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On the Chemistry of Ethanol on Basic Oxides: Revising Mechanisms and Intermediates in the Lebedev and Guerbet reactions

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A common way to convert ethanol into chemicals is by upgrading it over oxide catalysts with basic features; this method makes it possible to obtain important chemicals such as 1-butanol (Guerbet reaction) and 1,3-butadiene (Lebedev reaction). Despite their long history in chemistry, the details of the close inter-relationship of these reactions have yet to be discussed properly. Our present study focuses on reactivity tests, in situ diffuse reflectance infrared Fourier transform spectroscopy, MS analysis, and theoretical modeling. We used MgO as a reference

Introduction

Over the past decade, applications of ethanol as a platform chemical have aroused new interest because of both environmental concerns connected with petrochemical processes and new economic opportunities seen in bio-based feedstocks.^[1-5] Indeed, bio-ethanol has been demonstrated to be a promising and "green" reactant for both biofuels and biochemicals, particularly if it is derived from non-food crops and lignocellulosic materials (second-generation biomass).^[6-8] Despite the long history of ethanol in the chemical industry, the mechanism behind its catalytic upgrading on mixed oxide catalysts with basic features is still a subject of debate, as shown by the presence of several alternative mechanisms proposed in the literature.^[1,9-20] Ethanol can react on these materials to form various important chemicals, among which are butadiene (through the

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catalyst with pure basic features to explore ethanol conversion from its very early stages. Based on the obtained results, we formulate a new mechanistic theory able to explain not only our results but also most of the scientific literature on Lebedev and Guerbet chemistry. This provides a rational description of the intermediates shared by the two reaction pathways as well as an innovative perspective on the catalyst requirements to direct the reaction pathway toward 1-butanol or butadiene.

Lebedev reaction on bifunctional acid–base catalysts) and 1butanol (by the Guerbet route).

We reviewed the literature on the pathways proposed to justify the mentioned products, and it is noticeable that they share many features and a few key intermediates. We analysed the nature of the catalysts involved, and it emerges that a key role is played in the product formation by basic or dehydrogenating components such as MgO, CaO, Mg-Al-O (hydrotalcites), ZnO, Cr₂O₃, Ta₂O₅ and NiO.^[9-19] However, there is still a lack of detail on the specific role played by each catalyst component at every step along the reaction pathway. For instance, MgO is a good catalyst for the Guerbet reaction and is also often present in catalysts for the Lebedev process; it was claimed as a major component of the industrial catalysts used in the 1940s to produce butadiene.^[21] A few Mg-based catalysts reported in the literature are listed in Table S1; these data stress that typical Guerbet and Lebedev products or intermediates have been reported in the same downstream molecular pool and their respective distributions are related to reaction conditions and catalyst features.

The reaction network generally accepted in the literature for both reactions considers acetaldehyde as the first product formed from ethanol and its subsequent condensation to 3-hydroxybutanal (acetaldol; Scheme 1).

Hydrogenation is believed to occur by H-transfer from ethanol [Meerwein–Ponndorf–Verley (MPV) reaction], even though the hydrogen generated in situ might also play a role. However, other mechanistic options have been reported: acetaldol may undergo reduction by ethanol to form 1,3-butanediol,^[19] the dehydration of which possibly leads to either crotyl alcohol or 3-butene-2-ol. Notably, both compounds can be further dehydrated into butadiene. Additionally, a few authors have hy-



Scheme 1. Generally accepted pathway for ethanol transformation on basic oxides: Lebedev and Guerbet routes.

pothesised that the formation of C_4 compounds might be the result of a reaction between two molecules of ethanol or one molecule of ethanol and one of acetaldehyde.^[9,22]

Despite the sometimes detailed studies and the many techniques used, a definitive consensus on the most likely pathway has yet to be reached. Recently, Meunier et al.^[20] managed to rule out aldol condensation as the main path to 1-butanol formation by reactivity tests on hydroxyapatite catalysts and thermodynamic calculations, at least on heterogeneous catalysts at high temperature (350–410 °C).

In this paper, we report a mechanistic study performed on MgO as a model catalyst (i.e., one that shows pure basic properties) aimed to elucidate the key intermediates of ethanol conversion on mixed oxide catalysts with basic features. The existing correlation between the Lebedev and the Guerbet reactions was further analysed with the goal to gain a more complete view of the tangled mechanisms. Reactivity tests and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and MS were combined with computational studies, which allowed us to indicate, for the first time, additional details that led toward an alternative view of the complete mechanism for the processes involved. In particular, we discussed the key factors that govern the product distribution and reaction intermediates for the interconnected and competitive reactions that lead, alternatively, to 1-butanol/butenes or to butadiene.

Results and Discussion

Ethanol reactivity

After an initial screening to determine the dependence of catalyst performance on temperature, 250 and 400 °C were found to be the most representative temperatures (T) to evaluate the reaction pathways. Indeed, the lowest T value seemed to be the minimum needed to observe a detectable conversion of ethanol under the reaction conditions used, whereas MgO showed a good activity and a relatively limited yield to heavy products at higher T. As we wanted to investigate the very early stages of the reaction, we scanned the catalytic behaviour through the first hour of reaction and at uncommonly low contact times in comparison to those normally applied to max-

imise the yield of C₄ compounds. In this situation, however, poor carbon balance may be observed during the initial period of reactivity because of severe heavy-compound deposition on the catalyst surface.^[23,24]

The catalytic behaviour of ethanol on MgO at 250° C for different residence times is depicted in Figure 1. At contact times



Figure 1. Ethanol conversion at 250 °C on MgO. Symbols: ethanol conversion (\diamond); yields: acetaldehyde (+), 1-butanol (\triangle), crotyl alcohol (\bullet), 3-buten-1-ol (x), others (**u**). Others: 2-pentanol, 2-butanol and 3-buten-2-ol. Figure S1 shows the same results plotted as selectivity towards the products as a function of ethanol conversion.

lower than 0.4 s (calculated at the reaction *T*) the main product detected was acetaldehyde with traces of 1-butanol. At higher contact times, the formation of 1-butanol, 2-buten-1-ol (crotyl alcohol) and 3-buten-1-ol occurred, which was accompanied by the formation of other trace compounds. Neither C₄ aldehydes (3-hydroxybutanal, crotonaldehyde and butyraldehyde) nor C₄ olefins (butenes and butadiene) were detected.

