The Catalytic Activity of Some Mixed Oxides for Depolymerization of Paraldehyde

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Depolymerization of paraldehyde in benzene catalyzed by SiO_2–ZrO_2, SiO_2–TiO_2, Al_2O_3–ZrO_2, TiO_2–ZrO_2, Al_2O_3–TiO_2 (calcined at various temperatures) has been studied. It is observed that in all the cases the catalytic activity (first order rate constant, k) exhibited a maximum against the temperature of heat treatment of the catalyst. The acid sites at $pK_a \leqq -3.0$ correlate best with catalytic activity for depolymerization of paraldehyde.

It has been observed previously that mixed oxides show fairly strong acidic property on their surface and that the acidity changes remarkably on subjecting the samples to heat treatment.[1] In the present work an attempt has been made to study the depolymerization of paraldehyde in presence of some of these solid acids.

Depolymerization of paraldehyde proceeds in presence of mineral acids and carboxylic acids in nonaqueous media and can be followed by an accurate and easy method of analysis.[2,3] Depolymerization of paraldehyde in presence of solid acids like metal sulphates has been reported by Tanabe *et al.*[4,5] It was considered of interest to study this reaction in presence of mixed oxide catalysts for which no data exists. The rate constants have been correlated with the acidity of the catalysts.

Experimental

Materials. Paraldehyde and pure quality benzene were dried over sodium, distilled and used in this work. All other chemicals were extra pure grade reagents and were used as received.

Preparation of Catalysts. Silica gel was prepared by hydrolysis of dilute sodium silicate solution with 10% HCl.[6] Alumina was prepared from $Al(NO_3)_3 \cdot 9H_2O$ by precipitating $Al(OH)_3$ using ammonia water.[7] The precipitates obtained in the above two cases were heated for an hour and then filtered off and washed with distilled water till it was free from chloride and nitrate ions respectively. Finally the precipitates were dried at 100 °C for 20 hr and preserved. The binary oxides were prepared as follows.

1) Silica–titania: 85 g of SiO_2 gel prepared as above was suspended in 500 ml of distilled water and 18 ml of $TiCl_4$ was added. The mixture was boiled on a water bath for 1 hr and 50 ml of 28% ammonia water was added drop by drop to form the precipitate of titanic acid (H_4TiO_4). The final pH of the solution was near about 7.5. The mixture was heated for about an hour with continuous stirring and then the precipitate was filtered off and washed thoroughly with distilled water till it was free from chloride ions. The precipitate was dried at 100 °C for 20 hr and preserved. The weight % of TiO_2 in the mixture was calculated to be 15.

2) Silica–zirconia: 89 g of silica was suspended in 250 ml of distilled water and a solution of 26.9 g of $Zr(SO_4)_2 \cdot H_2O$ in 500 ml of water was added and to this mixture 46 ml of 28% ammonia was added dropwise with vigorous stirring. The mixture was heated for 2 hr. The final pH of the solution was 7.6. The precipitate was filtered off, washed with water until no sulfate ions were detected in the washings. The precipitate was dried as in 1). The weight % of ZrO_2 in the mixture was calculated to be 11.

3) Alumina–zirconia: This catalyst was prepared by the precipitation technique described above. 80 g of alumina prepared as above was suspended in 250 ml of distilled water and a solution of 48.9 g of $Zr(SO_4)_2 \cdot H_2O$ in 500 ml of water was added. The mixture was boiled on a water bath for 1 hr and 83 ml of 28% ammonia water was added dropwise until the pH of the solution was near about 7.2. The precipitate was washed and dried as in 1). The weight % of ZrO_2 in the mixture was calculated to be 20.

4) Titania–zirconia: The coprecipitated mixture of TiO_2–ZrO_2 was prepared as follows. 19.6 g of $Zr(SO_4)_2 \cdot H_2O$ was dissolved in 500 ml of distilled water and 20.5 ml of $TiCl_4$ was added to this solution. The solution was heated on a water bath for 2 hr and 322 ml of 28% ammonia water was added slowly with vigorous stirring to form a coprecipitate of the mixture. The final pH of the solution was near about 7.5. The precipitate was heated for 1 hr and was filtered off and washed thoroughly with distilled water until no chloride and sulfate ions were detected in the washings. The precipitate was dried at 120 °C for 20 hr. The weight % of ZrO_2 in the mixture was calculated to be 32.

