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To be cited as: *ChemCatChem* 10.1002/cctc.201601630

Link to VoR: http://dx.doi.org/10.1002/cctc.201601630

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ChemPubSoc Europe

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www.chemcatchem.org

Understanding the role of Gallium as a new promoter of MgO-SiO_2 catalysts for the conversion of Ethanol into Butadiene

Juliana Velasquez Ochoa,[a] Andrea Malmusi, [a] Carlo Recchi,[a] and Fabrizio Cavani*[a,b]

Abstract: This study explores the use of Gallium as a new component in MgO-SiO_2 catalysts for the Lebedev reaction (one-pot conversion of ethanol to butadiene). Several characterization techniques (XRD, NH_3-TPD, BET, ATR) and in-situ spectroscopic studies (DRIFTS-MS) were performed with the aim of correlating the properties of the modified materials with the catalytic results. It was concluded that the wet-impregnation of Ga^{3+} ion on the MgO-SiO_2 catalyst creates new Ga-O(H)-Si sites, that interact strongly with the alcohol and not only facilitate its dehydrogenation to acetaldehyde and transformation into the intermediate crotyl alcohol, but also enhance the dehydration of the latter compound because of an improved acidity. On the other hand, a proper amount of Ga oxide content is needed, in order to avoid excessive acidity which is conducive to an increased selectivity to ethylene.

Introduction

Because of the forecasted decrease in 1,3-butadiene (BDE) production by means of the conventional extraction from the C_4 fraction produced by naphtha cracking, as well as of the possible increase of demand for bio-sourced rubber, several alternative routes are currently under investigation for the synthesis of bio-BDE, starting from various renewable sources.[1] Several options are being investigated, such as (a) the direct fermentation route, (b) the one-step or two-step dehydration of butanediols – which appears to be one of the most promising routes [2,3] - and (c) the direct transformation of bio-ethanol.

Indeed, the interest in the development of better catalysts for the transformation of ethanol into BDE, has observed an exponential increase in the last decade due to the higher availability and lower cost of this 2nd generation bio-alcohol that constitutes an important renewable building block for a more sustainable chemical industry.[4,5] However, the reaction itself is not new, it is known since the early XX century when many countries were trying to overcome their dependence on natural rubber by developing a synthetic version, and the most successful formulations all contained BDE as monomer.

Synthetic BDE was produced at that time starting from acetylene via hydroformylation to 1,4-butynediol (Reppe process) or hydration to acetaldehyde and further condensation.[6] Instead, in Russia it was implemented the first successful one-pot process to obtain BDE directly either from grain ethanol or from potatoes.[7] The details of this process, known as Lebedev reaction (after the scientist Sergei Lebedev who developed it) were kept secret during several years since rubber was a very precious good especially during the war period. This type of approach was later on abandoned when the boom of petroleum made it economically less competitive until the beginning of the XXI century, when the trend started to go back to the use of renewable raw materials due to the economic and environmental problems related to the use of fossil-derived resources.[8–10] What it was revealed afterwards about the Lebedev process was not very detailed, it was only an indication on the composition of the catalysts used and of the reaction conditions. For this reason, during the last years several studies have been devoted to the optimization of the parameters for this process, but until now there is no general agreement on how it really works, that is, what is the real mechanism of this catalyzed reaction, and on reasons why the MgO-SiO_2 catalyst shows the best performance.[11,12] Nevertheless, what is sure is that the catalyst properties must be carefully tuned in terms of Mg/Si ratio, acid/base properties and incorporation of promoters.[13–15]

Among the metals that have been studied to increase the activity of MgO-SiO_2 catalysts, Cr[16–18], Ni[19], Zn[20], Cu[21,22] Ag[23,24] and Au[25] (or combinations such as Zn-Zr[26,27] or Cu-Ag[28]) have shown to give an acceptable performance (from 5 to 56% BDE yield). In this work, it is proposed the use of Ga due to its well-known dehydrogenating properties that have made it relevant in different catalytic applications, i.e., in olefins production by propane or ethane dehydrogenation[29–31], methane activation and aromatization[32], methanol to hydrocarbon conversion[33]. Ga oxide also shows acid properties, that make it active, amongst others, in Friedel-Crafts benzylation and acylation reactions.[34,35] The present study is an attempt to understand the behaviour of Ga oxide-modified MgO-SiO_2 catalysts.

Results and Discussion

A MgO-SiO_2 catalyst was prepared by means of wet kneading since it has been stated (and we verified as well, see Table S1) that this method produces more active catalysts for this reaction.[15,22] Figure 1 shows the X-ray diffraction patterns of the unmodified MgO-SiO_2 catalyst (MS-1, where 1 indicates the Mg/Si atomic ratio) and the samples containing different amounts of Ga, after calcination at 500°C for 3h. The MS-1 catalyst presents reflections attributable to MgO and a broad band typical of amorphous SiO_2. On the other hand, the

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[a] J. Velasquez Ochoa, A. Malmusi, C. Recchi. and F. Cavani
Dipartimento di Chimica Industriale "Toso Montanari"
Università di Bologna
Viale Risorgimento 4, 40136, Bologna, Italy.
E-mail: fabrizio.cavani@unibo.it
[b] Consorzio INSTM, Firenze, Research Unit of Bologna

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10.1002/cctc.201601630

impregnated samples were mainly amorphous with some broad reflections that seem attributable, with some uncertainty, to $MgSiO_3$ (JCPDS 00-047-1750), and $2MgO\cdot 3SiO_2\cdot 2H_2O$ (JCPDS 00-002-1009). However due to their broadness and low intensity, an unambiguous assignment could not be done. There was no evidence of any crystalline phase containing Ga. From the figure, it is clear that the impregnation method used caused changes in the original structure and that probably during the stirring of the catalyst with the $Ga(NO_3)_3$ solution, there was some hydration and re-dissolution of the Mg and Si phases creating new Mg-silicate compound with the Ga species dispersed in this matrix.