To confirm the lack of C₄ aldehydes, reactivity experiments were performed at 250°C with 0.6 s residence time for 24 h; the collected products were analysed by GC-MS and ESI-MS and presented no trace of these compounds. Indeed, the absence of 3-hydroxybutanal and crotonaldehyde poses important questions on the reaction mechanism as these are the generally accepted intermediates for C_4 -compound formation from ethanol. As the lack of C4 aldehydes might be also attributed to a fast conversion to crotyl alcohol (by MPV reduction) and then 1-butanol, these results are not exhaustive or able to rule out their role in the mechanism; further tests were thus deemed necessary and performed (vide infra). Nevertheless, it is important to highlight the direct formation of 1-butanol as a kinetic primary product, which goes against the mechanism accepted widely that postulates Guerbet alcohol formation by the in situ reduction of crotonaldehyde. This unexpected feature was also recently pointed out by other authors.^[1,20]

The products of ethanol transformation at 400 °C are shown in Figure 2. In order of abundance, ethylene was formed in large amounts, followed by acetaldehyde and 1-butanol, and finally butadiene as a consecutive product (additional informa-

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Figure 2. Ethanol conversion at 400 °C on MgO. Symbols: ethanol conversion (\blacklozenge); yields: ethylene (\bigtriangledown), acetaldehyde (+), 1-butanol (\triangle), 1,3-butadiene (\bigcirc), others (\blacksquare). Figure S2 shows the same results plotted as selectivity towards the products as a function of ethanol conversion.

tion on minor products is reported in the Supporting Information). Notably, ethylene formation was not expected on pure basic oxides and its presence was found previously not to be due to the result of a gas-phase homogeneous reaction. Also, acetaldehyde and 1-butanol appear to be kinetic primary products, even though selectivity extrapolation towards zero contact time may be ambiguous at such a high temperature.

Reactivity of proposed intermediates

To better comprehend the chemistry of ethanol condensation, we fed a few molecules proposed previously as possible intermediates during the formation of C_4 compounds.

The products obtained at 400 °C on feeding 1,3-butanediol (1,3-BDO), suggested to form from either the MPV reduction of acetaldol or the reaction of ethanol with acetaldehyde,^[4] are shown in Figure S3. As 1,3-BDO is much more reactive than ethanol, its residence time was kept lower than that of ethanol to maintain a low conversion. The two main products were ethanol and acetaldehyde; methyl vinyl ketone (MVK) and methyl ethyl ketone (MEK) were also formed, as well as minor amounts of other compounds, which include aromatics. Interestingly, the presence of ethanol and acetaldehyde suggests that 1,3-BDO undergoes a reverse addition. The catalytic behaviour of 1,3-BDO was also studied at 250 °C (Figure S4) and similar results were obtained. Only minor changes were observed in the product distribution even if ethanol and 1,3-BDO were co-fed in an equimolar amount; specifically, a slight increase in the yields of MVK, 2-butanone and aromatic compounds was noted. All in all, this evidence and the fact that we did not detect the formation of 1,3-BDO during ethanol transformation, suggest that this compound does not form under our reaction conditions. Any adsorbed intermediate compound that desorbs into the gas phase as 1,3-BDO would mainly decompose into ethanol and acetaldehyde.

Crotyl alcohol (2-buten-1-ol) was also suggested as a key intermediate. $^{[12,13]}$ Thus we reacted it on MgO at 250 and 400 $^\circ C$



Figure 3. Crotyl alcohol conversion at 400 °C on MgO. Symbols: crotyl alcohol conversion (\blacklozenge); yields: 1-butanol (\triangle), acetaldehyde (+),1,3-butadiene (\bigcirc). The distribution of the other products detected is shown in Figure S6.

to verify this possibility (Figure S5, and Figures 3 and S6, respectively). 1-Butanol was the major product detected; this could be obtained by MPV reduction of the carbonyl group in butanal, which was formed in a relatively large amount^[18,19,22] by tautomery of the alkenol obtained by the isomerisation of the double bond in crotyl alcohol. The MPV reduction can occur through the reaction with crotyl alcohol itself (which is dehydrogenated to crotonaldehyde), a hypothesis confirmed by a catalytic test performed by co-feeding crotyl alcohol and ethanol (molar ratio = 1:1) (Table 1). This did not show any significant difference from the test performed by feeding crotyl alcohol alone. Overall, the distribution of the products obtained by reacting crotyl alcohol on MgO was very similar to that obtained from ethanol.

Further catalytic tests were performed to elucidate additional key points in the mechanism. First, we examined the conversion of acetaldol (3-hydroxybutanal) under different conditions as it has been accepted for decades that this molecule is the key intermediate toward C4 molecules obtained by the aldol route, although it was not detected in the product mixture in our experiments or reported in the literature. From the results obtained at both 250 and 400 $^\circ\text{C}$ (Table 1), it is possible to see that the dehydration of the aldol to crotonaldehyde was only a minor reaction. Indeed, the main reaction observed was the reverse aldolisation to acetaldehyde, which indicates clearly that the aldol condensation is thermodynamically unfavourable at these temperatures. As no significant changes in the product distribution appeared even if ethanol and the aldol were co-fed, any option that presents acetaldol as a key intermediate in C4-compound formation could either be ruled out or its role limited only to a minor one. This idea has gained theoretical support recently.^[20]

