Electronic Supplementary Information

Highly Selective and Efficient Hydrogenation of Fatty acids to Alcohols using Pt supported over TiO_2 catalysts

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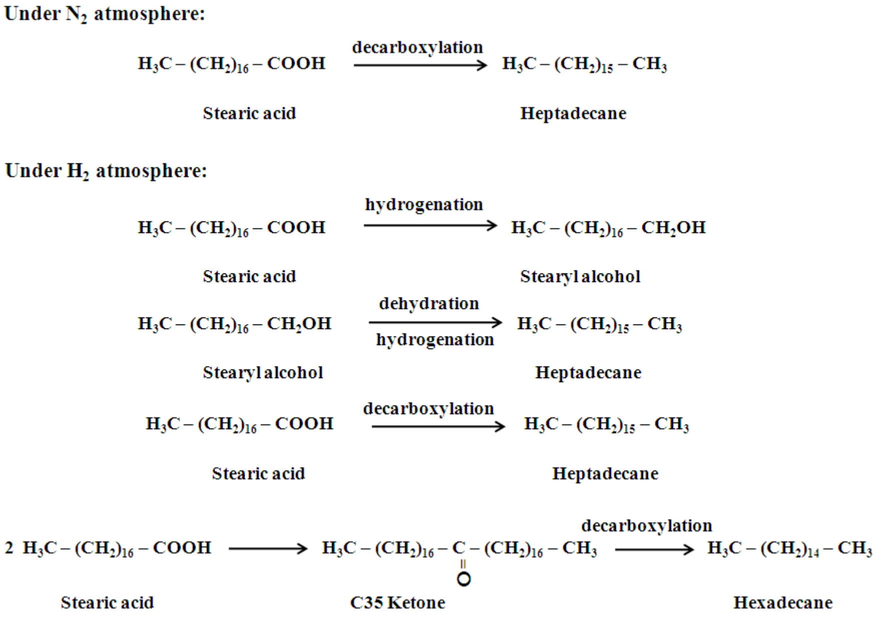
1. Introduction

The reaction pathways which can occur during the hydrogenation of aliphatic carboxylic acids are shown in **Scheme 1**. The observed reactions under a hydrogen atmosphere at 2 MPa pressure and 403 K on the 4%Pt-4%Re/TiO_2 catalyst surface were: (a) hydrogenation of stearic acid to stearyl alcohol, (b) monomolecular decarboxylation of stearic acid to heptadecane and bimolecular decarboxylation to hexadecane and (c) hydrogenation of stearyl alcohol to heptadecane. Selective hydrogenation of stearic acid to stearyl alcohol was the main reaction.



Scheme 1. Hydrogenation of Stearic acid to stearyl alcohol

2. Experimental

2.1. Chemicals and Catalysts

All chemicals were of AR grade and used without any further purification. Aliphatic carboxylic acids and dodecane were procured from Sigma-Aldrich. High purity H_2 was obtained from BOC. Pt and Pt-Re supported on titania catalysts with varying weight ratios of Pt and Re were synthesized in our lab by using sequential weight impregnation technique with Re followed with Pt impregnation on the surface of titania.

2.2. Hydrogenation procedure

Hydrogenation experiments were carried out in a 100 cm^3 Autoclave Engineers' high pressure reactor, which had a pressure range of 0-20 MPa gauge and maximum temperature limit of 573 K. In a typical experiment, catalyst was pre-reduced in situ before the reaction. 0.3 g of catalyst was suspended in 20 ml of dodecane and the reactor was purged three times with N_2, the mixture was agitated at 1500 rpm and heated to 393 K. After purging with H_2 three times, the reactor was pressurised to 2 MPa and the catalyst was reduced for 1 h. After pre-reducing the catalyst, the reactor was charged with 1.42 g (0.05 mol) of stearic acid and 20 ml of dodecane. As mentioned above, reactor was purged with N_2 followed with H_2 and heated to the reaction temperature while the impeller was set to 1500 rpm. At a desired temperature, the reactor was pressurised to the reaction pressure, which corresponded to t = 0. The reaction was monitored by sampling at regular time intervals, with analysis of the samples by GC equipped with a DB-1 capillary column and FID detector.

The reusability of monometallic and bimetallic catalysts was studied by recovering the catalyst at the end of stearic acid hydrogenation under typical experimental conditions as mentioned above. The recovered catalyst was regenerated by washing with acetone followed by an *in situ* pre-reduction under hydrogen atmosphere for 1 h., before being reused in subsequent recycles. In a separate set of reusability experiments, the recovered bimetallic catalyst was washed with acetone, dried at 393 K for 2 h. ,calcined in air at 773 K for 4 h. and subjected to an *in situ* pre-reduction under hydrogen atmosphere at 393K for 1 h., before being reused in subsequent recycles. The regenerated catalyst was tested for its activity in hydrogenation of stearic acid under identical experimental conditions. No makeup quantity of catalyst was added during subsequent recycles.

