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Poisoning of Ru/C by Homogeneous Brønsted Acids in Hydrodeoxygenation of 2,5-Dimethylfuran via Catalytic Transfer Hydrogenation

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Abstract

It has been proposed that the combination of metal and acid sites is critical for effective ring opening of biomass-derived furans to linear molecules, a reaction that holds promise for the production of renewable polymer precursors and alkanes. In this work, we use 2,5-dimethylfuran (DMF) as a model compound to investigate hydrogenolysis and hydrogenation pathways using a combination of H₂SO₄ and Ru-mediated catalytic transfer hydrogenation in 2-propanol. Acid-catalyzed hydrolytic ring opening of DMF to 2,5hexanedione (HDN) occurs readily at 80 °C with a selectivity of 89% in 2-propanol. Over Ru/C, HDN is fully converted after only 2 h at 80 °C, forming a mixture of both ring-closed products (~68% total yield), i.e., 2,5-dimethyltetrahydrofuran (DMTHF) and 2,5-dimethyl-2,3-dihydrofuran (DMDHF), as well as ring opened products (~28% total yield), i.e., 2,5-hexanediol (2,5-HDL) and 2-hexanol (HOL). Rather than observing sequential hydrolysis/hydrogenation reactions, we observe severe suppression of metal chemistry when having both Ru/C and H_2SO_4 in the reaction system. While minor leaching of Ru occurs in the presence of mineral acids, X-ray photoelectron spectroscopy coupled with CO chemisorption studies suggest that the primary cause of the lack of Ru-mediated chemistry is poisoning by strongly adsorbed sulfate species. This hypothesis is supported by the observation of Ru-catalyzed chemistry when replacing H₂SO₄ with Nafion, a solid Brønsted acid, as sulfonic acid groups tethered to the polymer backbone cannot adsorb on the metal sites.

Keywords: Ring opening, catalytic transfer hydrogenation, biomass, catalyst poisoning, dimethylfuran

1. Introduction

The conversion of biomass feedstocks to value-added carbon-neutral chemicals and fuels has demonstrated much promise. Owing to the complexity of biomass-derived substrates, many upgrade strategies require bifunctional catalysts, i.e., materials with two types of active sites, to achieve satisfactory activity and selectivity.[1-4] Not only can bifunctional catalysts reduce the overall number of reaction steps in a chemical process, but in some cases, they can also perform chemistry that cannot otherwise occur over mono-functional catalysts.[5-7] This is especially true in hydrodeoxygenation (HDO) processes which typically employ catalysts with both metal and acid/base characters to remove oxygenated functional groups in biomass-derived feedstocks. While many research groups have successfully implemented materials that fulfill these traits, fundamental understanding on the interplay between metal and acid sites is still lacking.

Recently, several groups have focused on the production of linear polyols, e.g., 1,6-hexanediol and 1,5-pentanediol, from biomass-derived furans such as 5-hydroxymethylfurfural (HMF) and furfural, respectively, which requires ring opening/hydrogenolysis of furans or cyclic ethers.[2, 8-11] These oxygenated furans can be derived from glucose and xylose, respectively, through a series of isomerization and dehydration steps.[12] However, ring opening typically requires high pressures of hydrogen, which leaves HMF and furfural susceptible to a variety of side products when exposed to metal catalysts, e.g. reduction of side groups. [9, 13, 14] Moreover, exposure of oxygenated furans to acids can lead to additional side products such as polymerization and etherification.[15] The use of model compounds has been proved helpful in understanding ring-opening chemistry due to the structural complexity of real biomass-derived substrates. 2,5-dimethylfuran (DMF) is a good substrate choice because it maintains HMF's furanic structure while eliminating reactive side groups. DMF is subject to ring opening via hydrolysis in Brønsted acidic conditions to form 2,5-hexanedione (HDN),[16, 17] although further hydrogenation is necessary to create linear alcohols or alkanes. Thus, exposing DMF to Brønsted acids, e.g. H₂SO₄, in the presence of hydrogenation catalysts, e.g. Ru/C, and a hydrogen source can, in theory, catalyze sequential ring opening and hydrogenation reactions to form linear alcohols. However, this hinges on the assumption that the two types of catalysts operate independent of each other, i.e., metal is capable of performing the hydrogenation reaction in the presence of Brønsted acids, or even better synergistically, i.e., they promote each other.

Herein, we report an experimental study on the ring opening of DMF on homogeneous Brønsted acids and Ru in isolation as well as in combination. 2-propanol is employed as the organic hydrogen source over Ru/C via catalytic transfer hydrogenation (CTH). We show that sulfuric acid is capable of catalyzing DMF ring opening facilely to HDN. HDN is susceptible to hydrogenation over Ru/C, leading to the formation of predominantly ring closed 2,5-dimethyltetrahydrofuran (DMTHF) rather than linear alcohols, e.g., 2-hexanol (HOL) or 2,5-hexanediol (2,5-HDL). Increasing the concentration of sulfuric acid drastically suppresses Ru-mediated chemistry, which is attributed to the poisoning by strongly adsorbed anions based on CO chemisorption and X-ray photoelectron spectroscopy results.

2. Materials and Methods

2.1 Catalytic Activity Evaluations

Activity tests for DMF HDO in this work were conducted in a 50 mL stainless steel pressure vessel (Parr Instruments). Reaction solutions were made by adding 1 wt% of reactant to 14 mL 2-propanol, where 2-propanol acts as both the solvent and the hydrogen source, as well as 80 mg of reduced Ru/C (5 wt% loading, Sigma Aldrich). For experiments where Brønsted acid was introduced, standard acid solutions in H₂O were prepared from 18 M H₂SO₄ (Sigma-Aldrich). Before sealing reactor, 0.5 mL of acid of a desired concentration was added to the reactor. The reactor was then sealed and purged 3 times with N₂ gas before being pressurized to a final pressure of 300 psig (N₂) at room temperature. Temperature of the reactor was then raised to the desired value and maintained for a predetermined period of time, followed by quenching the reaction in an ice bath. The catalyst was then filtered, and samples were placed in a vial for analysis in a gas chromatograph (GC) as well as in a gas chromatograph-mass spectrometer (GCMS). All chemicals were purchased from Sigma Aldrich and used without further purification.

Time-dependent data was acquired with a 160 mL stirred, pressurized vessel (Parr Instruments), installed with a dip tube equipped with a 0.20 μ m filter. Reaction solutions were made by adding 1 wt% of

reactant to 100 mL of pure 2-propanol and loading 500 mg of reduced Ru/C (5 wt% loading, Sigma Aldrich). Liquid samples were taken over the course of the reaction where volume and pressure changes were deemed negligible. Samples were subsequently placed in the GC for analysis.

