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The Reduction of Nitrile with 2-Propanol over Hydrous Zirconium Oxide

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The vapor-phase reduction of nitriles with 2-propanol proceeded efficiently over hydrous zirconium oxide to give the corresponding alcohols in high yields.

The reduction of nitriles was generally carried out by the reactions with metal hydrides, and with alkali metals in ammonia or amines, electrolic reduction, and catalytic hydrogenation. Although these reductions are useful to obtain amines or aldehydes from nitriles, diazotization of amine or further reduction of aldehyde are needed to obtain the corresponding alcohols from nitriles.

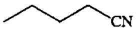
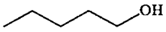
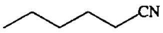
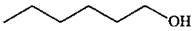
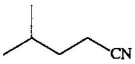
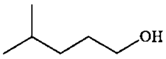
In our previous papers,$^{1-2)}$ we reported that hydrous zirconium oxide had catalytic activities for the reduction of aldehydes, ketones, and carboxylic acids with 2-propanol. These methods are expected to be applicable to the reduction of nitriles to corresponding alcohols in one step. In this paper, we report the reduction of nitriles with 2-propanol over hydrous zirconium oxide at 300 °C in the vapor phase. The reduction over hydrous zirconium oxide can be carried out heterogeneously and the products are easily isolated.

The hydrous zirconium oxide was prepared from an aqueous solution of zirconium oxychloride by precipitation with aqueous sodium hydroxide at room temperature followed by heating 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: 150-340 °C]. A solution of nitrile in alcohol (0.2 $mmol \cdot cm^{-3}$) with a hydrocarbon as an internal standard was fed into a reactor (5 $cm^3 \cdot h^{-1}$) by means of a microfeeder. The products were analyzed by gas chromatography. Activity and selectivity of the catalyst were determined at the steady states.

The results of the reductions of various nitriles with 2-propanol over hydrous zirconium oxide at 300 °C are listed in Table 1. The reduction of aliphatic nitriles proceeded efficiently to give the corresponding alcohols except for long-chain nitriles. The conversion and yield were lowered by increasing carbon chain lengths(Entries 1-4). The secondary and tertiary nitriles were reduced to give the *corresponding alcohols in high selectivity(Entries 5 and 6). The reduction of* phenylacetonitrile gave styrene together with 2-phenylethanol(Entry 7). Aromatic nitriles were also converted to the corresponding alcohols as main products. In the case of tolunitriles, isopropyl ethers of the produced alcohols and xylenes were observed in the products(Entries 9-11). It is interesting that the reduction of cyanopyridines mainly gave the corresponding picolines(Entries 12-14). These results are explained as follows. By analogy with other nitriles, cyanopyridines are reduced to give the corresponding pyridyl carbinol derivatives which are interconverted with the pyridyl carbocations on the catalyst. Because of stabilization due to the pyridine ring, these cations are easily attacked by hydride. Therefore, further reduction is expected to facilitate according to the stability of the pyridil carbocation. In fact, the yield of picolines increased in the order: 3-picoline>4-picoline>2-picoline, and this order is identical with that of the stability of the corresponding pyridil carbocations.3) In the case of conjugated nitriles, 1,4-reduction took place to lead to the saturated alcohols(Entries 15 and 16). The reduction of diphenylacetonitrile gave mainly the corresponding alcohol, however, the dehydration and rearrangement accompanied (Entry 17).

The results of the reduction of valeronitrile with different alcohols over hydrous zirconium oxide are shown in Table 2. Primary alcohol could be used as hydride source of the reaction. However, the ester was also obtained by a side reaction. The reaction with secondary alcohols gave the selectivity and conversion of the alcohol higher than that with primary alcohols. The reduction with 2-propanol whose steric hindrance is the smallest among secondary alcohols gave the alcohol in the highest yield. Tertiary alcohol did not act as hydride donor. In order to elucidate the dependence on reaction temperature, the reactions of valero-

Table 1. The Reduction of Nitriles with 2-Propanol over Hydrous Zirconium Oxide[a)]

