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Liquid-Phase Catalytic Transfer Hydrogenation of Furfural over Homogeneous Lewis Acid–Ru/C Catalysts

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The catalytic performance of homogeneous Lewis acid catalysts and their interaction with Ru/C catalyst are studied in the catalytic transfer hydrogenation of furfural by using 2-propanol as a solvent and hydrogen donor. We find that Lewis acid catalysts hydrogenate the furfural to furfuryl alcohol, which is then etherified with 2-propanol. The catalytic activity is correlated with an empirical scale of Lewis acid strength and exhibits a volcano behavior. Lanthanides are the most active, with $DyCl_3$ giving complete furfural conversion and a 97 % yield of furfuryl alcohol at 180 °C after 3 h. The combination of Lewis acid and Ru/C catalysts results in synergy for the stronger Lewis acid catalysts, with a significant increase in the furfural conversion and methyl furan yield. Optimum results are obtained by using Ru/C combined with VCl_3, $AlCl_3$, $SnCl_4$, $YbCl_3$, and $RuCl_3$. Our results indicate that the combination of Lewis acid/metal catalysts is a general strategy for performing tandem reactions in the upgrade of furans.

Introduction

Hydrogenolysis of biomass-derived furfural to platform molecules, such as 2-methylfuran (MF), is an essential step in the catalytic conversion of lignocellulosic biomass into transportation fuels and chemicals.[1] Furfural hydrogenolysis in the liquid phase has been studied with various single metal (Pt, Pd, Cu, Ru, Ir)[2] and bimetallic (Pt–Ru, Cu–Cr, Cu–Fe, Pt–Sn, Pt–Ge)[2b,3] catalysts on various supports. In most of the studies, high-pressure H_2 was used, and the MF yield was typically low and was modest (51 %) in only one study.[3e]

Despite the low cost of hydrogen due to the increased production of shale gas, the use of hydrogen donors for the hydrogenolysis of furfural may provide advantages, such as elimination of high hydrogen pressure and the associated compression cost, overcoming the unavailability of hydrogen in certain locations, and the possibility of an entirely green process (for example, with renewable butanol as a hydrogen donor).

In our recent study, a high MF yield of 76 % was observed through catalytic transfer hydrogenation (CTH) of furfural by using secondary alcohols (for example, 2-butanol or 2-pentanol) as hydrogen donors.[2f] The effective catalyst for the production of MF in high yields was found to be a combination of ruthenium oxide and metallic ruthenium supported on activated carbon.[2f,g] This is also the case for the hydrogenolysis of 5-hydroxymethylfurfural (HMF) to give high yields of 2,5-dimethylfuran (DMF),[4] which indicates that the coexistence of Lewis acid/metal sites is essential for the production of alkylated furans. Although the $Ru/RuO_2/C$ catalyst is fairly effective, the reduction of the oxide during the reaction makes fundamental studies complicated and the active sites remain elusive. An alternative to solid Lewis acid catalysts is the use of homogeneous Lewis acid catalysts, such as metal halides.

The beneficial effect of metal halides has been previously observed for the conversion of carbohydrates into a variety of versatile intermediate compounds for biofuels and chemicals.[5] For example, furfural production from xylose via xylulose can be substantially improved by using $CrCl_3$ in combination with HCl in aqueous media.[5a] Transition metal chlorides, such as $CrCl_3$, $FeCl_3$, and $CuCl_2$, as well as $AlCl_3$, were found to be effective for the conversion of cellulose into levulinic acid.[5c,d] To our knowledge, only recently, a related study of HMF hydrodeoxygenation to DMF reported a synergistic effect with a Lewis acidic $ZnCl_2$ and Pd/C dual catalyst.[6] With consideration of the effectiveness of the $Ru/RuO_2/C$ catalyst but the lack of understanding about the active site(s), it would be interesting to explore the synergy of homogeneous Lewis acid catalysts with heterogeneous metal catalysts for the upgrade of furfural.

Herein, we study the interaction of metal chloride Lewis acid and Ru/C catalysts for the CTH of furfural in the liquid phase and correlate the performance with an empirical scale of Lewis acid strength. The effect of reaction temperature, reaction time, and Al/Ru molar ratio on the furfural conversion and product distribution is presented. We demonstrate that Lewis acid catalysts can be very active for the hydrogenation of furfural to furfuryl alcohol and their activity exhibits a volcano-type behavior with Lewis acid strength. With a single outlier, hydrogenolysis of furfuryl alcohol to MF requires a metal catalyst. Interestingly, we find primarily synergistic effects between the metal chloride salts and the Ru/C catalyst but occasionally also antagonistic interactions.

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Results and Discussion

Catalysis over homogeneous Lewis acid catalysts

Furfural conversion and product distribution

Furfural conversion over Lewis acid catalysts in the absence of Ru/C was investigated at $T = 180\,^{\circ}C$ for a short reaction time of 3 h (Figure 1). Furfural conversion depends strongly on the Lewis acid catalyst and increases from 34 to 100 % following the order: $AlCl_3{\cdot}6\,H_2O < VCl_3 < ZnCl_2 < InCl_3 < MgCl_2 < CrCl_3{\cdot}6\,H_2O < LaCl_3 < SnCl_4{\cdot}5\,H_2O < YbCl_3 \approx DyCl_3 < RuCl_3$. The main product was furfuryl alcohol (FA). The yield of FA varies strongly (from 7 to 97 %) depending on the Lewis acid catalyst, in the order $RuCl_3 < SnCl_4{\cdot}5\,H_2O < VCl_3 < AlCl_3{\cdot}6\,H_2O < CrCl_3{\cdot}6\,H_2O < ZnCl_2 < InCl_3 < MgCl_2 < LaCl_3 < YbCl_3 < DyCl_3$.

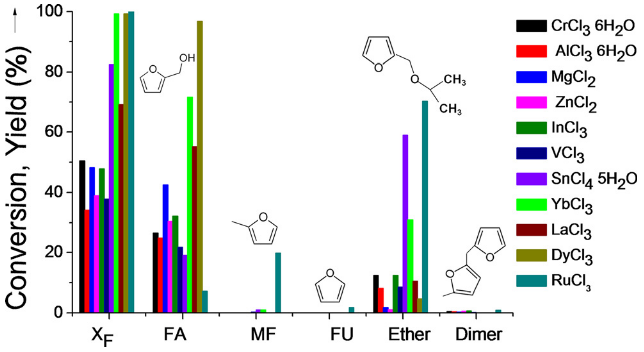


Figure 1. Furfural conversion and product yields for the indicated homogeneous Lewis acid catalysts. X_F: Furfural conversion; MF: 2-methylfuran; FA: furfuryl alcohol; FU: furan; ether: 2-(isopropoxymethyl)furan; dimer: 2-(2-furanylmethyl)-5-methylfuran. Experimental conditions: 1 wt % furfural in 2-propanol solution; $c_{\text{Lewis acid}} = 3.1$ mM; N_2 atmosphere (2.04 MPa); $T = 180\,^{\circ}C$; $t = 3$ h.