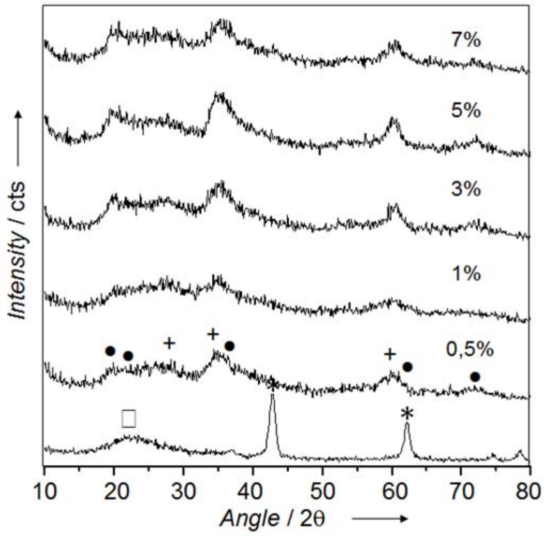


Figure 1. X-ray diffraction pattern of the MS-1 sample before impregnation (bottom) and after impregnation with different Ga content (wt% Ga) after calcination at 500°C. Symbols: *MgO, □SiO_2, •$2MgO\cdot 3SiO_2\cdot 2H_2O$, +$MgSiO_3$.

Table 1 presents the surface area for the unmodified and the impregnated samples. The structural change caused by the impregnation procedure resulted in higher area materials. The trend indicates that a low Ga content originated compounds with a higher surface area; conversely, at higher load of the metal, the area sensibly decreased probably due to the formation of Ga oxide aggregates.

The samples were tested in the direct conversion of ethanol to BDE (Lebedev process). Results are presented in Table 1. An increase of conversion was shown in the presence of Ga. Already at 0,5 wt% Ga, conversion was complete. BDE yield also increased in all cases with respect to the sample without Ga. However, the amount of by-products also increased (mainly ethylene and butenes). Indeed, the selectivity to BDE first declined, because of the remarkable increase of selectivity to ethylene, shown by sample with 0,5% Ga. However, a further increase of the Ga content led to a lower selectivity to ethylene (16 and 13% for samples with 5 and 7% Ga, respectively); catalyst MS-1+5%Ga was that one showing both the best yield and selectivity to BDE, higher than 50%. It is also important to notice that even though the higher activity of samples containing 0,5-3% Ga compared to MS-1 can be attributed to their higher surface area, this is not the case for catalysts containing > 3% Ga.

Table 1. Surface area and results of catalytic tests for samples impregnated with different Ga content.

Sample	Surface area (m^2/g)	Ethanol conv. [a] (mol %)	BDE Yield[a] (mol %)	BDE Selectivity[a] (mol %)	Ethylene Selectivity[a] (mol %)
MS-1	82	65,9	32,5	49,3	26,7
0,5% Ga	262	99,7	37,5	37,6	49,4
1,0% Ga	149	99,9	34,6	34,6	28,8
3,0% Ga	168	99,9	48,2	48,2	30,4
5,0% Ga	48	98,8	52,4	53,1	15,7
7,0% Ga	51	99,7	42,1	42,2	13,3

[a] Conditions: Feed 2% Ethanol in N_2, W/F 0,65 g s/mL, WHSV=0,07 $g_{EtOH}/(g_{cat}$ h), T 400°C. Average values of the last 3h of time-on-stream.

Other products obtained with higher yield for catalysts with Ga include butenes (the sum of the isomers), propylene and acetaldehyde (See Table S2). This indicates that Ga introduces dehydrogenating properties but also some acidity, and this was confirmed by the NH_3-TPD and pyridine adsorption tests (*vide infra*).

In similar studies by Larina et al.[36] for a Zn-modified MgO-SiO_2 catalyst, it was found that a 4%ZnO on a MgO:SiO_2 1:1 was the best compromise between the acid/base characteristics of the support and the dehydrogenating capacity of Zn.

The effect of temperature for the best performing catalyst (MS-1+5%Ga) was studied. Results presented in Table 2 confirm that 400°C is the more suitable temperature to maximize the yield to BDE. Below this temperature the conversion was lower whereas at higher temperatures the production of heavy compounds was greater (as seen from the C loss).

Table 2. Temperature effect for ethanol transformation with MS-1+ 5%Ga catalyst.

