TiO_2-supported Re as a heterogeneous catalyst for selective hydrogenation of carboxylic acids and their derivatives

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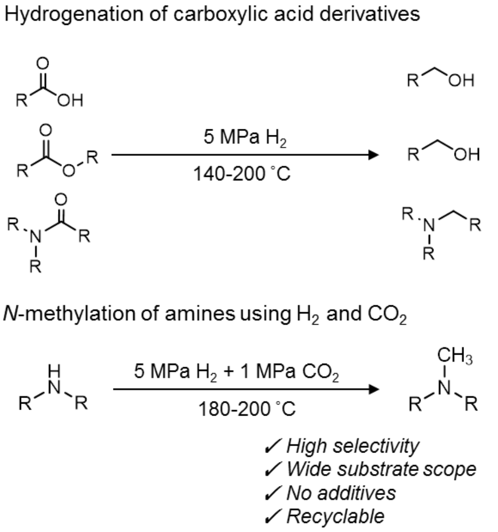
Abstract: TiO_2-supported Re, Re/TiO_2, has been found to promote selective hydrogenation of aromatic and aliphatic carboxylic acids to alcohols. Re/TiO_2 is superior to other transition metal-loaded TiO_2 and supported Re catalysts for selective hydrogenation of 3-phenylpropionic acid. This process produces 3-phenylpropanol in a 97% yield under mild condition (5 MPa H_2 at 140 ºC). Contrary to typical heterogeneous catalysts, Re/TiO_2 does not give dearomatized byproducts. The catalyst shows wide substrate scope toward the alcohol forming process (22 examples; up to 97% isolated yield) and is effective for selective hydrogenation of other carboxylic acid derivatives such as esters and amides.

Keywords: Rhenium, Selective hydrogenation, Carboxylic acid derivatives.

1. Introduction

Reduction of carboxylic acids to form alcohols is a key synthetic transformation for pharmaceutical and fine-chemical industries as well as for biomass conversion. Selective catalytic hydrogenation of carboxylic acids is a straight-forward and effective synthetic method. However, the required harsh conditions often lead to low selectivity to desired products. In particular, hydrogenation of aromatic rings occurs rather than hydrogenation of carboxylic acid groups when both moieties are present in substrates.

In this study, we propose a versatile heterogeneous catalytic system, comprised of TiO_2-supported Re (Re/TiO_2), which promotes selective alcohol forming hydrogenation reactions of carboxylic acids that contain aromatic and aliphatic moieties, as shown in Scheme 1.[1] Unlike previously-developed catalysts, TiO_2-supported Re has the advantage of being heterogeneous and, therefore, it can be readily recovered and recycled. Moreover, the catalyst is effective for selective hydrogenation of other carboxylic acid derivatives such as esters and amides.[2] The catalyst was also found to promote *N*-methylation of amines with H_2 and CO_2.



Scheme 1. Methods for hydrogenation of carboxylic acids containing aromatic ring(s).

2. Experimental

The Re/TiO_2 catalyst was synthesized by using a facile impregnation method employing NH_4ReO_4 and TiO_2 (JRC-TIO-8 supplied from Catalysis Society of Japan). Catalytic reactions were typically carried out using 1 mmol of a substrate and 2 mol% of catalyst (based on loaded Re) in a stainless autoclave (V = 10 cm^3; p_{H2} = 5 MPa; T = 140-200 ºC; t = 24 h). The products were analyzed by GC and GCMS. ^1H and ^{13}C NMR analysis

3. Results and discussion

High-angle annular dark-field scanning TEM (HAADF-STEM) analyses were performed to evaluate the element dispersion and particle size of Re in the Re/TiO_2, as given in Fig. 1. The results show that Re is present and that it is highly dispersed over the entirety of the TiO_2 particles. Hydrogenation reactions of 3-