Identification of the liquid phase products was performed on a GCMS (Shimadzu QP2010 Plus) system. The GC (Shimadzu GC2010) is equipped with an HP-INNOWax capillary column (30 m \times 0.25 mm id \times 0.50 µm film thickness) and interfaced directly to the MS (Shimadzu QP2010 Plus). Identification of the GCMS spectral features was accomplished by comparing the mass fragmentation pattern of the products with those in the built-in Wiley/NIST library.

Quantification of the liquid products was achieved using a GC (Agilent 7890A), equipped with an HP-INNOWax capillary column (30 m \times 0.25 mm id \times 0.5 μ m film thickness) and an FID detector. Response factors were determined using self-prepared solutions of known concentrations. Once response factors were determined, conversion was calculated based on the formula:

$$X = \frac{c_{\text{reactant},0} - c_{\text{reactant},\text{final}}}{c_{\text{reactant},0}} \cdot 100\%$$
[1]

Yields were calculated by the following formula:

$$Y_i = \frac{C_{i,\text{final}}}{C_{\text{reactant},0}} \cdot 100\%$$
 [2]

2.2 Catalyst Pre-treatment

Reduction of commercial Ru/C catalysts (Sigma-Aldrich, 5 wt% loading) was conducted *ex-situ* using a continuous-flow reactor. First, quartz wool was added to a quartz tube prior to the addition of Ru/C (~2 g) to prevent Ru/C from escaping. The loaded quartz tube was subsequently placed in a furnace and connected to a combined H₂ and He gas line, equipped with mass flow controllers. H₂/He flow was held constant at 20 sccm H₂ and 20 sccm He, and the furnace was heated to 300 °C with a temperature ramp of ~5 °C min⁻¹. After 3 h of reduction at 300 °C, H₂ flow was decreased to 0 sccm and left under He flow (40 sccm) to allow the catalyst bed to cool to room temperature. The Ru/C was then transferred to a vial and stored in a lab drawer until use in catalytic testing. This procedure was also described elsewhere.[4]

Acid-pretreated catalysts were prepared by mixing 14 mL of 2-propanol, 0.5 mL of various concentrations of acid, and 80 mg of Ru/C catalyst after reduction at 300 °C (see procedure in previous paragraph). After adequate mixing, the slurry was placed over a magnetic stirrer and allowed to stir, covered at room temperature, for 12 h. The mixture was then filtered, washed several times with 2-propanol, and allowed to dry. This catalyst was then placed directly into the reactor for catalytic testing.

2.3 X-ray Photoelectron Spectroscopic, Inductively Coupled Plasma Mass Spectrometric, and CO Chemisorption Measurements

X-ray photoelectron spectroscopic measurements were conducted in a Thermo Scientific K-Alpha+ spectrometer. XPS scans were taken using an accelerating voltage of 15 kV with Al K α X-rays as the excitation source (1486.7 eV). Spectra were collected with a 400 μ m spot size with a resolution of 0.05 eV. The XPS data were calibrated to adventitious carbon at 284.6 eV. Peaks were fitted using a blended exponential and Gaussian-Lorenzian shape profile with a Shirley background. Due to the significant overlap between C 1s and Ru 3d peaks, the peak fitting of the Ru 3d doublet was conducted as follows. One spectral band was assigned to Ru 3d_{5/2} and 3d_{3/2} each (without deconvoluting Ru with different oxidation states) with a full width at half maximum (FWHM) of 1.36 eV. Only the relative shift of the binding energy of the Ru 3d_{5/2} peak is used for discussion. Acid-treated and reduced catalysts were prepared as described in Section 2.2 and placed on carbon tape prior to analysis.

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) measurements were conducted on an Agilent 7500 Series instrument. Samples were prepared by pre-treating Ru/C in HCl (0.5 mL of 4 M HCl in 14 mL water) for 2 h at both room temperature and 80 °C followed by filtration of the remaining liquid. HCl, rather than H₂SO₄ or other sulfate salt, was employed due to incompatibility of sulfates with the instrument. Ru's 98 amu through 104 amu isotopes were scanned, where ¹⁰²Ru gave the greatest sensitivity. Ru standards in dilute HCl were acquired from VHG Labs and diluted for the ICP-MS calibration.

CO chemisorption experiments were conducted on an Altamira Instruments AMI-200ip instrument equipped with a thermal conductivity detector (TCD). Prior to dosing CO, the catalyst was reduced under 50% hydrogen in helium at 300 °C for 2 h. After reduction, the system was cooled to 30 °C under helium. Pulses of CO (25% CO in helium) were introduced and TCD spectra were collected and analyzed.

3. Results and Discussion

3.1 Brønsted Acid-catalyzed Hydrolysis of 2,5-dimethylfuran with Sulfuric Acid

	Reactant	Catalyst	<i>T</i> (°C)	<i>t</i> (h)	X (%)	Y(%)						
Entry						HON	HOL	HDN	DMTHF	DMDHF	2,5- HDL	C- balance
1	DMF	$H_2SO_4{}^a$	80	2	44	0	0	39	0	0	0	<mark>89</mark>
2	HDN	Ru/C	80	2	99	0	3.9	N/A	67	1.4	24	<mark>97</mark>
3	HDN	Ru/C	55	2	89	0	1.7	N/A	23	9.7	61	<mark>107</mark>
4	2,5-HDL (ref. [19])	Ru/C	80	2	76	0	1.8	0	74	trace	N/A	<mark>99</mark>
5	2,5-HDL (ref. [19])	Ru/C	55	2	5.5	0	0	0	3.6	0	N/A	<mark>65</mark>
6	DMF (ref. [19])	$\begin{array}{c} Ru/C + 0.5 \\ mL \ H_2O \end{array}$	80	2	99	0	22	0	33	0	53	<mark>108</mark>
7	DMF	$\begin{array}{l} Ru/C + \\ H_2SO_4{}^a \end{array}$	80	2	40	0	0	14	10	4.6	0	<mark>72</mark>
8	DMF (ref. [19])	Ru/C	80	2	99	1.3	19	0	73	0	0	<mark>94</mark>
9	HDN	$\begin{array}{c} Ru/C + 0.5 \\ mL \ H_2O \end{array}$	80	2	99	0	4.1	N/A	10	1.5	79	<mark>96</mark>
10	DMF	$Ru/C + ZnSO_4$	80	2	32	0	2.9	2.3	8.6	2.5	12	<mark>88</mark>
11	DMF	$Ru/C + Na_2SO_4$	80	2	96	19	0.4	0	59	2.2	10	<mark>94</mark>
12	DMF	Ru/C + NaHSO4	80	2	40	0	0	32	0	0	0	<mark>80</mark>
13	DMF	Ru/C + MgSO ₄	80	2	36	0	2.7	0	14	5.9	3.7	<mark>73</mark>
14	DMF	Ru/C ^b	80	2	NR	-	-	-	-	-	-	-

Table 1. Product distribution with various reactants and catalysts.