Temp. (°C)	Ethanol conversion[a] (mol %)	BDE Yield[a] (mol %)	BDE Selectivity[a] (mol %)	Ethylene Selectivity[a] (mol %)	C loss (mol %)
255	6,7	4,5	73,8	0,0	6,4
300	13,1	8,0	65,0	5,3	6,2
350	37,8	18,4	48,4	9,1	4,8
400	98,8	52,4	53,1	15,7	9,0
450	99,1	39,9	40,2	11,3	19,9

[a] Conditions: Feed 2% Ethanol in N_2, W/F 0,65 g s/mL, WHSV=0,075 $g_{EtOH}/(g_{cat}$ h). Average values of the last 3h of time-on-stream.

The introduction of 5% Ga was then carried out using different methods other than wet impregnation (WI). Specifically, the Ga source was directly added to the slurry during the synthesis of the catalyst (in-situ method), or deposited by means of incipient wetness impregnation (IWI). Figure 2 compares the XRD patterns for samples prepared with the three different methods used. It is observed that only the WI method produced changes in the structure of the sample; in fact, the other two samples presented the same diffraction pattern as the original MS-1, albeit with different intensity.

In recent studies it has been reported that the nature and amount of Mg-silicate phases formed during the synthesis procedure has a direct influence on the catalytic performance for this reaction.[37] Moreover, when this type of catalysts are modified with a dehydrogenating promoter, the formation of a solid solution with either SiO_2 or MgO might be responsible for the increased activity of these materials, as explained by Angelici et al.[38] They studied this reaction with a catalysts prepared supporting Cu on either SiO_2 or MgO prior to the addition of the other component during the wet-kneading, and found that materials where Cu was supported on MgO prior to wet-kneading with SiO_2 showed better overall performances and a large portion of Cu was found to be present in a $Cu_xMg_{1-x}O$ solid solution and CuO subnanometric clusters.

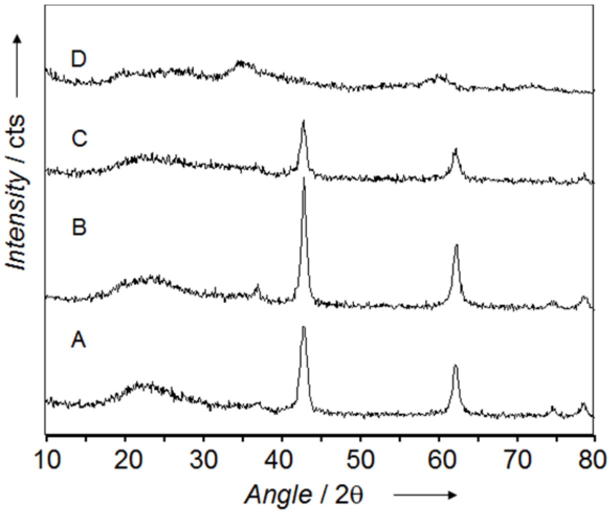


Figure 2. XRD pattern for sample MS-1 (A) and samples with 5% Ga introduced by the in-situ method (B; MS-1+5%Ga in-situ), by incipient wetness impregnation (C; MS-1+5%Ga IWI) and by wet impregnation (D; MS-1+5% Ga) (all patterns are on the same intensity scale).

The catalytic tests showed that the in-situ sample (Table 3, Entry 3) afforded a slightly lower conversion (96,5%) and it also formed more heavy-products (C loss). The BDE yield was higher for the in-situ sample compared to the IWI catalyst (36% vs 28%, Entries 3 and 4 of Table 3). Nevertheless, both samples presented a lower yield to BDE and the C balance was worse than in the case of the WI sample (entry 2 in Table 3).

Two more MgO-SiO_2 samples were used for the impregnation with 5% Ga, one synthesized by sol-gel and calcined at high temperature (forsterite, FS), and one synthesized by wet-kneading but with a higher Mg/Si ratio (MS-2). Catalytic results for FS without Ga showed an average of 19% yield to BDE (Entry 5, Table 3); Ga addition (Entry 6, Table 3) increased the conversion. However, there was a considerable amount of heavy compounds formed (measured as C-loss), that was even greater than BDE yield. For catalyst MS-2 the measured BDE yield was ca 32% (Entry 7) and in presence of 5% Ga the yield was 47% (Entry 8). These results are in line with recent findings (including our previous research work) that in this reaction the preparation method of MgO-SiO_2 and the Mg/Si ratio are critical parameters.[22,36,39]

Table 3. Results for direct ethanol transformation to BDE with Ga/MgO-SiO_2 catalysts prepared using different methods.

Entry	Sample	Ethanol Conv.[a] (mol %)	BDE Yield[a] (mol %)	BDE Sel.[a] (mol %)	Ethylene Sel.[a] (mol %)	C loss (mol %)
1	MS-1	65,9	32,5	49,3	26,7	3,8
2	MS-1+5% Ga	98,8	52,4	53,1	15,7	9,0
3	MS-1+5% Ga in-situ	96,5	36,2	34,4	13,8	23,1
4	MS-1+5% Ga IWI	98,6	28,4	28,8	5,3	41,9
5	FS (forsterite)	80,0	18,6	23,3	47,7	9,0
6	FS+5%Ga	99,9	28,0	28,0	8,0	37,0
7	MS-2	79,1	31,9	40,4	39,7	1,2
8	MS-2+5% Ga	98,8	46,5	47,1	9,6	18,5

[a] Conditions: Feed 2% Ethanol in N_2, W/F 0,65 g s/mL, WHSV=0,075 $g_{EtOH}/(g_{cat}$ h), T 400°C. Average values of the last 3h of time-on-stream.

