase in the content of Mg from MgSi-3 to MgSi-15 improved the selectivity to butadiene and, even though the conversion decreased, the yield to butadiene was slightly higher (13.2 vs 16.8% for MgSi-3 and MgSi-15, respectively, see Table S1). The selectivity to 1-butanol (including also the consecutive product of alcohol dehydration, butenes), showed a similar trend, with the exception of MgO, whose selectivity was higher than that shown by MgSi-30. This latter sample was the one providing the lowest overall yield to useful C_4 products, and the greatest yield to heavy compounds (see Table S1). Conversely, when the Si content was too high (at low Mg/Si ratio), the materials showed high yield and selectivity toward ethylene. The intermediate Mg/Si ratio values (samples MgSi-9 and MgSi-15) were those showing both the greatest selectivity to C_4 compounds and the lowest to ethylene. Silica gave high selectivity to acetaldehyde, but with low ethanol conversion. It is also noteworthy that while MgO showed some butadiene production, SiO$_2$ alone produced mainly acetaldehyde, diethylether, and some ethylacetate, but not butadiene (see Table S1).

The reaction network with MgO-SiO$_2$ catalysts

In order to extend the model previously proposed for MgO, a mechanistic study was performed on MgO-SiO$_2$ catalysts, investigating their catalytic behavior in function of contact time, under isothermal conditions. The main results for the MgSi-4 catalyst at 400°C are shown in Figure 6. Interestingly, when comparing kinetic results with those obtained with MgO,[4] the same products were obtained with the two catalysts, with similar trends also, even though the relative amount of each compound was different in the two cases: a result which may be clearly related to the introduction of acid properties.

The most abundant products detected for the whole range of residence time investigated were ethylene and butadiene followed by acetaldehyde and butenes, at lower and higher contact times, respectively, and by acetone and diethylether. Other minor by-products (not shown in the Figure) were 1-butanol, propylene, butyraldehyde, and the three alkenol isomers: 3-buten-1-ol, 2-buten-1-ol (crotyl alcohol) and 1-buten-3-ol. Taking into account all products, the C balance was in the 80-90% range, and was not much affected by the conversion degree; indeed, heavy compounds formed at all

conditions, and were not identified, although eluted in the GC column.
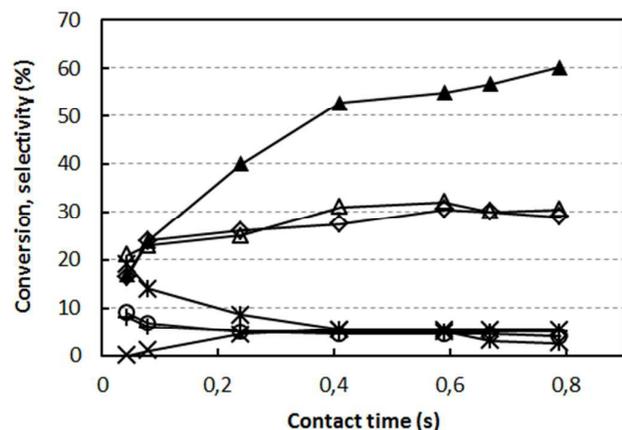
Figure 6. Effect of contact time on catalytic performance of MgSi-4 catalyst. Temperature 400°C, feed 2% ethanol in N_2. Symbols: ethanol conversion (▲), selectivity to butadiene (◇), ethylene (△), acetaldehyde (✳), acetone (+), butenes (✕), diethylether (○).

As expected, acetaldehyde appeared to be a kinetically primary product undergoing consecutive transformations, whereas both butadiene and butenes were consecutive products: indeed, the extrapolation of butadiene selectivity toward nil contact time was approximately zero, and butenes were not detected even at the lowest contact time value. Regarding ethylene, its behavior seemed to be the result of two contributions: when selectivity was extrapolated to nil residence time it was clearly higher than zero, indicating its kinetically primary nature; however, the selectivity trend increased with residence time, which is a typical behavior for a consecutive product.