^a0.5 mL of 2 M H₂SO₄ was added, ^bRu/C was pretreated with 5 M H₂SO₄ or Na₂SO₄ or ZnSO₄, ^cRu/C was pretreated with 5 M Na₂SO₄, ^dRu/C was pretreated with 5 M MgSO₄, ^eRu/C was pretreated with 5 M ZnSO₄. Entries 1, 2, 7, and 8 were taken from ref. [19]. DMF = 2,5-dimethylfuran, HON = 2-hexanone, HOL = 2-hexanol, HDN = 2,5-hexanedione, DMTHF = 2,5-dimethyltetrahydrofuran, DMDHF = 2,5-dimethyl-2,3-dihydrofuran, 2,5-HDL = 2,5-hexanediol.

Ring opening of DMF via hydrolysis to HDN occurs readily in the presence of sulfuric acid at 80 °C. After 2 h of reaction, ~44% conversion of DMF was achieved with a ~89% selectivity (~89% carbon balance) to HDN in 28:1 (vol/vol) mixture of 2-propanol and 2 M H₂SO₄, i.e., 0.07 M H₂SO₄ (Figure 1a and Table 1, Entry 1). This is in agreement with previous studies that report the facile hydrolysis of alkylated furans under acidic conditions.[16, 17] The high selectivity toward HDN supports the hypothesis that Brønsted acidity enhances the ability to ring open the furan to form linear alkyl chains. The use of H₂SO₄ also catalyzed the dehydration of 2-propanol to propylene, which consumed ~5.8% of 2-propanol to give ~5.3% yield to propylene (~91% selectivity). In addition, trace amounts of acetone and diisopropyl ether (DIIPE) were observed (Figure 1b). Though protons participate in dehydration reactions to convert ~5.8% of 2-propanol, plenty of free protons are available for DMF hydrolysis, as indicated by Figure 1a and Table 1, Entry 1 (44% conversion, 39% yield).

While Brønsted acidity alone is capable of opening the furan ring through hydrolysis, Brønsted acids cannot drive HDN hydrogenation to aliphatic alcohols or alkanes due to their inability to hydrogenate C=O bonds in the absence of Lewis acid or metal sites.[18] Thus, the combination of metal and Brønsted acid sites is expected to drive the production of alkyl alcohols from oxygenated furanic compounds. Dumesic et al., among others, proposed that the Brønsted acid/metal combination is responsible for the ring opening activity of the ReO_x/Rh catalyst.[2] 2-propanol and other secondary organic alcohols can function as effective hydrogen donors over metals such as Ru/C, eliminating the need for high pressure H₂.[18] To understand the interplay between the metal and acid catalysis, we first investigated the reactivity of HDN over Ru/C.



Figure 1. Product distribution of (a) DMF hydrolysis and (b) 2-propanol dehydration in the presence of homogeneous Brønsted acid. Reaction conditions: 1 wt% DMF in 14 mL 2-propanol with 0.5 mL of 5 M H₂SO₄, T = 80 °C, t = 2 h, $P_{N2} = 300$ psig.

3.2 2,5-hexanedione (HDN) Hydrogenation over Ru/C

Reduction of the carbonyl groups in HDN ensues readily over Ru/C. After 2 h of reaction at 80 °C, complete conversion of HDN was reached in the presence of 2-propanol with a 67% yield to 2,5-dimethyltetrahydrofuran (DMTHF), a 24% yield to 2,5-hexanediol (2,5-HDL), and a 4% yield to 2-hexanol (HOL) via CTH (Table 1, Entry 2). Thus, hydrogenation of HDN predominantly resulted in the ring closed DMTHF, rather than a linear molecule. In addition, high carbon balance was achieved after 5 h (>90%), suggesting that very few, if any, undetected byproducts formed. Interestingly, the time-dependent data collected over 24 h indicate that 2,5-dimethyl-2,3-dihydrofuran (DMDHF) is a reactive intermediate in HDN hydrogenation, peaking after only 20 min at 55 °C (Figure 2, purple trace). DMDHF formation from HDN could occur via several possible pathways. One such pathway involves the partial hydrogenation of one C=O bond in HDN to form 5-hydroxy-2-hexanone over Ru/C, which can then undergo ring closure and dehydration to DMDHF via Lewis acidic RuO_x sites. Although Ru/C catalysts were reduced at 300 °C prior to reaction, reduction was not conducted *in situ*. After reduction, 80 mg Ru/C was transferred to the reactor, which could introduce some oxide sites upon exposure to air during the transfer. However, based

on the experimental data, neither the precise catalytic sites for HDN ring closure to DMDHF nor the molecular-level reaction pathway can be determined. Yield of 2,5-HDL (Figure 2, green trace), via hydrogenation of both carbonyl groups of HDN, increased in the first 5 h to ~70% before its slow decline. Because DMDHF is the first intermediate to be observed in the time-resolved experiment, the formation of 2,5-HDL could also stem from the ring opening of DMDHF and subsequent hydrogenation. Although this pathway could not be determined experimentally, theoretical studies suggest that partially saturated furan rings can be ring-opened over metallic surfaces,[19] and thus it is a potential reaction pathway. DMTHF could form via two possible pathways (Figure 2, red trace): 1) ring hydrogenation of DMDHF, and 2) etherification of 2,5-HDL. Etherification reactions are typically catalyzed by acid sites, suggesting that 2,5-HDL cyclization to DMTHF might be facilitated by Lewis acidic sites on Ru in the form of RuO_x (Table 1, entries 4 and 5),[3, 4, 18, 20] which likely exist due exposure to air after pre-treatment of Ru/C. Trace amounts of HOL were also observed, likely due to either hydrogenolysis of 2,5-HDL or hydrogenolytic ring opening of DMDHF.



Figure 2. Product distribution of CTH of 2,5 hexanedione (HDN) as a function of time at 55 °C. Conditions: 1 wt% HDN in 100 mL 2-propanol, T = 55 °C, $m_{cat} = 500$ mg Ru/C, $P_{N2} = 300$ psig. Error bars included at t = 4 h to indicate representative uncertainty.