In conclusion, the main results obtained from reactivity experiments may be summarised as follows:

a) the main primary product of ethanol transformation was acetaldehyde; immediately after this, the main products

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 $C_4H_8O^{[c]}$

tr

tr

tr

tr

C₄H₁₀O^[c]

1

MVK^[c]

tr

tr

tr

tr

tr

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Table 1. Main catalytic results for potential key reaction intermediates in ethanol conversion on MgO (in the gas phase).									
Feed	T	τ	Conversion ^[a]	e ti e (b) (c)		Yie	ld [%] ^[a]	- · · · [c]	
	[°C]	[s]	[%]	C ₂ H ₄ O ^{(b),(c)}	C ₄ H ₆ O ^(c)	C ₄ H ₉ OH ^{ICJ}	$C_4H_6^{(c)}$	$C_2H_4^{(c)}$	
acetaldol	250	0.5	100	32 (+7)	9	tr	-	-	
acetaldol/ethanol	250	0.5	100	36 (+7)	8	tr	-	-	
acetaldol	400	0.2	100	11	2	-	tr	-	

3-buten-2-ol 400 0.3 58 1 tr 5 10 9 crotyl alcohol/ethanol 8 400 0.4 97 1 18 1 2 tr [a] If two different products are co-fed, conversion and yield refer only to the C4 compounds. [b] The yield obtained as paraldehyde is shown in parenthesis. [[]c] C₂H₄O, acetaldehyde; C₄H₆O: crotonaldehyde; C₄H₉OH: 1-butanol; C₄H₆: 1,3-butadiene; C₂H₄: ethylene; MVK: methyl vinyl ketone; C₄H₈O: 2-butanone; C₄H₁₀O: 2-butanol. tr: trace amount (yield < 1 %). Note: τ stands for contact time.

obtained were 1-butanol and crotyl alcohol. Conversely, butanal, crotonaldehyde and butadiene were all kinetically consecutive compounds (compared to acetaldehyde);

250

0.0

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- b) 3-hydroxybutanal (acetaldol), crotonaldehyde and gasphase 1,3-BDO are not key intermediates during the ethanol transformation to C₄ compounds over MgO;
- c) the intermediate compound that shows a product distribution closest to that shown by ethanol was crotyl alcohol.

DRIFTS

3-buten-2-ol

In situ DRIFTS experiments were performed to understand the way ethanol adsorbs on the surface of MgO and how it is further transformed with temperature (Figure 4). At room temperature (T = 30 °C), the observed bands correspond to un-dissociated H-bonded and O-bonded ethanol (a broad band between $\tilde{v} =$ 3500–3000 cm⁻¹ for the OH_v stretch and small bands at $\tilde{v} =$ 1377 and 1270 cm $^{-1}$ that correspond to OH_{δ} and $CH_{3\delta})$ and surface ethoxide (i.e., the product of ethanol dissociative adsorption), the bands of which at $\tilde{\nu} = 1062$ and 1103 cm⁻¹ can be assigned to coupled C-C and C-O stretching modes. Bands at $\tilde{\nu} = 2972$, 2928 and 2876 cm⁻¹ are caused by CH_{3v(a)}, CH_{2v(a)} and CH_{3v(s)} stretching modes.^[25]



Figure 4. DRIFT spectra of ethanol adsorption on MgO and desorption/transformation with increasing temperature.

After adsorption at 30°C, the alcohol feed was stopped and He was allowed to flow to remove the ethanol adsorbed physically. Then, the temperature program was started (up to 400 °C at 10°C min⁻¹) and desorption profiles were registered simultaneously by DRIFTS and MS (Figure 4 and Figure S7, respectively).

In a recent paper, Davis et al.^[11] reported a similar study that focussed on ethanol adsorption on MgO. Similar to our case, the bands at $\tilde{\nu} = 1058 - 1066 \text{ cm}^{-1}$ were attributed to molecular ethanol; moreover, the band at $\tilde{\nu} = 1119 - 1132$ cm⁻¹ was indicated to be caused by ethoxy species that disappear if T was increased from 200 to 440 °C. This allowed us to detect other species; for instance, we noticed bands that appear in the spectra at $\tilde{\nu} = 1718$ and 1143 cm⁻¹ as T was increased to 150 °C. Although the first of the two bands can be attributed to the C=O stretch of acetaldehyde,^[26] the second one corresponds to a species with a peculiar C–O stretch that is neither from ethoxy nor molecular ethanol. We anticipate that DFT calculations (vide infra) will allow us to tentatively attribute this band to the C-O stretch of a carbanion species formed by the abstraction of one H⁺ from the methyl group in ethanol (this hypothesis is developed in the following sections). This band seems to reach a maximum intensity and then shifts towards lower wavenumbers in the same way as some of the C-H vibration bands.

To have a clearer view of the bands with increasing intensity or that disappear with increasing T and highlight correlations among them, the different spectra were deconvoluted by using the built-in OPUS software fitting function, and the intensity of a few selected bands was plotted against T (Figure 5). This analysis confirmed that the first species observed were ethanol (bands at $\tilde{\nu} = 2972$ and 1270 cm⁻¹, with the maximum intensity at room temperature) and ethoxy (band at $\tilde{\nu} = 1105$ and 2925 cm⁻¹ with the maximum intensity at 100 °C). Thereafter, acetaldehyde appeared at 100 °C (bands at $\tilde{\nu} = 1718$ and 2813 cm⁻¹, also typical for aldehydes). In the middle range of temperatures (100-200 °C), we notice bands at $\tilde{\nu} = 2957$ and 1653 cm⁻¹; the latter was reported to be characteristic of the C=O stretch of acyl or acetyl species.[27] Upon increasing the temperature beyond 200°C, the acetyl band intensity decreased and the band attributed tentatively to a carbanion species began to shift towards lower wavenumbers (until $\tilde{\nu} = 1124 \text{ cm}^{-1}$ at $T > 300 \,^{\circ}\text{C}$). The intensity of the ethoxy bands decreased with no shift of the corresponding wavenum-

