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DEPOLYMERISATION OF PARALDEHYDE CATALYSED BY SOME SILICA AND ALUMINA BASED BINARY OXIDE CATALYSTS

By

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Abstract

Depolymerisation of paraldehyde in benzene catalysed by some silica and alumina based binary oxides has been studied. It is seen here that in all the cases, the acidity at pKa$\leqslant -3.0$ best correlates with catalytic activity (first order rate constant K) and is catalytically active for depolymerisation of paraldehyde. MoO_3, WO_3 and V_2O_5 supported on silica and alumina have acid sites at pKa$\leqslant -3.0$, hence these are catalytically active. Silica and alumina based MgO, BeO and ThO_2 have very little acid strength at pKa$\leqslant -3.0$ but have a number of weak acid centres at pKa$\leqslant +3.3$, and these relatively weak acid sites have been found to be catalytically inactive. The observed rate constant values in case of silica supported catalysts are greater than those of the alumina supported catalysts. It is further observed that the rate of depolymerisation of paraldehyde is directly proportional to the acidity of the catalysts at pKa$\leqslant -3.0$. The energies of activation have been found to be inversely proportional to the acidity of the catalysts.

Introduction

The surface acidity and acid strength distribution of silica and alumina supported binary oxide catalysts has already been reported by us.[1] In the present work an attempt has been made to study the catalytic property of these solid acids using them as catalysts in an acid catalysed reaction like the depolymerisation of paraldehyde in benzene. KAWAGUCHI and HASEGAWA[2] studied the acidic property and catalytic activity of zinc, cadmium and magnesium sulphates for depolymerisation of paraldehyde. Recently, SHIBATA and coworkers[3] have studied the acid property and catalytic activity of silica gel treated with ammonium salts. The catalytic activity of the treated and untreated silica gels for the depolymerisation of paraldehyde was studied in relation to the acidic property of the catalysts. A survey of literature reveals that very little work has been done on the depolymerisa-

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tion of paraldehyde by heterogeneous acids excepting the work on metal sulphates[4,5] and silica gel.[3]

In the present paper, depolymerisation of paraldehyde catalysed by some silica and alumina based binary oxides has been reported. The rate constants and energies of activation have been calculated and also the work has been extended to correlate the acidity of the catalyst, rate constant and energy of activation.

Experimental

Materials

Paraldehyde and Analar quality benzene were dried over sodium, distilled and used in this investigation.

Preparation of catalysts

The mixed oxides were prepared from Analar quality chemicals, by the precipitation and the impregnation technique. The mixtures of the precipitated hydroxides or the impregnated oxides were digested for several hours and then filtered, washed thoroughly and dried at 120°C for 20 hours. The samples thus obtained were powdered and only such samples collected between 100 and 150 mesh sieves were used. The powders were subjected

TABLE 1 Starting materials and method of preparation of binary metal oxides

Metal oxides	Starting materials	Preparation technique	Colour of the catalysts
SiO_2 gel	$Na_2SiO_3 \cdot 5H_2O$	Hydrolysis of sodium silicate by 10%HCl solution.	White
Al_2O_3	$Al(NO_3)_3 \cdot 9H_2O$	Precipitation as hydroxide by ammonia solution.	White
SiO_2-MoO_3	$SiO_2, (NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Impregnation	Light yellow
SiO_2-WO_3	SiO_2, H_2WO_4	Impregnation	-do-
SiO_2-V_2O_5	SiO_2, NH_4VO_3	Impregnation	Yellowish orange
SiO_2-MgO	$SiO_2, MgSO_4 \cdot 7H_2O$	Precipitation	White
SiO_2-ThO_2	$SiO_2, Th(NO_3)_4 \cdot 6H_2O$	Precipitation	White
SiO_2-BeO	$SiO_2, BeSO_4 \cdot 4H_2O$	Precipitation	White
Al_2O_3-MoO_3	$Al_2O_3, (NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Impregnation	Light yellow
Al_2O_3-WO_3	Al_2O_3, H_2WO_4	Impregnation	Light yellow
Al_2O_3-V_2O_5	Al_2O_3, NH_4VO_3	Impregnation	Yellowish orange
Al_2O_3-MgO	$Al_2O_3, MgSO_4 \cdot 7H_2O$	Precipitation	White
Al_2O_3-BeO	$Al_2O_3, BeSO_4 \cdot 4H_2O$	Precipitation	White
Al_2O_3-ThO_2	$Al_2O_3, Th(NO_3)_4 \cdot 6H_2O$	Precipitation	White

to heat treatment at desired temperatures by heating them for 6 hours in an electrical muffle furnace with temperature control arrangement. The samples after heat treatment were cooled in a desiccator and preserved in covered glass tubes under vacuum. The details of the starting materials used, the technique employed and the colours of the catalyst are given in Table 1.