3.3 Combined Metal and Homogeneous Brønsted Acid-catalyzed DMF Hydrogenation/Hydrogenolysis

Scheme 1. Reaction network from DMF (left) and 2-propanol (right) in the presence of both Ru/C and H₂SO₄, showing the formation of hydrolytic ring opening to HDN followed by hydrogenation in the DMF pathway and the emergence of propylene and sulfurous acid, bis(1-methylethyl)ether (SAE) in the 2-propanol pathway.

The combination of metal and homogeneous Brønsted acid, i.e., H₂SO₄, in the reaction mixture with DMF creates a complex reaction network (Scheme 1), whereby metal-catalyzed hydrogenation and hydrogenolysis occur in parallel with Brønsted acid-catalyzed hydrolysis. When 0 M H₂SO₄, i.e., pure water, was added to the reaction, full conversion of DMF was achieved, where DMTHF, HOL, and 2,5-HDL were formed with yields of 33%, 22%, and 53%, respectively (Table 1, Entry 6). At low acid concentrations (0.5 mL 1 M H₂SO₄ in 14 mL 2-propanol, final concentration of 0.36 M H₂SO₄) the combination of metal and acid catalysis did not enhance ring opening toward aliphatic alcohols, i.e., 2,5-HDL or HOL; instead, lower activity was observed after 2 h (~75% vs. 100% conversion on Ru/C) under otherwise identical conditions (Figure 3). In addition, DMTHF formed as the primary product (~31% yield), while yields toward HOL, 2,5-HDL, and HDN remained below 5% (Figure 3). This could be due to The ratio between stable products DMTHF and HOL is helpful in assessing the interplay between metal and acid catalysis because HOL production occurs solely over metal sites[13, 20, 21] while DMTHF production

can occur via a combination of metal and acid sites. Conversion of DMF on Ru/C resulted in roughly a 4:1 mixture of DMTHF to HOL at 80 °C in 2 h (Table 1),[20] whereas the ratio of DMTHF to HOL increased to 15:1 when the reaction was catalyzed by Ru/C with diluted H_2SO_4 (0.5 mL 1 M H_2SO_4 added in the reaction mixture) due to the HDN hydrogenation reaction to DMTHF (Figure 3). The enhanced selectivity for DMTHF indicates sequential acid and metal catalyzed reactions, i.e., HDN, formed from the hydrolysis of DMF by H₂SO₄, was subsequently converted to DMTHF on Ru/C. When 0.5 mL of 2 M H₂SO₄ was added (final concentration of 0.72 M H₂SO₄), both DMF conversion and DMTHF yield dropped considerably, resulting in a 40% conversion, a 10% DMTHF yield under otherwise identical conditions. Meanwhile, no HOL was observed, providing evidence of Ru's deactivation. In this case, the conversion is very similar to that when no Ru/C was added (~44%), which suggests that in the presence of both H_2SO_4 and Ru/C much of the initial DMF conversion proceeds via acid-mediated hydrolysis to HDN followed by partial hydrogenation and ring closure. It further suggests that the surface is only partially poisoned, inhibiting Ru's ability to catalyze hydrogenation reactions directly from DMF. An alternative explanation is that DMF and sulfate molecules might compete for sites on the Ru surface, making DMF's ability to access active Ru sites difficult. Meanwhile, protons in solution are available to perform hydrolysis to HDN. As evidenced by the product distribution, HDN can still be hydrogenated, followed by ring-closure to DMTHF, which suggests that HDN and sulfates do not appear to compete for the same type of Ru sites while DMF and sulfates do. HDN's ability to hydrogenate, however, suggest that the surface is only partially poisoned when 2 M H_2SO_4 (0.5 mL) was added, where some Ru sites are still catalytically active. Once the concentration of the added H₂SO₄ reached 5 M (final concentration of 1.78 M H₂SO₄), Rumediated catalysis was completely shut off, producing neither DMTHF nor HOL. Only acid-catalyzed hydrolysis occurred to form 31% yield of HDN.



Figure 3. Effect of the concentration of added sulfuric acid on DMF product distribution. Conditions: 1 wt% DMF in 14 mL 2-propanol with 0.5 mL of varying concentrations of H₂SO₄, T = 80 °C, t = 2 h, $m_{cat} = 80$ mg Ru/C, $P_{N2} = 300$ psig. Final concentration of H₂SO₄ in the mixture: 0.36 M (0.5 mL 1 M H₂SO₄), 0.72 M (0.5 mL 2 M H₂SO₄), 1.78 M (0.5 mL 5 M H₂SO₄)

Although water is added with varying concentrations of H₂SO₄, it does not contribute to the poisoning of Ru sites. Water, however, does play a role in tuning product selectivity of 2,5-HDL vs. DMTHF. In particular, when water is added (0 M H₂SO₄, Figure 3), yield of 2,5-HDL is 53% and yield of DMTHF is 33%, which is in stark contrast to that when no water is added (0% and 73%, respectively, Table 1, Entries 6 and 8). This could be due to one of two possibilities: (1) RuO_x phases form Ru(OH)_x species on the surface and contribute to 2,5-HDL formation,[20] or (2) increasing water concentration shifts equilibrium to favor 2,5-HDL over DMTHF, where water is a product of cyclization of 2,5-HDL to DMTHF. If the latter explanation holds, it is expected that using HDN as a starting material in a mixture of 2-propanol/water will result in a larger 2,5-HDL to DMTHF ratio, while yield to other hydrogenation products should remain similar. After reaction of HDN at 80 °C, full conversion of HDN was reached, and a 79% yield to 2,5-HDL and 10% yield to DMTHF was observed (Table 1, Entry 9). This 2,5-HDL to DMTHF ratio of 7.9 is drastically increased from 0.36 when no water was added (Table 1, entry 2). However, the sum of 2,5-HDL and DMTHF yields are very similar in both cases (89% vs. 91%), suggesting there is a similar degree of hydrogenation. In addition, HOL and DMDHF yields remained similar to that

when no water was used (4.1% and 1.5% versus 3.9% and 1.4%, respectively). These data suggest that water plays a negligible role in affecting Ru's hydrogenation ability, and likely only plays a role in affecting the equilibrium between DMTHF and 2,5-HDL.