We previously found that etherification between FA and the alcohol solvent to form 2-(isopropoxymethyl)furan (hereafter called the ether; Figure 1) is an important reaction competing with hydrogenolysis over the $Ru/RuO_2/C$ catalyst.[2f,g] In the case of the $Ru/RuO_2/C$ catalyst, etherification is enhanced at short reaction times and/or low temperatures and reverses at longer reaction times and/or higher temperatures to give FA and 2-propanol, with the FA converted eventually into MF. Herein, we find interesting differences in etherification between different Lewis acid catalysts. In particular, the ether yield is negligible for $ZnCl_2$ and $MgCl_2$, low for VCl_3, $AlCl_3{\cdot}6\,H_2O$, $CrCl_3{\cdot}6\,H_2O$, $LaCl_3$, $InCl_3$, and $DyCl_3$, and high for $YbCl_3$, $SnCl_4{\cdot}5\,H_2O$, and $RuCl_3$.

Furfural decarbonylation to furan (FU) occurs only with $RuCl_3$ (yield ≈ 2 %), and the formation of 2-(2-furanylmethyl)-5-methylfuran (hereafter called the dimer; Figure 1) is negligible for all Lewis acid catalysts, with yields lower than 1 %. These chloride salts do not catalyze hydrogenolysis to MF with the exception of the $RuCl_3$ catalyst, with which the MF yield is 20 %. Traces of MF were also detected for $YbCl_3$, $SnCl_4{\cdot}5\,H_2O$, VCl_3, $LaCl_3$, and $InCl_3$ (yields lower than 1 %).

Next, we turn to the product distribution resulting from the hydrogen donor. Figure S1 in the Supporting Information shows the 2-propanol conversion and product distribution at 180 °C for all of the Lewis acid catalysts investigated. 2-Propanol conversion varies from 0.5 to 1.2 % (a low conversion given the excess of the solvent) and follows the same trend as that of furfural conversion with the various Lewis acid catalysts, with the acetone yield reaching aprroximately 1.2 % with $DyCl_3$ (Figure S2 in the Supporting Information). Minor products of side reactions of 2-propanol include diisopropyl ether (alcohol self-etherification), propane (product of dehydration of 2-propanol to propylene followed by propylene hydrogenation), and isopropyl chloride, which is produced from 2-propanol with the Lewis acid catalyst in accordance with Equation (1).

$$MCl_x + x\,C_3H_7OH \rightarrow x\,C_3H_7Cl + M(OH)_x \tag{1}$$

The yield of isopropyl chloride, with respect to the initial metal chloride, is shown in Figure S3 in the Supporting Information.

In our previous study,[5a] it was found that, when $CrCl_3$ is dissolved in water, the pH value of the solution drops to approximately 2.1. This is because, in aqueous media, $CrCl_3$ forms hexa-aqua complexes characterized by ions, such as $[Cr(H_2O)_6]^{3+}$, which is hydrolyzed and results in Brønsted acidity, in accordance with Equation (2). This Brønsted acidity was found to catalyze the dehydration of xylulose to furfural.

$$[Cr(H_2O)_6]^{3+} \leftrightarrow [Cr(H_2O)_5OH]^{2+} + H^+ \tag{2}$$

In the present study, the metal chlorides were dissolved in 2-propanol in the absence of water, and therefore, pH measurement and estimation of the H^+ concentration was not possible. Currently, little is known about the formation of possible complexes upon dissolving metal halides in organic solvents. Our data clearly show that the Lewis acid catalyzed Meerwein–Ponndorf–Verley (MPV) reaction is dominant over homogeneous metal chloride catalysts, and thus, hydrogen protons are not expected to be present in noticeable concentrations to drive Brønsted acidity. To investigate the effect of the small fractions of water that are encapsulated in hydrated salts, select experiments were run over nonhydrated metal chlorides by adding the appropriate amount of water to achieve the same molar ratio of MCl_x/H_2O as that of the hydrated salt to the anhydrous salt (for example, VCl_3 and $VCl_3/H_2O = 1{:}6$); the results were similar. This provides strong evidence that the Lewis acid character and/or catalytic properties of the metal chlorides are not influenced by the presence of small fractions of H_2O contained in the hydrated structures.

Mechanistic insights

The hydrogenation of the CHO group of furfural on Lewis acid catalysts is well known to occur through the MPV interhydride transfer reaction between the carbonyl group of the compound and the OH group of 2-propanol.[7] The reaction is accompanied by acetone production, with furfural conversion increasing progressively with increasing acetone yield (Figure S2 in the Supporting Information). However, the number of acetone moles produced is, in all cases, higher than the number of moles of hydrogenation products (FA, MF, the ether, and the dimer; Figure S4 in the Supporting Information). This provides evidence that, in addition to the acetone produced through the MPV reaction, 2-propanol is dehydrogenated to produce acetone and H_2, which leads to hydrogen accumulation in the system. Based on the data (Figure S4 in the Supporting Information), we estimate that the fraction of acetone produced that is consumed in the hydrogenation of known products varies from approximately 57% (with Zn chloride) to about 98% (for example, with Yb chloride).

To explore the dehydrogenation activity of 2-propanol, the reactivity in neat conditions was investigated over $AlCl_3 \cdot 6H_2O$ catalyst. The results showed that 2-propanol is indeed dehydrogenated to form acetone (Figure S5 in the Supporting Information). However, the amount of acetone produced in the presence of furfural is significantly higher than that obtained in neat solvent through 2-propanol dehydrogenation. Byproducts of 2-propanol side reactions are in small fractions and are only slightly affected by the presence of furfural. The furfural interacts more strongly than 2-propanol with the Lewis acid catalyst, so its presence is expected to retard partially the 2-propanol dehydrogenation by blocking of the Lewis acid species. The enhanced quantities of acetone seen in the furfural experiments relative to those in the neat solvent experiments (Figure S5 in the Supporting Information), along with the hydrogen accumulation (Figure S4 in the Supporting Information), indicate that most of the 2-propanol reacts through the MPV reaction but a fraction undergoes dehydrogenation. The dehydrogenation activity is partially suppressed by furfural relative to that in neat conditions, and therefore, the fraction of each pathway contribution to 2-propanol conversion cannot be accurately estimated.