Spectroscopic studies: In order to correlate the properties of the catalysts and their performances, catalyst MS-1+5%Ga was further characterized and compared to MS-1. Figure 3 shows the DRIFT spectra of samples, recorded at both 85°C and 400°C (using KBr as background). For the sample containing Ga, a sharp band at 3672 cm^{-1} is present. This band has been ascribed to the vibration of surface OH multi-coordinated to Ga^{3+} in an octahedral environment.[40,41] The band at 3730 cm^{-1} may be assigned to mono-coordinated OH groups.[41]

For the same samples, attenuated total reflection IR spectra (ATR) were taken in order to observe the spectral range at lower wavenumbers that is difficult to analyze by means of DRIFTS. Spectra are shown in Figure 4; it is possible to observe that the presence of Ga caused the appearance of a Si-O-Si stretching band (at ca 1014 cm^{-1}), which is attributable to a newly developed interaction, i.e., to a Ga-O-Si bond. The fitting of the spectra in the region of this band (Figure S1) confirms that the component at lower wavenumber is not present in the sample without Ga.

In-situ DRIFT spectra of both samples, during ethanol adsorption at room temperature, are shown in Figure 5. The results (after subtraction of the catalyst spectrum) showed that the alcohol adsorbs molecularly as well as in its dissociated form (ethoxy group, $C_2H_5O^-$). The negative peak, clearly shown in spectra of both samples (at high wavenumbers), is due to the interaction of the free OH groups on the catalyst surface that become unavailable due to the interaction with the alcohol.

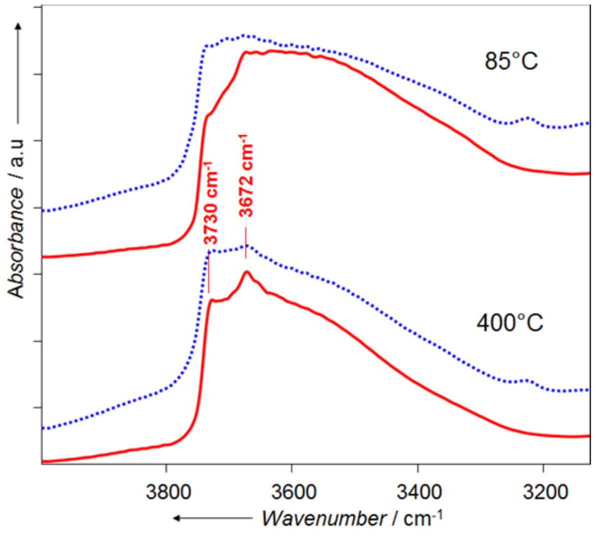


Figure 3. DRIFT spectra of samples MS-1 (Blue, dotted) and MS-1+5%Ga (Red, continuous) at 85 and 400°C under He flow.

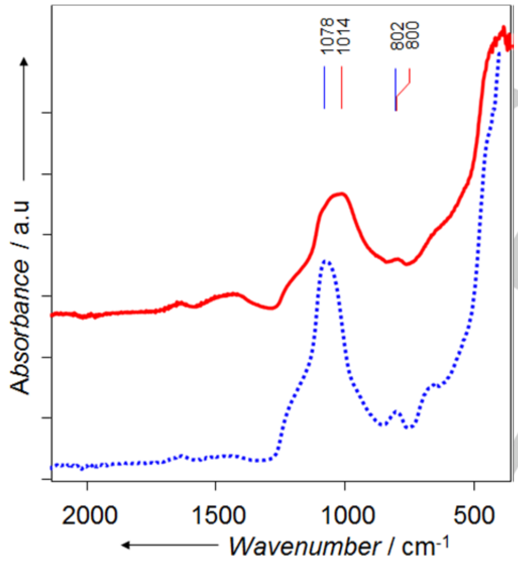


Figure 4. ATR spectra of samples MS-1 (Blue, dotted) and MS-1+5%Ga (Red, continuous).

Table 4 presents the assignment of the bands highlighting the most characteristic ones for each species, whereas some of them are in common to both adsorbed ethanol and ethoxy species.[42–44] The sample with Ga adsorbed more ethanol (more or less twice total intensity). This is also true if we consider that the quantity of sample used in the experiment was the same in the two cases, but the specific surface area was smaller for the sample with Ga (48 vs 82 m^2g^{-1} for MS-1+5%Ga and MS-1, respectively). Therefore, the Ga-modified sites are responsible for an additional direct interaction with the alcohol; in fact, the negative peak is more intense in the case of the Ga-containing sample. On the other hand, the peaks associated to the intermediate species (800-1500 cm^{-1}) seem to be less intense for the Ga-containing sample (compared to the negative peak, for instance). This could be due to the fact that in the case of MS-1+5%Ga, the adsorbed intermediates were more easily transformed and desorbed. This hypothesis was verified afterwards in the experiments carried out by increasing the temperature (*vide infra*).