5) Alumina–titania: 48.5 g of $AlCl_3 \cdot 6H_2O$ was dissolved in 360 ml of water and 7.8 ml of $TiCl_4$ was added. The solution was heated on a water bath for 1 hr and 290 ml of 28% ammonia water was added to the mixture in lots of 50 ml at a time. The last lot of ammonia water was added dropwise with continuous stirring until the pH of the solution was around 7.2. The mixture was boiled to complete the coprecipitation. The precipitate was washed and dried as in 4). The weight % of TiO_2 in the mixture was calculated to be 26.

The samples thus obtained in the above cases were powdered and only such samples collected between 100 and 150 mesh sieves were used. The powders were subjected to heat treatment in the temperature range of 120 to 1050 °C by heating for 6 hr 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.

Measurement of Surface Acidity and Acid Strength. The acidity (the number of acid sites) having an acid strength H_0 equal to or lower than the pK_a value of the indicator used were determined by using the amine titration method.[8,9]

Kinetic Studies. The procedure adopted was essentially the same as described by the earlier authors.[4,5] The reaction was studied at 25 °C by analyzing the acetaldehyde formed at various intervals of time by the bisulfite method.[10] Tests showed that none of the catalysts used, interfered with the determination of acetaldehyde by the above method.

Sufficient precautions were taken to study these reactions

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in the absence of moisture, since even traces of moisture could greatly retard or even stop the reaction altogether, especially when very effective catalysts were being used in low concentrations. Since the reaction is heterogeneous and the rate depends upon the condition of the experiment, the experiments were carried out under similar conditions throughout this investigation.

Results and Discussion

It has been observed that the rate of depolymerization of paraldehyde catalyzed by metal sulphates[4)] is of the first order and similarly with mixed 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 the depolymerization of paraldehyde catalyzed by SiO_2–ZrO_2, SiO_2–TiO_2, Al_2O_3–ZrO_2, TiO_2–ZrO_2, and Al_2O_3–TiO_2 are presented in Tables 1 and 2. It is seen from these tables that the acidity at $pK_a \leqq -3.0$, increases with increasing temperature of heat treatment and attains a maximum and then decreases with further rise in temperature. A reference to the rate constant value, k, in these tables indicates that there exists a correlation between acidity and the catalytic activity. When the catalyst was poisoned by dicinnamal acetone ($pK_a = -3.0$), it could not depolymerize paraldehyde. Therefore acid sites having an acid strength of $pK_a \leqq -3.0$ correlate best with catalytic activity for depolymerization of paraldehyde. This conclusion is in agreement with the one obtained by us in case of some silica and alumina based binary oxide catalysts[11–13)] and also with the one obtained by other workers with metal sulphates.[5)] The dependence of catalytic activity on the temperature of heat treatment of catalyst is shown in Tables 1 and 2. It is observed that in all cases the catalytic activity (first order rate constant, k) exhibited a maximum against the temperature of heat treatment of the catalyst. The decrease in the catalytic activity of these mixed oxides after heat treatment at elevated temperatures is due to a decrease in the number of acid sites and acid strength rather than to a decrease in their surface area.[14)]

It is interesting to note from the results presented in Tables 1 and 2 that acidity of 0.05 mmol/g or less at $pK_a \leqq -3.0$ is not effective for catalyzing this reaction. In case of Al_2O_3–ZrO_2 samples heat-treated at 260 and 800 °C have an acid value of 0.02 and 0.04 mmol/g respectively but these show no catalytic activity. Similarly in case of TiO_2–ZrO_2 and Al_2O_3–TiO_2 samples calcined at 120 and 220 °C have an acid value of 0.03 mmol/g but have no catalytic activity. It is further observed in case of SiO_2–TiO_2 that samples heat-treated at 120, 800, and 1000 °C have a number of acid sites having an acid strength of $pK_a \leqq +3.3$, but these samples show no catalytic activity. Similarly in case of Al_2O_3–TiO_2, TiO_2–ZrO_2 samples heat-treated at 120 and 800 °C have a number of acid sites having an acid strength of $pK_a \leqq +3.3$, but have no catalytic activity. A similar observation is made in case of Al_2O_3–ZrO_2 and Al_2O_3–TiO_2 for samples heat-treated at 260 and 220 °C respectively. Therefore even those relatively few acid sites at $pK_a \leqq -3.0$ (0.05 mmol/g or less) and those at $pK_a \leqq +3.3$ are catalytically inactive.