The catalysts were characterised by BET N_2 isotherm (Micromeritics ASAP 2010), TPO (Micromeritics Autochem 2910). The Temperature-programmed Oxidation (TPO) was measured using approximately 0.1 g of catalyst. The samples were placed in a U-shaped tube and cooled to -50 ^{o}C in helium. The catalyst was oxidised using 10% O_2 in He with the temperature being ramped from -50 to 800 ^{o}C at a rate of 10 ^{o}C min^{-1}. The oxygen uptake was monitored by a thermal conductivity detector (TCD).

3. Results and Discussion

3.1. Hydrogenation of Carboxylic acids

All hydrogenation reactions were performed in the kinetic regime. Experimental conditions were optimised for the reaction to be free from mass transfer and diffusion limitations. The rate of hydrogenation of stearic acid was linear with catalyst mass (**Fig. 1**) and the reaction rate did not change with speed of agitation and all reactions were performed at 1500 rpm. Identical linear dependence of rate of hydrogenation on catalyst mass was observed for decanoic acid as well, indicating that the reactions were free from mass transfer and diffusional limitations.

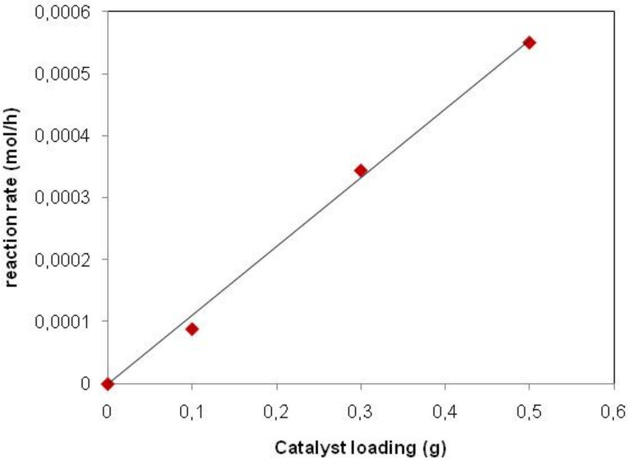


Fig.1 Effect of Catalyst loading on the reaction rate of hydrogenation of stearic acid Reaction conditions: Stearic acid 1.25 x 10^{-3} gmol/cm^{3}, dodecane 40 ml, 4%Pt-4%Re/TiO_2 (pre-reduced in H_2 at 393 K for 1 h.), temperature 403 K, hydrogen pressure 2 MPa, speed of agitation 1500 rpm.

3.2. Effect of other supports on the hydrogenation of stearic acid

Influence 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, and Al_2O_3 , CeO_2 and ZrO_2 were used as the catalyst supports with stearic acid conversion of < 2% even after 24 h. 4%Pt-4%Re/$CeZrO_4$ showed ~10% conversion after 5 h and only TiO_2 supported catalysts showed high conversions. A comparison of % conversion of stearic acid against time (hrs) is shown in Fig. 2,

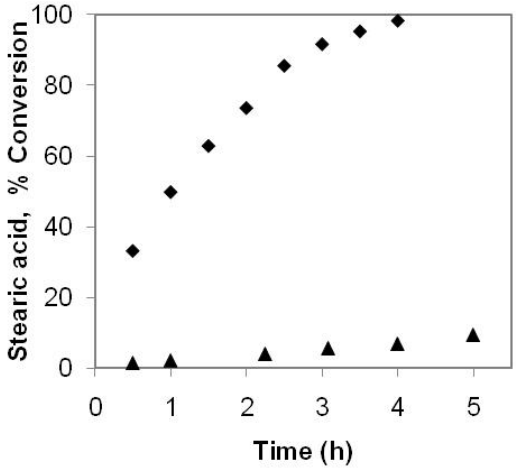


Fig. 2 Effect of support on the hydrogenation of stearic acid using ◆ - 4%Pt-4%Re/TiO_2 and ▲ – 4%Pt-4%Re/$CeZrO_4$ catalysts, is shown by the hydrogenation activity in terms of stearic acid conversion with respect to time (hrs).

