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THE MECHANISM OF DEPOLYMERIZATION OF
PARALDEHYDE CATALYZED
BY SOME MIXED OXIDE CATALYSTS

By

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Abstract

The catalytic depolymerization of paraldehyde by $\text{SiO}_2\text{-ZrO}_2$, $\text{ZrO}_2\text{-TiO}_2$, $\text{Al}_2\text{O}_3\text{-ZrO}_2$, $\text{TiO}_2\text{-ZrO}_2$, $\text{Al}_2\text{O}_3\text{-TiO}_2$ catalysts and also by MoO_3 , WO_3 , V_2O_5 oxides supported on SiO_2 and Al_2O_3 proceeds according to enzyme kinetics. The kinetic data with the above mixed oxides fit well the MICHAELIS-MENTEN's equation and hence the mechanism is considered similar to enzymatic reaction.

Introduction

Depolymerization of paraldehyde catalyzed by some mixed oxides has been investigated by us along with the acidic properties of the mixed oxides¹⁻⁴. TANABE and coworkers^{5,6} have studied extensively the mechanism of depolymerization of paraldehyde catalyzed by metal sulfates. The reaction was shown to follow enzyme kinetics and was entirely different from that of usual acid catalyzed reactions^{7,8}. The object of the present work is to investigate whether the mixed oxides behave in the same manner as the metal sulfates.

Experimental

Materials:

Paraldehyde and Analar quality benzene were dried over sodium, distilled and used in the present work.

Preparation of catalysts:

The mixed oxides were prepared from Analar quality chemicals, by the coprecipitation, precipitation and impregnation technique as described earlier^{1,4,9}.

Measurement of surface acidity:

For the quantitative measurement of surface acidity and acid strength the

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amine titration method developed by JOHNSON¹⁰) was used.

Kinetic studies:

The technique adopted was that described by earlier workers^{5,6}). The reaction was studied at two temperatures *i.e.*, 10°C and 20°C by analyzing the acetaldehyde formed by the bisulfite method¹¹).

Results and Discussion

It has been observed earlier in case of mixed oxides that the active sites having an acid strength of $pK_a \leq -3.0$ are catalytically active for the depolymerization of paraldehyde¹⁻⁴). The depolymerization of paraldehyde catalyzed by metal sulfates was shown to follow enzyme kinetics⁵). A similar observation was made in case of mixed oxides also and has been discussed in the light of the following experimental evidence.

Michaelis-Menten's plot:

In Fig. 1, the amount of acetaldehyde formed per unit milliequivalent of acid sites having a $pK_a \leq -3.0$ is plotted against time '*t*' over the range of various

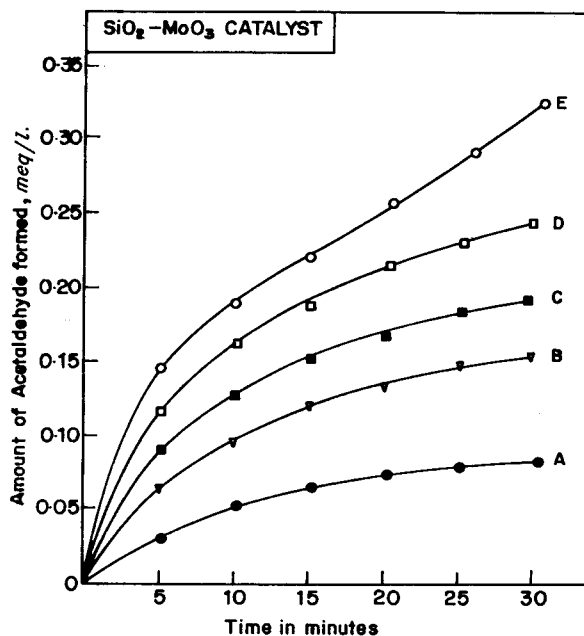


Fig. 1. Depolymerization of paraldehyde at 20°C. Initial concentration of paraldehyde: A—0.018 M, B—0.038 M, C—0.076 M, D—0.146 M, E—0.219 M.

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initial concentrations of paraldehyde from 0.018M to 0.219M for the catalyst $\text{SiO}_2\text{-MoO}_3$. Similar curves were obtained for all the other mixed oxide catalysts. The velocity 'V' was obtained from the tangent at the initial stages of the curve. In Fig. 2, the reciprocal, $1/V$, of the depolymerization velocity (V = the initial velocity per mmole of acid sites having $pK_a \leq -3.0$) was plotted against the

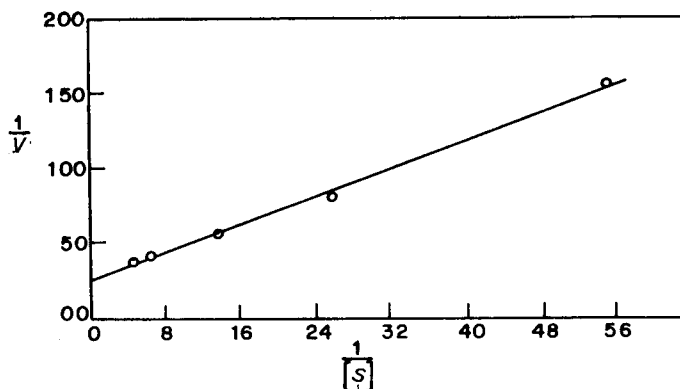


Fig. 2. The catalytic depolymerization of paraldehyde by silica-molybdena catalyst following enzyme kinetics.

