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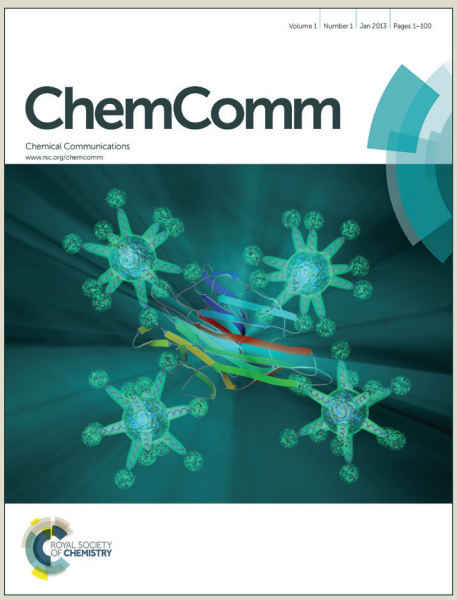

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ARTICLE TYPE

Role of water on metal catalyst performance for ketone hydrogenation. A joint experimental and theoretical study on levulinic acid conversion into gamma-valerolactone

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While Ru is a poor hydrogenation catalyst compared to Pt or Pd in gas phase, it is efficient in aqueous phase conditions to hydrogenate ketones such as the conversion of levulinic acid into gamma-valerolactone. Combining DFT calculations and experiments, we demonstrate that water is responsible for the enhanced reactivity of Ru in those conditions.

The swap from hydrocarbon based to biomass based feedstock triggers the development of novel catalysts and processes to transform oxygenates into valuable molecules.[1] Most of the time, those reactions with reactants extracted from biomass are conducted in water to efficiently solubilise reaction intermediates and products. We will show here that water can also play an essential role in the catalytic activity, focusing on the conversion of levulinic acid (LA) into γ-valerolactone (GVL)[2] (see Figure 1). LA can be obtained via cellulose hydrolysis and dehydration of such obtained glucose. GVL is an attractive platform molecule that can be derived from biomass and can be converted to a variety of chemicals, including biofuel additives.[3,4,5]

Galletti et al.[6] have established that with supported metal catalysts LA hydrogenation to GVL follows the scheme represented in Figure 1: (i) the metal catalyses the first step, i.e. the hydrogenation of the ketone moiety into 4-hydroxy pentanoic acid (ii) the cyclising esterification leads easily to the GVL. Another route is opened at higher temperatures (>200°C), starting with the cyclising dehydration of the enolic form of LA.[7,8,9] The C=C bond of the intermediary angelica lactone is then hydrogenated, leading to GVL. This alternative route is not accessible in our mild conditions.

In these conditions, it is striking that Ru is usually more active to convert LA to GVL than Pd and Pt in water,[9,10,11,12] while Ru is known to be poorly active compared to Pd and Pt to hydrogenate ketones in gas phase conditions.[13] Actually, the hydrogenation capability of Ru is strongly modulated by the reaction environment. Rooney et al. have shown that the hydrogenation of 2-butanone catalyzed by Ru/SiO_2 is 30 times faster in water than in heptane.[14] Thus, Ru is much more active in aqueous media, even more active than Pt or Pd, so that it is frequently used for aqueous phase hydrogenation of various ketones.[15]

This strong dependence of Ru activity upon solvent can also be transferred to our target reaction, the hydrogenation of LA

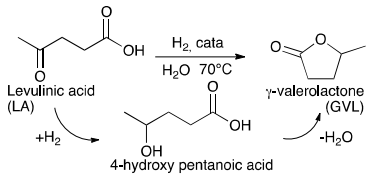

Figure 1. Conversion of levulinic acid into gamma-valerolactone

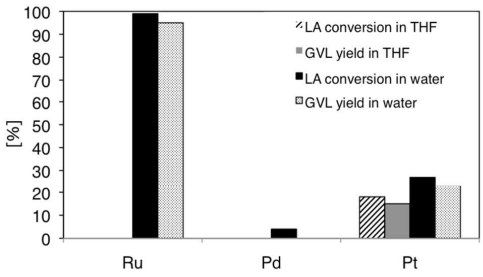

Figure 2. LA conversion and GVL yield in % for Ru, Pd, Pt in THF and in water solvent. No conversion was observed for Ru and Pd in THF solvent.