phenylpropionic acid (**1a**) were used to screen the properties of various catalysts in the initial phase of this effort. The results of this study show that the Re/TiO_2 produced 3-phenylpropanol (**2a**) and the corresponding ester (**3a**). **3a** was formed via an esterification reaction of the starting carboxylic acid by the formed alcohol. On the contrary, low yields of the alcohol and ester were observed when other precious metal (Pt, Ir, Ru, Rh and Pd) containing catalysts were employed. This was caused by competitive formation of products produced via dearomatization of benzene ring. Ag-, Cu-, Ni-, Co-loaded TiO_2 catalysts did not promote the reduction reaction. The time course of the hydrogenation reaction of 3-phenylpropionic acid over Re/TiO_2 is given in Fig. 2. Inspection of the profile shows that **2a** was efficiently generated from **1a** via a pathway involving initial formation of **3a**. The yield of **2a** reached 97% after 24 h. It has also been confirmed that the Re/TiO_2 catalyst can catalyze selective hydrogenation of carboxylic acid derivatives such as esters and amides having aromatic rings. In addition, Re/TiO_2 was found to promote *N*-alkylation of amines with carboxylic acids or esters in the presence of H_2. The reaction involves the hydrogenation of carboxylic acids (or esters) to give the corresponding alcohols in the presence of molecular H_2, followed by an *N*-alkylation of the amines with the generated alcohols. Re/TiO_2 also catalyzed the *N*-methylation of various amines in the presence of CO_2 and H_2.

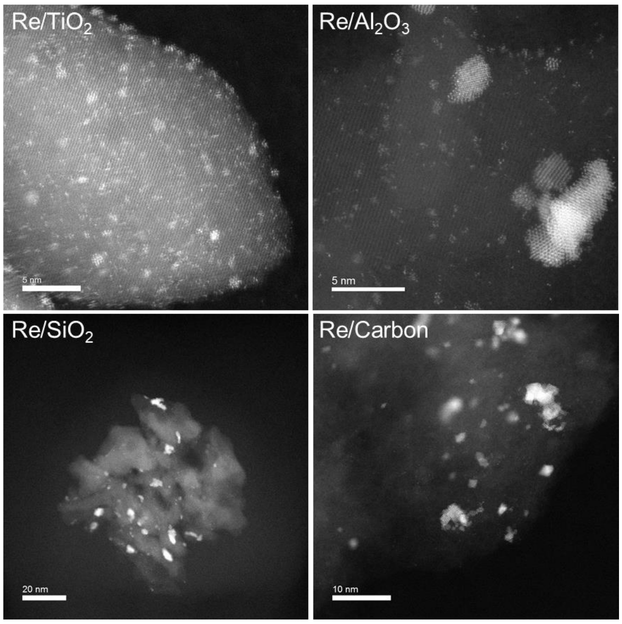


Figure 1. HAADF-STEM images of supported-Re catalysts on various supports.

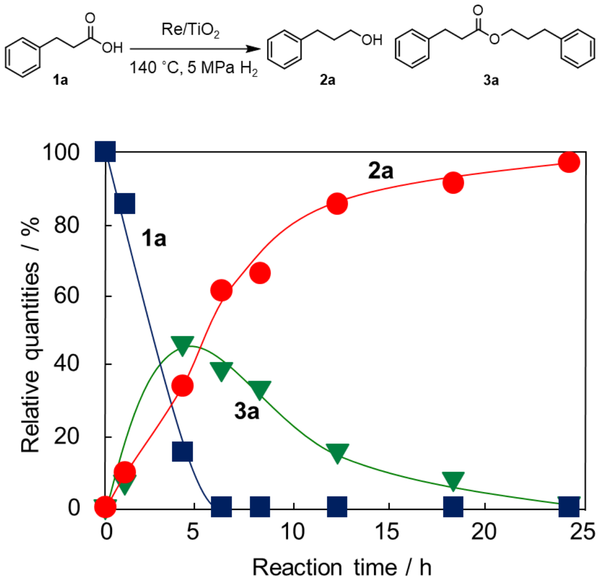


Figure 2. Time course of the hydrogenation reaction of phenylpropionic acid catalyzed by Re/TiO_2. Substances in the plot are 3-phenylpropionic acid (**1a**), 3-phenylpropanol (**2a**) and 3-phenylpropyl 3-phenylpropionate (**3a**).

4. Conclusions

We have developed a heterogeneous catalytic system that promotes selective alcohol forming hydrogenation reactions of carboxylic acids under mild conditions without the need for additives. In view of the importance of the process in both organic synthesis and industrial bulk chemical production, the new method for carboxylic acid hydrogenation should find wide utility and the findings should stimulate further studies targeted at the design of catalysts for selective hydrogenation reactions. In addition, Re/TiO_2 efficiently catalyzed the *N*-methylation of amines using a H_2/CO_2 mixture.

References

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