Highly selective and efficient hydrogenation of carboxylic acids to alcohols using titania supported Pt catalysts†

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Selective hydrogenation of carboxylic acids to alcohols and alkanes has been achieved under remarkably mild reaction temperatures and H_2 pressures (333 K, 0.5 MPa) using Pt/TiO_2 catalyst.

Catalytic hydrogenation is one of the most useful synthetic tools in the transformation of fats, in particular the synthesis of fatty alcohols from their corresponding carboxylic acids and esters.[1] Fatty alcohols are nonionic surfactants and are widely used in lubricants, resins, perfumes, cosmetics, shampoos and conditioners.[2] Recently, fatty alcohols have been explored for potential use in medicine, health supplements and biofuels.[3] The world market for fatty alcohols has been valued at \$1.87 billion with the scope of an annual growth rate of 7.3%.[4] In comparison with many carbonyl hydrogenations, hydrogenation of carboxylic acids to alcohols is difficult due to the fact that the carbonyl group has weak polarizability and has, consequently, lower reactivity. Therefore, extreme conditions are typically required where control of the selectivity of the process to the desired fatty alcohols is difficult. Commercially, fatty alcohols are produced from natural fatty acids/esters predominantly using copper chromite or zinc chromite catalysts at the hydrogen pressure of 20–30 MPa and temperatures 473–673 K.[5,6] In addition, ruthenium supported on carbon (6 MPa, 373 K), ruthenium dioxide (20–95 MPa, 423–523 K), ruthenium heptaoxide (25–35 MPa, 423–473 K) and bimetallic Ru–Sn on alumina (5–6 MPa, 523 K) catalysts have also been used for acid hydrogenation.[7] As a result there is a pressing need to develop alternative catalysts for more facile and selective hydrogenation of fatty acids to fatty alcohols at lower pressures and temperatures. In continuation of our long standing interest in liquid phase hydrogenations,[8] the hydrogenation of carboxylic acids to fatty alcohols has been studied using titania supported platinum group metal catalysts.

In the past decade, there has been a substantial increase in the use of reducible oxide supports, such as TiO_2, WO_3 and MoO_3, and/or promoters (Sn, Ge, Fe) to enhance the hydrogenation activity of platinum group metal catalysts.[9] Herein, we report a facile hydrogenation of a range of carboxylic acids with tunable high selectivities to alcohol/alkane as desired by using Pt/TiO_2 and $Pt–Re/TiO_2$ catalysts at low temperatures and H_2 pressures. Stearic acid ($C_{17}H_{35}COOH$) was chosen as a model substrate. A typical reaction profile of the hydrogenation of stearic acid using $4\%Pt/TiO_2$ catalyst at 403 K and a hydrogen pressure of 2 MPa is shown in Fig. 1A. The reaction went to completion in <20 h, with high selectivity to stearyl alcohol (93%) with the balance made up of linear alkanes with one or two C atoms (7%) fewer than stearic acid. It was possible to enhance the rate of hydrogenation using a bimetallic $4\%Pt–4\%Re/TiO_2$ catalyst; however, a significiantly reduced selectivity towards stearyl alcohol was observed. Complete conversion of stearic acid was achieved in <4 h with ~70% selectivity to stearyl alcohol, again with the balance due to the formation of alkanes. The experimental conditions for the hydrogenation reactions using $4\%Pt/TiO_2$ and $4\%Pt–4\%Re/TiO_2$ catalysts were optimised for the reactions to be under kinetic regime and free from mass transfer and diffusional limitations. The rate of hydrogenation of stearic acid was linear with catalyst mass (100–500 mg) and the reaction rate did not change with speed of agitation > 1100 rpm (ESI†).