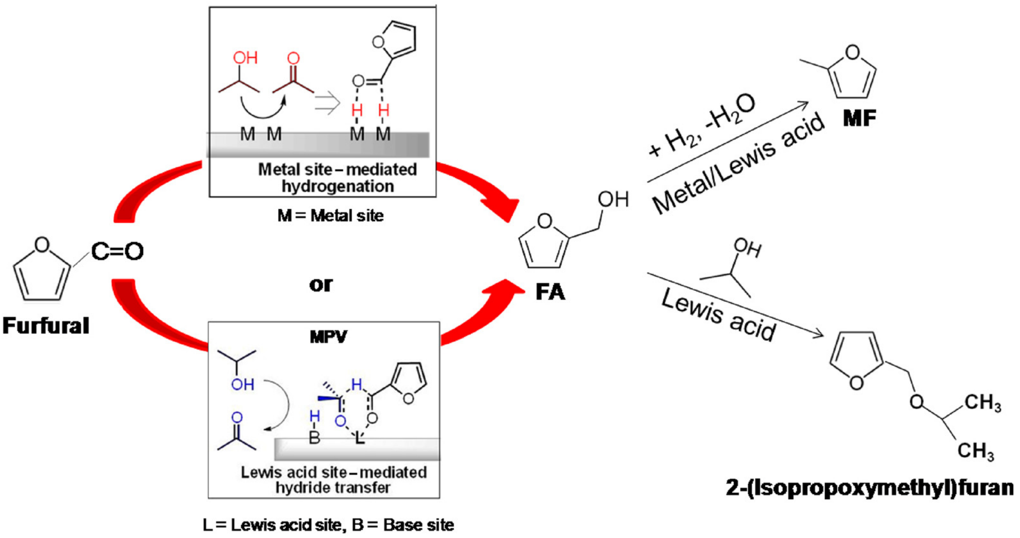
In summary, what our results indicate is that these homogeneous Lewis acid catalysts are capable of the hydrogenation of furfural to FA through the MPV reaction followed by etherification with the solvent (Scheme 1). In addition, they are reasonably effective catalysts in the dehydrogenation chemistry of the solvent, a property that is not typically associated with them. In the presence of furfural, the dehydrogenation activity of 2-propanol is reduced and furfural hydrogenation proceeds mainly through the MPV reaction. Finally, these catalysts are not effective in producing side products of 2-propanol, as observed from the slow alcohol dehydration and hydrogenation of the resulting propylene and the slow self-etherification.

Correlation of performance with Lewis acid strength

To understand the effect of the Lewis acid catalysts on furfural conversion, a descriptor of catalytic activity was exploited. Zhang[8] proposed that the Lewis acid strength could be composed of some electrostatic and covalent properties. The electrostatic force between a positive charge and a negative charge is approximately proportional to z/r_k^2, in which z is the charge number of the atomic core (that is, the number of valence electrons) and r_k is the ionic radius.[8,9] With regard to the covalent force, it has been suggested that, because the σ bond is formed by sharing of an electron pair between the metal ion and the ligand, its strength increases with the tendency of the cation to take on electrons, that is, with the increasing electronegativity of the metal ion.[8] The quantity z/r_k^2 was calculated (Table 1) and plotted as a function of the metal electronegativity X_z (Figure S6 in the Supporting Information). The regressed Equation (3) was used to define the equation for classification, and the function Z, as an empirical metric of the Lewis acid strength, is calculated with Equation (4).[8]

$$z/r_k^2 = 2.99 \times X_z - 0.67 \quad (3)$$

$$Z = z/r_k^2 - 2.99 \times X_z + 0.67 \quad (4)$$



Scheme 1. Scheme of the proposed reaction network in furfural hydrogenolysis with a mixture of Lewis acid/metal catalysts.

Table 1. Metal electronegativity, z/r_k^2, and estimated Lewis acid strength *Z*.

Metal	Metal electronegativity X_z (Pauling scale)	z/r_k^2	Lewis acid strength *Z*
Zn	1.65	3.652	−0.83965
In	1.78	4.152	−0.73946
Mg	1.31	2.704	−0.742
Dy	1.22	2.711	−0.45821
V	1.63	5.479	1.048859
La	1.1	2.184	−0.61616
Cr	1.66	5.263	0.740596
Yb	1.1	2.953	0.152837
Al	1.61	6.584	2.215368
Sn	1.96	5.806	0.360967
Ru	2.2	5.06	−1.12314

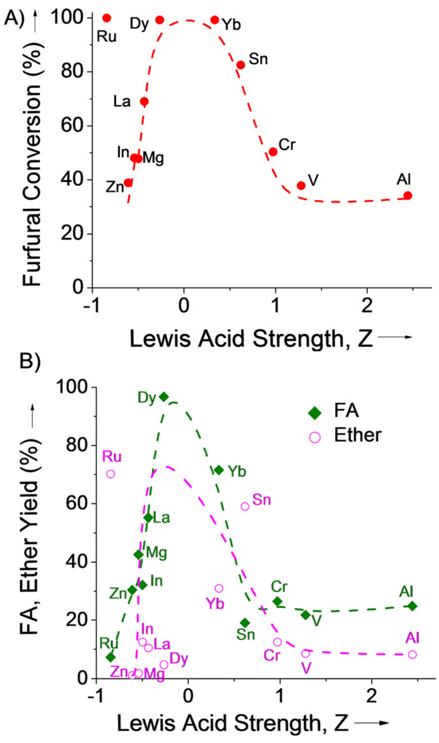


Figure 2. A) Furfural conversion and B) FA and ether yields as a function of the Lewis acid strength in the absence of Ru/C catalyst. Experimental conditions were the same as those given in Figure 1.

The strength ***Z*** of the Lewis acids was calculated for all of the metal chlorides investigated (Table 1) and was correlated with furfural conversion and the FA and ether yields (Figure 2).

In all cases, the furfural conversion is nearly equal to the sum of the FA and ether yields (an indication of a lack of any major byproducts), with the exception of $RuCl_3$, which produces a noticeable yield of MF. It is observed that the catalytic activity goes through a maximum (Figure 2A) at around the strength of $DyCl_3$ and $YbCl_3$; that is, it exhibits a volcano type of behavior. $RuCl_3$ also exhibits 100% furfural conversion, but a significant fraction of the furfural is converted into MF. The volcano-type curve can be rationalized by the classic Sabatier principle, in which the stronger the Lewis acid, the stronger the adsorption of furfural, the lower the reaction barrier and, consequently, the higher the conversion of furfural to reaction products. However, above a certain Lewis acid strength, furfuryl alcohol (the product) adsorption becomes so strong that it may block the catalytically active sites, which results in lower activity.

