Why Is Ruthenium an Efficient Catalyst for the Aqueous-Phase Hydrogenation of Biosourced Carbonyl Compounds?

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Supported or unsupported ruthenium catalysts were seldom employed in the past to carry out hydrogenation reactions in petrochemistry and chemical synthesis. Instead, these reactions were usually achieved in the gas phase or in organic solvents over platinum, palladium, rhodium, and nickel catalysts tailored to obtain optimum activities and selectivities toward desired products. Triggered by the threat of dwindling fossil resources and by the hope to decrease CO_2 emissions, many attempts have been made during the past two decades to produce chemicals by catalytic conversion of platform molecules obtained from polysaccharides or lignocellulosic materials by depolymerization, fermentation, and pyrolysis processes.[1] These water-soluble, biosourced molecules were converted into chemicals currently produced from fossil resources, such as succinic acid and derivatives,[2] or into new bioproducts that had no synthetic counterpart, such as isosorbide and lactic acid derivatives.[3]

A literature survey of the aqueous-phase hydrogenation of biosourced molecules shows that ruthenium metal particles supported on various carbons and oxides were the most efficient catalysts to achieve a rapid and selective conversion of carbonyl functionalities into the corresponding alcohols.[1d] For instance, the hydrogenation of glucose into sorbitol,[4] of levulinic acid (LA) into γ-valerolactone (GVL),[5] and of lactic acid into 1,2-propanediol[5c,6] were achieved with a much higher yield on ruthenium than with any other metal catalysts. Measurements in a high-throughput reactor of the rates of aqueous-phase hydrogenation reactions of acetaldehyde, propanal, acetone, and xylose over alumina-supported, monometallic catalysts showed that ruthenium-based catalysts showed the highest activity for the hydrogenation of carbonyl groups.[7] Several investigations of the solvent effect in the hydrogenation of carbonyl functionalities pointed out a marked enhancement of the reaction rate of Ru catalysts in water solutions. Thus, the rate of 2-butanone hydrogenation in the presence of a 5 wt % Ru/SiO_2 catalyst was 7 and 33 times larger in water than in methanol and isopropyl alcohol, respectively.[8] A systematic study of the influence of water on the activity of Ru/C catalysts in the hydrogenation of model oxygenates derived from bio-oils such as 2-butanone was carried out,[9] and the highest hydrogenation activity was measured in water, followed by alcohols, whereas in aprotic, apolar solvents, a much lower activity was observed. The conversion of LA to GVL over a Ru/C catalyst was faster in ethanol–H_2O and butanol–H_2O mixtures than in pure ethanol and butanol, respectively.[10]

On the basis of a recent survey of experimental and theoretical investigations, this article is intended to review the interpretations possibly accounting for the superior activity of ruthenium catalysts in the aqueous-phase hydrogenation of carbonyl compounds.

To interpret the beneficial role of water on the rate of 2-butanone hydrogenation over a Ru/SiO_2 catalyst, Akpa et al.[8] carried out density functional theory (DFT) calculations to follow the reaction energies and activation barriers for the different reaction pathways involved in the hydrogenation of 2-butanone over a model Ru(0001) surface. It was shown that the interaction of water molecules with the hydroxylbutyl intermediate considerably decreased the energy barriers, thus accounting for the enhanced reaction rate in water compared with reactions performed either in the absence of solvent or in the presence of isopropyl alcohol. The increase in the proton diffusion coefficient in water was identified as an additional factor favoring higher reaction rates.

From a very detailed kinetic investigation of solvent effects in low-temperature hydrogenation of various model carbonyl compounds over a Ru/C catalyst, Wan et al.[9] showed that the highest hydrogenation activity was observed in protic solvents, water giving the maximum rate enhancement. A correlation between the initial hydrogenation rate of 2-butanone and hydrogen-bond donor capability of the solvents was observed, which was consistent with the hypothesis that the strong interaction between water and 2-butanone by hydrogen bonding lowers the activation energy barrier and leads to high hydrogenation rates.