Several studies on the reaction mechanism of ethanol dehydration to ethylene over acid catalysts have been reported in literature, but this mechanism is still controversial.[17] The major controversy lies in whether ethylene is directly generated from ethanol or also consecutively from diethylether (DEE), which is the main by-product of the process with several acid catalysts. In order to verify DEE involvement as an intermediate molecule for ethanol conversion into ethylene on our catalytic systems, the ether was fed over MgSi-4 at the reaction temperature of 400°C and 0.4s residence time. A low DEE conversion of 7% was observed, with ethylene actually being the main reaction product. In our case, therefore, direct ethanol dehydration appears to give the greatest contribution to ethylene formation. However, a minor contribution deriving from DEE cracking should also be taken into account.

As mentioned above, we recently suggested that the formation of butadiene occurs by reaction between acetaldehyde and ethanol; an adsorbed species, chemically related to 1,3-butanediol, is formed which, however, dehydrates and desorbs into the gas phase, yielding the precursors of butadiene. With regard to this latter step, the

dehydration of 1,3-butanediol can give rise to three different isomers: 3-buten-1-ol, 2-buten-1-ol (crotyl alcohol), and 1-buten-3-ol. It is expected, however, that these three compounds are not formed in equal amounts, with the formation depending on the two types of mechanism by which dehydration occurs (either acid- or basic-catalyzed). Therefore, in order to infer more details on the reaction mechanism with MgO-SiO_2 catalysts, the three C_4 alkenols were fed over MgSi-4, at 400°C and 0.4 s residence time (results reported in Table 2). Crotyl alcohol was more efficiently dehydrated into butadiene, showing a yield up to 86% at total conversion. 1-Buten-3-ol was also converted into butadiene quite efficiently (68% yield at total conversion) but a greater formation of heavy compounds was observed. Conversely, 3-buten-1-ol behaved in a very different manner showing a much lower yield into butadiene (only 13% at 95% conversion) together with an extensive formation of heavy compounds. Moreover, significant yields to propylene and crotonaldehyde were obtained. This might suggest that the final dehydration step (from alkenols to butadiene) preferably occurs in the presence of acid sites; in fact, if an anionic-type mechanism via H^+ abstraction by a basic site would take place, the dehydration of 3-buten-1-ol should lead to the formation of butadiene. Conversely, an acid-catalyzed dehydration would occur preferably on crotyl alcohol, because of the delocalization of the positive charge generated on the primary C atom after water elimination, and on 1-butene-3-ol as well, because of the formation of a cation on the secondary C atom.

Table 2. Reactivity of alkenols at 400°C and 0.4 s contact time.

Reagent	Conversion (%)	Yield (%)		
		butadiene	propene	2-butenal
2-buten-1-ol	99,9	86	0,3	Traces
3-buten-1-ol	95	13	15	9
3-buten-2-ol	99,9	68	0,3	-

Kinetic experiments were also performed by co-feeding water with ethanol on MgSi-4. Since water is generated during the transformation of ethanol into butadiene and other by-products, the aim of this experiment was to determine whether the presence of water may affect the reactivity of the catalyst. Therefore, we co-fed an amount of water which corresponds to approximately 70% of the amount which is generated in-situ during the reaction. The results of these experiments are reported in Table 3, and compared with tests without co-fed water carried out under the same conditions.

When water was co-fed, a poisoning effect was shown; indeed, the presence of water led to a considerable decrease in ethanol conversion and also greatly affected product selectivity. A selectivity increase was recorded for ethylene, and also, to a minor extent, for the other kinetically primary products such as DEE and acetaldehyde, and for acetone as well. On the other hand, a drop in the selectivity of secondary products such as butadiene, butenes, and propylene was also observed. This effect may in part be related to the strong

decrease in ethanol conversion, but also to the change in the nature of active sites, as in the case of ethylene, whose formation mainly comes from Brφnsted-type acid sites. These results, together with FTIR spectra recorded during water + pyridine adsorption, reveal that water generated during reaction is responsible for the in-situ generation of Brφnsted sites; unfortunately, this leads primarily to the strong increase in ethylene selectivity.

