CHEMISTRY LETTERS, pp. 1141-1144, 1989.

Reduction of Carboxylic Acid with 2-Propanol over Hydrous Zirconium Oxide

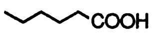
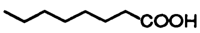
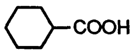
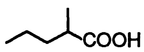
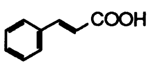
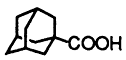
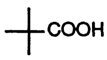
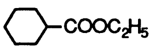
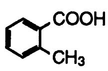
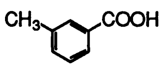
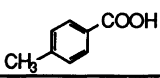
Kyoko TAKAHASHI, Makoto SHIBAGAKI, Hideyuki KUNO, and Hajime MATSUSHITA
Life Science Research Laboratory, Japan Tobacco INC.,
6-2 Umegaoka, Midori-ku, Yokohama, Kanagawa 227

The vapor-phase reduction of carboxylic acids with 2-propanol was found to proceed efficiently over hydrous zirconium(IV) oxide, and the corresponding alcohols were obtained in high yield. Esters were also reduced.

In previous papers, we reported[1-3] that the reduction of aldehydes and ketones and the amidation of carboxylic acids proceeded efficiently over hydrous zirconium(IV) oxide. The reaction of carboxylic acids with alcohols was also reported to proceed efficiently to give the corresponding esters by catalysis with the oxide.[4] During our studies to clarify the scope and the limitation of those reactions and to characterize the hydrous zirconium(IV) oxide, it was found that the reaction of carboxylic acids with 2-propanol at a temperature above 250 °C causes the reduction to give the corresponding alcohols. Generally, the reduction of carboxylic acid was carried out by use of metal hydride or by catalytic hydrogenation. Disadvantages of the former reaction are the need of a stoichiometric amount of the reductant and of acid treatment in the work-up procedure. The latter reaction proceeds under high temperature and high pressure. It is not known if the reduction of carboxylic acid can proceed with alcohol as a hydrogen source. The reduction by our method has several advantages; it can be carried out heterogeneously and the products are easily isolated, and it can proceed under atmospheric pressure. In this paper, we report that the reduction of carboxylic acid and ester with 2-propanol over hydrous zirconium(IV) oxide in vapor phase gives the corresponding alcohol. Some other solid catalysts were also examined.

The hydrous zirconium(IV) oxide was prepared by the treatment of aqueous solution of zirconium oxychloride with aqueous sodium hydroxide at room temperature, and was heated at 300 °C for 5 h.[1] Some characteristic properties were mentioned in a previous paper.[1] The reaction was carried out in a glass flow reactor (7 mm in diameter) with a fixed-bed catalyst [flow rate of nitrogen carrier gas: 60 $cm^3 \cdot min^{-1}$; catalyst: 2.0 g, 24-60 mesh; reaction temperature: 275-350 °C]. A solution of carboxylic acid or ester in 2-propanol (0.2 $mmol \cdot cm^{-3}$) and a

Table 1. Reduction of Carboxylic Acid or Ester over Hydrous Zirconium Oxide[a]

Entry	Reactant	Temperature	Conversion	Selectivity/%	
		°C	%	Alcohol	Ester
1		300	100	81	tr.
2		300	100	64	10
3		300	100	34	19
4		300	100	95	4
5		300	100	84	tr.
6		300	100	78	tr.
7		300	89	53	2
8		300	100	98	tr.
9		300	100	80	-
10		300	100	92	-
11		300	43	0	67
12		300	98	25	59
13		300	100	31	33

a) Catalyst; 2.0 g, carboxylic acid or ester; 0.2 $mmol \cdot cm^{-3}$ in 2-propanol (50 cm^3), sample feed; 5 $cm^3 \cdot h^{-1}$.

hydrocarbon as an internal standard was fed, by a means of a microfeeder, into a reactor (5 $cm^3 \cdot h^{-1}$). The analysis of the product was carried out by gas chromatography (a capillary column PEG 20M 30m). Activity and selectivity of the catalyst were determined after the steady states were reached.

