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Vapor-Phase Reduction of Aldehydes and Ketones with 2-Propanol over Hydrous Zirconium Oxide

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

Vapor-phase reduction of aldehydes and ketones with 2-propanol was carried out over hydrous zirconium oxide. The reduction proceeded efficiently to give corresponding alcohols. The oxide worked continuously for 10 h without being inactivated.

The reduction of aldehydes and ketones with 2-propanol in the existence of aluminium isopropoxide is well known as Meerwein-Ponndorf-Verley reduction. This method is prominent in terms of compatibility with many different types of functional group, selectively for carbonyl reduction, and low cost of 2-propanol.[1] Disadvantage in the reduction is the need of strong acidic treatment to neutralize the alkoxide salt as well as tedious workups. To avoid the disadvantages, the use of heterogeneous catalysts was reported.[2] In previous paper, we reported the liquid-phase reduction of aldehydes and ketones over hydrous zirconium oxide.[3] Although most of aldehydes and ketones were efficiently reduced to corresponding alcohols, sterically hindered or conjugated ketones resisted the reduction. It was also reported that the raising the reaction temperature increased the reaction rate, and the vapor-phase reduction was examined in order to proceed the reduction at higher temperature. In the vapor-phase reactions, several advantages are expected such as (1) continuous reaction (2) easy product isolation (3) avoidance of mechanical breakage of the catalyst (4) suppression of undesired side reaction because of a short time contact to the catalyst.

In this paper, we will describe the vapor-phase reduction of aldehydes and ketones[4] with 2-propanol by the catalysis of hydrous zirconium oxide. Some characteristic properties and a preparation of the hydrous zirconium oxide were mentioned in the previous paper.[3)] The vapor-phase reduction was carried out in a glass flow reactor (7 mm in diameter) with fixed-bed catalyst [flow rate of nitrogen carrier gas: 60 $cm^3 \cdot min^{-1}$; catalyst: 1.0 g, 10-30 mesh; reaction temperature: 100-200 °C]. Initially, the catalyst bed was pretreated by 2-propanol vapor with nitrogen gas stream (60 $cm^3 \cdot min^{-1}$) at the reaction temperature for 0.5 h, and a solution of aldehyde or ketone in 2-propanol (0.1 $mol \cdot dm^{-3}$) was fed (10 $cm^3 \cdot h^{-1}$) into the reactor with a microfeeder. The solution was passed to the catalyst bed after vaporizing on the entrance of the reactor at 220 °C. The analysis of the products was carried out by a gaschromatography. Steady state was reached after feeding of the solution for 2 h, and then the reaction was continued for 10 h without deactivation of the catalyst. The results are listed in Table 1.

Every aldehyde was quantitatively reduced to be corresponding alcohol (run 1-5). In the case of liquid-phase reductions of some aldehydes, a certain amount of condensed products were observed. In the case of vapor-phase reduction, the side-reactions might be suppressed because of short-time contact of the reactants or products with the catalyst, although the reaction temperature was high. Most of ketones were also reduced efficiently to be corresponding alcohols, although the stereoselectivity was relatively low. With raising the reaction temperature from 100 °C to 150 °C, a small amount of styrene was obtained in the case of acetophenon, although the conversion was increased from 83% to 100% (run 7 and 8). Run 12 shows that 64% of camphor was converted to borneol and isoborneol at 150 °C. At 200 °C, the conversion became 88%, but the reaction induced the dehydration and isomerization of those products to camphene (run 13). The reduction of 3,5,5-trimethyl-2-cyclohexen-1-one (run 14) at 150 °C gave three dehydrated products of the corresponding alcohol, while

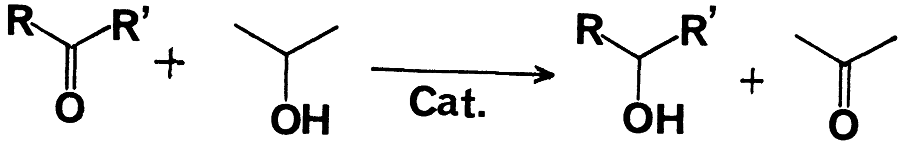
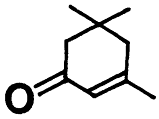
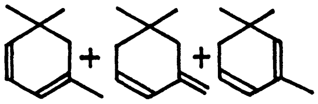


Table 1. Vapor-Phase Reduction of Aldehydes and Ketones$^{a)}$

Run	Aldehyde or ketone	Temp/°C	Conv./%	Products and selectivity/%$^{b)}$
1	Benzaldehyde	150	99.0	Benzylalcohol (100)
2	Hexanal	150	99.6	Hexanol (100)
3	Octanal	150	98.8	Octanol (100)
4	Decanol	150	99.6	Decanol (100)
5	Cyclohexylaldehyde	150	99.6	Cyclohexylmethanol (100)
6	Cyclohexanone	100	99.4	Cyclohexanol (100)
7	2-Metylcyclohexanone	100	98.7	2-Metylcyclohexanol (100) (*trans* : *cis* = 44 : 56)
8	4-Metylcyclohexanone	100	99.4	4-Metylcyclohexanol (100) (*trans* : *cis* = 73 : 27)
9	Acetophenone	100	83.0	2-Phenylethanol (100)
10	Acetophenone	150	100	2-Phenylethanol (98), Styrene (2)
11	3-Decanone	150	73.8	3-Decanol (100)
12	3-Decanone	170	92.6	3-Decanol (100)
13	2-Hexanone	200	97.0	2-Hexanol (100)
14	4-Methyl-2-pentanone	150	87.2	4-Methyl-2-pentanol (100)
15	Camphor	150	64.0	Borneol (41), Isoborneol (59)
16	Camphor	200	88.0	Borneol (29), Isoborneol (15), Camphene (56)
17		150	99.8	 (100)

a) Catalyst; 1.0 g, reactant; 0.1 mol·dm^{-3}, (in 2-propanol solution), sample feed; 10 cm^{3}·h^{-1}, carrier gas; 60 cm^{3}·min^{-1}. b) Determined by gaschromatography using decane as an internal standard.

the product of the reduction at 100 °C was messy. These results indicated that conjugated or sterically hindered ketones, which resisted the reduction in liquid-phase, could be reduced in vapor-phase, but that the dehydration was also competed at higher reaction temperature.

Although the hydrous zirconium oxide is convertible into zirconia by loss of water, the hydrous zirconium oxide in 2-propanol vapor does not loss the catalytic activity for the reduction under 200 °C.

References

1) A. L. Wiles, Org. React., 2, 178 (1944).
2) Several reports were listed in our previous paper.3)
3) M. Shibagaki, K. Takahashi, and H. Matsushita, Bull. Chem. Soc. Jpn., in press.
4) At a high temperature, a slow attainment of equilibrium between alcohol and carbonyl compound without catalyst and acceleration of the reaction with ceric oxide or sodium acetate were known.1)

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