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Figure 5. Ethanol on MgO. IR band intensity as a function of temperature.

bers. This assignment was further confirmed by the behaviour of the intensity of the bands (Figure 5) and by the adsorption experiment performed at high temperature (Figure S9), which shows that at 400 °C the band at $\tilde{\nu} = 1124 \text{ cm}^{-1}$ was prevalent, whereas those attributed to ethoxy species were less intense. Therefore, it can be suggested that the acetaldehyde/acetyl and the carbanion may react together to form adsorbed crotyl alcohol as the band at approximately $\tilde{\nu} = 1620 \text{ cm}^{-1}$ (which appears after 250 °C) was also observed if crotyl alcohol was fed over MgO (Figure S8). Conversely, bands of adsorbed crotonaldehyde were not observed except perhaps if T was higher than 350 °C (Figure S8). Later on, the formation of consecutive products (such as crotonaldehyde, acetone, butanal and butadiene) was detected as indicated by bands at $\tilde{v} = 1672$ and 1649 cm⁻¹ characteristic of C=O and C=C stretching, and by the mass desorption profiles recorded during the temperatureprogrammed desorption (TPD) experiment (Figure 4).

Additional clues that emerge from the TPD experiments are that 1-butanol is a primary product (especially at low temperature), that butadiene formation starts only if T > 250 °C and that crotonaldehyde is observed only in traces at high temperatures. Acetyl species may also decompose into CO and methyl, which may form acetone (band at around $\tilde{\nu} = 1649$ cm⁻¹, T > 350 °C)^[28] according to Equations (1), (2) and (3).

$$CH_3CHO \rightarrow CH_3CO_{ads} + H_{ads}$$
 (1)

$$CH_{3}CO_{ads} \rightarrow CH_{3ads} + CO_{ads}$$
(2)

$$CH_{3}CO_{ads} + CH_{3ads} \rightarrow CH_{3}COCH_{3}$$
(3)

With respect to lighter species, the formation and partial adsorption of carbonates in the range of temperatures considered is evidenced by both the broadening of the band at around $\tilde{v} = 1600 \text{ cm}^{-1}$ and the CO₂ detected in the TPD and that the ethanol observed at T < 250 °C may be related to both the desorption of the molecularly adsorbed fraction and the recombination of the ethoxy species with protons. Other products observed were ethylene (only at low temperature if ethanol was also present), hydrogen, methane and CO_2 . The latter may be formed both by the decomposition of surface carbonates and by the "reforming" of ethanol or other products because of the water generated in the reaction medium (e.g., by ethanol dehydration).

With no traces of acetaldol or crotonaldehyde revealed in the spectra and, instead, the formed intermediates that resemble crotyl alcohol, the in situ DRIFTS study appears to confirm that the aldol condensation is not the key mechanism to lead to the formation of C_4 compounds from ethanol on basic oxide materials.

To conclude our experimental investigation, a set of experiments that involve feeding ethanol continuously on MgO at 400 °C was performed while the mass signal of the desorbed products was monitored (so-called "operando mode", Figures S9-S11). These tests differed from those that involved lowtemperature adsorption because the effective contact time of reactants is much shorter. In this respect, in the continuous feeding mode, reaction conditions were certainly closer to those achieved in the flow reactor, albeit they may make the identification of reaction intermediates more difficult because of their fast transformation. Nevertheless, experiments at 400 °C generated spectra that are similar to those recorded using the TPD approach at lower temperature, and thus support the hypothesis that intermediates observed during experiments under such conditions are likely precursors for the formation of the final products (see detailed discussion in the Supporting Information). To support this conclusion, the feasibility of the reaction pathways that involve the unknown intermediate (identified tentatively as a carbanion) adsorbed on MgO was further investigated by DFT calculations.

Theoretical modelling

As a result of the complexity of the tangled reaction set that involves ethanol on basic oxides, our computational study attempted to, at least, clarify the very early stages of ethanol conversion. We did this by focusing on likely transient species and their production mechanism from gas-phase ethanol. A few reactive pathways that may lead to the products detected experimentally were also investigated and linked to the experimental results. The technical details of our theoretical investigation are given in the Experimental Section.

Alcohol dehydrogenation

As the first step, we investigated the dehydrogenation reaction that generates the detected aldehydes using an approach validated previously.^[29] The reaction (ΔE) and transition state (TS) energetics for ethanol dehydrogenation with respect to two alternative energy zeros are shown in Table 2; the optimised stationary points are shown in Figure 6.

A lower barrier (by 4.4 kcal mol⁻¹) and ΔE are calculated if ethanol dehydrogenation takes place close to the O3C site. The energetic ordering shown in Table 2 changes if we refer to the gas-phase ethanol/MgO cluster as energy zero because of the adsorption energies. Nevertheless, both catalytic sites

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Table 2. Alcohol adsorption, reaction and TS energies for the process that leads to the dehydrogenation of ethanol and methanol on $Mg_{10}O_{10}$ and for the formation of a carbanion by methyl deprotonation in ethanol $L^{[a]}$

Alcohol/site	Adsorption energy [kcal mol ⁻¹]	$\Delta E^{ ext{b]}}$ [kcal mol $^{-1}$]	Barrier ^(b) [kcal mol ⁻¹]				
Dehydrogenatio	n						
EtOH/Mg3C	39.5	38.1 (-1.4)	44.7 (5.2)				
EtOH/O3C	23.9	29.4 (5.5)	40.4 (16.5)				
MeOH/O3C	25.1	37.0 (11.9)	44.5 (19.4)				
MeOH/Mg3C	40.4	45.9 (5.5)	51.4 (11.0)				
Carbanion formation							
EtOH/Mg3C		31.3 (-8.2)	33.4 (-6.1)				
EtOH/O3C		36.4 (12.5)	36.7 (12.8)				
[a] The zero of the energy for the processes is assumed to be the ad-							

sorbed alcohol with the OH dissociated. [b] In parentheses, there are energetic quantities that refer to the gas-phase alcohols plus $Mg_{10}O_{10}$ as reactants.

should be considered as active thanks to the high temperature (400 $^{\circ}$ C) employed during the reaction, and the Mg3C site is likely to produce more aldehydes, comparatively, thanks to the lower barrier from the feed reactants.