3.2. Reusability of monometallic 4%Pt/TiO_2 and bimetallic 4%Pt-4%Re/TiO_2 catalysts

The reusability of monometallic 4%Pt/TiO_2 and bimetallic 4%Pt-4%Re/TiO_2 catalysts was studied by using a recovered catalyst at the end of hydrogenation of stearic acid under typical experimental conditions. The results obtained for monometallic 4%Pt/TiO_2 catalyst are shown in **Fig. 3A** and bimetallic 4%Pt-4%Re/TiO_2 catalyst shown in **Fig. 3B**.

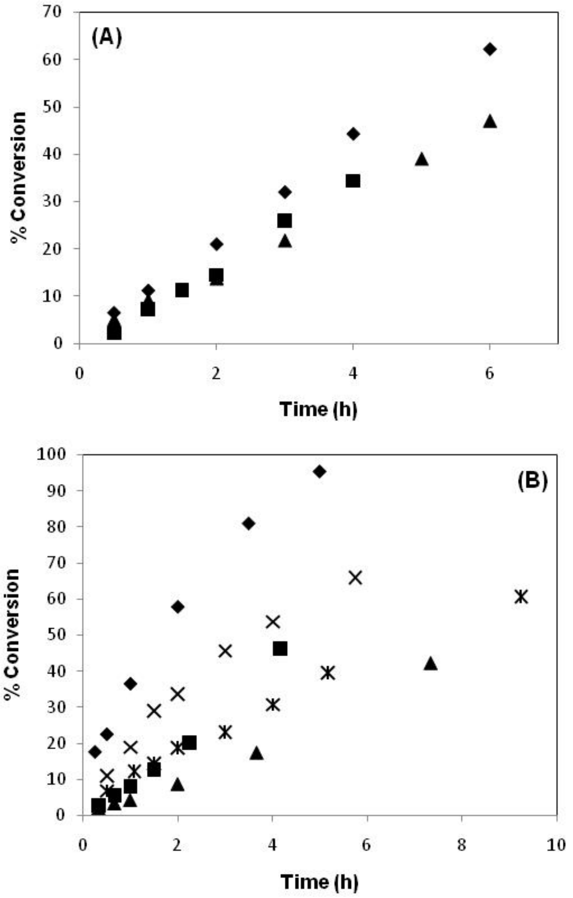


Fig. 3 Reusability of monometallic 4%Pt/TiO_2 catalyst (A) and bimetallic 4%Pt-4%Re/TiO_2 catalyst (B) is shown by the hydrogenation activity in terms of stearic acid conversion with respect to time. ◆ - Fresh catalyst, ■ - 1st reuse (pre-reduced at 393K), ▲ – 2nd reuse (pre-reduced at 393K), × - 1st reuse (calcined at 773K and pre-reduced at 393K), ∗ - 2nd reuse (calcined at 773K and pre-reduced at 393K); Stearic acid 1.25 x 10^{-3} gmol/cm^3, dodecane 40 ml, catalyst loading 0.0125 g/cm^3, temperature 403 K, hydrogen pressure 2 MPa, speed of agitation 1500 rpm.

3.3. TPO analysis of monometallic 4%Pt/TiO_2 and bimetallic 4%Pt-4%Re/TiO_2 catalysts

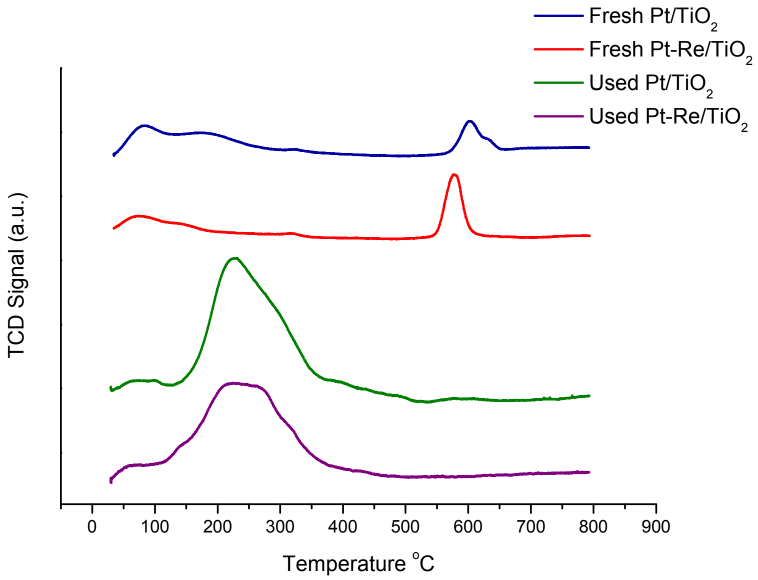


Fig. 4 TPO profiles for fresh and used monometallic 4%Pt/TiO_2 and bimetallic 4%Pt-4%Re/TiO_2 catalyst.