ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 3613–3615

www.rsc.org/chemcomm

COMMUNICATION

Synergy between the metal nanoparticles and the support for the hydrogenation of functionalized carboxylic acids to diols on Ru/TiO_2†

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Received 26th November 2010, Accepted 24th January 2011
DOI: 10.1039/c0cc05206j

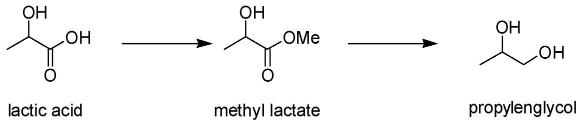
Ruthenium nanoparticles supported on titania are over three times more active than conventional ruthenium on carbon for the hydrogenation of lactic acid. This superior catalytic activity can be due to a combined action of small ruthenium nanoparticles and the titania support.

Diols, such as ethylene glycol and 1,2-propanediol, are monomers of polyester resins used in antifreeze and deicing fluids, liquid detergents and in the manufacture of food,[1] drug and cosmetic products. The demand for 1,2-propanediol, currently produced by ring opening of propylene oxide with water, has recently increased.[2] The actual production route links the price of 1,2-propanediol to the price of oil. It would be convenient to have alternative production routes for diols based on renewable resources.

Fermentation of glucose can produce large quantities of lactic acid (2-hydroxypropanoic acid) and it is expected that the cost will decrease as advances in fermentation and separation technologies occur. Thus, lactic acid is considered a platform product derived from biomass from which a series of derivatives could be obtained. It is of interest to transform the carboxylic group of lactic acid into a hydroxyl group to produce 1,2-propanediol. Thus, if a suitable catalyst is found, an economically feasible route for producing 1,2-propanediol from biomass would be available.

Reductions of carboxylic acids to alcohols are usually accomplished through a two-step process wherein the carboxylic acid is first converted into a more readily reducible derivative, such as an ester or anhydride, before carrying out the hydrogenation (Scheme 1).

Hydrogenation of carboxylic acids and esters are often performed under vigorous reaction conditions due to the low reactivity of the carboxylic acid group with hydrogen.[3] More specifically, the hydrogenation of ethyl lactate to propylene glycol has been carried out at 150–250 °C and high hydrogen pressures (200–300 bar) over copper/chromium oxide and RANEY® nickel catalysts, with 80% yield of propylene glycol. Broadbent *et al.*[4] reported the first catalytic hydrogenation of free lactic acid over an unsupported rhenium black catalyst at 150 °C and 270 bar hydrogen pressure, achieving yields of propylene glycol as high as 80%. It is clear from the above that the development of active catalysts for hydrogenation of esters and acids to the corresponding alcohols under milder reaction conditions is a matter of great interest.



Scheme 1 Two step process of the reduction of lactic acid to propylenglycol.

Here we present that by using a bifunctional ruthenium supported catalyst where the support activates the carbonyl group and the small ruthenium particles on the support (average crystal size 2.0 ± 0.1 nm) efficiently dissociate H_2, it is possible to increase more than three times, the activity of the conventional Ru/C catalyst, while preserving selectivities above 95%. Ruthenium based catalysts have received much attention for the hydrogenation of a wide variety of carboxylic acids and esters, due to their excellent intrinsic hydrogenation activity.[5] When using Ru(5%)/C (Aldrich), that has been reported as a very active and selective catalyst,[6] or other Ru(0.6–2%)/C catalysts, high conversions and selectivities (see Fig. 1) were obtained with a TOF of 14 h^{-1} calculated, from the initial reaction rate, as the number of propylenglycol molecules formed per hour and per ruthenium atom. However, with the catalyst synthesized here, Ru(0.64%)/TiO_2, that contains small ruthenium nanoparticles (2.0 nm) supported on TiO_2 (anatase, Aldrich), the TOF was larger (51 h^{-1}), while lactic acid is converted to propylenglycol under milder reaction conditions.