towards GVL. We analysed three noble metal catalysts (Ru, Pt, Pd) supported on titania in two different environments (water and tetrahydrofuran (THF)) in mild conditions (70°C, 50 bar of hydrogen, details in ESI†). The catalysts were prepared in a way that the particle size effect could be minimized since all metal particles possess similar size (2.1-3.2nm). With the same support and particle size, the experiments here provide a consistent case of comparison on two solvents in similar conditions, hence avoiding other effects on the hydrogenation activity. TEM images (ESI†) generally demonstrated a homogeneous distribution of the active phase on the support. The results of the catalytic activity are presented in Figure 2. The Ru catalyst activity is strongly dependent on the reaction media. While it is not active in THF, Ru is the most active in water (99% LA conversion, 95% GVL yield). Pt and Pd activities are not sensitive to the solvent: around 15-20% of GVL yield together with a 20-30% conversion of LA is obtained using Pt and negligible activity is observed using Pd. Note that Pd was active for this reaction but at higher

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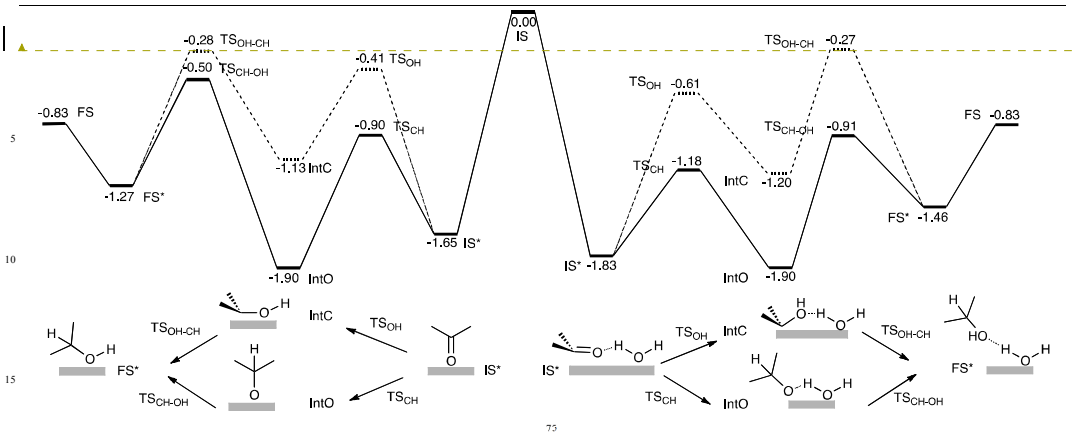

Figure 3. Reactions paths for the hydrogenation of acetone on Ru(0001) in absence (left) and in presence of a water molecule (right). The reference energy is common and includes the acetone and a H_2 molecule in gas phase, three bare Ru(0001) slabs and a 'hydrated' slab bearing a chemisorbed water molecule.

temperatures (190°C) and conserving the same order of reactivity: Ru > Pt > Pd. Finally, the trends upon metal and solvent are similar for the LA conversion into GVL and the ketone hydrogenation, indicating that the first step (i.e. the ketone hydrogenation, see Figure 1) is the rate determining step of this reaction.

To our knowledge, this striking dependence of the relative activity of Ru, Pt and Pd for ketone hydrogenation on the reaction medium is not yet well understood. In this paper, we aim at explaining the apparently unique behaviour of Ru in the presence of water using DFT calculations. Several strategies are possible to model solvent effects. Implicit models take into account the dielectric constant and its capability to stabilize charges.[16] Explicit models include solvent molecules increasing the number of atoms and accessible configurations.[17] The increase of activity of Ru in aqueous phase compared with organic solvent lies probably in the hydrogen bond effect of liquid water. An implicit model cannot grasp this kind of effect easily. However, an explicit modelling of liquid water is highly expensive. We propose here to use a micro-solvation approach, including only the most important solvent molecule, following our previous works on the influence of water on alcohols dehydrogenation.[18,19,20] The ketone was modelled by acetone, since both molecules show very similar trends upon metal and solvent changes, implying that the acid group is not affecting the hydrogenation of the ketone function.