Table 3. Ethanol conversion (%) and selectivty to products (%) at 400°C over MgSi-4 at 0.4s contact time: effect of water in the inlet feed.

Feed	Ethanol 2% in N_2	Ethanol 2% + 0,5% H_2O in N_2
Ethanol conv.	53	24
Sel. Butadiene	27.5	18
Sel. Ethylene	32	49
Sel. Butenes	5.5	Tr
Sel. Propylene	3	Tr
Sel. Acetaldehyde	5.5	10
Sel. Acetone	4.5	9
Sel. Diethylether	5	8
Sel. 1-Butanol	1	1
Heavies (from mass balance)	15	5

In-Situ DRIFTS studies

Figure 7 shows the spectra of catalysts at 400°C (after a pre-treatment at 450°C in He), which were recorded after feeding ethanol (see Experimental for details). Here, the parent MgO shows a band at 3745 cm^{-1} assigned to a Mg-OH hydroxyl group in which the oxygen is mono-coordinated with Mg. It is usually agreed that OH stretching is highest for terminal OH groups, whereas intermediate and low frequencies indicate bridging OH groups.[18,19] When there was a small amount of Si in the material, the OH stretching shifted to 3678 cm^{-1} which indicates an increase in the coordination number of oxygen, but in this case the OH group is multi-coordinated to Mg and Si atoms (or the Mg-OH is affected by the neighbouring Si^{4+}). However, when Si content increased, the intensity of this band decreased and the band at 3738 cm^{-1} started to rise, a phenomenon which might be due to the presence of isolated Si-OH groups on the surface.

The presence of this acid group correlates with the tendency of materials to produce ethylene (which means that the presence of free terminal Si-OH induces dehydration). The band at 3481 cm^{-1} may be assigned to OH groups which interact with O^{2-} species,[19] and this band is only present when Mg/Si > 4.

In order to understand the interaction of alcohol with the surface of this catalysts, some experiments were performed by adsorbing ethanol at 85°C (See Figure 8, top), heating it up to 400°C for 2 min, and then cooling it down to 85°C in order to record the spectrum again (as in Figure 8, bottom). The

spectrum of the catalyst was subtracted, so the bands observed correspond to the surface species created by ethanol adsorption and transformation.
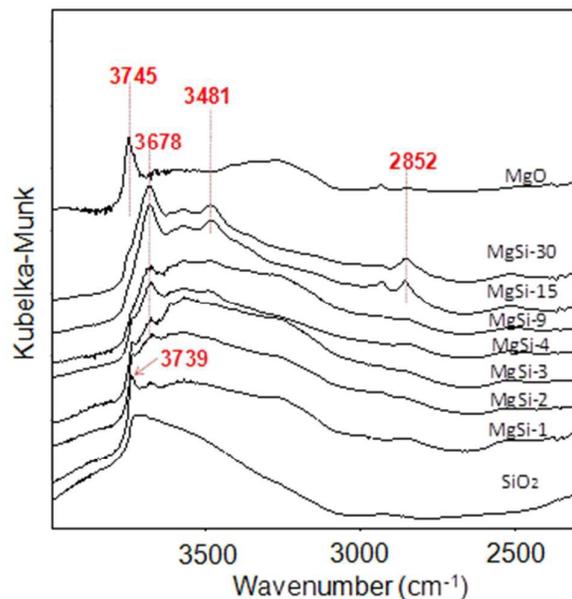