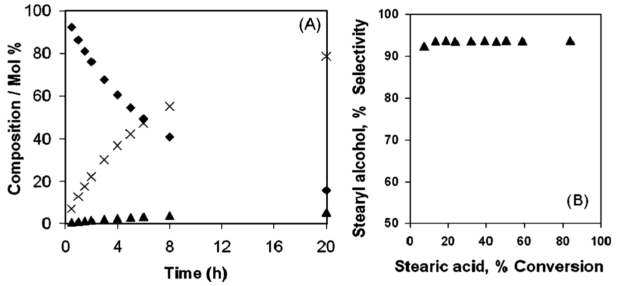

Fig. 1 Reaction composition–time profile (A) of the hydrogenation of stearic acid, ◆: stearic acid, ×: stearyl alcohol, ▲: heptadecane and (B) selectivity to stearyl alcohol as a function of the % conversion of stearic acid. Reaction conditions: stearic acid 0.005 mol, dodecane 40 cm^3, $4\%Pt/TiO_2$ 300 mg (pre-reduced in H_2 at 393 K for 1 h.), 403 K, H_2 pressure 2 MPa.

In order to examine whether it was possible to enhance the catalytic activity whilst maintaining the high selectivity towards the alcohol, a range of catalyst supports as well as the influence of different Pt–Re weight ratios was examined. The effect of support was studied for the hydrogenation of stearic acid at 2 MPa and 403 K using 4%Pt and 4%Pt–4%Re supported on SiO_2, Al_2O_3, CeO_2, ZrO_2, $CeZrO_4$ and TiO_2. The reaction rate was found to be negligible when SiO_2, Al_2O_3, CeO_2 and ZrO_2 were used as the catalyst supports with stearic acid conversion of <2% even after 24 h. Addition of rhenium to these catalysts did not result in any further reaction. $4\%Pt–4\%Re/CeZrO_4$ showed ~10% conversion after 5 h (ESI†)

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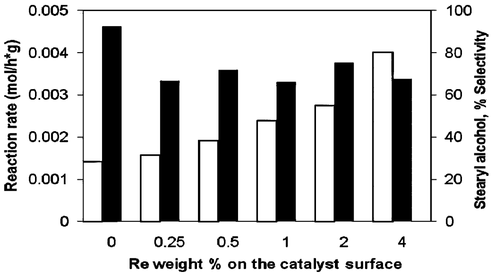


Fig. 2 Effect of increasing weight % of Re in the Pt–Re/TiO_2 catalyst on the reaction rate (left hand side axis, ☐) for the hydrogenation of stearic acid and selectivity towards stearyl alcohol obtained at ~80% conversion (right hand side axis, ■).

and only TiO_2 supported catalysts showed high conversions. TiO_2 support was found to play a critical role in the activity of the catalyst. It should be noted that no reaction was found over the titania in the absence of any metal. In addition, different rhenium loadings in the bimetallic systems were investigated under otherwise identical experimental conditions in the hydrogenation of stearic acid. When only Re was present, *i.e.* 4%Re/TiO_2, no reaction was observed under any conditions for stearic acid. Fig. 2 compares the reaction rate and selectivity to stearyl alcohol as a function of the rhenium loading from 0 to 4 wt%. In all cases (Re > 0 wt%) the reaction went to completion in <5 h and the reaction rates increased linearly with Re loading. However, in the presence of rhenium the selectivity to stearyl alcohol was in the range of 65–75% and was found to be independent of the rhenium loading. Importantly, these selectivities were maintained over a wide range of temperatures (333–423 K) and hydrogen pressures (0.5–3 MPa) although the rates were found to decrease as the temperature (Fig. 3) and hydrogen pressure were lowered, as expected.

Using all the catalysts tested, the hydrogenation of stearic acid could be successfully performed even at very low H_2 pressures, of the order of 0.5 MPa at 403 K, and low temperatures of 333 K at 2 MPa H_2 pressures, demonstrating the high activity of both monometallic and bimetallic catalysts (Fig. 3). To the best of our knowledge this is the first report on hydrogenation of aliphatic carboxylic acids to the corresponding alcohols at such low hydrogen pressure (0.5–2 MPa) and temperature (333–403 K).