3.4. Deactivation of Ru/C in Homogeneous Brønsted Acids

The deactivation of Ru/C in the presence of sulfuric acid could be attributed to site-blocking by adsorbed sulfate or bisulfate anions, which could potentially be facilitated by the reaction between protons and oxide phases, e.g., RuO_x , on the surface. When replacing H_2SO_4 with a sulfate salt soluble in 2propanol, e.g., ZnSO₄, in the identical concentration to that of H₂SO₄, significant decrease in DMF conversion was observed in comparison to that when no additive was added while maintaining a high carbon balance (~88%) (Figure 4a and Table 1, Entry 10). In contrast to using H_2SO_4 , only partial loss in metal activity was observed in the presence of sulfates, likely due to the incomplete blocking of metal sites by adsorbed sulfate. While lower yields for DMTHF and HOL were observed (8.6% and 2.6%, respectively – Table 1, Entry 10), the ratio between the two products remained similar to that when H_2SO_4 was absent (\sim 3:1 vs. \sim 4:1), indicating that site blocking is likely the primary cause of deactivation. When ZnSO₄ was replaced with a salt that is insoluble in 2-propanol, e.g., Na₂SO₄, no appreciable change in product distribution is observed after reaction (Table 1, Entry 11), most likely due to the lack of sulfate ions in solution. Replacing H₂SO₄ with an equimolar concentration of NaHSO₄ resulted in a very similar product distribution to that of H_2SO_4 , i.e., high selectivity for hydrolysis product (HDN) but no hydrogenation products (Figure 4a and Table 1, Entry 12). Thus, protons likely facilitate site blocking by interactions with Ru sites. Alternatively, it is possible that protons increase Ru's electron density near the surface, hindering its catalytic performance. Such a phenomenon has been observed by Karim et al. when Pt was used for aqueous-phase reforming of glycerol in acidic conditions.[22]

While a significant amount of propylene (0.18 mol) was detected in the presence of H_2SO_4 , its participation in Ru/C's deactivation through proton-mediated oligomerization reactions is likely minimal. In the post-reaction mixture when both 80 mg Ru/C and 0.5 mL of 2 M H_2SO_4 was added, propylene (5.3%

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yield), acetone (0.1% yield) and DIIPE (0.1% yield) were formed from 2-propanol (5.8% conversion), resulting in a very high carbon balance (95% with respect to converted 2-propanol), where the majority of propylene was detected in the liquid phase. Therefore, it is possible that the liquid-phase propylene could react with protons in the solvent to form polypropylene or oligomers. However, such undetected products formed from these reactions, if any, make up only a small portion of the carbon balance and are unlikely to be the main cause of catalyst deactivation. In addition, the acid sites which can catalyze propylene oligomerization exist homogeneously in solution, rather than on the catalyst (Ru/C) surface.[23] Thus, longer alkyl chains that form in solution are unlikely to subsequently adsorb on Ru sites and inhibit hydrogenation reactions. Experiments performed using sulfate salts in place of H₂SO₄ provide further evidence that propylene, along with oligomers derived from it, do not contribute significantly to catalyst poisoning. When alcohol-soluble sulfate salts, e.g., ZnSO₄ and MgSO₄, are co-fed with Ru/C, negligible propylene is observed due to a lack of homogeneous Brønsted acid sites; moreover, severe deactivation of Ru sites is still observed (Figure 4a and Table 1, entries 10 and 13), which subsequently leads to the conclusion that sulfates, rather than propylene-based oligomers, play a key role in catalyst poisoning.

Halides also showed similar deactivating effect on Ru-mediated hydrogenation, evidenced by minimal hydrogenation products when introducing halide acids and halide salts (Figure 4b). Adding 0.5 mL of 4 M of HCl, HBr, or HI as the homogeneous Brønsted acid produced >90% selectivity to HDN and no conversion of DMF to hydrogenation or hydrogenolysis products, suggesting that halides are similarly capable of poisoning Ru sites. Similar deactivation by halides was observed by Karim et al. due to strong binding of the anion to metallic surfaces.[22] Halide salts, i.e., NaCl, LiBr, etc., were more effective in deactivating the Ru sites than sulfates at similar concentrations, which is likely due to the strong binding of halides to the metal.



Figure 4. (a) Effect of acids and salts on DMF conversion and product distribution. (b) Effect of halide-based salts and acids on DMF conversion and product distribution, illustrating very pronounced loss in activity. Conditions: 1 wt% DMF in 14 mL 2-propanol with 0.5 mL of 5 M acid or salt (in water), T = 80 °C, t = 2 h, $m_{cat} = 80$ mg reduced Ru/C, $P_{N2} = 300$ psig.

When Ru/C catalysts were pre-treated *ex-situ* by sulfuric acid or sulfate salts (as described in the Experimental Section), similar deactivation toward DMF hydrogenation was observed, further supporting the hypothesis of deactivation of Ru by site blocking. Pretreatment of Ru/C catalysts was conducted by soaking the catalyst in a mixture of 14 mL 2-propanol and 0.5 mL 5 M acid or salt solution at room temperature for 2 h. Following filtering, washing, and drying of the H₂SO₄, Na₂SO₄, or ZnSO₄ treated catalyst, minimal DMF conversion and no products were detected (Table 1, Entry 14). This suggests that

upon drying of the catalysts, sulfuric acid or sulfate salt is able to irreversibly block or remove the active sites on Ru/C. However, over these treated catalysts, HDN can still be converted (>99%) to form DMTHF (~23% yield), 2,5-HDL (~38%), and DMDHF (~6%), although carbon balance is significantly lower (~67%). This suggests that available Ru sites are significantly poisoned and cannot hydrogenate DMF effectively. However, hydrogenation of HDN to HDL can still occur, followed by ring-closure. Pulse CO chemisorption experiments indicate that the treatment of Ru/C with both sulfate salt and acid pre-treatments drastically reduces the availability of metal sites. Reduced Ru/C catalysts adsorbed 73 µmol_{CO}/g, which was in excellent agreement with Ru/C catalysts pre-treated with only 2-propanol (70 μ mol_{CO}/g). However, Ru/C catalysts that were pre-treated with ZnSO₄, Na₂SO₄, and H₂SO₄ adsorbed only trace amounts of CO (<1 μ mol_{CO}/g), which indicates that either: (a) sulfates are strongly bound to the surface, covering metal sites irreversibly, or (b) sulfate salts and acids cause severe leaching of Ru from the support. The latter possibility was tested via inductively coupled plasma mass spectrometry (ICP-MS). Analysis of the filtrate in ICP-MS showed that only ~1.4% Ru is removed by acid treatment at room temperature, and ~6% of Ru is removed at 80 °C. Thus, leaching of Ru is unlikely the main cause of the complete deactivationThis is supported by CO chemisorption experiments where negligible CO was adsorbed on pre-treated catalysts even after the catalysts were reduced at 300 °C for 3 h *in-situ* prior to pulsing CO. It should be noted that 300 °C is a high enough temperature to completely reduce RuO_x in H₂.[24] Leaching of Ru to the solution could lead to Ru-phase redistribution and morphology changes on the catalyst surface, subsequently deactivating the catalyst. However, this possibility cannot explain the complete loss of CO chemisorption onto the surface ($<1 \mu mol_{CO}/g$) and complete loss of Ru-mediated activity (Figure 3), although some losses could be expected. In addition, this possibility can be ruled out by experiments where sulfate/halide salts were employed. In these cases, no protons are available to drive leaching and reassembly of Ru molecules on the surface, and yet strong deactivation of metal sites was observed (Figure 4). Thus, it is most likely that sulfates/halides are bound strongly to the surface after being pre-treated with acid and dried.