The yields of FA and the ether are plotted as a function of Lewis acid strength in Figure 2B. Although it is expected that the formation of both FA and the ether takes place on the same species and that FA is an intermediate in the production of the ether, FA etherification is noticeable only on $RuCl_3$ and $SnCl_4$. The rest of the metal chlorides are either not very active or stop the chemistry at furfuryl alcohol (for example, $DyCl_3$). The activity of a catalyst in the MPV reaction does not correlate with the ability of the catalyst for etherification. As we recently showed theoretically for solid Lewis acid sites of alumina,[10] the strength of Lewis acids of a certain crystal correlates linearly with the binding energy and also with the dehydration reaction barrier but does not correlate well with the etherification reaction barrier, probably because of the reaction being bimolecular, that is, as a result of stereochemical hindrance and modification of the electronic properties from adsorption of the first molecule.

Interaction of Ru/C and homogeneous Lewis acid catalysts

Furfural conversion and product distribution

The interaction of Ru/C catalyst with different Lewis acids in the transformation of furfural was investigated at $T = 180\,^{\circ}C$ for 3 h of reaction time. Figure 3 compares the performance of the Ru/C catalyst (in the absence of Lewis acid catalyst) with those of the Lewis acid/metal mixtures. The catalytic activity of Ru/C is significantly enhanced with the addition of small amounts of the Lewis acids. In particular, the furfural conversion increases from 41 to 100% following the order: $InCl_3 <$ Ru/

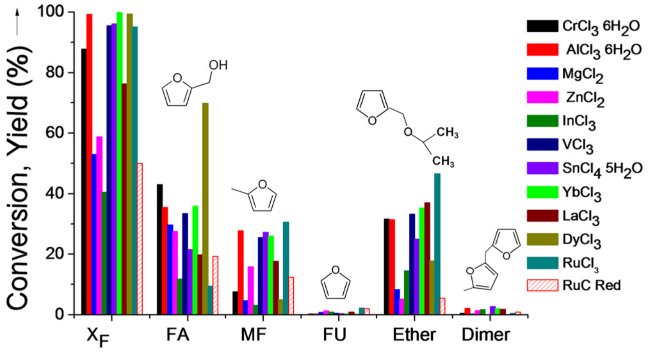


Figure 3. Effect of the addition of Ru/C catalyst on furfural conversion and product yield for the indicated homogeneous Lewis acid catalysts. Experimental conditions: 1 wt% furfural in 2-propanol solution; $c_{\text{Lewis acid}} = 3.1$ mM; $c_{\text{Ru/C}} = 4.1\ g\,L^{-1}$; N_2 atmosphere (2.04 MPa); $T = 180\,^{\circ}C$; $t = 3$ h.

$C < MgCl_2 < ZnCl_2 < LaCl_3 < CrCl_3{\cdot}6\,H_2O < RuCl_3 < VCl_3 < SnCl_4{\cdot}5\,H_2O < DyCl_3 < AlCl_3{\cdot}6\,H_2O < YbCl_3$. A comparison of Figure 1 and Figure 3 shows that the addition of metallic Ru/C results in the formation of MF for all Lewis acids examined. In most cases, the MF yield is higher than that obtained if only Ru/C catalyst is used (12 %). Moderate MF yields of 26–31 % are achieved by using Ru/C combined with VCl_3, $AlCl_3$, $SnCl_4$, $YbCl_3$, and $RuCl_3$. Significant amounts of FA and the ether are also formed.

The performance of the combined Ru/C and Lewis acid catalysts was correlated with the Lewis acid strength ***Z*** described above (Figure 4). It was found that furfural conversion increases rapidly with increasing Lewis acid strength and reaches a plateau above a certain value of ***Z*** (Figure 4 A). The FA yield goes through a maximum for $DyCl_3$ with increasing Lewis acidity (Figure 4 B); it follows a similar trend to that obtained in the absence of Ru/C (Figure 2 B) but reaches higher values in the presence of Ru/C. The ether yield reaches a plateau above a certain Lewis acid strength (Figure 4 B). This is most possibly related to the fact that Ru/C itself is able to etherify FA with the 2-propanol solvent, most probably on the carbon support.[2g] In our previous study, an experiment was conducted over activated carbon with FA as the reactant and it was found that FA is mainly etherified with 2-propanol on the surface of the carbon support; a conversion of 41 % was observed, with a 32 % yield of the ether and a 2 % yield of MF. The MF yield (Figure 4 C) also exhibits a plateau at high values of ***Z***.

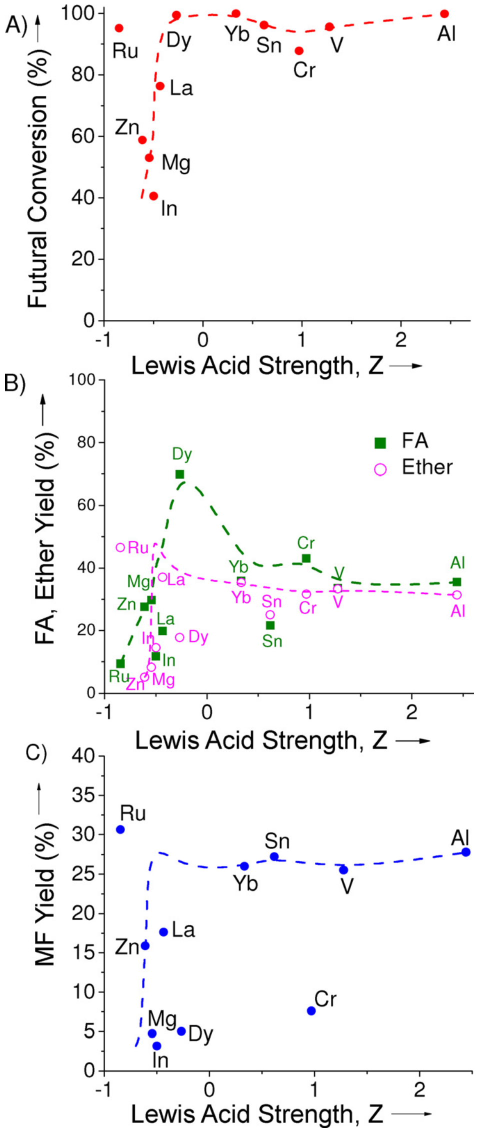


Figure 4. A) Furfural conversion, B) FA and ether yields, and C) MF yield as a function of the Lewis acid strength with a mixture of Lewis acid and Ru/C catalysts. Experimental conditions were the same as those in Figure 3.