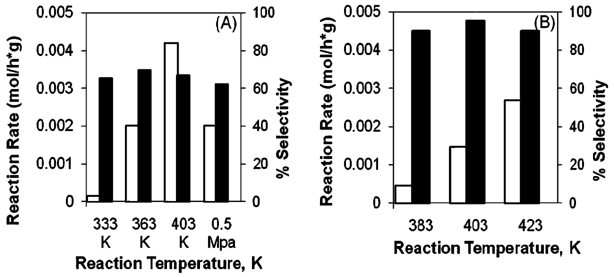
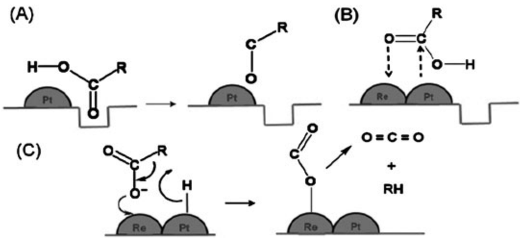


Fig. 3 Variation of reaction rate as a function of the reaction temperature and the influence of increasing reaction rate (LHS, white) on the selectivity (RHS, black) to stearyl alcohol using (A) 4% Pt–4% Re/TiO_2 catalyst; and (B) 4% Pt /TiO_2 catalyst, ☐: reaction rate, ■: % selectivity. All other reaction conditions were same as shown in Fig. 1.

In order to establish the reaction pathway both acid and alcohol substrates were reacted over the catalyst under a hydrogen and nitrogen atmosphere. Following the reaction of stearic acid in a nitrogen atmosphere at 0.6 MPa pressure and 403 K using 4%Pt–4%Re/TiO_2 catalyst pre-reduced in H_2 at 393 K for 1 h, decarboxylation of stearic acid to heptadecane only occurred with ~14% conversion of stearic acid in 2 h. This rate is lower than the rate of formation of heptadecane under hydrogen indicating that a second process must also contribute to the alkane formation. No reaction was found using stearyl alcohol under a nitrogen atmosphere; however, under hydrogen 2 MPa pressure and 403 K using 4%Pt–4%Re/TiO_2 catalyst pre-reduced in H_2 at 393 K for 1 h, complete conversion was observed in 2 h to heptadecane as the only product observed *via* dehydration and then rapid hydrogenation of the intermediate alkene. The suggested reaction pathways are shown in the ESI.† This is in agreement with previous reports wherein decarboxylation of aliphatic long chain carboxylic acid to alkanes with loss of 1 or 2 carbon atoms was found to occur in supercritical water in an Ar atmosphere at the reaction temperature of 523–673 K in the presence of metal oxides such as ZrO_2, CeO_2 and Y_2O_3.[10]

The enhanced hydrogenation activity associated with the TiO_2 support is thought to be due to the interaction of the carbonyl oxygen of the acid with the support metal ion/oxygen vacancy created in the reducible oxide by low temperature reduction activated *via* the presence of the platinum.[11] This interaction weakens the C=O and promotes hydrogenation and carbon–oxygen bond cleavage. The increased activity in the presence of Re may be due to the increased oxyphilicity of the surface associated with the Re cations which interact with the lone electron pair of carbonyl group oxygen, as depicted in Scheme 1. The interaction of the substrate with rhenium on the catalyst surface favours the formation of alkanes, indicating two different hydrogenation mechanisms proceeding on Pt/TiO_2 and Pt–Re/TiO_2 monometallic and bimetallic catalysts.

The scope of the liquid-phase hydrogenation using Pt monometallic and Pt–Re bimetallic catalysts supported on titania was further extended to various other aliphatic and cyclic carboxylic acids (Table 1). In all cases, high activity at low hydrogen pressures and temperatures was found with similar reaction rates; however, again for the majority of substrates



Scheme 1 Hydrogenation of carboxylic acid proceeding *via* the interaction of the oxygen atom of the carbonyl group with the oxygen vacancies created by hydrogen spill-over by Pt metal (A), the interaction of the oxygen atom of the carbonyl group with Re cations on the surface of Pt–Re/TiO_2 bimetallic catalyst (B) and the decarboxylation of carboxylic acid on the surface of Re on the surface of Pt–Re/TiO_2 bimetallic catalyst (C).