Enol formation

The enolic form of acetaldehyde would be important if the C_4 formation proceeded through the aldolic pathway, and DFT calculations indicate that C_4 formation on Mg3C should release energy (2 kcal mol⁻¹) and require a low barrier to be surmounted (6.6 kcal mol⁻¹; see Figure 7 for the optimised structures). It is thus likely that a fast equilibrium may exist between the two molecules.

Carbanion formation

The basic MgO surface sites may cleave a C–H bond heterolythically in the ethanol methyl group, and our calculations (Table 2 and Figure 8) indicate that such a process generates a carbanion 31.3 and 36.4 kcalmol⁻¹ above the adsorbed ethanol in the vicinity of the Mg3C and O3C sites, respectively. Deprotonation close to the Mg3C site generates a product that is 6.8 kcalmol^{-1} lower in energy than acetaldehyde plus adsorbed H₂ compared to MgO/gaseous ethanol; the TS barriers for such processes also have the same order of energy. The carbanion produced close to the O3C site, instead, is higher by 7.0 kcalmol⁻¹ than acetaldehyde/adsorbed H₂, although the TS barriers have the same order as that close to Mg3C. Notably, the barrier for carbanion formation near O3C is just 0.3 kcalmol⁻¹ above the energetic requirement for the reaction.

The data reported in Table 2 suggest that both Mg3C and O3C sites may produce the two intermediates, albeit with different activities. In fact, the global energy profiles suggest that carbanion formation on the Mg3C site ought to be the most likely process, followed by ethanol dehydrogenation on the same site and carbanion formation on O3C.

The idea of a carbanion formation by the deprotonation of the methyl group was considered previously by Iglesia and Gines,^[30] albeit from an adsorbed aldehyde. In their study, the catalyst was a basic oxide (MgCeO_x) modified with Cu and K, and they used ${}^{12}C_2H_5OH/{}^{13}C_2H_4O$ reactant mixtures to establish that condensation reactions can proceed by the direct reaction of ethanol without the intermediate formation of gas-phase acetaldehyde. This means that acetaldehyde condensation may occur and that ethanol direct condensation contributes to the formation of the products. Besides, they discussed that the condensation reactions become easier than dehydrogenation in presence of a metal (e.g., Cu) as the metal helps to remove the hydrogen as H₂.

The suggestion of carbanion formation on the MgO surface rationalises several experimental observations, the simplest one of which is the production of ethylene. We have located two TS that lead from the Mg3C-adsorbed carbanion to ethylene and dissociated water (see Figure 9 for the reactant/TS structures) with fairly low barrier heights (3.7 and 6.5 kcal mol⁻¹). Such a finding places the barrier to be surmounted during the carbanion formation plus dehydration sequence at 4.8 kcal mol⁻¹ below the barrier that leads to acetaldehyde plus H₂. Thus, the dehydration of ethanol is a competitive process compared to its dehydrogenation even onto the purely basic MgO. Besides, the carbanion normal mode at $\tilde{\nu}$ = 1165 cm⁻¹ also helps to assign the IR feature at $\tilde{\nu} = 1143$ cm⁻¹, the evolution of which is in line with the reactivity expected from such species (vide supra, DRIFTS Section and Figure S12, which show the simulated IR spectrum of the carbanion). Similarly, the position of the two peaks around $\tilde{\nu} = 1220 \text{ cm}^{-1}$ in the spectrum shown in Figure S12 correlates well with the location of a shoulder that appears and then disappears in the DRIFT spectrum upon increasing the temperature. Notably, the relative intensities in the $\tilde{\nu} = 1143 - 1220 \text{ cm}^{-1}$ region are not reproduced well by the calculations. We consider that this finding is most likely because the shoulder modes involve the displacement of the proton on MgO that interacts directly with the anionic carbon atom; the effect of such motion on the molecular dipole may be estimated improperly by DFT due to of shortcomings in the description of electronic correlation. Instead, the lack of any feature in the DRIFT spectra around $\tilde{v} =$ 1380 cm⁻¹ (Figure S12), a mode connected to the wagging of OH-bearing CH₂ in the carbanion, remains for the moment unclear.

With the quantitative results discussed, it is possible to draw a partial conclusion with respect to the importance of the aldolic path toward C₄ formation on MgO. The higher energetic cost to be paid to produce two molecules of acetaldehyde compared to a single carbanionic species or a carbanion and an acetaldehyde ought to make the surface concentration of the acetaldehyde/enol pair substantially less than that of the carbanion/acetaldehyde couple (or the carbanion/ethanol pair, vide infra). In turn, this suggests that the aldolic pathway is less likely than the one that involves the carbanion. Additional arguments against the aldolic scheme come from the fact that the adsorbed aldol lies substantially higher in energy than the adsorbed 1,3-BDO and that our DFT calculations predict the al-

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Figure 6. Reactant, TS and product (from left to right) of the alcohol (a and b, ethanol; c and d, methanol) dehydrogenation process on MgO near the Mg3C (a and c) and O3C (b and d) sites.