Ru that is leached into solution by interactions with protons is only mildly active for hydrogenation reactions. This is evidenced by reactions conducted with supernatant solutions created by refluxing Ru/C

in 14 mL 2-propanol solutions containing 0.5 mL of 5 M H₂SO₄ for 2 h at 80 °C. After filtering the Ru/C from the resulting mixture, DMF was added to the liquid to make the concentration 1 wt%, and the mixture subsequently was added to the reactor vessel, pressurized with N_2 (300 psi), and heated to 80 °C for 2 h. Post-reaction analysis revealed that DMF conversion was 45%, with 32% yield to HDN, 6% yield to DMTHF, and 5% yield to HDL. The DMF conversion is similar to that when no leached Ru is available in solution, which suggests that the leached Ru does not effectively hydrogenate DMF. Instead, it is likely that HDN is first formed via homogeneous Brønsted acid sites, and homogeneous Ru sites can hydrogenate C=O bonds to form HDL. HDL can then undergo proton-mediated ring closure to form DMTHF. In reactions where DMF was left to react in the presence of both Ru/C and 0.5 mL of 5 M H₂SO₄, no hydrogenation products were observed (Figure 3). This can be rationalized by the low concentration of homogeneous Ru sites at the start of the reaction when both Ru/C and H₂SO₄ were co-fed with DMF. Over the course of the reaction, a small amount of Ru is gradually leached into solution. Thus, only at longer reaction times are there sufficient Ru sites to perform hydrogenation reactions, at which point the reaction is quenched. When supernatant solutions are used, the reaction begins with a relatively high Ru concentration in solution, where both hydrolysis and hydrogenation reactions can occur at a faster rate than the cases not using supernatant solutions.

X-ray photoelectron (XPS) spectral features of H_2SO_4 - or sulfate salt-treated catalysts strongly indicate that sulfate molecules are bound to the surface after pre-treatment. The XP spectra of each of the pre-treated Ru/C catalysts showed a prominent band at 169.8 eV (Figure S1), which is characteristic of the S 2p_{3/2} band of sulfate.[25-27] In addition, the cations of the salts used to treat Ru/C catalysts were also observed in the XP spectra. This is evidenced by a doublet feature in the XP spectra of ZnSO₄-treated catalysts located at 1022.1 and 1045.2 eV, respectively assigned to Zn 2p_{3/2} and 2p_{1/2} (Figure S2a).[28, 29] Similarly, a band corresponding to Na 1s was observed at 1071.0 eV in the Na₂SO₄-treated catalyst, which is in good agreement with reports in literature (Figure S2b).[30, 31] Chemical shifts in the Ru 3d bands were observed in the XP spectra of pre-treated Ru/C catalysts, which could be explained by chemical shifts induced by chemically bonded sulfate. To diagnose the impact sulfate deposits on Ru, the Ru 3d and C 1s spectral features were investigated. The Ru 3d region overlaps significantly with that of C 1s (Ru⁰ $3d_{5/2}$ peak at ~280 eV[32] and the C 1s peak of graphitic carbon at 284-285 eV[33, 34]),[24, 35] which introduces uncertainty in the peak deconvolution and quantitative analysis. Rather than quantitative assessment of atomic ratios, only the general envelope of the Ru 3d peaks was fit and the binding energy (BE) of Ru $3d_{5/2}$ was used in the comparison of oxidation state of Ru in various catalysts.[24] The reduced Ru/C sample shows a $3d_{5/2}$ band at 281.0 eV, which indicates Ru is at least partially oxidized,[24, 32, 35] (Figure 5a). This is likely due to the oxidation of the reduced Ru catalyst upon air exposure when transferring the sample to the XPS chamber for the ex situ characterization. In Ru/C catalysts pre-treated with sulfuric acid or sulfate salts, a ~0.5 eV shift of the Ru $3d_{5/2}$ peak to higher



Figure 5. XPS spectra of Ru 3d binding region for (a) untreated, reduced Ru/C, (b) $ZnSO_4$ -treated Ru/C, (c) Na_2SO_4 -treated Ru/C, (d) H_2SO_4 -treated Ru/C, where (e) shows a schematic of catalysts with sulfate deposits onto the surface.

BE in was observed as compared to the reduced Ru/C sample (Figure 5b-d), which is likely caused by the adsorption of sulfate on Ru. The downshift of the O 1s peak is also consistent with the chemical shifts in the Ru 3d_{5/2} peak (Figure S3). Prior to the sulfate pre-treatment, the most prominent peak in the O 1s region appeared at 533.0 eV, which was assigned to C-O bonds in the carbon support.[36, 37] A downshift of the O 1s peak to ~532.0 eV was observed after pre-treatment with the sulfate, which was attributed to the addition of oxygen from adsorbed sulfate.[38, 39] No noticeable changes are observed in the C 1s envelope, indicating that most sulfate adsorbs on the metal, rather than the carbon support (Figure S4).