A comparison of Figure 2 and Figure 4 indicates clear synergistic effects of mixtures of strong Lewis acid and Ru/C catalysts. Specifically, physical mixtures of Ru/C and chloride salts of Al, V, Sn, and Cr exhibit much higher activities and increased yields of all products with an FA/ether ratio close to 1. Ru and Yb exhibit a complex interaction with Ru/C to give a higher yield of MF and a different ether/FA ratio than as standalone catalysts. An outlier among the strong Lewis acids is $CrCl_3$, which is very active but exhibits an antagonistic effect with Ru/C that results in a low MF yield.

The 2-propanol conversion and acetone yield are higher in all cases in the presence of Ru/C catalyst, with the exception of the reaction with $DyCl_3$ for which the values are comparable (Figure S7 in the Supporting Information). It has been found that Ru/C catalyst exhibits high activity for the dehydrogenation of secondary alcohols to produce a ketone and equivalents amounts of H_2.[2f] It can, therefore, be suggested that, in the presence of both metal (Ru/C) and Lewis acid catalysts, acetone is produced through MPV and 2-propanol dehydrogenation reactions. The hydrogenation of the CHO group of furfural may occur with hydrogen produced through 2-propanol dehydrogenation on metallic Ru sites and the MPV interhydride transfer reaction on Lewis acid sites (Scheme 1). For example, in the case of $YbCl_3$, although furfural conversion is complete both in the presence and in the absence of Ru/C, the product distribution differs. The addition of Ru/C results in the production of MF at the expense of FA. The 2-propanol conversion and acetone yield are higher in the presence of both Ru/C + $YbCl_3$ in the reactant suspension, which indicates that H_2 produced from 2-propanol dehydrogenation is consumed for MF production. This is also the case for $RuCl_3$, for which both the MF and acetone yields are enhanced with the addition of Ru/C. As in the absence of Ru/C catalyst, the number of acetone moles produced is higher than the number of moles of furfural hydrogenation products (Figure S4 in the Supporting Information) for all Lewis acids examined. Irrespective of the reaction by which acetone is produced, the MF yield increases with the increasing acetone yield (Figure 5), in agreement with our previous studies.[2f,g]

The fraction of H_2 produced that is consumed in the hydrogenation of known products was estimated based on the data of Figure S4 in the Supporting Information, and it was found to vary from approximately 43 % for the less active catalysts (such as $InCl_3$) to about 96 % (for example, with $LaCl_3$).

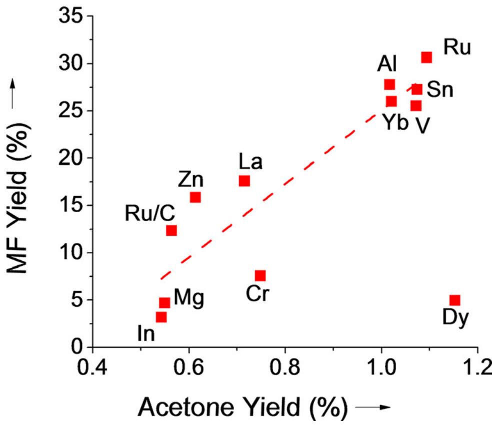


Figure 5. MF yield as a function of acetone yield for mixtures of Lewis acid and Ru/C catalysts. Experimental conditions were the same as those given in Figure 3.

Mechanistic insights

The results in Figure 1 and Figure 3 clearly indicate that MF production requires a combination of metal/Lewis acid catalyst. This is more pronounced in the cases of $AlCl_3$ and VCl_3, for which neither the metallic Ru alone nor the Lewis acid alone are capable of catalyzing effectively the production of MF from furfural (Figure 6), but in coexistence, they are capable of carrying out the hydrogenolysis.

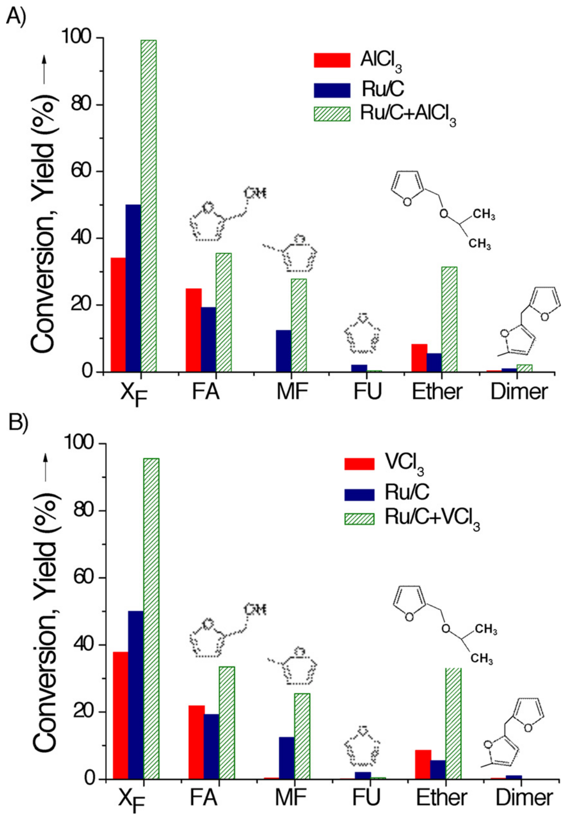


Figure 6. Synergism of the Lewis acid and Ru/C combination relative to reduced Ru/C catalyst with A) $AlCl_3$ and B) VCl_3 catalysts. Experimental conditions were the same as those given in Figure 3.

The results are in general agreement with recent work on the hydrodeoxygenation of HMF to DMF with tetrahydrofuran as the solvent and external hydrogen as the hydrogen source.[6] It was found that the combination of Lewis acidic $ZnCl_2$ and Pd/C completely converted HMF and exhibited a high DMF selectivity of 85 %. Under comparable reaction conditions, Pd/C alone produced only 27 % DMF, whereas $ZnCl_2$ alone did not catalyze deoxygenation or hydrogenation of HMF, which suggests a strong synergistic effect between the two catalysts.