Figure 7. Reactant, TS and product for the enol formation from acetaldehyde near the Mg3C site. Note the presence of two near-degenerate isomers for the enol coordinated onto the Mg3C site.

dolic condensation to be nearly energy neutral in the gas phase (see Figure S12 and related discussion). Notably, this finding is valid whatever the catalyst employed and suggests that the presence of reduced metals (e.g., see work by Iglesia and Gines^[30] and the butadiene catalyst by Ivanova et al.^[31]) may only favour the formation of acetaldehyde to be consumed along paths alternative to the aldolic one.

Carbanion reactivity

As suggested, the in situ generation of a carbanion from ethanol may open alternative channels, among which are the attack to the acetaldehyde carbonyl group and to the hydroxyl-bearing carbon atom in another ethanol molecule. The first reaction would lead to the alkoxide precursor of 1,3-BDO, whereas 1-butanol would be obtained by the S_N2-like attack of the Mg-coordinated and activated ethanol. The energetics for these two processes are provided in Table 3, and the relevant structures are shown in Figure 10. Although both processes are exergonic with respect to the reactants because of the formation of a C-C bond, the carbonyl attack appears to be substantially more facile than the S_N2-type reaction because of the electronic structure of the aldehydic group and the fact that the charge-bearing carbon atom in the carbanion has to detach from the stabilizing lattice Mg to approach the OH-bearing carbon atom in ethanol (Figure 10).

With the zero set as two vapour ethanol molecules plus the MgO clusters, the energy profiles place the products of the ethanol/carbanion and acetaldehyde/carbanion reactions at -54.1 and -21.2 kcal mol⁻¹, respectively. Thus, the adsorbed 1butanol plus dissociated water is

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Figure 8. Reactant, TS and product for the carbanion formation from ethanol near the Mg3C (top) and O3C (bottom) sites. Notice the presence of two near-degenerate isomers for the carbanion coordinated onto the Mg3C site.

Table 3. TS barrier heights and energetics of the carbanion attack to the acetaldehyde carbonyl and hydroxyl-bearing carbon atom in ethanol gauged from the co-adsorbed reactive species in the vicinity of the corner site.^[a]

Reactants	TS barrier ^(b) [kcalmol ⁻¹]	$\Delta E^{\rm [b]}$ [kcal mol ⁻¹]
acetaldehyde/carbanion	11.4 (19.1)	-28.9 (-21.2)
ethanol/carbanion	41.0 (28.9)	-42.0 (-54.1)
acetaldehyde/enol	7.2 (6.3)	-10.6 (-11.5)

[a] The energetics of the stationary points for the aldolic pathway are also shown. [b] The energies that refer to two ethanol molecules in the gas phase plus the MgO cluster are shown in parentheses.

more stable than the dissociated 1,3-BDO because of the dehydrogenation energy (Table 2). On the same energy scale, the TS barrier for the two processes becomes 28.9 and 19.1 kcal mol⁻¹, respectively; hence, either the two pathways have a similar activity, at least based on the energy requirement alone, or the process for 1,3-BDO is somewhat faster than that for 1-butanol. This suggestion agrees well with the results shown in Figure 1, in which a slightly lower yield is obtained for 1-butanol than for 3-buten-1-ol plus crotyl alcohol. Importantly, these compounds are likely to be produced by the dehydration of the deprotonated 1,3-BDO by carbanion formation (Figure 10) as discussed in the Supporting Information.

An additional consequence of the fact that adsorbed 1,3-BDO lies only 21.2 kcal mol⁻¹ below the common energy zero is the possible retro-dissociation into ethanol and acetaldehyde, a process that requires only -0.3 kcal mol⁻¹ on MgO and is apparent in both Figures S3 and S4. Importantly, this conclusion does not contradict the proposed mechanism of 3-buten-1-ol and crotyl alcohol formation (Supporting Information), as these are formed in the vicinity of corner sites. Feeding 1,3-BDO directly onto MgO is instead likely

to lead toward terrace adsorption, at least initially; in such a situation, the diol may gather the energy to decompose easily.

Guerbet versus Lebedev reactions: Common features and differences in mechanisms

From the data collected so far by reactivity tests, DRIFTS, TPD, MS and theoretical modelling, it is possible to suggest a new mechanism able to explain not only the evidence reported in this work but also the data published in many decades of literature on both the Lebedev and Guerbet reactions.

First, ethanol is adsorbed on the basic oxide surface and dissociates into acetaldehyde and hydrogen; this is a rate-determining step and it requires a relatively high temperature (> 200 °C) to take place. Adsorbed acetaldehyde is in equilibrium with the related enolic form. At the same time, ethanol can be adsorbed on the catalyst surface as an ethoxide onto low-coordination sites, although this anion always remains in equilibrium with its un-dissociated alcoholic form. This happens especially near O3C (the alcoholic oxygen atom is coordinated on a Mg4C site), and the molecular ethanol may undergo a proton abstraction from the α -carbon atom to generate a carbanion, the negative charge of which is stabilised by the



Figure 9. Reactants and TS for the dehydration of ethanol starting from the Mg3C-adsorbed carbanion.

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Figure 10. Reactants, TS and products of the reaction between the carbanion and an adsorbed ethanol molecule (top) or acetaldehyde (middle). Also shown, are the two carbanions obtained from 1,3-BDO (bottom).

cations present in the oxide lattice as the near-sp³-type orbital that contains the lone pair electrons points towards one of them. The carbanion may undergo three different reactions, and each path is facilitated or hindered depending on temperature, catalyst acid-base features and the likelihood of molecular encounter (vide infra):

- a) the hydroxyl group present in the carbanion reacts with the H⁺ dissociated previously (adsorbed on the catalyst surface) to produce water and ethylene, which desorb in the gas phase (route 1 in Scheme 2);
- b) the carbanion reacts with another ethanol molecule by an S_N 2-like attack to lose a water molecule to produce 1-butanol directly (route 2 in Scheme 2);
- c) the carbanion reacts with an acetaldehyde molecule to produce an adsorbed species directly, which desorbs to produce either crotyl alcohol (route 3 in Scheme 2 or 3-buten-1-ol and a water molecule. Alkenols may then dehydrate to 1,3-butadiene or rearrange into 3-buten-2-ol.