Reactivity studies coupled with *ex-situ* characterization techniques suggest that the deactivation of Ru/C proceeds through the blocking of Ru sites by strongly adsorbed, negatively charged sulfate species. While fresh Ru exists primarily as an oxide in the form of RuO₂ (Figure 5a), Ru can be reduced by CTH under reaction conditions[24] and is therefore likely to exhibit both metallic and oxide phases. The use of sulfuric acid or sodium bisulfate strongly deactivated Ru/C (Figure 4a). We hypothesize that when these acidic species are used as co-catalysts, protons facilitate site blocking by removing oxygen from RuO_2 via removal of water (Scheme 2), leaving a site available for a sulfate molecule to bind. By extension, increasing the concentration of protons, and therefore sulfate anions, should result in a more pronounced loss in catalytic activity, which is consistent with the reactivity data shown in Figure 3. Meanwhile, when sulfate salts, in the absence of proton, are used in identical concentration to sulfuric acid, a milder loss in activity was observed. Rather than removal of water through proton-mediated dehydration of the surface, we propose that sulfate salts can only interact with metallic Ru after partial reduction of the surface by CTH. In this case, we attribute the site blocking to negatively charged sulfate ions, rather than to the adsorption of propylene-derived oligomers. When using sulfate salts, propylene formation from 2-propanol cannot occur due to the lack of proton in solution, and thus propylene oligomers are unlikely to play any major role in site blocking. In addition, ex-situ characterizations by pulsing CO onto a sulfate salt-treated Ru/C catalyst after reduction at 300 °C reveal that sulfate is bound very strongly to the Ru surface. Thus, we propose that at least two mechanisms could be at play: (1) proton-mediated water removal and subsequent covalent sulfate bonding, and (2) CTH-mediated reduction of Ru followed by non-covalent



Scheme 2. Proposed mechanisms for deactivation where (a) protons can remove water to allow for sulfate adsorption, and (b) reduction of RuO_x phases by CTH precedes weak sulfate binding.

sulfate-Ru interactions. When acids are used, both mechanisms can occur, resulting in a more pronounced loss in activity; salts, on the other hand, can only proceed by the second mechanism due to the lack of proton, leading to a milder loss in activity.

Our work reveals that the presence of mineral acids has an inhibitive effect on Ru/C, wherein strong adsorption of sulfate or halide anions block Ru sites such that DMF hydrogenolysis cannot occur effectively. Mechanisms previously proposed for ring opening have suggested that bifunctional catalysis is necessary, where Brønsted acidity facilitates either the binding of the substrate[40-42] or the protonation of the furan ring.[5] In our system, enhancement of ring opening activity was not observed in the presence of both metal and a mineral acid. While both were added to the reaction mixture, coexistence of both kinds of sites did not exist under reaction conditions; instead, Ru sites were eliminated by adsorbed anions, such as sulfate. This hypothesis is supported by employment of a solid acid with tethered sulfonic acid groups that cannot come in direct contact with the Ru surface, i.e., Nafion. A physical mixture of Nafion beads and Ru/C should in principle provide both metal and acid sites and eliminate interaction between sulfonic groups and metal. Thus, both acid and metal chemistry is expected to occur. Adding 2.5 g Nafion NR50, which corresponds to ~2 mmol H⁺ based on the ion exchange capacity (IEC), resulted in a 18% conversion and a 13% HDN yield in the absence of Ru/C (Figure 6, dark blue bars). While the total number of protons was identical to that of 0.5 mL of 2 M H₂SO₄, a considerable drop in conversion and yield is observed

compared to that of 2 M H₂SO₄ (Figure 6, dark red bars). This difference in activity is likely due to either the reduced acid strength of the tethered sulfonic groups, as compared to H₂SO₄, or the slow diffusion of DMF into the pores of Nafion beads. Nonetheless, combining both 80 mg Ru/C and 2.5 g Nafion NR50 in one pot resulted in a ~42% combined yield of ring opened products (21% yield to HOL, 24% yield to 2,5-HDL) after 2 h of reaction, maintaining full DMF conversion (Figure 6, light blue bars). In this case, DMF conversion can proceed either via direct Ru-mediated hydrogenation/hydrogenolysis to form DMTHF, DMDHF, and HOL, or via sequential reactions consisting of proton-mediated hydrolysis to HDN and Rumediated hydrogenation to 2,5-HDL, DMDHF, and DMTHF. Thus, the rather high yield (21%) to HOL provides strong evidence that the Ru/C surface remains fully active because this yield is very similar to that observed when no acid (solid or homogeneous) was added (Table 1, entry 8). In addition, HDN's hydrogenation/ring closure to DMDHF and DMTHF can be attributed to participation from Ru or RuO_x sites (Figure 2), although the mechanistic details of this transformation cannot be distinguished based on our experimental data. The presence of 2,5-HDL is likely due to the hydrogenation of HDN, produced by acid-catalyzed hydrolysis, on Ru, providing evidence that both acid and metal catalysis proceed unimpeded. However, the desired enhancement of ring opening was not observed; instead, serial reactions (DMF hydrolysis to HDN, followed by HDN hydrogenation) occur.

Bimetallic catalysts which contain both acid and metal sites co-impregnated on a common support, e.g., Rh-Re or Ir-Re supported on SiO₂, exhibit synergy between both phases, likely due to the close proximity of these two types of sites. Mechanisms proposed by Dumesic et al.[5], Tomishige et al.[40] and others,[41] suggest that acid sites such as ReO_x provide protons to activate the cyclic ether in tetrahydrofuran while metal sites perform the necessary hydrogenation steps, resulting in α , ω -diols. Therefore, it is likely the proximity of the metal and acid sites on the molecular level is needed to enable the operative chemistry favoring the ring opening pathway. In our system, the solution-phase protons can exist near the Ru sites to perform such chemistry; however, the anion component of the homogeneous acid severely inhibited Ru sites from conducting the necessary hydrogenation. Alternatively, using Nafion instead of sulfuric acid prevented sulfate-mediated site-blocking, as well as the proximity between acid and metal sites, which leads to sequential reactions rather than the desired synergistic effect. Thus, our results highlight the importance of synthesizing bifunctional catalysts with atomically mixed metal and acid sites for selective ring opening catalysis.

4. Conclusions

In this study, we show that mineral acids combined with Ru/C do not act synergistically in facilitating the ring opening of DMF. High selectivity toward a ring closed product, e.g. DMTHF, was observed, rather than enhanced selectivity toward alcohols in the presence of dilute sulfuric acid and Ru/C. Severe deactivation of Ru-mediated hydrogenation and hydrogenolysis chemistry was observed in the



Figure 6. Reactivity of DMF in both homogeneous and heterogeneous acids in the presence (or absence) of Ru/C. Conditions: 1 wt% DMF in 2-propanol at 100 °C for 2 h, $P_{N2} = 300$ psig, $m_{Ru/C} = 80$ mg, $m_{nafion} = 80$ mg.

presence of high concentrations of mineral acids. Metal sulfates and halides are also able to poison Ru sites, however, not as efficiently as the corresponding acids. XPS and CO chemisorption results indicate that site blocking by sulfate and halide anions on Ru sites is likely the main cause of poisoning. This hypothesis is supported by the lack of catalyst poisoning when replacing mineral acids with a solid acid, i.e., Nafion, because the tethered sulfonic groups cannot adsorb on Ru sites. However, the lack of the proximity between the acid and metal sites in this case leads to sequential acid and metal mediated reactions, rather than promoting the ring opening chemistry.