The reason for the ineffectiveness of acid sites with weaker acid strength than $pK_a = -3.0$ is probably to be found in the fact that no paraldehyde molecule will give a conjugated acid at any of these weaker sites, since the pK_a value of paraldehyde is about -3.3.[15)] Similar correlations between activity and acid amount over limited ranges of acid strength were evident in both the hydration of propylene,[16)] polymerization of isobutyl vinyl ether[17)] catalyzed by various sulphates, and also hydrolysis of aliphatic esters catalyzed by

TABLE 1. ACIDIC PROPERTY OF MIXED OXIDE CATALYSTS AND DEPOLYMERIZATION OF PARALDEHYDE AT 25 °C

Catalyst and paraldehyde concentration	Calcination temperature °C	Acid amount, mmol/g		Rate constant ($k\times10^3$ $min^{-1}\cdot g^{-1}$)
		$pK_a \leqq +3.3$	$pK_a \leqq -3.0$	
SiO_2–ZrO_2 Paraldehyde concn=0.073 M	110	0.18	0.08	4.02
	240	0.28	0.12	9.86
	320	0.39	0.16	18.48
	440	0.45	0.20	26.32
	500	0.52	0.30	42.50
	600	0.48	0.26	35.20
	710	0.40	0.24	32.50
	820	0.32	0.20	27.50
	1000	0.20	0.09	7.20
SiO_2–TiO_2 Paraldehyde concn=0.063 M	120	0.20	—	—
	260	0.31	0.12	8.45
	380	0.34	0.14	10.06
	440	0.37	0.16	12.34
	500	0.38	0.17	18.86
	550	0.42	0.20	26.52
	600	0.39	0.16	19.07
	700	0.37	0.08	8.42
	800	0.32	—	—
	1000	0.24	—	—

Table 2. Acidic property of mixed oxide catalysts and depolymerization of paraldehyde at 25 °C

Catalyst and paraldehyde concentration	Calcination temperature °C	Acid amount, mmol/g		Rate constant ($k\times 10^3$ $\mathrm{min}^{-1}\cdot\mathrm{g}^{-1}$)
		$\mathrm{p}K_a\leqq+3.3$	$\mathrm{p}K_a\leqq-3.0$	
Al_2O_3–ZrO_2 Paraldehyde concn=0.093 M	120	0.12	—	—
	260	0.20	0.02	—
	380	0.33	0.08	8.26
	500	0.38	0.16	21.68
	610	0.31	0.12	17.92
	710	0.26	0.08	9.84
	800	0.14	0.04	—
	1000	0.04	—	—
TiO_2–ZrO_2 Paraldehyde concn=0.080 M	120	0.11	0.03	—
	220	0.18	0.09	6.45
	360	0.25	0.12	9.86
	440	0.30	0.15	18.82
	520	0.24	0.13	14.89
	600	0.18	0.09	10.08
	700	0.08	0.06	4.68
	800	—	—	—
Al_2O_3–TiO_2 Paraldehyde concn=0.096 M	120	0.18	—	—
	220	0.22	0.03	—
	320	0.26	0.06	4.60
	420	0.32	0.10	12.66
	500	0.30	0.07	7.34
	600	0.24	0.02	—
	700	0.18	0.01	—
	800	0.10	—	—

mixed oxides.[18)] In these cases catalytic activities were found to be proportional to the activities at $-3.0\leqq H_0\leqq+1.5$, at $-5.6\leqq H_0\leqq-3.0$ and at $H_0\leqq-3.0$ respectively.[16–18)]

These observations show that every reaction requires acid sites of a particular acid strength for a particular reaction and hence it can be concluded that acidity and acid strength play an important role in every acid catalyzed reaction.

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