As far as the first path is concerned, the harder the cation is, the more stable the carbanion; this is why calcium oxide pro-

duces much more ethylene than magnesium oxide.^[15] Importantly, the aldol condensation (which is endergonic by 33.8 kcal mol⁻¹ according to the level of theory used)^[1] can be definitely ruled out as the main path in the Lebedev process as the encounter of two molecules of acetaldehyde is hindered because of their scarce concentration on the surface (the Tishchenko dimerisation to ethyl acetate is slow for the same reason) and the large prevailing concentration of adsorbed ethanol. This is activated either as ethoxide or carbanion species. A reaction between the former and acetaldehyde is indeed possible, even though it would yield the hemiacetal (a possible precursor of ethyl acetate, which we observed only in traces). Its formation, however, is thermodynamically hindered at high temperatures.

The second reaction is the main path followed by ethanol to produce Guerbet alcohols, that is, mainly 1-butanol. This reaction is, therefore, aided by catalysts able to stabilise the carbanion (but not too much to avoid ethylene formation) and by the lack of acetaldehyde on

a vicinal site. These conditions may be reached by decreasing the temperature to limit ethanol dehydrogenation to acetaldehyde (see different selectivity to 1-butanol in Figures 1 and 2) and/or by tuning catalyst features. For example, hydroxyapatite^[15] shows the highest yield to 1-butanol because, as pointed out by the authors, Lewis acid sites (Ca²⁺) and basic sites (O²⁻) have a greater atomic distance than MgO, which might play an important role in the likelihood of molecular encounter. Moreover, for hydroxyapatite with a high Ca/P ratio, the acid sites needed to perform alcohol dehydration are almost nil, which avoids consecutive reactions that might possibly take place from 1-butanol or crotyl alcohol, of which the latter is a competitive path.

Route 3 leads to 1,3-butadiene from ethanol, that is, the Lebedev reaction; the latter process has been demonstrated clearly to require complex catalysts able, firstly, to dehydrogenate to acetaldehyde, secondly, to condense C_2 intermediates and, lastly, to dehydrate the formed C_4 .^[1,18] Moreover, it is well known that acetaldehyde has a beneficial effect on 1,3-butadiene yield, which is why this aldehyde is recycled to the reactor in the industrial process.^[32] All this evidence is confirmed by our model. Acetaldehyde must react with the ethanol carb

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Scheme 2. Hypothesised reaction pathways that lead to ethylene (route 1), 1-butanol (Guerbet reaction, route 2) and crotyl alcohol, precursor of butadiene (Lebedev reaction, route 3).

anion to form crotyl alcohol as the key intermediate, and the precursor for butadiene formation by further dehydration. The final and kinetically consecutive dehydration of the alkenol to butadiene is likely to involve a mechanism quite similar to that observed for both ethanol and 1,3-butanediol dehydration.

The reaction between acetaldehyde and ethanol is in competition with the direct production of 1-butanol, which is why an external source of aldehyde is needed to decrease the probability of the reaction of the carbanion with ethanol and increase the selectivity to butadiene. The condensation features of catalysts must be carefully tuned as the atomic distance of two active sites (one bound to the aldehyde and the other to the carbanion) must be right to facilitate the process. Lastly, dehydration properties are essential to dehvdrate the intermediate alkenol by shifting the equilibrium to 1,3-butadiene. In the case of the purely basic system investigated here, the yield and selectivity to butadiene are much lower than those observed with mixed acid-base systems (e.g., Mg/Si/O). However, the presence of acid sites is required only to perform the consecutive steps that concern alcohol dehydration (e.g., to lead to 1,3-butadiene), whereas they are not involved in the generation of primary products and intermediates shared by both the Lebedev and the Guerbet reactions.

The dehydration of alcohols on acid systems involves energy barriers similar to those calculated with MgO;^[33] this means that with bifunctional catalysts, an additional, acid-catalysed pathway leads to higher butadiene (and butene) selectivity and less by-product formation than with a purely basic catalyst, with which several other side reactions contribute to the formation of a wide spectrum of products.

Finally, the mechanism proposed by Meunier et al.^[20] for the Guerbet reaction, based mainly on thermodynamic calculations, has analogies with the mechanism proposed here. In particular, it was reported that at least two reaction pathways take place simultaneously, the main pathway

involves the condensation of two ethanol molecules with no intermediate gaseous compounds (so-called "direct" route), whereas a minor "indirect" route involves the condensation of ethanol with acetaldehyde (formed from ethanol dehydrogenation) to form butenol, which is converted subsequently to butanol by hydrogen transfer from a sacrificial ethanol molecule.

Conclusions

A new mechanism for the transformation of ethanol into C_4 compounds over MgO, as a model basic catalyst, has been

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proposed based on the results of reactivity tests, in situ diffuse reflectance infrared Fourier transform spectroscopy and theoretical modelling. This approach made it possible to draw a unifying picture of the different routes that lead to either 1-butanol (a transformation known as the Guerbet reaction), butadiene (the main product in the Lebedev process) or ethylene. The suggested mechanism discards the key role of both acetaldol and crotonaldehyde as the reaction intermediates, usually accepted to be shared between the two pathways that lead either to the alcohol or the diolefin. Conversely, we have found that the two reactions involve different intermediate species. Crotyl alcohol and 3-buten-1-ol are the key intermediates of the Lebedev process and precursors for butadiene formation. However, the reaction between ethanol and its activated form (the carbanion) might explain the formation of the Guerbet alcohol as a kinetic primary product.

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The reactions involved are summarised in Scheme 3, which show in a simplified scheme the stoichiometries for the formation of main products; an overview of all reactions involved is shown in Figure S14, as inferred from reactivity experiments performed on both ethanol and the intermediates.