Figure 7. DRIFT spectra of Mg-Si catalysts at 400°C recorded after feeding ethanol at room temperature.
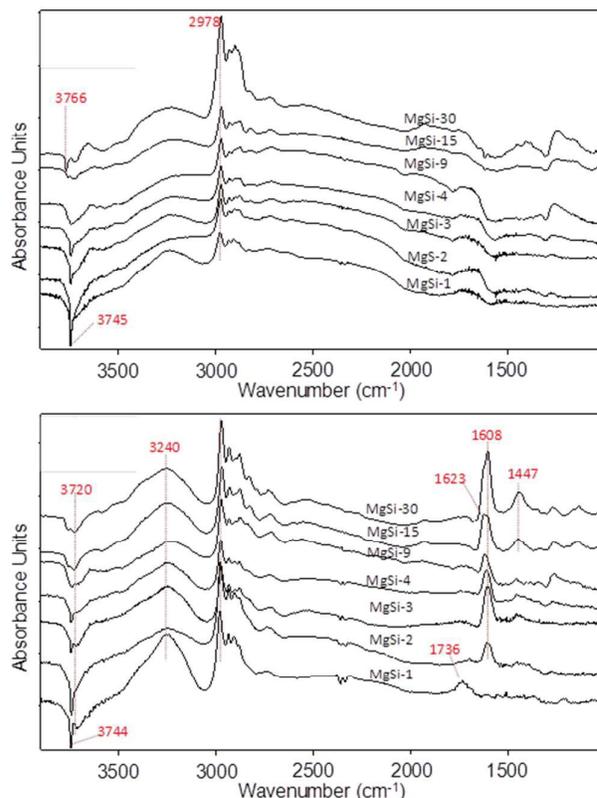

Figure 8. Ethanol adsorbed at 85°C on the different Mg-Si materials (top) and after thermal treatment at 400°C (bottom).

During the adsorption of ethanol at 85°C, a sharp negative band in the OH stretching region appeared for MgSi-1 (3745 cm^{-1}). This negative band suggests that the alcohol interacts with the terminal OH groups. When the Mg/Si ratio increased, the intensity of this band decreased and it became broader, suggesting that the adsorption of ethanol was less strong and that it took place at different sites, including the multi-coordinated OH groups observed before (Figure 7). The fact that some OH groups were disappearing (OH negative band), especially for low Mg/Si ratio materials, might indicate that direct dehydration reaction plays an important role when the Si content is high. After the thermal treatment at 400°C and quench, the negative band still was present suggesting that the loss of the hydroxyl group was an irreversible process. In this case, also some bands in the low frequency region appeared (Fig. 8 bottom). For MgSi-1, the band at 1743 cm^{-1} can be attributed to a C=O stretching of acetaldehyde (thus in this case it does not desorb as easily). Starting from MgSi-2 a band appeared at 1604 cm^{-1} (see Figure S4) whose intensity increased for MgSi-3 but then decreased when the Mg/Si ratio was ≥4, and a band at around 1623 cm^{-1} started to appear and grow. This band has been previously assigned to an adsorbed form of crotyl alcohol, which is the butadiene precursor.[4] Starting from MgSi-9 and above, a band at 1605 cm^{-1} increased again but in this case it might be attributed to the formation of carbonates in the most basic materials or even acetates (as shown by the presence of other bands at 1447 and 1338 cm^{-1}, the OCO $\nu_{(s)}$ and CH$_3$ $\delta_{(s)}$ typical of this moiety). Therefore, catalyst basicity should be strong enough to favor the dehydrogenative pathway until crotyl alcohol, but when it is too strong (as for the MgSi-30), it favors the formation of acetates and carbonates and lowers butadiene selectivity as well. DRIFT spectra of in-situ adsorption of CO$_2$ at 400°C corroborated the stronger basicity of samples with high Mg/Si ratio (see below).