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References

- [1] I. Klein, C. Marcum, H. Kenttämaa, M.M. Abu-Omar, Green Chem 18 (2016) 2399-2405.
- [2] S. Sawadjoon, A. Lundstedt, J.S.M. Samec, Acs Catal 3 (2013) 635-642.
- [3] P. Panagiotopoulou, D.G. Vlachos, Applied Catalysis A: General 480 (2014) 17-24.

[4] M.J. Gilkey, P. Panagiotopoulou, A.V. Mironenko, G.R. Jenness, D.G. Vlachos, B. Xu, ACS Catal 5 (2015) 3988-3994.

- [5] M. Chia, Y.J. Pagan-Torres, D. Hibbitts, Q. Tan, H.N. Pham, A.K. Datye, M. Neurock, R.J.
- Davis, J.A. Dumesic, J Am Chem Soc 133 (2011) 12675-12689.
- [6] M.M. Sullivan, A. Bhan, ACS Catal 6 (2016) 1145-1152.
- [7] B. Saha, C.M. Bohn, M.M. Abu-Omar, Chemsuschem 7 (2014) 3095-3101.
- [8] M.I.H. Zaki, Muhammad A.; Pasupulety, Lata, Langmuir 17 (2001) 4025-4034.
- [9] J. Tuteja, H. Choudhary, S. Nishimura, K. Ebitani, ChemSusChem 7 (2014) 96-100.
- [10] T. Mizugaki, T. Yamakawa, Y. Nagatsu, Z. Maeno, T. Mitsudome, K. Jitsukawa, K. Kaneda, ACS Sustainable Chemistry & Engineering 2 (2014) 2243-2247.
- [11] S. Yao, X. Wang, Y. Jiang, F. Wu, X. Chen, X. Mu, ACS Sustain Chem Eng 2 (2014) 173-180.
- [12] R.J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, Chemical reviews 113 (2013) 1499-1597.
- [13] D.A. Bulushev, S. Beloshapkin, J.R.H. Ross, Catal Today 154 (2010) 7-12.
- [14] T. Thananatthanachon, T.B. Rauchfuss, Angewandte Chemie 49 (2010) 6616-6618.

- [15] P. Panagiotopoulou, N. Martin, D.G. Vlachos, Journal of Molecular Catalysis A: Chemical 392 (2014) 223-228.
- [16] D.S.P. Eftax, A.P. Dunlop, J Org Chem 30 (1965) 1317-1319.
- [17] N. Nikbin, S. Caratzoulas, D.G. Vlachos, Chemsuschem 6 (2013) 2066-2068.
- [18] M.J. Gilkey, B. Xu, ACS Catal 6 (2016) 1420-1436.
- [19] G.R. Jenness, W. Wan, J.G. Chen, D.G. Vlachos, Acs Catal 6 (2016) 7002-7009.
- [20] M.J. Gilkey, A.V. Mironenko, L. Yang, D.G. Vlachos, B. Xu, ChemSusChem 9 (2016) 3113-3121.
- [21] J. Luo, L. Arroyo-Ramírez, R.J. Gorte, D. Tzoulaki, D.G. Vlachos, AIChE J 61 (2015) 590-597.
- [22] A.M. Karim, C. Howard, B. Roberts, L. Kovarik, L. Zhang, D.L. King, Y. Wang, Acs Catal 2 (2012) 2387-2394.
- [23] J. Skupinska, Chem Rev 91 (1991) 613-648.
- [24] J. Jae, W. Zheng, A.M. Karim, W. Guo, R.F. Lobo, D.G. Vlachos, Chemcatchem 6 (2014) 848-856.
- [25] C.-C. Chang, S.K. Green, C.L. Williams, P.J. Dauenhauer, W. Fan, Green Chem 16 (2014) 585.
- [26] S. Zhong, R. Daniel, H. Xu, J. Zhang, D. Turner, M.L. Wyszynski, P. Richards, Energy Fuels 24 (2010) 2891-2899.
- [27] T.S. Hansen, K. Barta, P.T. Anastas, P.C. Ford, A. Riisager, Green Chem 14 (2012) 2457.
- [28] G.J. Coyle, T. Tsang, I. Adler, N. Ben-Zvi, J Electron Spectrosc 24 (1981) 221-236.
- [29] M.I. De Barros, J. Bouchet, I. Raoult, T. Le Mogne, J.M. Martin, M. Kasrai, Y. Yamada, Wear 254 (2003) 863-870.
- [30] M. Toupin, T. Brousse, D. Belanger, Chem Mater 16 (2004) 3184-3190.
- [31] L. Yang, Z. Zhang, X. Gao, Y. Guo, B. Wang, O. Sakai, H. Sakai, T. Takahashi, J Membr Sci 252 (2005) 145-154.
- [32] S. Akbayrak, S. Ozkar, Acs Appl Mater Inter 4 (2012) 6302-6310.
- [33] T. Buntara, I. Melián-Cabrera, Q. Tan, J.L.G. Fierro, M. Neurock, J.G. de Vries, H.J. Heeres, Catal Today 210 (2013) 106-116.
- [34] S.G. Wang, V. Vorotnikov, D.G. Vlachos, Green Chem 16 (2014) 736-747.
- [35] S. Iqbal, S.A. Kondrat, D.R. Jones, D.C. Schoenmakers, J.K. Edwards, L. Lu, B.R. Yeo, P.P.
- Wells, E.K. Gibson, D.J. Morgan, C.J. Kiely, G.J. Hutchings, ACS Catal 5 (2015) 5047-5059.
- [36] W. Xia, Y. Wang, R. Bergsträßer, S. Kundu, M. Muhler, Appl Surf Sci 254 (2007) 247-250.
- [37] R. Blume, D. Rosenthal, J.-P. Tessonnier, H. Li, A. Knop-Gericke, R. Schlögl, ChemCatChem 7 (2015) 2871-2881.
- [38] S. Contarini, J.W. Rabalais, J Electron Spectrosc 35 (1985) 191-201.
- [39] Y. Uwamino, T. Ishizuka, J Electron Spectrosc 34 (1984) 67-78.
- [40] L. Zhang, A.M. Karim, M.H. Engelhard, Z. Wei, D.L. King, Y. Wang, J Catal 287 (2012) 37-43.
- [41] B. Pholjaroen, N. Li, Y. Huang, L. Li, A. Wang, T. Zhang, Catal Today 245 (2015) 93-99.
- [42] J. Jae, E. Mahmoud, R.F. Lobo, D.G. Vlachos, Chemcatchem 6 (2014) 508-513.