MEERWEIN-PONNDORF REDUCTION OF BENZALDEHYDE OVER METAL OXIDES

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The Meerwein–Ponndorf reduction of benzaldehyde by 2-propanol in the liquid phase was studied in the presence of metal oxides as the catalysts. Except for alumina, all the eight metal oxides tested were found to be nearly inactive. The activity of the alumina–magnesia catalysts decreased with the decreasing alumina content. No correlation was observed between the basic properties of the alumina–magnesia catalysts and their activity in the reduction of benzaldehyde.

The Meerwein–Ponndorf reduction of aldehydes and ketones is known to be catalysed in solution by metal alkoxides[1]. Aluminium 2-propoxide is generally used in the synthetic practice. The mechanism of this reaction involving a cyclic electron transfer was suggested first by Woodward[1]. Recently, alumina has been reported to exhibit catalytic activity in this reaction[2,3]. The surface Al^{3+} ions presumably act as the active sites and thus an analogous mechanism can be considered.

During the adsorption of alcohols on surfaces of some metal oxides, molecular species possessing an alkoxide structure were observed by means of IR spectroscopy[4,5]. These surface alkoxides are supposed to play an important role in the dehydrogenation of secondary alcohols over metal oxides[6]. For this reason, it can be expected that metal oxides exhibiting catalytic activity in the dehydrogenation of alcohols may also be active as catalysts in the Meerwein–Ponndorf reduction.

The aim of this work was to test the catalytic activity of a series of metal oxides and of alumina–magnesia catalysts that have been suggested for the heterogeneous catalytic aldol condensation[7,8]. During the condensation reaction, side reactions possessing characteristics of the Meerwein–Ponndorf reduction could occur. The reduction of benzaldehyde by 2-propanol was chosen as the test reaction.

EXPERIMENTAL

Aluminium oxide, chromium(III) oxide and iron(III) oxide as well as the alumina–magnesia catalysts were prepared by adding dilute ammonium hydroxide to the corresponding metal nitrate solutions. The precipitated metal hydroxides were decanted in distilled water, filtered off, dried at 120°C and calcined at 500°C for 4 h. Other metal oxides were commercial products (Lachema Brno; Merck-Schuchardt, FRG). Also these metal oxides were calcined at 500°C before use. Fractions with a particle diameter of 30—70 μm were used throughout all measurements. The specific surfaces of metal oxides were determined by the BET method (BaO 2·5 m^2 .

. g^{-1}; ZnO 0·5 m^2 g^{-1}; Fe_2O_3 65 m^2 g^{-1}; Cr_2O_3 60 m^2 g^{-1}; TiO_2 10 m^2 g^{-1}; CeO_2 15·5 m^2 . . g^{-1}; La_2O_3 3·0 m^2 g^{-1}; ZrO_2 0·8 m^2 g^{-1}). Specific surfaces of alumina and alumina–magnesia catalysts are listed in Table I. Benzaldehyde was carefully purified by rectification in an atmosphere of nitrogen; all other chemicals were of the analytical purity grade. Testing of the catalytic activity of metal oxides and the measurement of kinetics of the reduction reaction were conducted in a stainless-steel, magnetically stirred microreactor[9] allowing experiments to be carried out under an elevated pressure (0·3 MPa of nitrogen) at 120°C. The reactants were diluted with toluene; identical initial concentrations (0·1 mol l^{-1}) of benzaldehyde and 2-propanol were used. The volume of the reaction mixture was 8 ml and the weighed amount of the catalyst was 0·5 g throughout all the test experiments. During the activity testing, samples were taken after 0·5, 1 and 2 h. The gas-chromatographic analyses of samples were carried out at 150°C using a 2 m column packed with 7% Silicone OV-17 on Gas Chrom Q. Hexadecane was used as the internal standard.

RESULTS AND DISCUSSION

Except for alumina, all the eight metal oxides tested were found to be nearly inactive under the given conditions of the reduction reaction. The rate of the benzaldehyde reduction over alumina and alumina–magnesia catalysts was quite consistent with the second-order kinetics. The rate constants obtained by linearisation of dependences of the substrate conversions upon time were expressed in the form of relative specific activities. In Table I, the resulting values are compared with the relative specific activities inherent to the same catalysts in the decomposition of diacetone alcohol[10]. The decomposition of diacetone alcohol is known to be a base catalysed reaction

TABLE I

Relative Specific Reactivities k_{rel} of Alumina–Magnesia Catalysts in Decomposition of Diacetone Alcohol (A) and Reduction of Benzaldehyde (B)

Content of Al^{3+} % mol.[a]	Specific surface m^2 g^{-1}	k_{rel} A[b]	k_{rel} B
100	220	1·0	1·0
94	220	6·1	0·95
85	220	18·1	0·91
75	210	54·2	0·74
60	140	36·2	0·41
0	20	14·9	0·01

[a] % Mol. = $100n_{Al}/(n_{Al} + n_{Mg})$ where n_{Al} and n_{Mg} is the number of Al^{3+} and Mg^{2+} ions, respectively, in a weight unit of the catalyst; [b] reaction conditions for the decomposition of diacetone alcohol are given in ref.[10].

and that is why this reaction has been suggested for testing the catalytic activity of basic sites[11,12].

From Table I it follows that in the benzaldehyde reduction by 2-propanol the catalytic activity of the alumina-magnesia catalysts rises with the increasing alumina content; on the contrary, in the base catalysed decomposition of diacetone alcohol the activity of the same catalysts goes through a maximum. This fact clearly demonstrates the specific role of aluminium oxide in the heterogeneous catalytic Meerwein–Ponndorf reduction. It is further clear that the catalytic activity of the alumina-magnesia catalysts is not affected by the overall surface basicity. The finding that alumina functions as a specific catalyst in the heterogeneous catalytic Meerwein–Ponndorf reduction merits a detailed explanation; the same concerns the importance of the pretreatment of alumina[2,3] allowing high activity to be achieved under mild conditions. An analogy was thus offered to the homogeneous catalytic reduction of aldehydes and ketones[1] in which various metal alkoxides, such as tin, titanium, zirconium, antimony(V) and iron(III) ethoxide, proved to have catalytic activity. However, also here the aluminium alkoxides were much more active[1].

Alumina is the principal component of catalysts suggested for the base catalysed aldol condensation reactions[7,8]. Lowering the alumina content in these catalysts suppresses the potential side reactions, such as the Meerwein–Ponndorf reduction, which might occur between the aldol and the starting aldehyde or ketone during the condensation reaction.

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