Measurement of acidity and acid strength

The acidity (the number of acid sites) having an acid strength H_0 equal to or lower than the pKa value of the indicator used were determined by using the amine titration method developed by JOHNSON[6].

Kinetic studies

The technique adopted was essentially the same as described by the earlier authors[4,5]. The reaction was studied at two temperatures, 10°C and 20°C by analysing the acetaldehyde formed by the bisulphite method[7].

Precautions were taken to study these reactions in the absence of moisture, since trace quantities of moisture could greatly retard or even stop the reaction altogether, especially when very effective catalysts were being used in low concentrations. All the catalysts were re-activated before use by heating them at the desired temperatures, they were cooled in a desiccator and were immediately used in the reaction in view of the foregoing criterion.

Results and Discussion

It has been observed that the rate of depolymerisation of paraldehyde catalysed by metal sulphates[5] is first order. Similarly with silica and alumina based binary oxides the rate was found to be of the first order with respect to paraldehyde concentration, as straight line graphs were obtained for the $\log(a-x)$ against time 't' plots.

The results of depolymerisation of paraldehyde catalysed by silica and alumina based binary oxides are given in Table 2. A reference to the rate constant values 'K' indicates that there exists a correlation between acidity and catalytic activity. The acid sites having acid strength equal to or stronger than $pKa = -3.0$ best correlate with catalytic activity and are catalytically active for depolymerisation of paraldehyde.

In case of molybdenum oxide, tungstic oxide, and vanadium pentoxide supported on silica and alumina, it is seen that they have acid strength of $pKa \leqslant -3.0$; hence these are catalytically active for depolymerisation of paraldehyde. Silica and alumina based MgO, BeO and ThO_2 mixed oxides

TABLE 2 Depolymerisation of paraldehyde catalysed by some binary metal oxides.

Concentration of Paraldehyde: 0.05 M. Amount of Catalyst: 1 g.

Catalyst		Temp. of heat treatment °C	Acidity m. moles/g at pKa $\leqslant -3.0$	$K_1 \times 10^3 \text{min}^{-1}$ at 10°C	$K_2 \times 10^3 \text{min}^{-1}$ at 20°C	Energy of activation Calories per mole
SiO_2-MoO_3	(81%-19%)	450	0.500	38.450	98.420	18540
SiO_2-WO_3	(86%-14%)	400	0.440	32.780	94.520	20840
SiO_2-V_2O_5	(85%-15%)	450	0.380	20.038	70.120	24550
SiO_2-MgO	(72%-28%)	500	0.062	—	—	—
SiO_2-ThO_2	(85%-15%)	400	0.048	—	—	—
SiO_2-BeO	(78%-22%)	450	0.032	—	—	—
Al_2O_3-MoO_3	(74%-26%)	450	0.450	34.860	95.690	19860
Al_2O_3-WO_3	(84%-16%)	400	0.400	24.080	78.080	23280
Al_2O_3-V_2O_5	(83%-17%)	450	0.340	16.280	65.420	27350
Al_2O_3-MgO	(70%-30%)	500	—	—	—	—
Al_2O_3-BeO	(75%-25%)	450	—	—	—	—
Al_2O_3-ThO_2	(83%-17%)	400	—	—	—	—

have very little acid strength at $pKa = -3.0$ and have a number of acid centres weaker than $pKa = +3.3$[1]. Therefore, those relatively weak acid sites are considered to be catalytically inactive. The catalysts were poisoned with dicinnamal acetone ($pKa = -3.0$) and then used as catalysts in the depolymerisation of paraldehyde. No depolymerisation took place in the presence of these poisoned catalysts. This confirms our earlier observation[1] that acid centres of $pKa \leqslant -3.0$ alone are catalytically active for depolymerisation of paraldehyde in accordance with the earlier studies[5]. Again the present experimental evidence shows that the reaction of depolymerisation of paraldehyde is selective for solid acids and selectivity of catalysts plays an important role in every reaction.

A reference to the rate constant values of all these catalysts shows that the observed rate constant values in case of silica supported catalysts are greater than those of the alumina supported catalysts, obviously for the reason that the silica supported catalysts are more acidic in acid strength distribution than the corresponding alumina supported catalysts. In Fig. 1 are given the plots of the rate constant K againsnt the acidity measured at $pKa \leqslant -3.0$ for all the mixed oxide catalysts for depolymerisation of paraldehyde in benzene solution. These plots give a straight line indicating that the rate of depolymerisation of paraldehyde is directly proportional to the acidity of the catalysts at $pKa \leqslant -3.0$. A similar linear dependence of