We start by the elementary steps for acetone hydrogenation on the Ru(0001) surface. We modelled gas phase hydrogenation with a periodic slab approach (see ESI†). The two possible reaction paths are represented in Figure 3, both starting in the centre of the figure and evolving towards the left, the reference being the Ru(0001) and acetone and hydrogen in gas phase. In the alkyl path, the chemisorbed acetone (IS*) is hydrogenated on the oxygen first through the transition state TS_{OH}. It leads to an alkyl radical IntC. In the second step, the carbon is hydrogenated (TS_{OH-CH}) resulting in the weakly chemisorbed isopropanol (FS*, E_{ads}=-0.44eV). This route is disfavoured by high lying transition states (TS) of energy -0.41eV and -0.28eV relative to the

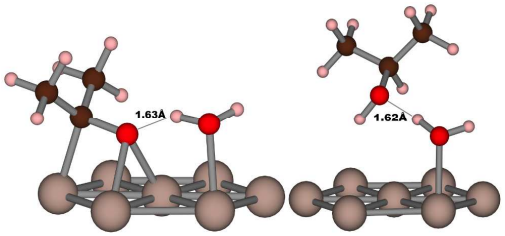

Figure 4. Co-adsorption structures of acetone and water (left) and isopropanol and water (right) on Ru(0001)

reference. The second TS is the highest, 1.37eV higher than chemisorbed acetone. In the alkoxy path, the carbon is hydrogenated first (TS_{CH}), leading to a very stable alkoxy intermediate (IntO, 0.25eV more stable than the chemisorbed as the energy difference between the TD-TS and the TD-I of a catalytic cycle. The smaller the energetic span, the higher the rate and the more efficient is the corresponding catalyst. More details on the procedure are given in the Computational Details section of the ESI†. This approach shows that the two paths are equally disfavoured with an energetic span of 1.37eV for the alkyl route and 1.40eV for the alkoxy one.

To grasp the major effect of the water solvent, we used the simplest possible approach and added a chemisorbed water molecule to our model. The chemisorptions of acetone is strongly modified. In absence of water, acetone exhibits two iso-energetic chemisorbed structures (E_{ads}=-0.47eV; the C=O bond parallel to the surface or perpendicular to the surface). In presence of water, the most stable situation for acetone corresponds to the configuration parallel to the surface forming a H-bond with the chemisorbed water molecule. (See Figure 4 left). This configuration is 0.18 eV more stable than the separated adsorption of water and acetone. The co-adsorption of the resulting isopropanol and water is in line with previous studies on Pt(111)[18] and Rh(111)[19,20] : the alcohol is H-bonded to the chemisorbed water and shows no direct interaction with the surface. Here again, the two possible hydrogenation paths starting from this configuration are represented in Figure 3 starting in the

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centre and going towards the right, the reference being the Ru(0001) slab with water already chemisorbed and acetone and hydrogen in gas phase. The chemisorbed acetone (IS*) is stabilised by ~0.2eV. The TS_{OH} of the alkyl path is also stabilized by ~0.2eV. However, the second transition state $TS_{OH\text{-}CH}$ is not affected and is still lying high in energy (-0.27eV relative to the reference). Thus, the overall effective barrier is increased by 0.2eV. The situation is more favourable on the alkoxy path. The two transition states are lying lower in energy in the presence of water. In addition, the formation of the alkoxy intermediate is less exothermic. Then, the effective barrier markedly decreases by 0.41eV (from 1.40 to 0.99eV). To conclude, the presence of co-adsorbed water slightly inhibits the alkyl path and strongly favours the alkoxy path. The effective activation barrier is diminished by 35%, leading to a strong increase of the predicted activity of Ru(0001). The addition of a single chemisorbed water molecule hence allows us to capture the origin of the enhanced activity of Ru in aqueous conditions observed for the hydrogenation of ketones[14] or for the conversion of LA into GVL as already exposed. To go beyond this initial model, we have refined the most favourable alkoxy route. Adding the surrounding aqueous environment as a continuum model[21] does not change the energetic span significantly (see Table S2 and S3, ESI†). Then, we increased the number of water molecules to 11 to include the first solvation sphere as suggested by Hu and co-workers.[22] Here again, the energetic span is not strongly affected (Figure S3 ESI†). A single water molecule is enough to grasp the Ru catalyst activation. An alternative route could involve the dissociation of a water molecule (Figure S4, ESI†). For instance, the hydrogen-bonded water could dissociate and transfer the proton involved in the hydrogen bond to the alkoxy (second elementary step of the alkoxy route) leading to the isopropanol and a surface hydroxyl. However, surface hydroxyl groups cannot accumulate at the catalyst surface and have to be eliminated. Their hydrogenation is as energy demanding as the hydrogenation of the alkoxy intermediate.