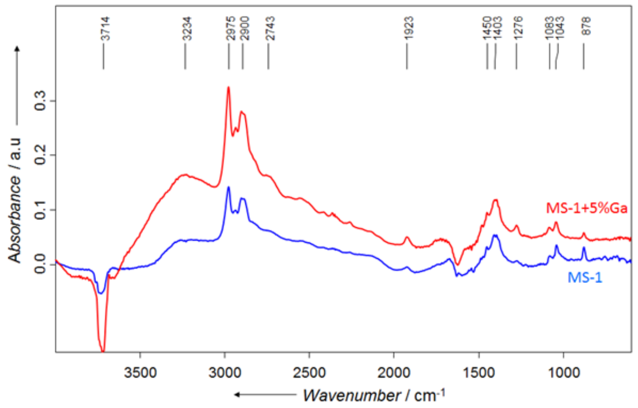


Figure 5. DRIFT spectra of ethanol adsorption at room temperature for samples MS-1 (Blue, bottom) and MS-1+5%Ga (Red, top).

After the saturation with ethanol at room temperature, the cell temperature was increased until 400°C at a rate of 10°C min^{-1} (with continuous flow of ethanol in He). Figure 6 shows the results of ethanol reaction at different temperatures for MS-1 and MS-1+5%Ga. The spectra were obtained after subtraction of the background (bare catalyst mixed with KBr), registered at each temperature.

At high wavenumbers, there was a negative band that corresponds, in both catalysts, to an interaction of the alcohol with the free OH groups. This interaction is stronger in the case of the catalyst with Ga, due to the presence of additional Ga-OH groups that can react with ethanol, and even at high temperature the intensity of this negative band continued to be strong, whereas in the case of MS-1 (top spectra), it became less intense with the increasing temperature. One important difference is that the sample with Ga showed a band at around 1610 cm^{-1} that has been attributed to the ν_{as} of an adsorbed crotyl alcohol species, precursor of BDE formation. [11,39] This band can be seen at lower temperature (starting at 300°C) in comparison with the sample without Ga, which presents this band only at 400°C. Moreover, the formation of this band is concomitant with the disappearance of the bands attributable to the ethoxy species (1039-1076 cm^{-1}), which according to our previous proposed mechanism of reaction [11] is the precursor of acetaldehyde. Therefore, this demonstrates that the sample modified with Ga is more active for two reasons: it has a higher dehydrogenating power (which explains the higher conversion) and it also readily transforms the intermediates into crotyl alcohol which is then dehydrated to BDE, due to the newly developed acidic character. Figure S2 shows a comparison for the spectra of the two samples recorded at 350°C.

Table 4. Assignment of the bands after ethanol adsorption on samples.

Vibration	Wavenumber (cm^{-1})
Metal-O	878
ν_{as}(C-O)$_{bident}$/ν_{as}(C-C) ethoxy	1043
ν_{as}(C-O)$_{monodent}$ ethoxy	1083
δ(OH) in ethanol	1276
δ_s(CH$_3$) in ethanol	1403
δ_{as}(CH$_3$)	1450
δ_{as}(CH$_2$)	1479
δ_s(H$_2$O) (negative)	1630
ν_{as}(α-C-H) ethoxy	2743
ν_s(CH$_2$)	2885
ν_s(CH$_3$)	2900
ν_{as}(CH$_2$)	2933
ν_{as}(CH$_3$) in ethoxy	2975
ν(OH) in ethanol	3234
ν(free OH) (negative)	3714

Another set of experiments was performed; in this case, ethanol was sent at low temperature as a pulse (0,6 µl min^{-1} for 15 min). Afterwards, the samples were left under He flow until weakly adsorbed ethanol was removed (ca 30 min) and then a temperature program was performed (until 400°C, ramp 10°C min^{-1}). Figure 7 shows the result of this ethanol-TPD experiments for MS-1 and MS-1+5%Ga. In this case, samples were not diluted in KBr. For both samples, at low temperature the bands corresponding to adsorbed ethanol and ethoxy species were present, even if some of the characteristic bands below 1000 cm^{-1} were not seen probably due to the high absorbance of the undiluted samples in this region.

There were two main differences between the samples; the first is the way the OH groups interact with ethanol (negative band at around 3730 cm^{-1}): a sharper band was observed for the sample with Ga, which might indicate that ethanol interacts preferentially with only one type of OH group, the one mono-coordinated with Ga (observed in the spectra of catalysts before ethanol adsorption (Figure 3)). Instead, in the sample without Ga this band was broader and less strong, indicating an interaction of ethanol with different types of surface OH (Mg-OH or Si-OH). The second difference was that the sample with Ga showed a band at around 1617 cm^{-1} that has been ascribed to the formation of an adsorbed crotyl alcohol, precursor for BDE formation; this band was observed already at 300°C.