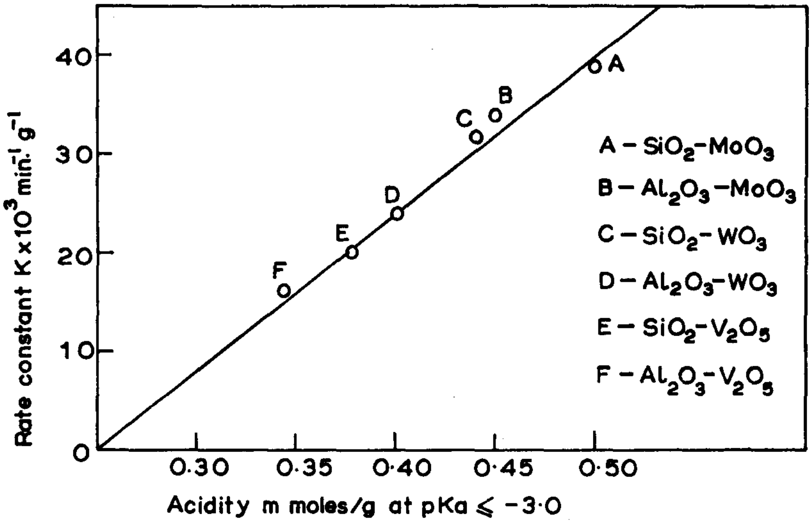

Fig. 1. The dependence of catalytic activity for depolymerisation of paraldehyde on the number of acidic centres on SiO_2 and Al_2O_3 supported catalysts.

activity and acid amount is observed in case of the decomposition of ethyl and isopropyl alcohols on SiO_2-ZrO_2 catalyst which has an acidity with acid strength $H_0 \leqslant -8.2$[8]. Similarly WATANABE *et al.*[9] have shown that the propylene polymerisation rates at 100°C are proportional to the amount of the acid on nickel sulphate at $H_0 \leqslant +1.5$.

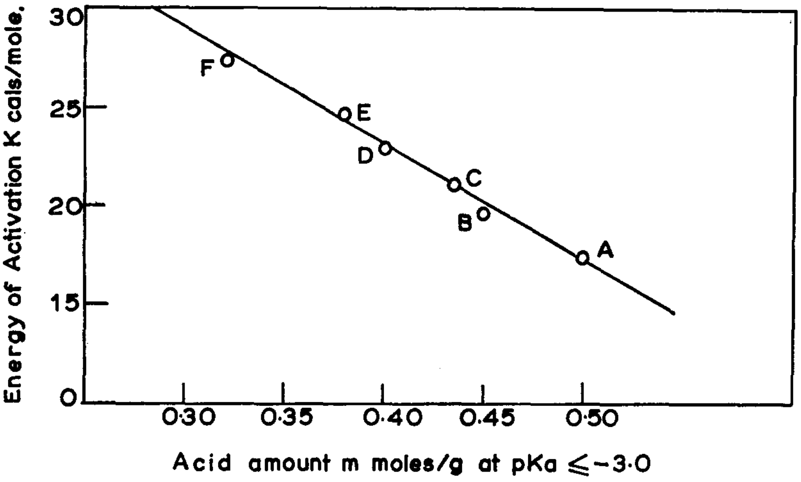

Fig. 2. Energy of activation versus number of acidic centres.

It is observed from Table 2 that the energy of activation is inversely proportional to the acidity of the mixed oxides. Figure 2 gives the plot of energy of activation E against the acidity measured at $pKa \leqslant -3.0$ for all catalysts. These plots give a straight line suggesting that the energy of activation is inversely proportional to the acidity of the catalysts. A similar relationship was obtained by FISHER *et al.*[10] in the study of decomposition of formic acid over silica-alumina catalyst. Energy of activation was inversely proportional to the acid amount as determined by amine titration using *p*-dimethylamino-azobenzene ($pKa = +3.3$) as indicator.

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References

1) S. P. WALVEKAR and A. B. HALGERI, Paper presented to the Convention of Chemists (Bombay), Abstract No. P-71-33 (1971).
2) T. KAWAGUCHI and S. HASEGAWA, Tokyo Gakugei Daigaku Kiyo, **21**, 63 (1969).
3) K. SHIBATA, T. KIYOURA and Y. HAYASHI, This journal, **19**, 29 (1971).
4) K. TANABE and A. ARAMATA, *ibid.*, **8**, 43 (1960).
5) K. TANABE and C. MUGIYA, *ibid.*, **14**, 101 (1966).
6) O. JOHNSON, J. Phys. Chem., **59**, 827 (1955).
7) I. E. FRIEDMANN, M. COTONIO and G. A. SCHAFFER, J. Biol. Chem., **73**, 342 (1927).
8) V. A. DZISKO, Proc. 3rd Intern. Congr. Catalysis, **1**, 422 (1964).
9) Y. WATANABE and K. TANABE, This journal, **12**, 56 (1964).
10) J. B. FISHER and F. SEBBA, Actes Congr. Intern. Catalyse, 2 Paris I, No. 29 (1960).