To better understand the periodic trends for the influence of water, the same paths were computed for a larger series of late transition metals (Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu) on the corresponding close-packed surfaces ((111) for fcc metals and (0001) for hcp ones). For most of the metals under consideration, the two routes are almost equally probable in the absence of water, with a small preference for the alkyl path (except for Rh and Ir). The energetic span of the most favourable path is provided in the absence and presence of water and for each metal under consideration in Figure 5 (more details in ESI†, Table S2). At the bare metallic surface, the most active catalysts are Ir, Pt and then Cu and Rh according to their respective energetic span while Ni, Pd, Ru and Co are much less active catalysts. This is in good agreement with experimental observations for gas phase acetone hydrogenation.[13] For the common subset of metals, experiment gives the activity order Pt > Rh > Pd ~Ru > Ni ~ Co while calculations show Pt > Rh > Ni > Pd ~ Ru> Co so that only Ni is slightly misplaced. Last, one can notice that the activity for the alkyl paths is mainly controlled by the acetone adsorption (IS*) as TOF-determining state and the TS for the second hydrogenation on the carbon ($TS_{OH\text{-}CH}$) as TOF-determining-TS while the alkoxy paths are controlled by the oxygen

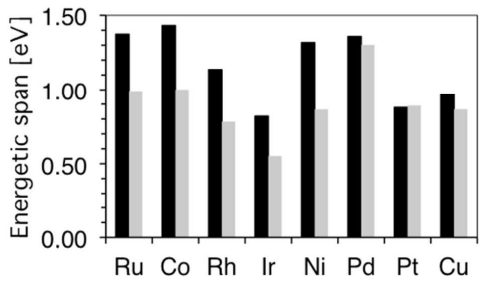

Figure 5. Energetic (in eV) for the acetone hydrogenation at the bare metallic surface (in black) and in presence of one chemisorbed water (in grey) for a series of transition metals.

hydrogenation TS ($TS_{CH\text{-}OH}$) and the chemisorbed acetone (IS*) or the alkoxy state (IntO) for more oxophilic metals such as Co, Ni, Ru.

The presence of one water molecule strongly modifies the energetic span values and the alkoxy route is clearly preferred over the alkyl one for all metals (see ESI†, Table S3). This inversion results from an activation of the alkoxy route with a concomitant deactivation of the alkyl route. The influence of water on the energetic span of the most favourable route is summarized on Figure 5. We have already seen that the capability of Ru to hydrogenate acetone is strongly enhanced by the presence of a single chemisorbed water. On the other hand, the less-oxophilic metals (Pd and Pt) are barely affected. The promotion of the alkoxy route is not strong enough to facilitate the acetone hydrogenation: Pt is as active as in the absence of water; Pd is still inactive. This is in line with our experimental findings: Pt is active to some extent in both THF and water while Pd is not in both environments in our mild conditions. Calculations clearly show the promotion of Ru vs Pt in aqueous phase. However, from the intrinsic error bar of DFT-GGA (0.15 eV) it is not possible to determine in absolute value which metal is the most active one in aqueous conditions, since the calculated barriers only differ by 0.1 eV. Other aspects, as the coverage of hydrogen, could also slightly alter the relative energies of the hydrogenation transition states. This goes beyond the scope of this communication.

Our wider screening of transition metals shows in addition that the promotion effect seen for Ru can be generalized to the other oxophilic metals such as Co and Ni. The higher the energy of the d-band centre is, the more oxophilic a metal is. The variation of the energetic span of the alkoxy path upon water assistance nicely correlates with the d-band centre of the metal under consideration (Figure S5, ESI†). Surface species on those metals are more strongly affected by the co-adsorption of a water molecule. The TD-TS ($TS_{CH\text{-}OH}$) is stabilized while the TD-I (mainly IntO) is often destabilized. Therefore, the energetic span is strongly reduced (up to ~0.4eV) and those metals become good candidate catalysts for acetone hydrogenation in aqueous environment. This result clears up the difference in the catalytic reactivity order of metal for acetone hydrogenation in gas phase[13] and in aqueous phase.[15] As discussed above, in gas phase, Ru, Co, Ni and Pd are poorly active.[13] Things change completely in aqueous phase

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experiments and Ru, Co, Ni become excellent catalysts while Pd remains poor.[15] The calculated assistance of water for oxophilic metals hence shed light on experimental observations.