In order to verify that the band at about 1620 cm^{-1} is associated to intermediates for butadiene formation, more realistic conditions were reproduced by continuously feeding ethanol during the temperature program (Figure S5). It was observed that the formation of intermediates such as ethoxy (band at 1065 cm^{-1}), ethanol anion (1143 cm^{-1}) and adsorbed crotyl alcohol (1620 cm^{-1}) took place much more easily in the case of MgSi-15 compared to materials with low Mg/Si ratio, indicating that the former has a more appropriate balance of acid/base properties to promote the dehydrogenative pathway instead of the dehydration (ethylene) or condensation (butanol) routes.

Further tests were made by adsorbing CO$_2$ over MgSi-1 and MgSi-15 (Figure S6). The amount of CO$_2$ adsorbed at 400°C on the latter catalyst was significantly higher than that shown for MgSi-1, which demonstrates the higher basicity of MgSi-15 sample and also makes it possible to exclude the formation of carbonates in previous experiments, while facilitating the assignment of the bands observed.

Discussion

A model for the nature of active sites in MgO-SiO$_2$

In regard to the nature of active sites, Kvisle et al.[20] studied the mechanical and chemical mixtures of Mg and Si oxides and concluded that it is unlikely that their synergic effect is solely due to the presence of MgO in the SiO$_2$ or vice versa. Conversely, they mentioned the possibility that this result is related either to defects created on the MgO structure during synthesis or to new Mg–O–Si interactions. The review by Sels and co-workers states that the synthesis procedure should promote the formation of Mg–O–Si species, at the same time keeping the remaining MgO highly dispersed.[5] Natta and Rigamonti also mentioned a relation between the activity and high dispersion of magnesia on silica and the presence of a limited amount of amorphous magnesia hydrosilicate phase resulting from the interaction of dissolved Mg^{2+} with the silanols of the silica surface.[21]

With the information discussed and the results obtained so far, it is possible to propose a model for these complex heterogeneous catalysts. In samples showing a high Mg/Si ratio, new sites characterized by a Lewis-type acidity are generated, associated with Mg^{2+}-O-Si^{4+} pairs; the acid strength of this site is related to the number of neighbouring Si^{4+} sites. These sites interact with the water generated in the reaction environment and are transformed into Brφnsted acid sites; the latter possess the acid strength needed for the dehydration of intermediately formed alkenols into butadiene. Conversely, when the content of Si is too high, it segregates as forsterite and also as SiO$_2$ domains, creating a stronger acidity, which is detrimental for selectivity, because it favours ethanol dehydration to ethylene. Therefore the optimal acid strength is neither too weak (not sufficient for an efficient dehydration and leading mainly to the formation of heavy compounds, in an amount even greater than that observed with MgO only, as for MgSi-30) nor too high, because, in this case, the formation of ethylene becomes the prevailing reaction. Thus the optimal acidity is observed for Mg/Si values between 15 and 9, i.e. when the catalyst is made of Si^{4+} dispersed in MgO, and the formation of forsterite is either not yet shown or minimal.

Relationship between acid-basic properties and catalytic behavior

In our previous work,[4] we reported that ethanol activation and transformation into ethylene, 1-butanol, or butadiene (the latter via alkenols as intermediate compounds) may occur on a MgO catalyst with the involvement of basic sites only.

Combining the information reported in the present work, with the reaction mechanism that we proposed for butadiene formation,[4] we can state what follows:

(a) The activation of ethanol occurs with the contribution of both basic sites, especially in samples showing the greater basic strength (i.e., those with the higher Mg/Si ratio), and acid sites, especially in samples showing the greater acid strength (i.e., those with the lower Mg/Si ratio). Basic sites extract the proton either from the OH group, so generating an ethoxide species which is the precursor for acetaldehyde, or from the methyl group with formation of a carbanion species. The latter

reaction is as energetically demanding as the ethoxide dehydrogenation to acetaldehyde.[4] The carbanion may then react with either another molecule of ethanol, generating 1-butanol, or with acetaldehyde, with formation of crotyl alcohol, in both cases after elimination of one water molecule. Instead, acid sites contribute to ethanol dehydration to ethylene. The most active catalyst was MgSi-1, which showed the greater surface area. Silica was less active than MgSI-1 because of both its relatively low surface area and the absence of basic sites, whereas catalysts with higher Mg/Si atomic ratio were less active than MgSi-1, despite the stronger basicity, because of both the lower surface area and the lower number of acid sites.

