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The Catalytic Reduction of Aldehydes and Ketones with 2-Propanol over Silica-Supported Zirconium Catalyst

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Reduction of aldehydes and ketones with 2-propanol proceeded efficiently over silica-supported zirconium catalyst, and the corresponding alcohols were obtained in high yields. In the reduction of aldehyde, the acetalization did not occur and the side reaction, the aldol condensation, was inhibited.

The reduction of aldehydes and ketones with 2-propanol in the presence of aluminium isopropoxide is well known and is called the Meerwein-Ponndorf-Verley reduction.[1] This method is widely used because of its compatibility with many different types of functional group, its selectivity for carbonyl reduction, and the low cost of 2-propanol.[2] However, the disadvantages of this reaction are the need for strong acidic treatment to neutralize the alkoxide salt as well as a tedious work-up.

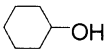
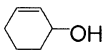
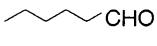
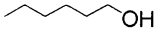
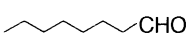
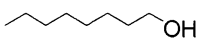
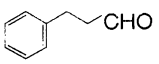
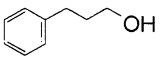
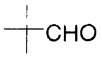
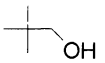
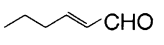
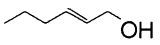
As a method avoiding these disadvantages, we reported the reduction of aldehydes and ketones over hydrous zirconium oxide in previous papers.[3-5] However, in most cases, sterically hindered ketones did not react to give the corresponding alcohols in high yields.

In this paper, we describe the reduction of aldehydes and ketones with 2-propanol using a silica-supported zirconium catalyst. This catalyst was prepared as follows: Silica gel (25 g) was put into a 2-propanol solution (500 cm^3) containing zirconium tetra-*i*-propoxide (0.1 mol/m^3), and the mixture was heated under gentle reflux for 5 h. The resulting product was filtered, and washed with 2-propanol and hexane, finally dried *in vacuo* at room temperature. About thirty one grams of the catalyst were obtained.

A typical procedure for the reduction is as follows: Silica-supported zirconium catalyst (0.1 g) was put into a 10 cm^3 round bottomed flask equipped with a reflux condenser together with acetophenone (0.5 mmol), 2-propanol (2 cm^3), and a n-tridecane (0.05 mmol) as an internal standard. The contents were heated under gentle reflux. Portions of the reaction mixture were

removed at certain times after refluxing, and the concentrated products were analyzed by GLC (a capillary column PEG 20 M 30 m). The identification of the products was made by comparison of retention times in gas chromatography with those of authentic samples.

Table 1. Reduction of Ketones or Aldehydes with 2-Propanol over Silica-Supported Zirconium Catalyst[a)]

Entry	Reductant	Product	Conversion /% (h) [c)]	Selectivity /%	k[d)] /10^{-5} s^{-1}
1			87(1.5)	100	14.2
2			44(8)	100	0.882
3			56(24)	100	0.867
4			86(6)	100	3.67
5			51(8)	84	0.811
6 b)			57(2)	98	4.13
7 b)			67(6)	97	1.65
8 b)			96(6)	72	6.38
9 b)			56(4)	100	1.95
10			94(6)	94	5.36

a) Reductant (0.5 mmol), catalyst (0.1 g), in 2 cm^3 of 2-propanol under reflux.

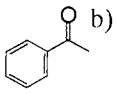
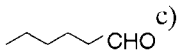
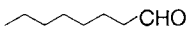
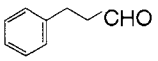
b) Reductant (1.25 mmol), catalyst (0.05 g), in 5 cm^3 of 2-propanol under reflux.

c) Reaction time. d) Rate constant.

The reductions of several aldehydes and ketones with 2-propanol were carried out over silica supported zirconium catalyst, and the results are listed in Table 1. In each reaction, the corresponding alcohol was obtained in a high yield.

In order to compare the silica-supported zirconium catalyst with the hydrous zirconium oxide and zirconium alkoxide, the reductions of acetophenone, hexanal, octanal, and phenylacetaldehyde with 2-propanol were carried out over these catalysts. These results are shown in Table 2. The reduction of sterically hindered ketones, such as acetophenone, was not efficient when hydrous zirconium oxide was used as catayst but the efficiency greatly improved over silica-supported zirconium catalyst. Diisopropylacetal was yielded at early stage in the

Table 2. Comparison of the Catalytic Activity of Several Catalysts[a)]

Reductant	Catalyst		Conversion	Selectivity /%		
		/g	/%	Alcohol	Acetal	Aldol
 b)	Hydrous Zirconium Oxide	0.1	17	100	0	0
	Silica-Supported Zirconium Catalyst	0.1	86	100	0	0
	Zirconium tetra-*i*-propoxide	0.1	68	100	0	0
	Silica gel	0.1	0	-	-	-
 c)	Hydrous Zirconium Oxide	0.15	79	39	45	10
	Silica-Supported Zirconium Catalyst	0.05	57	98	0	2
	Zirconium tetra-*i*-propoxide	0.05	57	61	0	39
	Silica gel	0.15	0	-	-	-
	Hydrous Zirconium Oxide	0.05	79	24	59	5
	Silica-Supported Zirconium Catalyst	0.05	67	97	0	1
	Zirconium tetra-*i*-propoxide	0.05	51	77	0	11
	Hydrous Zirconium Oxide	0.05	91	40	49	5
	Silica-Supported Zirconium Catalyst	0.05	96	72	0	14
	Zirconium tetra-*i*-propoxide	0.05	97	48	0	26

a) Reductant 1.25 mmol, 2-propanol 5 cm^3, reflux for 6 h. b) Acetophenone 0.5 mmol, 2-propanol 2 cm^3. c) Reflux for 2 h.

reaction over hydrous zirconium oxide in the cases of hexanal, octanal, and phenylacetaldehyde. The aldol condensation competed with the reduction in the reaction with zirconium tetra-*i*-propoxide. On the other hand, over silica-supported zirconium catalyst, the acetalization did not occur, and the aldol condensation was inhibited. The silica gel of the carrier was inert. In each case, the silica-supported zirconium catalyst exhibited the highest catalytic activity.

The specific surface area of the silica-supported zirconium catalyst was measured by means of BEL JAPAN micrometrics BELSORP28, and listed in Table 3. The surface area of silica-supported zirconium catalyst was larger than that of hydrous zirconium oxide. Although it is feasible that the difference in surface area is one of the causes of the difference in catalytic activity, we conjecture that the active sites of silica-supported zirconium catalyst are different from those of hydrous zirconium catalyst from the difference in the selectivity.

Table 3. Specific Surface Areas of Hydrous Zirconium Oxide and Silica-Supported Zirconium Catalyst

Catalyst	Specific surface area /m^2 g^{-1}
Hydrous Zirconium Oxide	207
Silica-Supported Zirconium Catalyst	270
Silica gel	287

It is concluded that the silica-supported zirconium catalyst is superior to hydrous zirconium oxide or zirconium tetra-*i*-propoxide for the reduction of aldehydes and ketones with 2-propanol.

References

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