There are two variables that can determine the difference in activity observed between Ru(0.5–5%)/C and Ru(0.64%)/TiO_2 catalyst. One is the crystallite size of the ruthenium and the other is the nature of the support. In the case of hydrogenations catalyzed by ruthenium, only few reports discuss that small ruthenium nanoparticles are potentially more active than catalysts with larger particles and that the agglomeration of the metal produces an activity decay.[7] In our study, the crystallite size of the ruthenium on TiO_2 has been changed by sintering the Ru in Ru(0.64%)/TiO_2 at high temperature (400 °C), as well as by increasing the ruthenium content. Indeed, both methods produce an increase in the average crystallite size, as can be seen in the TEM pictures given in ESI.† The crystal size of the

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c0cc05206j

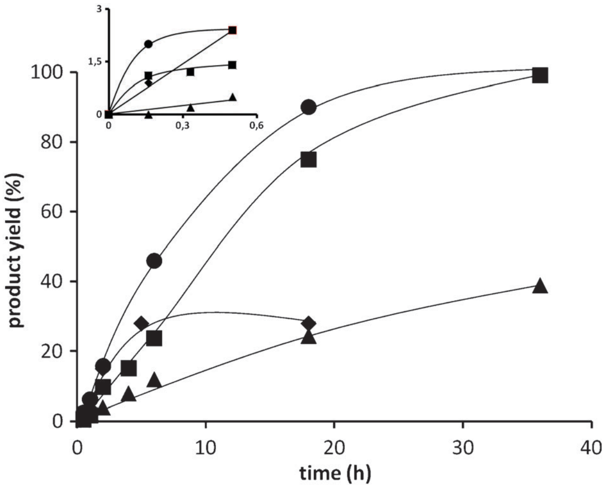


Fig. 1 Plots of 1,2-propanediol yield *vs.* time for the catalysts: (●) Ru(0.64%)/TiO_2, (■) Ru(1%)/TiO_2, (◆) Ru(5%)/C and (▲) Ru(0.64%)/TiO_2 calcined. Reaction conditions: 0.4 mol%Ru, 150 °C and 32 bar H_2 pressure.

Ru/TiO_2 samples under study ranged from 2 to 30 nm. Assuming the full-shell model,[8] and hexagonal particles, the percentage of surface ruthenium atoms on the samples with different crystallite sizes can be estimated. When the ratio between the initial rate and the surface ruthenium atoms is plotted *versus* the surface metal atoms, for the Ru/TiO_2 catalysts with different metal crystallite sizes, a constant value is obtained as it can be seen in Fig. 2. Then, this is a confirmation that the metal dispersion is a key parameter controlling the catalytic activity of the material.

In addition, when the TOF values for the ruthenium catalysts based on TiO_2 (30 m^2 g^{-1}) were compared with other supports such as active carbon (700 m^2 g^{-1}) or CeO_2 (253 m^2 g^{-1}), one can observe that the TOF values for the former are clearly higher, at least for samples with Ru $\leq$ 2 wt% (Fig. 3) indicating that besides a possible influence on the Ru crystallite size, the support also plays a direct role. In fact, the average particle size for Ru/C at different loadings from 0.5 to 5 wt% is almost constant (average 2.3 nm) (see ESI†) while due to the much smaller surface area of TiO_2, the average particle size of Ru(5%)/TiO_2 is 5 nm. H/D exchange experiments performed on Ru(1%)/TiO_2, Ru(2%)/CeO_2 and Ru(5%)/C samples show similar hydrogen dissociation activities (*ca.* 50% at 25 °C), suggesting that hydrogen activation is not limiting the hydrogenation activities on the ruthenium catalyst due to the high efficiency of the metal to activate hydrogen. If this is so, then the hydrogenation step should be the one controlling the rate of the overall process. Thus, a catalyst that, besides dissociating H_2, is able to activate the carboxy group of the lactic acid, should improve the observed reaction rate with respect to another catalyst that does not perform such activation. To study if Ru/TiO_2 is able to activate a carboxylic group, we have adsorbed propanoic acid (as a model for lactic acid) from the gas phase on the TiO_2 support as well as on Ru(0.64%)/TiO_2 and Ru(2%)/CeO_2 for comparative purposes.