Conclusions

Ru is widely used to hydrogenate biomass sourced oxygenates such as levulinic acid while this metal is known to be a poor hydrogenation catalyst of acetone in gas phase. Combining experiments in THF and water together with DFT calculations, we showed that this metal activity is highly sensitive to its environment. The presence of a H-bonded water molecule dramatically reduces the energetic of the reaction pathway, hence enhancing the catalytic activity. We predict that this activation can be generalized to other oxophilic metals such as Co or Ni while Pt and Pd are insensitive to their aqueous environment.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental Section ; TEM images ; Computational Details ; Energetic Span definition ; energetic spans of each path and each metal, without and with water ; energetic spans of each path with an implicit solvent for Ru(0001) ; transition states structure for the hydrogenation of the alkoxy on Ru(0001) in presence of 3 water molecules and in presence of 11 water molecules ; alternative route to the alkoxy path in presence of water on Ru(0001) ; correlation of the energetic span variation for the alkoxy path with the d-band center ; all calculated structures together with their absolute energies.]. See DOI: 10.1039/b000000x/

1 D.M. Alonso, J.Q. Bond, and J.A. Dumesic, *Green Chemistry*, 2010, **12**, 1493
2 W.R.H. Wright, and R. Palkovits, *ChemSusChem*, 2012, **5**, 1657
3. I. T. Horvath, H. Mehdi, V. Fbos, L. Boda, L. T. Mika, *Green Chemistry*., 2008, **10**, 238.
4 D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Green Chemistry*., 2013, **15**, 584.
5. J.-P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, *Angewandte Chemie International Edition* 2010, **122**, 4581.
6 A.M. Raspolli Galletti, C. Antonetti, V. De Luise and M. Martinelli, *Green Chemistry* 2012, **14**, 688
7 W. Luo, U. Deka, A. M. Beale, E.R.H. van Eck, P. C.A. Bruijnincx, B. M. Weckhuysen *Journal of Catalysis*, 2013, **301**, 175
8 V. Mohan, C. Raghavendra, C. V. Pramod, B. D. Raju and K. S. R. Rao *RSC Adv.*, 2014, **4**, 9660
9 P. P. Upare, J.-M. Lee, D. W. Hwang, S. B. Halligudi, Y. K. Hwang and J.-S. Chang, *Journal of Industrial and Engineering Chemistry*, 2011, **17**, 287
10 L. Corbel-Demailly, B.-K. Ly, D.-P. Minh, B. Tapin, C. Especel, F. Epron, A. Cabiac, E. Guillon, M. Besson, and C. Pinel *ChemSusChem* 2013, **6**, 2388.
11 J. M. Tukacs, R. V. Jones, F. Darvas, G. Dibo, G. Lezsak and L. T. Mika, *RSC Advances*, 2013, **3**, 16283
12 L.E. Manzer *Applied Catalysis. A* 2004, **272,** 249
13 N.N. Rimar, and G.N. Pirogova, *Russian Chemical Bulletin*, 1998, **47**, 398
14 B.S. Akpa, C. D'Agostino, L.F. Gladden, K. Hindle, H. Manyar, J. McGregor, R. Li, M. Neurock, N. Sinha, E.H. Stitt, D. Weber, J.A. Zeitler, and D.W. Rooney, *Journal of Catalysis*, 2012, **289**, 30
15 J. Lee, Y. Xu, G.W. Huber, *Applied Catalysis B*, 2013, **140**, 98
16 J. Tomasi, B. Mennucci, and R. Cammi, *Chemical Reviews*, 2005, **105**, 2999.
17 C.D. Taylor, and M. Neurock, *Current Opinion In Solid State & Materials Science*, 2005, **9**, 49-65
18 S. Chibani, C. Michel, F. Delbecq, C. Pinel, and M. Besson, *Catalysis Science & Technology*, 2013, **3**, 339
19 C. Michel, F. Auneau, F. Delbecq, and P. Sautet, *ACS Catalysis*, 2011, **1**, 1430
20 D. Loffreda, C. Michel, F. Delbecq, and P. Sautet, P. *Journal of Catalysis*, 2013, **308**, 374
21 K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias, and R. G. Hennig. *Journal of Chemical Physiscs* 2014, **140**, 084106
22 J. Liu, X.-M. Cao, and P. Hu, *Physical Chemistry Chemical Physics*, 2014, **16**, 4176

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