On the basis of these results and on the hypothesis suggested, one might expect MgO to be a good catalyst in crotyl alcohol dehydration to butadiene if the alkenol is fed directly to the reactor. However, this was not the case as shown by the results in Figure 3. This is because, in addition to dehydration, many other reactions occur on adsorbed crotyl alcohol, such as double-bond isomerisation, dehydrogenation on the enol species, which result in a variety of products.



Scheme 3. Stoichiometries of the main reactions that occur at low temperature (top) and high temperature (bottom) if ethanol is fed over MgO.

The mechanism suggested here also explains the formation of dehydration compounds even on purely basic materials. Furthermore, the mechanism proposed does not include Htransfer (Meerwein–Ponndorf–Verley) reactions from ethanol to any reaction intermediate.

Experimental Section

Catalyst preparation and characterisation

The catalyst was prepared by precipitation from an aqueous solution that contained the corresponding nitrate salt, $Mg(NO_3)_2 \cdot 6 H_2O$. The solution was added dropwise to another solution that contained Na_2CO_3 dissolved in distilled water. As the first solution was added to the second one, the pH was adjusted continuously to keep it close to 10.0. Under these conditions, the precipitation of $Mg(OH)_2$ occurred. The obtained slurry was stirred for 40 min. The precipitate was separated from the liquid by filtration and washed with distilled water (6 L) at 40 °C. The solid was then dried at 110 °C overnight and calcined at 450 °C for 8 h in air.

The surface area was measured by the BET single-point method (N₂ adsorption at the temperature of liquid N₂) by using a Sorpty 1750 Fisons Instrument. The surface area of the calcined sample was $86 \text{ m}^2\text{g}^{-1}$.

Bench-scale plant tests

Reactivity experiments were performed by using a continuous-flow reactor made of glass that operated under atmospheric pressure. Catalyst (0.10–1 g) was loaded in pellet (30–60 mesh) form. Residence time (calculated as the ratio between catalyst volume [mL] and total gas flow [mLs⁻¹], which was measured at the reaction temperature) varied. The inlet feed molar ratio was constant and set at 2 mol% organic+98% nitrogen.

Downstream products were fed to an automatic sampling system for GC analysis. This was performed by using an Agilent-5890 instrument equipped with a flame ionisation detector (FID) and a thermal conductivity detector. Agilent chromatographic columns HP-5 (50 m, 0.20 mm) and HP-plot Al₂O₃-KCl (30 m, 0.50 mm) were used for product separation. Qualitative analysis were performed by bubbling effluent gas through two in-series abatement devices, which were filled with acetone (but in some cases either water or dichloromethane was used) and held at a temperature of 0-2 °C. Compounds were identified by GC–MS and the injection of pure reference standards for the comparison of retention times in the GC column.

DRIFTS-MS

The sample was pre-treated at 450 °C in a He flow (10 mLmin⁻¹) for 45 min to remove any molecules adsorbed on the material. Then the sample was cooled to RT, and ethanol was fed at $0.6 \,\mu$ Lmin⁻¹. Subsequently, it was left to flow until weakly adsorbed ethanol was evacuated, and then the temperature program started (until 450 °C at 10 °Cmin⁻¹). The following selected MS signals were monitored continuously with time (and temperature): *m/z* 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 record-

ed by using a mercury cadmium telluride (MCT) detector after 128 scans with 2 cm⁻¹ resolution. The mass spectrometer was an EcoSys-P from European Spectrometry Systems. The second type of experiment was performed by pre-treating the sample in the same way and then setting the temperature at 400 °C before the ethanol feed was started (30 min at 0.6 μ L min⁻¹). As stated briefly in the discussion, the spectra were deconvoluted by using the built-in OPUS software fitting function. The model was optimised using Lorentzian peak shapes and the Levenberg–Marquardt algorithm. We also divided each spectrum at each temperature into three frequency ranges to fit them separately. The criteria to accept them was a residual root-mean-square (RMS) error lower than 0.0009.

DFT calculations

The modelling of the processes involved in the reactivity of ethanol on MgO was performed by employing gas-phase electronic structure calculations by using the Gaussian 09^[34] suites of codes at the DFT level. Specifically, we used the B3LYP DFT functional^[35] together with the 6-31 + +G(d,p) basis set, a level of theory employed commonly for similar tasks.^[36, 37]

As performed previously,^[29] MgO nanocrystals were modelled using a cluster approach mainly with $\mbox{Mg}_{10}\mbox{O}_{10}$ as the model of the crystal corners (Mg3C and O3C sites; Figure 9). Whenever edge-proximity effects may have introduced a bias in the energetic profile studied, the largest Mg₁₆O₁₆ cluster (Figure 10) was used to limit polarisation-induced artefacts. The geometrical parameters of the clusters (right angles and $d_{\rm MgO}$ = 2.1084 Å) were kept frozen^[36] while the degrees of freedom of the adsorbed species were optimised. In many cases, putative TS structures were generated by means of relaxed scans along chosen reaction coordinates (e.g., atom-atom distances) and subsequently optimised fully by using analytical second derivatives of the energy surface. All stationary points were characterised using frequency calculations. As these interesting processes involve heavy atoms or groups, no correction for zero point effects was introduced. Relative TS and product energies are provided with respect to the reactants of the specific process under investigation and with respect to the species fed into the reaction environment (i.e., the MgO clusters and ethanol molecules). The second type of energy scale allows a direct comparison between alternative reaction pathways.

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Lebedev and Guerbet: what's the difference? The multifaceted approach used to study the mechanism of the Lebedev and Guerbet reactions indicates that the two processes share the same anionic intermediate but evolve along different reaction pathways, which avoid the thermodynamically hampered aldolic route.



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On the Chemistry of Ethanol on Basic Oxides: Revising Mechanisms and Intermediates in the Lebedev and Guerbet reactions