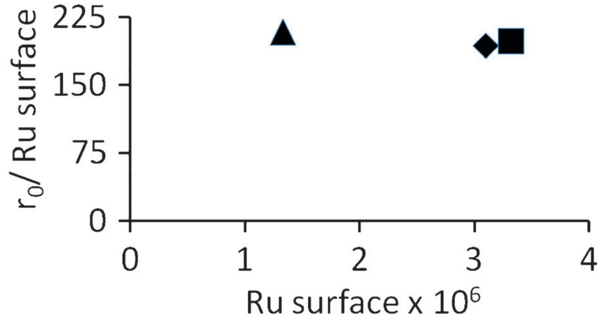


Fig. 2 Plot of the ratio between the initial rate and the surface ruthenium atoms (r_0/Ru surface) *vs.* surface Ru atoms for the catalysts with different ruthenium crystallite size: (■) Ru(0.33%)/TiO_2, (◆) Ru(0.64%)/TiO_2 and (▲) Ru(1%)/TiO_2.

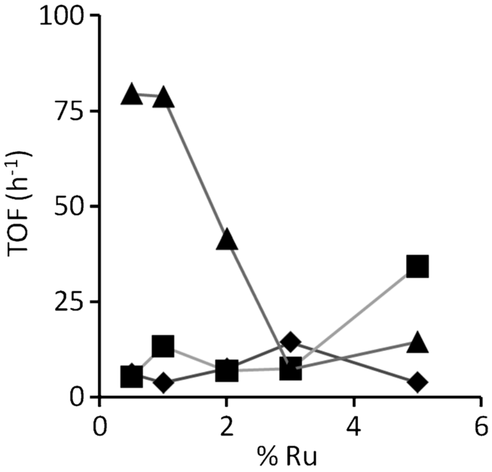


Fig. 3 Influence of the support and Ru loading on the TOF value: (■) active carbon, (▲) TiO_2, (◆) CeO_2. (Experiments done at 40 bar hydrogen pressure.)‡

The corresponding IR spectra are presented in Fig. 4.§ On TiO_2 a weak activation of the carbonyl group (IR band at 1717 cm^{-1}) together with a lower amount of more strongly activated carbonyl species (IR band at 1656 cm^{-1}) are observed. On Ru/TiO_2 a strong activation of the carbonyl group is mainly favoured (IR band at 1656 cm^{-1}),with a minor contribution of the less activated mode at 1717 cm^{-1}. From the IR spectra we can deduce that both activation modes proceed on the TiO_2 support. On CeO_2, carboxylate species (IR bands at 1594 and 1556 cm^{-1}), strongly adsorbed on the catalysts support, are mainly formed. This could be related to the higher basicity of the CeO_2 support. Therefore, the IR spectroscopic data show that the formation of carboxylate group is

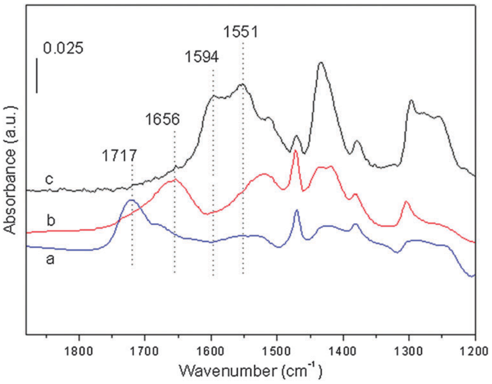


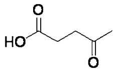
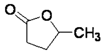
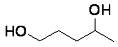
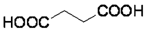
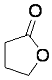
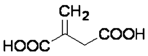
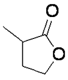
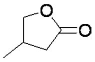
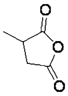
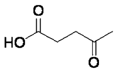
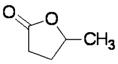
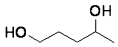
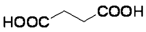
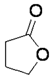
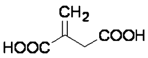
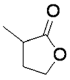
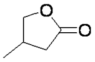
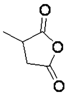
Fig. 4 IR spectra of 1 mbar propanoic acid adsorbed on (a) TiO_2, (b) Ru(0.64%)/TiO_2 and (c) Ru(2%)/CeO_2 samples.