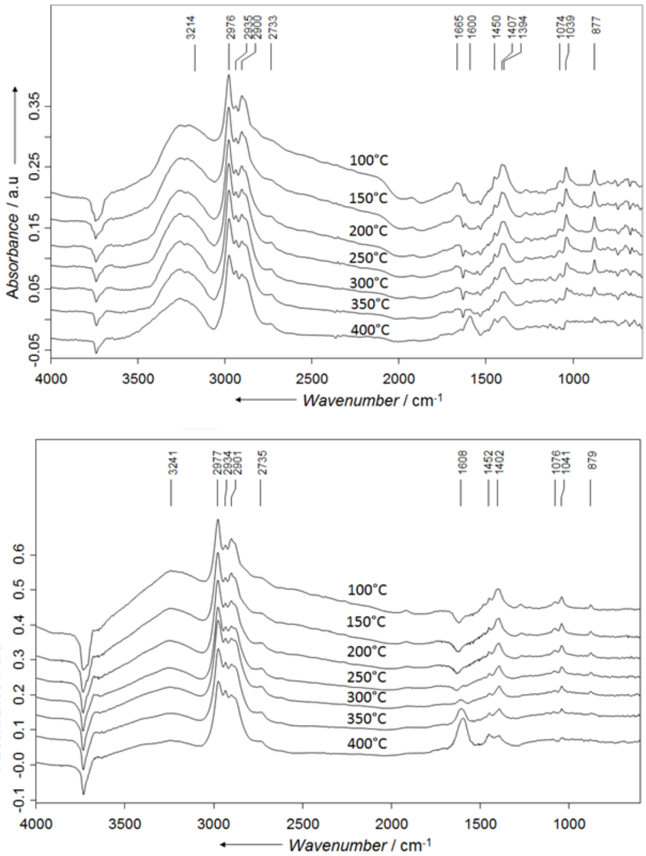


Figure 6. DRIFT spectra of samples MS-1 (Top) and MS-1+5%Ga (Bottom) during ethanol adsorption at increasing temperatures.

During the ethanol-TPD experiments, the desorbed products were followed with an on-line quadrupole (mass spectrometer). The main products detected for the two samples are shown in Figure 8. It can be inferred that for both catalysts, desorption of unreacted ethanol and acetaldehyde formation and desorption occurred at low temperature (slightly lower for the sample MS-1+5%Ga). Ethylene formed as well with both samples; the profile of the MS signal for this molecule was particular since it formed at least in two stages; the first one was probably due to the acid-catalysed ethanol dehydration, whereas the second one can be explained by a particular mechanism of ethanol adsorption and activation to generate a carbanion species, which then may either decompose to ethylene (Scheme 1) or react with acetaldehyde.[11]

On the other hand, it can be observed that ethylene and BDE (the two main products of the reaction) showed similar trends for the two samples, but both compounds were released earlier for the sample with Ga (see Figure S3 for a comparison), and this is in agreement with the spectroscopic observations regarding the easier formation of BDE precursor (i.e., crotyl alcohol) in the case of MS-1+5%Ga. However, this observation can also suggest a higher acidity of this sample, since acidity is an essential property for both the formation of ethylene and the dehydration of crotyl alcohol to BDE.

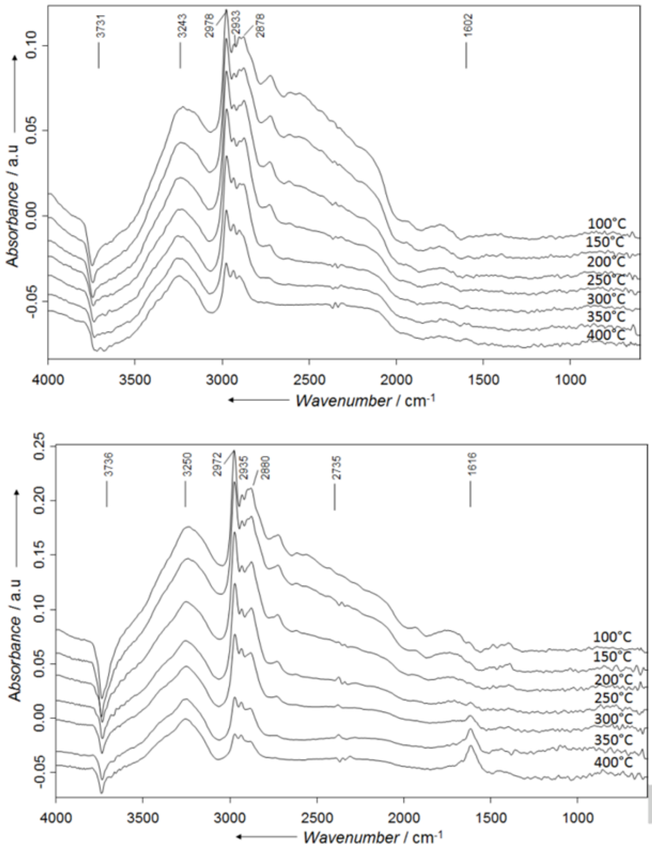


Figure 7. DRIFTS spectra of samples MS-1 (Top) and MS-1+5%Ga (Bottom).during ethanol TPD.