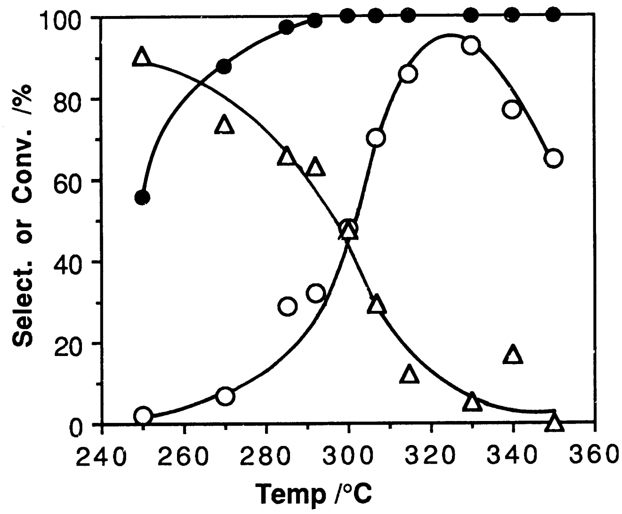


Fig. 1. The temperature dependence.

2-Ethylhexanoic acid; 0.2 $mmol \cdot cm^{-3}$ (2-propanol solution), feed; 5 $cm^3 \cdot h^{-1}$, cat.; 2.0 g.
○ ; Selectivity of the alcohol
Δ ; Selectivity of the ester
● ; Conversion

The results are listed in Table 1. The reduction of primary carboxylic acids proceeded efficiently to give the corresponding alcohols and the yield increased with decreasing carbon chain length (Entries 1-3). The secondary carboxylic acids also reduced efficiently (Entries 4 and 5). The reaction of pivalic acid with 2-propanol gave high selectivity of the corresponding alcohol, however, adamantanecarboxylic acid was not reduced efficiently (Entries 7 and 8). These results suggested that the selectivity was subject to some steric effect, which was also shown from the reduction of toluic acids (Entries 11-13). Esters, as well as the carboxylic acids, were efficiently reduced to corresponding alcohols (Entries 9 and 10).

In order to elucidate the dependence on reaction temperature, the reactions of 2-ethylhexanoic acid with 2-propanol were carried out at several temperatures. It was interesting that the reaction of carboxylic acid with 2-propanol led to the esterification below 250 °C and to the reduction at higher temperature, as shown in Fig. 1. With an increase in temperature the yield of the ester decreased, and that of the reduction was superior above 300 °C. The yield of the alcohol, which was highest at 330 °C, decreased at further higher temperatures. It is worth noting that the dehydration of alcohols hardly occurred over the hydrous zirconium(IV) oxide at such high temperatures.

In order to compare the catalytic activities, the reductions of cyclohexanecarboxylic acid with 2-propanol were carried out over several heterogeneous catalysts. The results are shown in Table 2. Except for the hydrous zirconium(IV) oxide, the reduction did not proceed at all, and some catalysts, known as solid acids, caused the dehydration of 2-propanol. It was concluded that the hydrous zirconium(IV) oxide was the best catalyst for the reduction of carboxylic acid with 2-propanol among the catalysts examined.

Table 2. Comparison of the Catalytic Activity of Several Catalysts in the Reduction of Cyclohexanecarboxylic Acid with 2-Propanol[a)]

Catalyst	g	Conversion/%	Yield/%		
			Alcohol	Ester	Aldehyde
Hydrous Zirconium(IV) Oxide	1	85	29	35	3
Hydrous Cerium(IV) Oxide	1	38	0	13	0
Hydrous Alminium(III) Oxide	1	24	0	3	tr.
Hydrous Iron(III) Oxide	1	15	0	tr.	0
Hydrous Niobium(V) Oxide	1	3	0	3	0
Hydrous Zirconium(IV) Oxide	2	100	95	4	1
Hydrous Titanium(IV) Oxide	2	19	0	0	0
Silica gel	2	6	0	6	0
Zeolite,A-4	2	22	0	22	tr.
Al_2O_3	2	0	0	0	0
MgO	2	83	0	83	tr.

a) Reaction temperature; 300 °C, N_2; 60 $cm^3 \cdot min^{-1}$, cyclohexanecarboxylic acid; 0.2 $mmol \cdot cm^{-3}$ in 2-propanol (50 cm^3), sample feed; 5 $cm^3 \cdot h^{-1}$.

References

1) M. Shibagaki, K.Takahashi, and H.Matsushita, Bull. Chem. Soc. Jpn., 61, 3283 (1988).

2) M. Shibagaki, K.Takahashi, H.Kuno, and H.Matsushita, Chem. Lett., 1988, 1633.

3) K.Takahashi, M. Shibagaki, H.Kuno, H. Kawakami, and H.Matsushita, Bull. Chem. Soc. Jpn., 62, 1333 (1989).

4) K. Takahashi, M. Shibagaki, and H.Matsushita, Bull. Chem. Soc. Jpn., in press.

(Received March 24, 1989)