more reluctant to undergo hydrogenation on CeO_2, than when the carbonyl group was activated on Ru/TiO_2. These spectroscopic data agree very well with the catalytic results. Therefore, according to the data obtained on the influence of Ru particle size and the C=O shift in IR, the high activity observed with the Ru/TiO_2 catalyst may arise from the synergism of small ruthenium crystallite size to activate the H_2 and the role of the TiO_2 support to adsorb and activate the acid, probably in the periphery of the metal crystallites.

To evidence the heterogeneous nature of the hydrogenation taking place in our system and to check if the homogeneous catalysis can take place, two different leaching tests were performed. The hot filtration test consists in stopping the reaction at half conversion, and filtering off the catalyst without cooling the solution, so to avoid re-deposition of the ruthenium particles on the support. As shown in ESI,† after hot filtration of the solid catalyst, no further conversion was observed, indicating the absence of active species in the solution formed by metal leaching.

When ICP analysis is performed to the reaction mixture with Ru/TiO_2 catalyst after 5 hours of reaction, only 0.1% of the total ruthenium contained in the fresh catalyst was determined in the solution. This amount is much lower than for the commercial Ru(5%)/C, where 0.6% of leaching was determined for the same reaction. The results indicate that differences in activity cannot be due to homogeneous reactions. Additionally, a study of catalyst productivity was carried out by performing the reaction with a ratio lactic acid/catalyst of 3482, and a turnover number of 893 was achieved with the $Ru(0.64\%)/TiO_2$ catalyst. Also, the recyclability of the catalyst was proved by performing three consecutive runs without any loss of activity.

Table 1 Comparison of the catalytic activity of Ru(5%)/C and $Ru(0.6\%)/TiO_2$ for the catalytic hydrogenation of three functionalized carboxylic acids. Reaction conditions: 0.4 mol%Ru, 150 °C and 35 bar H_2 pressure

Substrate	Conversion (%)/TON	Selectivity (%)		
		Catalyst Ru(5%)/C		
Levulinic acid	100/106	90	10	
				
Succinic acid	75/12.5	90		
				
Itaconic acid	100/28.6	30	44	25
				
		Catalyst $Ru(0.6\%)/TiO_2$		
Levulinic acid	100/247	93	7	
				
Succinic acid	100/38	98		
				
Itaconic acid	100/68	32.4	58	9.6
				

The scope of the catalyst has been demonstrated by carrying out the hydrogenation of various acids. The results are summarized in Table 1. It can be seen there that high yields to the corresponding lactones are generally obtained with TONs at least twice as high for $Ru(0.64\%)/TiO_2$ than for Ru(5%)/C.

From the results presented above, it can be concluded that $Ru(0.64\%)/TiO_2$ is the most active catalyst for the reduction of the hydroxycarboxylic acids reported until now. The catalytic activity of $Ru(0.64\%)/TiO_2$ can be explained from the synergism between the small particle size of Ru crystallites and the activation of the carbonyl group on the TiO_2. This synergetic effect between the metal and the support enhances more than three times the catalytic activity of $Ru(0.64\%)/TiO_2$ (TOF per surface metal atom) with respect to the conventional Ru supported on active carbon.

Financial support by the Spanish MICNN (Consolider-Ingenio 2010 (Proyecto MULTICAT)) and Generalidad Valenciana (Prometeo/2008/130) is gratefully acknowledged. A.P. thanks the Generalitat Valenciana for a Prometeo research associate contract.

Notes and references

‡ All the catalysts have been submitted to exhaustive washings until they are free of chloride based on the silver nitrate test.

§ Due to the lack of carbon transparency and experimental limitations, IR spectroscopy was found to be unsuitable to study propanoic acid adsorption on Ru/C samples.

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