The samples without Ga and with 0,5 and 5% Ga were analyzed by means of NH_3-TPD in order to evaluate their acidic properties. From Figure 9 and Table 5 it is observed that the sample containing the lower amount of Ga (0.5%) holds a greater number of acid sites, which are of moderate-high strength (i.e., with higher temperature of desorption); this can explain its higher selectivity to ethylene. On the other hand, the sample with 5% Ga has a lower number of acid sites but a higher acid site density. However, it is important to notice that the acid strength of these sites was relatively weak (T_{max}= 265-270°C vs 305-310°C for the other two samples). This might explain its better performance in the Lebedev reaction (i.e., with lower selectivity to ethylene and better selectivity to BDE), which agrees with our previous research work in the sense that selectivity to BDE is favoured by a higher acid site density but of low/moderate strength.[39] These results are also in line with recent findings concluding that a delicate balance between the amount and strength of the acid sites in $MgO-SiO_2$ catalysts is needed in order to be selective in the Lebedev reaction.[14,24,36]

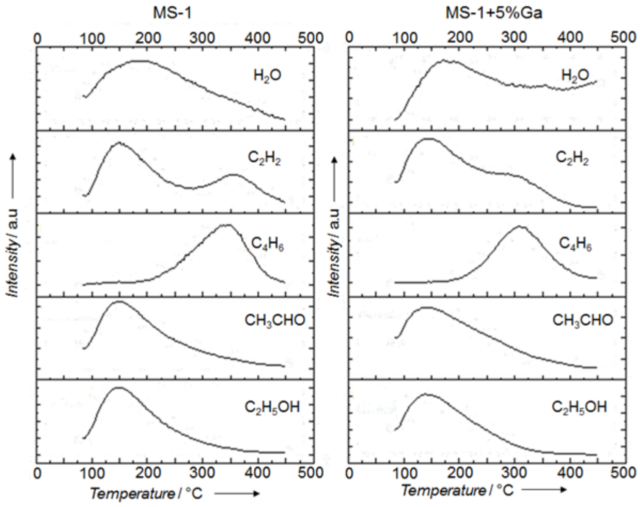
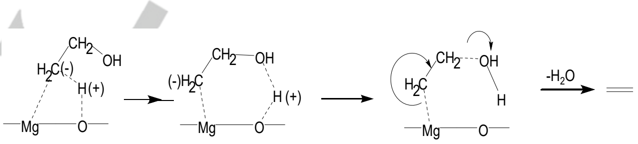


Figure 8. Main products (signal from the mass spectrometer) during the ethanol-TPD experiment for samples MS-1 (Left) and MS-1+5%Ga (Right).



Scheme 1. Formation of ethylene from ethanol via carbanion.[11]

As regards pyridine adsorption (Figure S4), it was observed that MS-1+5%Ga contains a small amount of Brϕnsted sites which are absent in $MgO-SiO_2$,[30] and might correspond to Ga-OH groups; besides, the Lewis acid sites are slightly stronger (blue shifted). An interesting observation is a band usually assigned to pyridone species [45] which indicates the presence of very reactive OH species or acid/base pairs in the case of the sample with Ga.

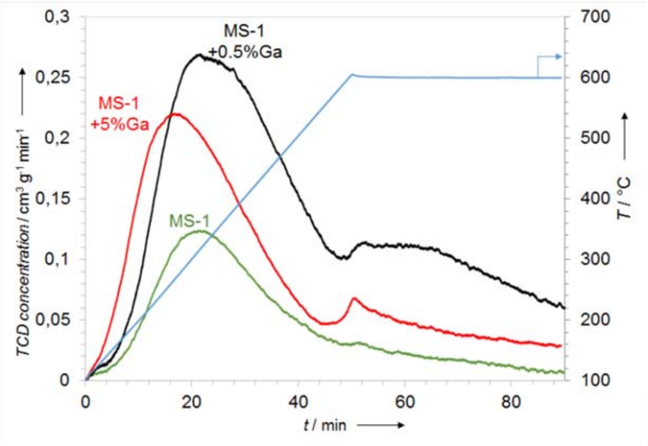


Figure 9. Ammonia-TPD for samples MS-1, MS-1+0.5%Ga and MS-1+5% Ga.

Table 5. Results of ammonia-TPD tests for the samples impregnated with different Ga content.

Sample	Surface area (m^2/g)	Acid sites number (10^{-5} mol/g)	Acid sites density (10^{-5} mol/m^2)
MS-1	82	7,6	0,093
MS-1+0,5%Ga	262	11,5	0,044
MS-1+5%Ga	48	8,9	0,185

Conclusions

When Ga is deposited on $MgO-SiO_2$ catalysts by means of the wet impregnation method, it affects the structure and creates new surface Ga-OH groups (and Ga-O(H)-Si bonds) that strongly interact with ethanol. This interaction seems to be more effective on the OH groups coordinated to only one Ga cation. This modification of the sample affects positively the performance for BDE production. In general, it enhances BDE yield by increasing the adsorption of ethanol on catalysts surface, its dehydrogenation to acetaldehyde, and further transformation to the adsorbed intermediate, crotyl alcohol. Moreover, Ga modifies the acidic properties of the catalyst. These properties can be tuned by changing the amount of Ga in the sample. In particular, 5% of Ga was found to give an optimal balance between acid sites density and strength, thus increasing not only the rate of ethanol dehydrogenation, but also the selectivity to BDE and decreasing ethylene formation.

The main limits of the direct Lebedev technology still remain (a) the moderate selectivity to BDE, (b) the relevant number of by-products formed (ranging from ethylene to heavier hydrocarbons, such as aromatics), and (c) the low productivity, mainly due to the low inlet concentration of ethanol used.

