CHEMISTRY LETTERS, pp. 839-840, 1993.

Reduction of Carboxylic Acid with 2-Propanol over Zirconia-Titania

Kyoko TAKAHASHI, Makoto SHIBAGAKI, Hideyuki KUNO, and Hajime MATSUSHITA
Life Science Research Laboratory, Japan Tobacco INC.,
6-2 Umegaoka, Midori-ku, Yokohama, Kanagawa 227

The reduction of long carbon chain carboxylic acids or the esters with 2-propanol proceeded efficiently over zirconia-titania at atmospheric pressure, and the corresponding alcohols were obtained. Methyl 9-octadecenoate was reduced to give 9-octadecen-1-ol in a 58% yield.

The reductions of carboxylic acid to the corresponding alcohol are generally carried out using metal hydrides or by catalytic hydrogenation using catalysts such as copper chromite. However, the former reaction is unsuitable for a large scale reaction and the latter needs a high hydrogen pressure. Furthermore, it is difficult to convert unsaturated carboxylic acids or esters to the unsaturated alcohols by catalytic hydrogenation. ZnO-Cr_2O_3,[1] Ru-Sn-Al_2O_3,[2] and Ru-Sn-B-Al_2O_3[3] have been reported as catalysts for the selective reduction of 9-octadecenoic acid or its ester; however, high hydrogen pressure was required. In a previous paper,[4] we reported that the reductions of carboxylic acids or esters with 2-propanol gave the corresponding alcohols. This reduction could be carried out under atmospheric pressure over the hydrous zirconium oxide. However, it was difficult to reduce long chain carboxylic acids efficiently. In this paper, we report that zirconia-titania is an active catalyst for the reduction of long chain carboxylic acids or esters with 2-propanol at atmospheric pressure and that selective reduction of unsaturated carboxylic acid to the unsaturated alcohol can be performed.

Zirconia-titania catalysts were prepared by the treatment of an aqueous solution of zirconium oxychloride and titanium tetrachloride with aqueous sodium hydroxide or aqueous ammonium hydroxide, drying the precipitate, and calcination at 300 °C for 5 h. The reduction was carried out in a glass flow reactor (7 mm in diameter) with a fixed-bed catalyst [flow rate of nitrogen carrier gas:60 cm^3 min^{-1}]. A solution of carboxylic acid or the ester in 2-propanol was fed, by means of a microfeeder, into a reactor. The analysis of the product was carried out by gas chromatography. Activity of the catalyst was determined after the steady state had been

Table 1. Reduction of Carboxylic Acids and Esters over Zirconia-Titania Catalyst[a)]

Entry	Reactant	Conversion/%	Yield/%		
			Alcohol[b)]	Isomeric alcohol	Isopropyl ester
1	$CH_3(CH_2)_8COOH$	100	85	-	6
2	$CH_3(CH_2)_{12}COOCH_3$	100	78	-	11
3	$CH_3(CH_2)_{14}COOCH_3$	100	72	-	24
4	$CH_3(CH_2)_{16}COOCH_3$	100	49	-	34
5	CH_2:$CH(CH_2)_8COOH$	100	71	26	1
6	CH_2:$CH(CH_2)_8COOCH_3$	100	70	17	10
7	$CH_3(CH_2)_7CH$:$CH(CH_2)_7COOCH_3$	100	58	-	29

a) Reactant; 0.05 mol dm^{-3} in 2-propanol, sample feed; 10 cm^3 h^{-1}, temperature; 250 °C, zirconia-titania catalyst(Ti/Zr=5/10); 4.0 g, carrier gas; N_2 60 cm^3 min^{-1}. b) The corresponding alcohol.

reached.

In order to investigate the dependence on the Ti/Zr ratio, the reductions of decanoic acid were carried out over Ti/Zr ratios ranging from 1/10 to 12/10. As a result, it was determined that the catalytic activity is dependent on the Ti/Zr ratio and that an atomic ratio of Zr to Ti of 1:0.5 gives maximum activity and selectivity for the alcohol formation. Table 1 lists the results of the reductions of several carboxylic acids and esters over zirconia-titania catalyst(Ti/Zr=5/10). The corresponding alcohols were obtained in these reactions. The yield of decanol was 85%, which is higher than that(34%) using hydrous zirconium oxide[4)] as a catalyst. Saturated methyl esters were largely reduced to the corresponding alcohol, and the by-product was the corresponding isopropyl ester. The yield of the alcohol decreased with increasing carbon chain length of the reactant. The reduction of 10-undecenoic acid or its methyl ester proceeded to give 10-undecen-1-ol as the major product. Although the isomerization of double bond occured, undecanol was not detected. The reduction of methyl 9-octadecenoate gave 9-octadecen-1-ol in a 58% yield at atmospheric pressure.

References

1) J. Sauer and H. Adkins, *J. Am. Chem. Soc.*, **59**, 1 (1937).

2) K. Y. Cheah, T. S. Tang, F. Mizukami, S. Niwa, M. Toba, and Y. M. Choo, *J. Am. Oil. Chem. Soc.*, **69**, 410 (1992).

3) V. M. Deshpande, K. Ramnarayan, and C. S. Narasimhan, *J. Catal.*, **121**, 174 (1990).

4) K. Takahashi, M. Shibagaki, H. Kuno, and H. Matsushita, *Chem. Lett.*, **1989**, 1141.

(Received February 18, 1993)