(b) The distribution of products is affected by the number and strength of both acid an basic sites, in a non-obvious manner. In the reaction pathway leading to butadiene, acidity plays a role in causing the dehydration of the intermediately formed alkenols. The presence of a small amount of Si^{4+} (in MgSi-30) led to an increased surface area compared to MgO, and to the generation of acid sites, albeit of weak strength (Figure 3). In this case, only a limited increase in selectivity to butadiene was shown when compared to MgO, but the selectivity to 1-butanol (whose formation may occur with involvement of basic sites only)[4] was lower than with MgO, while, at the same time, the formation of heavier compounds was considerably enhanced. A further increase in Si content, in samples Mg/Si-15, -9 and -4) led to an increased acidity in terms of number, density, and strength of sites, which fostered the dehydration of intermediately formed alkenols to butadiene, thus finally leading to a strongly enhanced formation of butadiene, still with a low yield to ethylene. An even higher acidity, in samples with low Mg/Si ratio (< 4), led to a considerably increased contribution of the acid-catalyzed dehydration of ethanol to ethylene: a reaction which greatly prevailed over the formation of C_4 compounds. The same was true for 1-butanol dehydration to butenes; in samples with the highest Mg/Si ratio, 1-butanol selectivity largely prevailed over butenes, while the opposite was true for Mg/Si ratios lower than 9. Therefore, the greater selectivity to butadiene was shown by those samples which combined a strong basicity –necessary to dehydrogenate the ethoxide to acetaldehyde and to generate the carbanion species- with a medium strength acidity and moderate density of acid sites, needed to efficiently dehydrate alkenols, while limiting ethylene formation.

DRIFTS experiments confirmed the stronger interaction of ethanol with catalysts having the greater Si content, which induced to the preferred dehydration to ethylene. Both key species previously identified with MgO, crotyl alcohol and the carbanion formed by deprotonation of the methyl group, were also identified with MgO-SiO$_2$ catalysts, an event which confirms that the same mechanism formerly proposed for ethanol to C_4 compounds with MgO, is also valid with these bifunctional catalysts. Spectroscopic measurements also validated that the pathway leading to butadiene was the preferred one with catalysts having higher Mg/Si atomic ratio, i.e., with MgSi-9 and MgSi-15, which agrees with the greater selectivity shown by these samples.

Previously Niiyama et al.[7] reported that a catalyst with 79 wt% of MgO (Mg/Si atomic ratio 5.7) showed a good acid–base balance, reaching a high butadiene formation rate, since at lower values ethylene formation was too high and after this value, butadiene formation decreased. Unfortunately, 5.7 was the highest Mg/Si molar ratio investigated and the yield of products was not reported in this case.

A thorough analysis of the role of basic and acid sites in MgO-SiO$_2$ catalysts was also reported by Angelici et al[13]. These authors found that the best performing catalysts are those containing a small amount of strong basic sites, combined with an intermediate amount of acidic sites. This statement is in line with our findings, with the difference that our results led us to conclude that the best Mg/Si ratio, showing the optimal combination of the different sites needed, is obtained for higher Mg/Si ratios than those reported in literature, at least with our sol-gel catalysts.

