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H-ZSM-5-Catalysed Shape-Selective Acetalisation of Aldehydes

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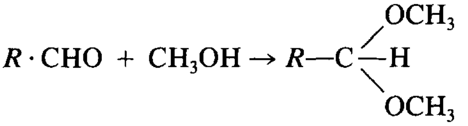
The paper describes acetalisation of aliphatic and aromatic aldehydes with methanol catalysed by H-ZSM-5 at room temperature. The reactions are characterised by the following features:

(1) The reaction rates are faster with aromatic aldehydes relative to the aliphatic aldehydes.
(2) The reaction exhibits shape selectivity for aliphatic aldehydes.

The phenomenon of shape selectivity with the aliphatic aldehydes studied has been corroborated by carrying out kinetics of adsorption of the aldehydes and the product acetals. The activity and selectivity pattern of H-ZSM-5 has been compared with other acid catalysts. The utility of the shape selective acetalisation of H-ZSM-5 in selectively reducing one aldehyde in presence of the other with sodium borohydride is also pointed out.

INTRODUCTION

Zeolites have established themselves as industrial catalysts for over two decades for a variety of hydrocarbon processing reactions where acidity and shape selectivity are important factors. It is only in recent years that the utility of zeolites for organic synthesis is recognised for producing specific organic intermediates and fine chemicals in high selectivity (*1*). Some of the examples include acylation of arenes (*2*), halogenation and nitration of arenes (*3, 4*), esterification of acids (*5*), skeletal rearrangement of paraffins and olefins (*6*), pinacolone rearrangement (*7*), and rearrangement of epoxides (*8*). In the present paper, we report H-ZSM-5 catalysed acetalisation of aldehydes:



$$R\cdot\mathrm{CHO} + \mathrm{CH_3OH} \rightarrow R\text{—}\mathrm{C}(\mathrm{OCH_3})_2\text{—H}$$

(R = alkyl or aryl).

We also report shape selectivity in acetalisation reaction, which implies that H-ZSM-5 could differentiate between certain aldehydes towards the acetalisation reaction. The acetalisation reaction is often used by organic chemists to protect the aldehyde group in presence of other functional groups so that subsequent reactions could be selectively performed on the latter (*9*). For example, a ketone could be reduced to alcohol in presence of an aldehyde using $NaBH_4$ if the aldehyde is protected as an acetal. ZSM-5-catalysed acetalization seems to offer a unique possibility to differentiate between two equally reactive aldehydes by virtue of shape-selective effects. This aspect becomes apparent as we discuss some of our results later in the paper. The present paper is an extension of our earlier work (*9*) on heteropolyacid-catalysed acetalisation/ketalisation reactions.

EXPERIMENTAL

Materials

The aldehydes were all procured from either Fluka (Switzerland) or Aldrich Chemical Co. (UK) and were 99.5% pure. A.R. grade methanol was obtained from British Drug House, India. H-ZSM-5 (SiO_2/Al_2O_3 = 90) was kindly supplied by Dr. P. Ratnasamy of National Chemical Laboratory, Pune, India. The BET surface area of the

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sample is 415 m^2/g and the adsorption capacity for water was found to be only 8% by weight of the Zeolite. The Zeolite HY was procured from Strem Chemicals Co. (USA). Silica–alumina (Al_2O_3 = 25% by weight) and γ-Al_2O_3 were procured from Ketjen (Netherlands) and Harshaw Chemie (Netherlands), respectively. Tungstosilicic acid was obtained from British Drug House, India. The dimethyl acetals of the aldehydes hexanal, hexahydrobenzaldehyde and 2-ethyl hexanal were prepared using our procedure reported earlier (9) and used for the adsorption experiments.

Reaction Procedure

In a typical reaction using benzaldehyde, 5 mmol of the substrate was mixed with 10 ml of methanol in a round-bottom flask. H-ZSM-5, 40 mg, was added and the mixture was kept stirred on a magnetic stirrer. Samples were withdrawn from time to time for analysis of the products.

Analysis

The products were analysed by GC using a 6-ft-long column PEG 400 on Chromosorb. At the end of the reaction, the solid catalyst was filtered out, the methanol was evaporated on a rotary evaporator, and the isolated acetal was identified by IR and NMR.