To understand why Ru/TiO_2 catalysts were particularly active in the aqueous phase hydrogenation of levulinic acid, Michel et al.[5e] performed DFT calculations taking acetone as a model carbonyl compound adsorbed on a Ru(0001) surface. As a chemisorbed water molecule was added to the model, the chemisorption of acetone was strongly modified as well as the hydrogenation intermediate (iso-propoxy) and product (iso-propanol). On Ru(0001), the reaction was controlled by the hydrogenation step of the alkoxy intermediate. In the absence of water, the isopropoxy was strongly adsorbed in the hollow site of the oxophilic Ru(0001). In the presence of a chemisorbed water molecule, an isoenergetic configuration appeared where the alkoxy intermediate was chemisorbed on the top site, with the oxygen forming an H-bond with the chemisorbed water molecule. This "hydrated" configuration

opens the road to an easier hydrogenation path, the overall barrier being decreased by 0.41 eV. On the other hand, with the less oxophilic platinum, the hydrogenation did not follow the same reaction route, going through a hydroxyl-alkyl intermediate. The overall barrier of this path was controlled by the ketone adsorption and the hydrogenation of the carbon of the hydroxyl-alkyl intermediate. The presence of chemisorbed water stabilized the ketone adsorption and destabilized the transition state corresponding to the C—H bond formation, leading to an increase in the effective barrier along this path. Concomitantly, the chemisorbed water facilitated the other path of hydrogenation sufficiently to make it easier, but not enough to really affect the resulting overall barrier of hydrogenation on platinum. The energetic gain on the overall barrier provided by a chemisorbed water molecule correlated nicely with the oxophilicity of the metal (d-band center). These calculations clearly accounted for the promotion of ruthenium activity in aqueous phase while less-oxophilic metals such as platinum were barely affected. Interestingly, it was shown that the hydrogenation activity of nickel should also be promoted in water solutions in agreement with literature data indicating that nickel was widely employed in the aqueous-phase hydrogenation of water-soluble carbonyl compounds, for instance, in the industrial hydrogenation of glucose into sorbitol.[4a,11]

In the three investigations discussed above,[5e,8,9] the high activity of ruthenium in the aqueous-phase hydrogenation of carbonyl compounds was attributed to the interactions, via hydrogen bonds, between the C=O group adsorbed on the metal surface and adjacent adsorbed water molecules, leading to a decrease in the energy barriers. However, these calculations did not take into account the possible dissociation of water molecules adsorbed on the ruthenium surface, as suggested from theoretical and experimental investigations. On the basis of DFT calculation, Feibelman[12] reported that the wetting layer on Ru(0001) did not consist of undissociated water molecules, but of an energetically more stable half-dissociated monolayer wherein water molecules and hydroxyl fragments were hydrogen-bonded in a hexagonal structure and hydrogen atoms were bound to surface Ru atoms.

Michaelides et al.[13] also found by DFT calculations that a partially dissociated OH—H$_2$O overlayer on Ru(0001) was thermodynamically more stable than H$_2$O bilayers. Experimentally, using a sensitive temperature-programmed desorption technique to probe the adsorbed species on a Ru(0001) crystal face covered with water at low temperature, Denzler et al.[14] showed that after the total desorption of water molecule at 220 K, molecular hydrogen desorbed from the surface above 350 K, indicating that dissociated hydrogen was present on the surface. Tatarkhanov et al.[15] have studied by scanning tunneling microscopy (STM) and X-ray absorption spectroscopy (XAS) the structures produced by the dissociation of water on a Ru(0001) crystal face; XAS revealed the presence of hydroxyl groups with an O—H bond essentially parallel to the surface, and STM images showed that the mixed H$_2$O—OH structures consisted of long narrow stripes aligned with the three crystallographic directions perpendicular to the close-packed atomic rows of the Ru(0001) surface.