Conclusions

The reactivity of MgO-SiO$_2$ materials prepared by means of the sol-gel method, used as catalysts for the one-pot ethanol transformation into butadiene, was affected by the nature and amount of both basic and acid sites. The best catalysts, showing the greater selectivity to butadiene, were those which combined a limited number of medium-strength acid sites with strong basic properties. Samples showing these features were those characterised by a Mg/Si atomic ratio between 9 and 15. In fact, a greater content of Si (like in samples having Mg/Si ratio lower than 9) led to the formation of either forsterite or silica domains, with a considerable fraction of strong acid sites which finally gave rise to the preferred formation of ethylene. Conversely, in samples having a Mg/Si ratio higher than 15, the generation of a limited number of weak acid sites did not provide the acidity feature needed to efficiently dehydrate intermediately formed alkenols. An important role is played by Lewis acid sites of medium strength generated by Mg-O-Si pairs; these transform into Brφnsted sites by interaction with the water generated during the reaction.

References

1. C. Angelici, B.M. Weckhuysen and P.C.A. Bruijnincx, *ChemSusChem*, 2013, **6**, 1595-1614.

2. Y. Wang and S. Liu, *Journal of Bioprocess Engineering and Biorefinery*, 2012, **1**, 33-43.

3. M.D. Jones, C.G. Keir, C. Di Iulio, R.A.M. Robertson, C.V. Williams and D.C. Apperley, *Catalysis Science & Technology*, 2011, **1**, 267-272.

4. A. Chieregato, J. Velasquez Ochoa, C. Bandinelli, G. Fornasari, F. Cavani and M. Mella, *ChemSusChem*, 2015, **8**, 377-388.

5. E. V. Makshina, M. Dusselier, W. Janssens, J. Degrève, P.A. Jacobs and B.F. Sels, *Chemical Society reviews*, 2014, **43**, 7917-7953.

6. W. Janssens, E. V. Makshina, P. Vanelderen, F. De Clippel, K. Houthoofd, S. Kerkhofs, J. a. Martens, P. a. Jacobs and B. F. Sels, *ChemSusChem*, 2014, **8**, 994-1008.

7.   H. Niiyama, S. Morii and E. Echigoya, *Bulletin of the chemical society of Japan*, 1972, **45**, 655-659.
8.   R. Brambilla, C. Radtke, J. H. Z. dos Santos and M. S. L. Miranda, *Powder Technology*, 2010, **198**, 337-346.
9.   F. Ciesielczyk, M. Przybysz, J. Zdarta, A. Piasecki, D. Paukszta and T. Jesionowski, *J Sol-Gel Sci Technol*, 2014, **71**, 501-513.
10. T. López, R. Gómez, M.E. Llanos, E. García-Figueroa, J. Navarrete and E. López-Salinas, *Materials Letters*, 1999, **39**, 51-57.
11. T. López, R. Gomez, M.E. Llanos and E. López-Salinas, *Materials Letters*, 1999, **38**, 283-288.
12. S. Mitra and S. Sampath, *Journal of Materials Chemistry*, 2002, **12**, 2531-2537.
13. C. Angelici, M.E.Z. Velthoen, B. M. Weckhuysen and P. C. a. Bruijnincx, *Catal. Sci. Technol.*, 2015, **5**, 2869-2879.
14. C. Angelici, M.E.Z. Velthoen, B. M. Weckhuysen and P. C. a. Bruijnincx, *ChemSusChem*, 2014, 2505-2515.
15. G. Busca, *Physical Chemistry Chemical Physics*, 1999, **1**, 723-736.
16. E.V.V. Makshina, W. Janssens, B. F. F. Sels and P. a. A. Jacobs, *Catalysis Today*, 2012, **198**, 338-344.
17. M. Zhang and Y. Yu, *Industrial & Engineering Chemistry Research*, 2013, **52**, 9505-9514.
18. G. Busca, *Catalysis Today*, 1998, **41**, 191-206.
19. O. Diwald, M. Sterrer and E. Knözinger, *Physical Chemistry Chemical Physics*, 2002, **4**, 2811-2817.
20. S. Kvisle, A. Aguero and R.P.A. Sneeden, *Applied Catalysis*, 1988, **43**, 117-131.
21. G. Natta and G. Rigamonti, *La Chimica e l'Industria*, 1947, 239 - 244.

Green Chemistry Accepted Manuscript