reciprocal $\left[\frac{1}{S}\right]$ of the initial concentration of paraldehyde $[S]$. As shown in Fig. 2, the plots lie on a good straight line. Similar observation was made with other mixed oxide catalysts, indicating that the observed kinetic data fit the well known MICHAELIS-MENTEN'S equation, as has been suggested by TANABE⁶⁾ in case of metal sulfates. MICHAELIS constants were calculated from K_m/V_{max} and $1/V_{max}$ (which were obtained from the graphs; K_m/V_{max} is the slope of the graph and $1/V_{max}$ is the intercept on the Y-axis) which are given in Table 1. A reference to the values of energies of activation given in Table 1 shows that these are in keeping with the general trend of values (21040 and 27350 cal/mole) obtained in case of metal sulfates¹²⁾. The main difference between homogeneous and heterogeneous acid catalyzed reactions is indicated by the large difference in the energy of activation of these two different processes. In homogeneous acid catalyzed reaction the value of energy of activation is of the order 14300 cal/mole and this value is comparatively less than the values obtained in the present investigation and also those for the metal sulfates (Table 1). It can be concluded from our results as has been done by TANABE *et al.*⁶⁾ that the reaction involves an intermediate paraldehyde-solid acid complex formation as an intermediate. The kinetics and hence the mechanism inferred was thus different from that of usual homogeneous acid catalyzed reactions^{7,8)}.

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TABLE 1. Relationship between acidity, MICHAELIS constant and energy of activation

Sl. No.	Catalyst and its composition	Temp. of heat-treatment. °C	Acidity at $pK_a \leq -3.0$ mmole/g.	MICHAELIS constant K_m	Energy of activation cal/mole
1.	SiO ₂ -ZrO ₂ (89%-11%)	500	0.30	0.3664	18170
2.	SiO ₂ -TiO ₂ (85%-15%)	550	0.20	0.8375	19190
3.	Al ₂ O ₃ -ZrO ₂ (80%-20%)	500	0.16	0.0875	21040
4.	TiO ₂ -ZrO ₂ (68%-32%)	440	0.15	0.220	22390
5.	Al ₂ O ₃ -TiO ₂ (74%-26%)	420	0.09	0.166	25560
6.	SiO ₂ -MoO ₃ (81%-19%)	450	0.50	0.0932	18540
7.	Al ₂ O ₃ -MoO ₃ (74%-26%)	450	0.45	0.136	20840
8.	SiO ₂ -WO ₃ (86%-14%)	400	0.44	0.138	24550
9.	Al ₂ O ₃ -WO ₃ (84%-16%)	400	0.40	0.210	19860
10.	SiO ₂ -V ₂ O ₅ (85%-15%)	450	0.38	0.214	23280
11.	Al ₂ O ₃ -V ₂ O ₅ (83%-17%)	450	0.34	0.220	27350
12.	NiSO ₄ ¹²⁾ *	350	0.056	0.045	26900
13.	CuSO ₄ ¹²⁾ *	300	0.072	0.120	21700
14.	CCl ₃ COOH ¹²⁾ *	—	—	—	14300

* Reference numbers.

The present experimental results show that in the depolymerization of paraldehyde, selectivity of the acid sites play an important role. A well known strong solid acid like silica-alumina whose acid strength ($pK_a \leq -8.2$) is stronger than those of the present mixed-oxides, was found to be much less active catalytically than the latter for depolymerization of paraldehyde. Our observations that acid centres of $pK_a \leq -3.0$ are necessary for depolymerization of paraldehyde implies selectivity in the use of acid centres of particular acid strength for particular reaction and this agrees with an earlier observation that acid centres of $pK_a \leq -3.0$ are necessary in the ester hydrolysis¹⁴⁾, where also it has been shown that there is selectivity in the utilization of acid centres. The reaction of enzyme with the substrate is selective, whereas the selectivity of that kind has never been seen in homogeneous acid catalyzed reactions¹²⁾. It has been shown in the present work that solid acids behave very much similarly as an enzyme does; it might be considered as suggested by TANABE *et al.*¹³⁾ that the C-O bonds are weakened not only by the adsorption of oxygen atoms of paraldehyde on active centres (both BRÖNSTED and LEWIS acid sites) on the catalyst, but also by some interactions between sites other than active centres and some part of the paraldehyde molecule. It is characteristic of enzyme action that there are some inter-

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actions between substrate and a site remote from the active centres of enzyme action^{15,16}). Our present conclusions support the views of earlier workers in the study of depolymerization of paraldehyde by metal sulfates^{5,6}).

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