Table 1 Hydrogenation of carboxylic acids under the reaction conditions in Fig. 1

Substrate	Catalyst metal/TiO_2	Time/h	[a]Acid conv. (%)	Selectivity (%) Alcohol	Selectivity (%) Alkanes
Octadecanoic acid	4%Pt	12	82	93	7
Hexadecanoic acid	4%Pt	14	79	90	10
Tetradecanoic acid	4%Pt	6	83	91	9
Decanoic acid	4%Pt	8	79	90	10
Cyclohexanecarboxylic acid	4%Pt	6	80	88	12
3-Cyclohexylpropanoic acid	4%Pt	18	80	8	92
Octadecanoic acid	4%Pt–4%Re	2.5	86	67	33
Hexadecanoic acid	4%Pt–4%Re	2.5	84	61	39
Tetradecanoic acid	4%Pt–4%Re	3	83	90	10
Decanoic acid	4%Pt–4%Re	4	79	75	25
Cyclohexanecarboxylic acid	4%Pt–4%Re	1	84	70	30
3-Cyclohexylpropanoic acid	4%Pt–4%Re	3	85	6	94

[a] Using 4%Pt–4%Re/TiO_2, all reactions went to completion in $<$5h, while using 4%Pt/TiO_2 all reactions went to completion in $<$20 h.

the Pt–Re/TiO_2 catalysts were found to have a significantly reduced selectivity towards the respective alcohol compared with the monometallic Pt/TiO_2 catalyst.

The reusability of 4%Pt/TiO_2 and 4%Pt–4%Re/TiO_2 catalysts was studied with the recovered catalyst regenerated by washing with acetone followed by an *in situ* pre-reduction in H_2 at 393 K for 1 h and then the hydrogenation of stearic acid repeated. The regenerated 4%Pt/TiO_2 catalyst showed good reusability with similar reaction rates and the selectivity towards stearyl alcohol on the recycle (ESI†). In contrast, the regenerated 4%Pt–4%Re/TiO_2 catalyst showed loss in the hydrogenation activity with an associated decrease in reaction rate. A further loss in the hydrogenation activity was observed on recycling the catalyst for a second time. However, the selectivity towards stearyl alcohol remained constant on recycle (ESI†). Some of the decrease in activity is likely to be due to the presence of strongly adsorbed carbonaceous residue on the catalyst. The temperature programmed oxidation profile of the spent catalyst showed a broad peak located at 140–370 °C and calcination of the catalyst at 773 K and then pre-reduction in H_2 at 393 K did lead to some recovery of the activity but not to the rate of the fresh catalyst (ESI†). N_2 sorption analysis of fresh and recovered 4%Pt–4%Re/TiO_2 catalysts did not show any pore blocking or reduction of the surface area and ICP results showed that the leaching of the active metal was below 1 ppm. Therefore, it is most likely that the majority of the deactivation is due to a loss of the interaction between the Re and Pt. It should be noted that since the selectivity does not change on recycle, it is unlikely that complete loss of contact between the Re and Pt occurs as this would lead to an increase in the selectivity for stearyl alcohol.

Pt and Pt–Re supported on titania catalysts have shown excellent activity for the reduction of various carboxylic acids under low hydrogen pressures and reaction temperature compared with that for previously reported catalysts. In particular, the monometallic 4%Pt/TiO_2 demonstrates excellent selectivity towards corresponding alcohols. The reaction conditions can also be successfully tuned with 100% selectivity to obtain alkanes by decarboxylation of carboxylic acids under nitrogen atmosphere. The liquid phase hydrogenation methodology reported here shows a huge potential for such difficult hydrogenations under safer and more economical reaction conditions.

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