The results of the present study agree with and provide further support for our previous findings, in which it was demonstrated that the effective catalyst for high MF yields is a combination of Ru (metal) and RuO_2 (Lewis acid).[2f,g] Whereas the origins of the synergy of these homogeneous Lewis acid/metal catalysts are currently unknown, our results provide insights into the development of heterogeneous catalysts for donor-based hydrogenolysis. They underscore the fact that not all Lewis acid catalysts combined with a metal are effective in carrying out hydrogenolysis. Rather, strong Lewis acid catalysts are essential for this. At the same time, the results in Figure 4 provide evidence that, above a certain Lewis acid strength, MF production cannot be further improved, at least under the present experimental conditions; thus, a minimum Lewis acid strength is essential but hydrogenolysis activity does not scale up with the Lewis acid strength. Higher reaction temperature or longer reaction time, as well as different Lewis acid/metal ratios, may be required; thus, the effect of these parameters is investigated in the following sections.

Effects of operating conditions and metal/Lewis acid catalyst ratio

Effect of reaction time

The effect of the reaction time on the catalytic activity and product distribution has been investigated at $T = 180\,^{\circ}C$ over $AlCl_3$, both in the absence and in the presence of Ru/C catalyst. In the former case (Figure 7 A), furfural conversion increases from 31 to 97 % with an increase in the reaction time from 1 to 9 h. The main reaction products detected were FA and the ether.

The addition of Ru/C catalyst (Figure 7 B) results in an almost complete furfural conversion already after 3 h and is accompanied by MF production, with its yield increasing from 13 to 45 % with an increase in the reaction time from 1 to 9 h. The yield of the ether increases up to 32 % at $t = 9$ h, which is lower than that observed with $AlCl_3$ catalyst alone, whereas the opposite is observed for shorter reaction times. This is most probably related to the enhancement of FA hydrogenolysis to form MF at longer times by the synergism of the Ru/C and $AlCl_3$ catalysts. Both the ether and MF are produced from FA, the yield of which decreases as a function of time. FU and the dimer were also detected, but their yields are low at all times.[2g] The 2-propanol conversion and the acetone yield increase with the reaction time, and both are enhanced with the addition of Ru/C (Figure S8 in the Supporting Information).

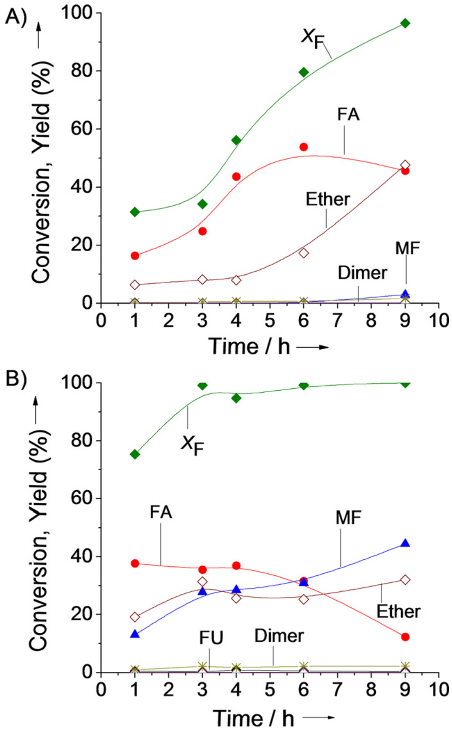


Figure 7. Effect of reaction time on furfural conversion and product yields over A) $AlCl_3$ and B) $AlCl_3$ and Ru/C catalysts. Experimental conditions: 1 wt% furfural in 2-propanol solution; $c_{Lewis\ acid}=3.1$ mm; $c_{Ru/C}=0$ (A) or 4.1 g L^{-1} (B); N_2 atmosphere (2.04 MPa); $T=180$ °C.

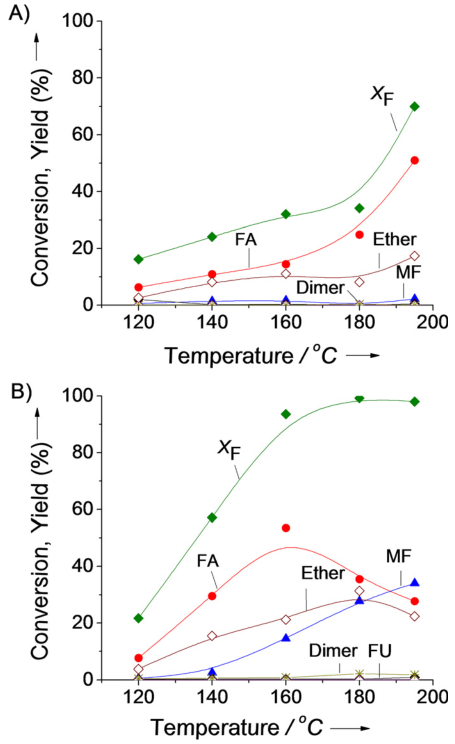


Figure 8. Effect of reaction temperature on furfural conversion and product yields over A) $AlCl_3$ and B) $AlCl_3$ and Ru/C catalysts. Experimental conditions: 1 wt% furfural in 2-propanol solution; $c_{Lewis\ acid}=3.1$ mm; $c_{Ru/C}=0$ (A) or 4.1 g L^{-1} (B); N_2 atmosphere (2.04 MPa); $t=3$ h.

Effect of reaction temperature

The effect of the reaction temperature was investigated in the range of 120–195 °C over $AlCl_3$, both in the absence (Figure 8 A) and in the presence (Figure 8 B) of Ru/C catalyst. In the former case, the furfural conversion and FA yield increase with an increase in the temperature and reach 70 and 51%, respectively, at $T=195$ °C. The yield of the ether takes comparable values with those of FA up to $T=160$ °C but is not further increased at higher reaction temperatures. The MF yield is only 2.5% at $T=195$ °C.

The addition of Ru/C results in significantly higher furfural conversions over the entire temperature range examined and is accompanied by MF production at temperatures higher than $T=130$ °C, with a yield of 35% achieved at $T=195$ °C. The yield of FA increases up to 53% at $T=160$ °C and then decreases to 28%, as a result of its consumption in the production of MF and the ether through hydrogenolysis and etherification with 2-propanol, respectively. The yield of the ether is higher than that obtained in the absence of Ru/C catalyst. As in the case of the time-dependent experiments, the 2-propanol conversion and acetone yield increase with reaction temperature and are enhanced with the addition of Ru/C (Figure S9 in the Supporting Information).