Adsorption

The adsorption measurements were carried out in carbon tetrachloride as the solvent (since methanol itself is a reactant) using isooctane (Fluka; Switzerland) as the internal standard. It was independently confirmed that isooctane does not adsorb inside the ZSM-5 channels.

Kinetics of adsorption was carried out as follows: To 0.1 m.mol of aldehyde in 1 ml of carbon tetrachloride, 0.1 m.mol of isooctane were added. The sample was withdrawn from time to time and analysed by GC as described above. Adsorption experiments with benzaldehyde were carried out with toluene as the solvent instead of carbon tetrachloride since the solution of benzaldehyde in carbon tetrachloride was suspected to be slightly hazy. It is known that toluene adsorbs inside the zeolite channels. Hence the isooctane added serves as the internal standard.

TABLE 1

Rate and Conversion Data for Acetalisation of Aldehydes on H-ZSM-5

Substrate[a]	Initial rate ($mol\ mg^{-1}\ min^{-1}$)	Acetal[b] (%)
1. Benzaldehyde	5.0	85.0
2. *o*-Tolualdehyde	5.5	85.5
3. *p*-Tolualdehyde	5.5	84.0
4. Hexanal	0.15	84.0
5. Hexahydrobenzaldehyde	0.09	91.9
6. 2-Ethyl hexanal	0	0

[a] 0.005 mol of substrate, 40 mg of catalyst, and 10 ml of methanol.

[b] Acetal percentages correspond to steady-state conversions; steady state is attained within 240–300 min for the aromatic aldehydes while it takes more than 20 h for the aliphatic aldehydes.

RESULTS

Table 1 assembles the data for the acetalisation of a number of aldehydes on H-ZSM-5. It may be seen that aliphatic as well as aromatic aldehydes undergo acetalisation with the yields of the product ranging from 84–91%. The table also gives the initial rates of the acetalisation of the individual aldehydes, derived from our kinetic plots. In general, aromatic aldehydes react very much faster than the aliphatic aldehydes, although the steady-state conversions are more or less comparable for all the aldehydes. 2-Ethyl hexanal, however, does not undergo reaction.

The aliphatic aldehydes took almost 24 h to reach steady state. This could be due to their low reactivity or a possible indication of diffusion controlled reaction rates. Thus, acetalisation of mixtures of aliphatic aldehydes was carried out in order to explore shape selectivity effects. In addition, kinetics of adsorption of aldehydes and the acetals were also carried out to find out if diffusion had any role to play.

Figure 1 shows the kinetics of competitive acetalisation of a mixture of hexanal and hexahydrobenzaldehyde. Clearly hexanal

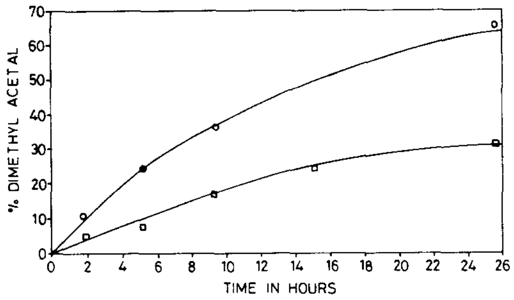

FIG. 1. Kinetics of competitive acetalisation of a mixture of hexanal and hexahydrobenzaldehyde, (○) Acetal of hexanal; (□) acetal of hexahydrobenzaldehyde. Conditions: $T = 26°C$, 0.01 M each of hexanal and hexahydrobenzaldehyde in 10 ml of methanol; H-ZSM-5: 40 mg.

reacts faster than hexahydrobenzaldehyde. The initial rates are: 0.15 mol-mg^{-1}-h^{-1} for hexanal and 0.05 mol-mg^{-1}-h^{-1} for hexahydrobenzaldehyde. Table 2 assembles the initial rates of acetalisation and steady-state conversions for the mixtures of aldehydes derived from kinetic plots similar to Fig. 1. It may be seen that on H-ZSM-5 catalyst, hexanal reacts much faster than hexahydrobenzaldehyde (entry 1). It may be seen that the conversions at steady state fall for hexanal and hexahydrobenzaldehyde in presence of 2-ethyl hexanal. (Compare Tables 1 and 2.) The fall is more pronounced for hexahydrobenzaldehyde. Further it was found that 2-ethyl hexanal did not react at all on H-ZSM-5. This could be utilised to acetalise hexanal or hexahydrobenzaldehyde in presence of 2-ethyl hexanal (entries 2, 3, and 4). This is in contrast to the result obtained on tungstosilicic acid wherein 2-ethyl hexanal does react and at a slightly faster rate than hexanal (entry 5). On γ-Al_2O_3 catalyst 2-ethyl hexanal also was found to react at a rate a little faster than that of hexanal although conversions were limited to 5–6% only.