A recent STM investigation by Maier et al.[16] showed that hydrogen liberated by the water dissociation adsorbs mostly on the Ru sites located between the H$_2$O—OH stripes, although occasionally, H atoms can be trapped at the center of water hexagons, as proposed in previous theoretical models of the partial dissociation of a complete water bilayer.[12,13] In contrast

with the previous studies pointing to water dissociation, Kim et al.,[17] on the basis of spectroscopic studies of adsorbed probe molecules, concluded that water adsorbed on Ru(0001) was capable of generating a proton transfer reaction. These surface science studies, although they were conducted at temperatures well below those used in the catalytic hydrogenation of carbonyl compounds, should certainly be taken into account to interpret the specificity of the ruthenium catalyst in aqueous phase hydrogenation.

The participation of water in the mechanism of hydrogenation of carbonyl groups was supported by an isotope labeling experiment reported by Tan et al.[18] Because the hydrogenation of LA to GVL over a Ru/TiO$_2$ catalyst was carried out in D$_2$O solution, product analysis showed that a deuterium atom was detected on the carbon C5 of GVL. Because an H/D exchange between GVL and D$_2$O was ruled out in a separate experiment, this study pointed to a mechanism whereby D atoms originating from D$_2$O were added to the C=O bond of LA.

The mechanism of hydrogenation of a carbonyl group on ruthenium catalysts could be even more complex because experiments indicate that surface RuO$_x$ species may also be involved in hydrogenation reactions. Thus, Vlachos et al.[19] carried out furfural hydrogenation of methylfuran by catalytic hydrogen transfer using secondary alcohols over a Ru/RuO$_2$/C catalyst. The mechanism of reaction was interpreted by a synergy between Lewis acid sites (RuO$_x$) and metallic Ru sites, resulting in higher methylfuran yields. The presence of RuO$_2$ species on the catalyst surface detected by temperature-programmed reduction was confirmed by XPS and EXAFS spectroscopy.[20] To elucidate the role of the Lewis acidity in the reduction of furfuryl alcohol to 2-methylfuran, DFT calculations on the RuO$_2$ (110) surface showed that the rate-limiting step was the scission of the C—O bond of the side chain and that the reaction was made easier by the activation of the furan ring via the insertion of a hydrogen atom.[21]

The combined experimental and theoretical investigations mentioned previously[5e,8,9] provide a rational interpretation of the superior hydrogenation activity of ruthenium in water solution in terms of the interaction of the carbonyl group with water molecules lowering activation energy barriers. These investigations are coherent and sound, but do not take into account surface science results pointing to a dissociation of water molecules, resulting in hydroxyl groups and hydrogen atoms coadsorbed on the Ru surface[12−16] and, more importantly, the compelling evidence that hydrogen atoms issued from water dissociation saturate the carbonyl functionalities to yield alcohols.[18]

To understand why ruthenium is surprisingly so active in aqueous-phase hydrogenation of carbonyl compounds in comparison with other Pt-group metals, we are now at a crossroad where two mechanisms involving water should be evaluated. On one hand, coadsorbed water molecules could merely lower energy barriers, leading to an easier hydrogenation of carbonyl groups by dissociated hydrogen; on the other hand, the dissociation of water increases the surface concentration in hydrogen atoms, thus favoring the hydrogenation process.

To unravel the respective importance of these two mechanisms and, particularly, to confirm the role of water as a source of hydrogen, further isotope labeling experiments on Ru catalysts in comparison with other metal catalysts will be required, and an improved theoretical description of the

different mechanisms occurring at the water/ruthenium interface should be achieved. From a more general standpoint, the development of fundamental research on the catalytic conversion of biomass-derived platform molecules, rich in carbonyl functionalities, is required to make this value chain competitive with respect to the traditional synthesis of chemicals from fossil fuels that has been improved steadily for more than a century.

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Notes
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