Effect of the ratio of Lewis acid/metal catalysts

The effect of the Al/Ru molar ratio on the furfural hydrogenolysis activity was investigated at $T=180$ °C for $t=3$ h, either by varying the $AlCl_3$ concentration (1–10.5 mm) while keeping the Ru/C concentration (0.4% w/v) constant (Figure 9 A) or by varying the Ru/C concentration (0.2–1.65% w/v) while keeping the $AlCl_3$ concentration (3.1 mm) constant (Figure 9 B). In both cases, the furfural conversion increases with an increase in the Al/Ru molar ratio, whereas the product distribution depends on whether the concentration of $AlCl_3$ or Ru/C is being varied. In the former case, the FA yield decreases from 53 to 34% with an increase in the Al/Ru molar ratio in the range of 0.5–5.0, whereas the opposite is observed in the latter case. The yield of the ether increases from 18 to 49% with an increase in the concentration of $AlCl_3$ while the Ru/C concentration is kept constant. In contrast, the yield of the ether varies slightly with the increase in the concentration of Ru/C while the $AlCl_3$ concentration is kept constant, which indicates that FA etherification with 2-propanol is favored on Lewis acid sites relative to metal sites. On the other hand, the MF yield increases moderately (from 19 to 28%) with an increase in the $AlCl_3$ concentration (Figure 9 A) but decreases considerably (from 44 to 18%) with a decrease in the Ru/C concentration (Figure 9 B), providing evidence that metallic Ru contributes significantly on FA hydrogenolysis to MF. However, the MF yield is only 12% for an Al/Ru molar ratio of 0, which indicates that it is the synergy of Lewis acid and metal sites that is responsible for the high MF yield. Although the results of the present study cannot elucidate the details of the interplay between metal/Lewis acid sites, such a synergy possibly arises from a molecular interaction between the two catalysts as a result of adsorption of the

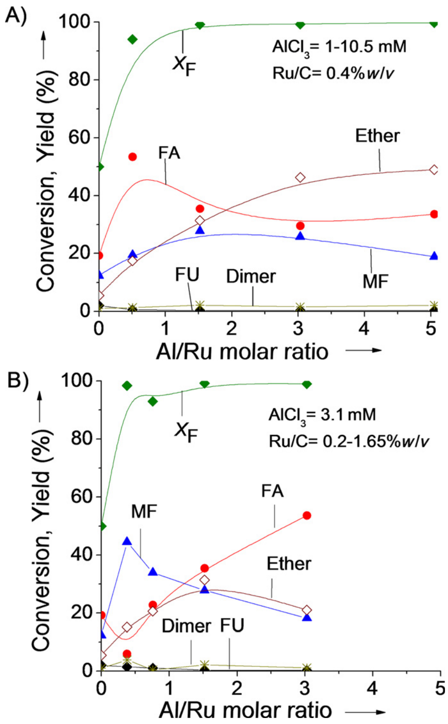


Figure 9. Effect of Al/Ru molar ratio on furfural conversion and product yields by varying the concentration of A) $AlCl_3$ and B) Ru/C catalysts. Experimental conditions: 1 wt% furfural in 2-propanol solution; N_2 atmosphere (2.04 MPa); $T=180$ °C; $t=3$ h.

Lewis acid on the metal. Further work will be needed to understand the molecular origin of this interaction.

The 2-propanol conversion and acetone yields are higher with higher Ru/C concentrations, most probably as a result of the parallel occurrence of the MPV and 2-propanol dehydrogenation reactions (Figure S10 B in the Supporting Information). As expected, isopropyl chloride formation is favored for higher $AlCl_3$ concentrations (Figure S10 A in the Supporting Information).

Catalyst stability

Catalyst stability has been examined by conducting catalyst recycling experiments over Ru/C + $AlCl_3$ catalysts at $T=180$ °C for 3 h of reaction time. The catalyst was recovered after the reaction by filtration, washed with 2-propanol several times, and reused after drying at $T=100$ °C (hereafter called the spent catalyst). Fresh Ru/C catalyst (< 10 wt% of total catalyst) was added to replenish the catalyst mass lost during recovery. Fresh $AlCl_3$ was then added, and the experiment was repeated. The results are summarized in Figure 10. On the spent catalyst, the furfural conversion remains practically unchanged (≈99%), whereas the MF yield decreases from 28 to 12.5%. The decrease in the MF yield is accompanied by an increase in the FA yield from 36 to 48% and a slight increase in the ether yield from 32 to 34%. Our results demonstrate that, although the furfural conversion over the spent catalyst does not decrease, FA production increases at the expense of MF. We hypothesize that this change in selectivity is due to modification of the Ru catalyst and may be a result of residual Cl ions left on the Ru catalyst. Importantly, the product distribution is completely recovered after catalyst regeneration (regenerated catalyst) following the same pretreatment used for the fresh catalyst (reduction for 3 h at 300 °C in H_2 flow). The results indicate that the Ru/C catalyst deactivation is reversible and the catalyst is recyclable after regeneration.

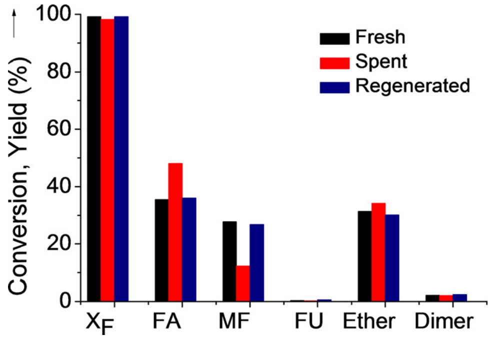


Figure 10. Furfural conversion and product yields over the fresh, spent, and regenerated catalysts. Experimental conditions are the same as those given in Figure 3.

Conclusions

We have studied the effect of homogeneous chloride-based Lewis acid catalysts, as well as the interaction of these Lewis acid catalysts with Ru/C catalyst, on the hydrodeoxygenation of furfural in the liquid phase through catalytic transfer of hydrogen (CTH) with 2-propanol as the solvent and hydrogen donor. We have shown that homogeneous Lewis acid catalysts effectively convert furfural into furfuryl alcohol (FA) and its ether with 2-propanol. These catalysts are ineffective in the hydrogenolysis of FA to form 2-methylfuran (MF) except for $RuCl_3$. The catalyst activity exhibits a volcano-like behavior versus Lewis acid strength. The most active catalysts are salts of Ru, Sn, Yb, and Dy. Hydrogenation of furfural proceeds primarily through the MPV interhydride transfer. However, direct dehydrogenation of 2-propanol leading to the production of gaseous H_2 occurs in parallel and could result in some hydrogenation of the CHO side group of furfural.