Experimental Section

Synthesis: The $MgO-SiO_2$ sample with a Mg/Si molar ratio of 1 (labelled MS-1) was prepared as follows: The Mg source was $Mg(OH)_2$ prepared by precipitation of $Mg(NO_3)_2{\cdot}6H_2O$ with NH_3. The Si source was obtained by precipitation of TEOS with NH_3. Afterwards, the Mg and Si sources, in molar ratio 1/1, were mixed under stirring in water for 4h and then dried at 120°C during the night to be finally calcined at 500°C for 3h in static air. The MS-1 catalyst was impregnated with different loading of Ga. The method used was the wet impregnation (WI) with aqueous solutions of $Ga(NO_3)_3$ in different weight percentage (of Ga), from 0.5 to 7%. Further impregnation methods were as well explored: i) Incipient wetness impregnation (IWI): dissolving the Ga source in the minimum amount of water needed to wet the catalyst, then dropping this solution onto the catalyst. ii) In situ: the Ga source was added directly during the synthesis of the Mg-Si catalyst.

Characterization: The XRD measurements were carried out using a Philips PW 1710 apparatus, with Cu Kα (λ = 1.5406 Å) as radiation source in the range of 5°<2θ<80°, with steps of 0.1 grade and acquiring the signal for 2 seconds for each step. Reflects attribution is done by the Bragg law, using the d value: 2d senθ = nλ. The specific surface area was measured applying the single point BET method. The instrument used for this analysis was a Carlo Erba Sorpty 1700. In the analysis around 0.5g of the sample was placed inside the sample holder and then heated at 150°C under vacuum (4 Pa) in order for it release the water, air or other molecules adsorbed. Afterwards the sample was put in liquid nitrogen and the adsorption of the gaseous N_2 was carried out. NH_3-temperature-programmed desorption (TPD) measurements were obtained with a TPD/TPR/TPO Micromeritics instrument. 100–300 mg of catalysts were pre-treated at the calcination temperature for 45 min under He flow. After cooling down to 100 °C, NH_3 was adsorbed by flowing of a 10% NH_3 in He gas mixture for 20 min (30 mL min^{-1}, NTP), with subsequent He treatment for 60 min to remove physisorbed molecules. Catalysts were then heated under He flow (50 mL min^{-1}, NTP) at a heating rate of 10 °C min^{-1} up to 600°C. Attenuated total reflectance spectra of the materials were recorded at room temperature with an ALPHA-FTIR instrument at a resolution of 2 cm^{-1}. First a background was taken to eliminate the contribution of atmospheric water and carbon dioxide. Later on, the powder was put in intimate contact with the crystal to perform the measurement. DRIFTS-MS: In a typical experiment, the 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 mL min^{-1} and vaporized. Subsequently, He was left to flow until weakly adsorbed ethanol was evacuated. The temperature was raised to 400°C at 10°C min^{-1} while registering the spectra (DRIFT and on-line MS). 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. 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.

Catalytic tests: Reactivity experiments were carried out using a continuous flow reactor, operating under atmospheric pressure. Ethanol percent was fixed to a 2 mol.% in N_2. The catalyst amount and flux of the carrier were varied in order to achieve the desired residence time. Most of the experiments were performed at W/F 0,65 g s/mL, WHSV=0,075 $g_{EtOH}/(g_{cat}$ h), at 400°C. Downstream products were continuously monitored by online gas chromatography (GC) using an Agilent-6890 instrument equipped with two columns (HP-5 50 m, 0.20 mm and HP-plot Al_2O_3-KCl 30 m, 0.50 mm) and two detectors (FID and TCD). Compounds were identified by means of GC-MS and then quantified by external standard calibration curve. The values reported were taken as the average of the last 3h of time on stream in a 4h run (stationary state). Figure S5 shows the catalytic performance in function of time-on-stream for samples MS-1 and MS-1+5%Ga.

Keywords: Lebedev • Butadiene • Ethanol • DRIFTS

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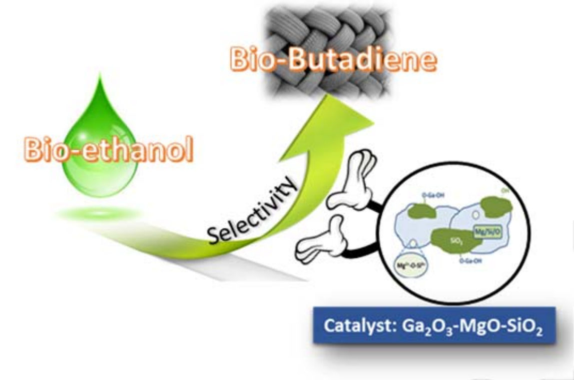
10.1002/cctc.201601630

FULL PAPER

Gallium oxide is an activity and selectivity promoter for MgO-SiO_2 catalysts for the direct transformation of ethanol into butadiene (Lebedev process).



*Juliana Velasquez Ochoa, Andrea Malmusi, Carlo Recchi, Fabrizio Cavani**

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Understanding the role of Gallium as a new promoter for the catalytic conversion of Ethanol into Butadiene