Entry	Nitrile	Conv./%	Product (Select. /%)
1		98	 (73)
2		89	 (78)
3		92	 (83)
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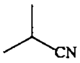
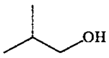
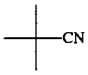
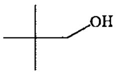
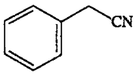
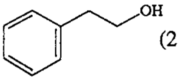
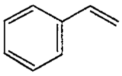
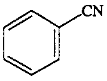
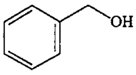
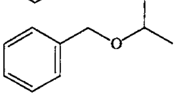
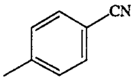
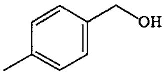
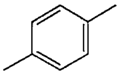
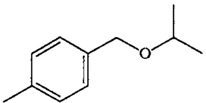
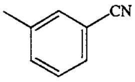
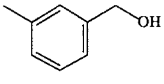
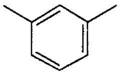
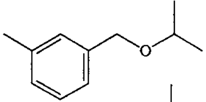
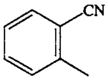
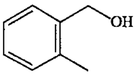
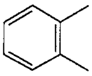
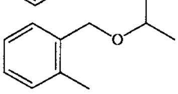
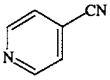
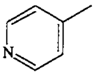
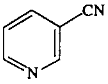
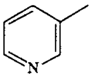
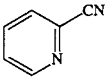
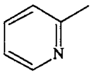
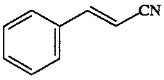
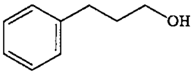
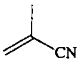
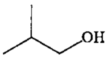
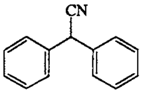
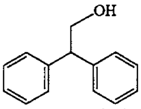
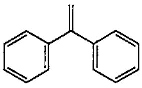
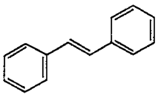
5		98	 (95)
6		89	 (90)
7		100	 (29)  (39)
8		98	 (64)  (5)
9		83	 (54)  (8)  (11)
10		86	 (71)  (2)  (6)
11		79	 (58)  (2)  (7)
12		100	 (39)
13		100	 (50)
14		66	 (30)
15		100	 (46)
16		88	 (88)
17		100	 (43)  (21)  (29)

a) Nitrile; 0.2 mmol cm^{-3} in 2-propanol, catalyst; 2.0 g, sample feed; 5 $cm^3 \cdot h^{-1}$, temperature; 300 °C.

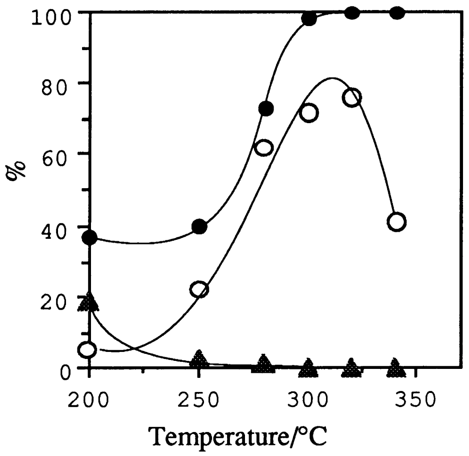


Fig. 1. The temperature dependence.

Valeronitrile: 0.2 mmol·cm^{-3} (in 2-propanol), sample feed: 5 cm^3·h^{-1}, catalyst: 2.0 g.
●: Conversion ○: Yield of pentanol ▲: Yield of isopropyl valerate.

Table 2. The Reduction of Valeronitrile with Several Alcohols[a)]

Alcohol	Conv./%	Yield/%
methanol	33	0.5
ethanol	73	40
2-propanol	98	72
cyclohexanol	71	54
a-phenethylalcohol	20	20
tert-butanol[b)]	0	0

a) Catalyst: 2.0 g, valeronitrile: 0.2 mmol·cm^{-3} in alcohol, sample feed: 5 cm^3·h^{-1}, temp: 300 °C.
b) Temp : 250 °C.

nitrile with 2-propanol were carried out at several temperatures. The results are shown in Fig. 1. The reaction of the nitrile with 2-propanol mainly led to esterification below 250 °C and to reduction in the range of about 300 °C to 320 °C. This temperature dependence is similar to that of the reduction of carboxylic acid.[2)]

In order to estimate the durability of the hydrous zirconium oxide, the reaction of valeronitrile with ethylalcohol was carried out at 250 °C. As a result, the activity of the catalyst was maintained without appreciable decrease for more than 92 h.

References

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