Neither the metallic Ru/C alone nor a Lewis acid alone is capable of effectively catalyzing the hydrodeoxygenation of furfural to MF, which is consistent with our previous results demonstrating that the coexistence of both catalysts is essential.[2f,g,4] The synergy of Lewis acid and metal catalysts significantly increases both the furfural conversion and the MF yield, with VCl_3, $AlCl_3$, $SnCl_4$, $YbCl_3$, and $RuCl_3$ exhibiting better results. The MF yield increases with an increase in the reaction time or temperature and can be further optimized by selecting the molar ratio of Al/Ru. The highest MF yield was approximately 45%.

Catalyst recycling experiments showed that furfural conversion remains complete over the spent catalyst and the FA yield increases at the expense of the MF yield. However, the catalyst performance is regained completely after catalyst regeneration.

Our results support a picture whereby the Lewis acid catalyst is mainly responsible for the hydrogenation of furfural to FA, along with the etherification (a side and reversible reaction of FA and 2-propanol), and the Lewis acid/metal catalyst synergy drives the hydrogenolysis of FA to MF. This synergy extends beyond that of heterogeneous catalysts that we discovered before to homogeneous Lewis acid/heterogeneous metal catalysts and, as such, opens up new possibilities for carrying out this cascade of reactions in a single pot. Our results reveal for the first time that good catalysts require a strong Lewis acid functionality and optimization of the ratio of the two functionalities.

Experimental Section

The CTH of furfural was carried out in a Parr batch reactor with 2-propanol (Sigma–Aldrich) as the hydrogen donor. Although 2-propanol is less effective as a hydrogen donor, the larger availability of experimental data of prior work render its selection desirable. Briefly, in a typical experiment, an alcohol solution of furfural (1 wt%; 24 mL) containing a Lewis acid catalyst (3.1 mM; VCl_3, $AlCl_3{\cdot}6H_2O$, $ZnCl_2$, $MgCl_2$, $InCl_3$, $CrCl_3{\cdot}6H_2O$, $LaCl_3$, $SnCl_4{\cdot}5H_2O$, $YbCl_3$, $DyCl_3$ (all Sigma–Aldrich), or $RuCl_3$ (Strem Chemicals)) and Ru/C catalyst (0.1 g) was added to the reactor, which was sealed under N_2 pressure (2.04 MPa) and heated in a temperature-controlled oil bath. The reaction was stopped at the desired times, the reactor was cooled down in an ice bath, and the suspension was collected, filtered, stored in sealed vials, and analyzed by using both gas chromatography (GC; Agilent 7890A) and gas chromatography–mass spectrometry (GC–MS; Shimadzu QP2010 Plus). The metal catalyst used was 5 wt% Ru/C (Sigma–Aldrich), which, prior to each experiment, was treated for $t=3$ h at $T=300\,^{\circ}C$ in an H_2 flow of 40 $cm^3\,min^{-1}$. Details of methods can be found elsewhere.[2f,g] In most experiments, the carbon material balance in the liquid products is 88–100%. Some higher loss of carbon is observed only at high Al/Ru ratios in Figure 9.

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[1] Y. Nakagawa, M. Tamura, K. Tomishige, *ACS Catal.* **2013**, *3*, 2655–2668.
[2] a) M. Hronec, K. Fulajtarová, *Catal. Commun.* **2012**, *24*, 100–104; b) M. Hronec, K. Fulajtarová, T. Liptaj, *Appl. Catal. A* **2012**, *437–438*, 104–111; c) V. V. Ordomsky, J. C. Schouten, J. van der Schaaf, T. A. Nijhuis, *Appl. Catal. A* **2013**, *451*, 6–13; d) P. Reyes, D. Salinas, C. Campos, M. Oportus, J. Murcia, H. Rojas, G. Borda, J. L. G. Fierro, *Química Nova* **2010**, *33*, 777–780; e) M. M. Villaverde, N. M. Bertero, T. F. Garetto, A. J. Marchi, *Catal. Today* **2013**, *213*, 87–92; f) P. Panagiotopoulou, N. Martin, D. G. Vlachos, *J. Mol. Catal. A* **2014**, *392*, 223–228; g) P. Panagiotopoulou, D. G. Vlachos, *Appl. Catal. A* **2014**, *480*, 17–24.
[3] a) A. Merlo, V. Vetere, J. Ramallo-López, F. Requejo, M. Casella, *React. Kinet. Mech. Catal.* **2011**, *104*, 467–482; b) A. B. Merlo, V. Vetere, J. F. Ruggera, M. L. Casella, *Catal. Commun.* **2009**, *10*, 1665–1669; c) C. Xu, L. Zheng, J. Liu, Z. Huang, *Chin. J. Chem.* **2011**, *29*, 691–697; d) K. Yan, A. Chen, *Energy* **2013**, *58*, 357–363; e) K. Yan, A. Chen, *Fuel* **2014**, *115*, 101–108.
[4] J. Jae, W. Zheng, A. M. Karim, W. Guo, R. F. Lobo, D. G. Vlachos, *ChemCatChem* **2014**, *6*, 848–856.
[5] a) V. Choudhary, S. I. Sandler, D. G. Vlachos, *ACS Catal.* **2012**, *2*, 2022–2028; b) Q. Ren, Y. Huang, H. Ma, J. Gao, J. Xu, *Chin. J. Catal.* **2014**, *35*, 496–500; c) H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* **2007**, *316*, 1597–1600; d) L. Peng, L. Lin, J. Zhang, J. Zhuang, B. Zhang, Y. Gong, *Molecules* **2010**, *15*, 5258–5272; e) Y. J. Pagán-Torres, T. Wang, J. M. R. Gallo, B. H. Shanks, J. A. Dumesic, *ACS Catal.* **2012**, *2*, 930–934.
[6] B. Saha, C. M. Bohn, M. M. Abu-Omar, *ChemSusChem* **2014**, *7*, 3095–3101.
[7] a) A. Corma, M. E. Domine, L. Nemeth, S. Valencia, *J. Am. Chem. Soc.* **2002**, *124*, 3194–3195; b) A. Corma, M. E. Domine, S. Valencia, *J. Catal.* **2003**, *215*, 294–304; c) J. Jae, W. Zheng, R. F. Lobo, D. G. Vlachos, *ChemSusChem* **2013**, *6*, 1158–1162.
[8] Y. Zhang, *Inorg. Chem.* **1982**, *21*, 3889–3893.
[9] a) E. G. R. A. L. Allred, *J. Inorg. Nucl. Chem.* **1958**, *5*, 264–268; b) Y. Zhang, *Inorg. Chem.* **1982**, *21*, 3886–3889.
[10] G. R. Jenness, M. A. Christiansen, S. Caratzoulas, D. G. Vlachos, R. J. Gorte, *J. Phys. Chem. C* **2014**, *118*, 12899–12907.

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