Entry 6 shows the difference in reaction rates between benzaldehyde and hexahydrobenzaldehyde on H-ZSM-5 which is quite substantial in favour of the former.

Table 3 assembles the data of acetalisation rate of benzaldehyde on various solid acid catalysts. The reaction rates cannot be compared since the strength and number of acid sites on these solid acids are important factors which should be taken into consideration for a realistic comparison.

Kinetics of Adsorption

Figure 2 compares the kinetics of adsorption of hexanal and hexahydrobenzaldehyde. Clearly, the initial rate of hexanal adsorption is faster, which is also reflected in the acetalisation rates. (The initial rates are:

TABLE 2

Relative Rate and Conversion Data for Competitive Acetalisation of Mixture of Aldehydes[a]

Entry no.	Catalyst	Substrate 1	Substrate 2	Relative[b] rate	Acetal[c] of substrate 1 (%)	Acetal[c] of substrate 2 (%)
1	H-ZSM-5 (40 mg)	Hexanal	Hexahydrobenzaldehyde	3.0	66.0	32.0
2	H-ZSM-5 (80 mg)	Hexanal	2-Ethyl hexanal	—	29.6	0
3	H-ZSM-5 (120 mg)	Hexanal	2-Ethyl hexanal	—	80.0	0
4	H-ZSM-5 (80 mg)	Hexahydrobenzaldehyde	2-Ethyl hexanal	—	15.0	0
5	Tungstosilicic acid (40 mg)	Hexanal	2-Ethyl hexanal	0.8	73.0	88.8
6	H-ZSM-5 (80 mg)	Benzaldehyde	Hexahydrobenzaldehyde	5.8	56.0	14.0

[a] 0.005 mol each of the substrate and 10 ml of methanol are taken.

[b] This is the ratio of initial rate of acetalisation of substrate 1 to that of substrate 2.

[c] Acetal percentages refer to the steady-state conversions.

TABLE 3

Comparison of Acid Catalysts for Acetalisation of Benzaldehyde[a]

Catalyst	Initial rate ($mol\ mg^{-1}\ min^{-1}$)	Acetal[b] (%)
1. H-ZSM-5	5.0	85.0
2. HY	1.9	70.0
3. Silica-Alumina	1.0	60.0
4. γ-Al_2O_3	0.5	45.0

[a] 0.01 mol of benzaldehyde, 40 mg of catalyst, and 10 ml of methanol.

[b] Percentages correspond to steady-state conversions which were attained in most of the cases in 300–400 min.

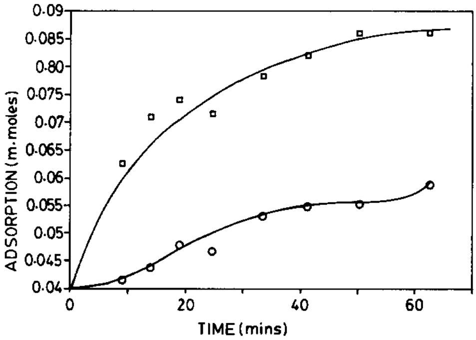

FIG. 3. Kinetics of competitive adsorption of hexanal and 2-ethyl hexanal; (□) hexanal, (○) 2-ethyl hexanal. Conditions: $T = 26°C$, 0.1 mmol each of the absorbates in 1 ml of carbon tetrachloride; H-ZSM-5: 200 mg.

4.3×10^{-5} mmol-mg^{-1}-min^{-1} for hexanal and 7×10^{-6} mmol-mg^{-1}-min^{-1} for hexahydrobenzaldehyde).

Interestingly, it was found that 2-ethyl hexanal does get adsorbed although it does not react to form any acetal on H-ZSM-5. So the kinetics of competitive adsorption kinetics of a mixture of hexanal and 2-ethyl hexanal was carried out and the plots are shown in Fig. 3. The initial rate of hexanal is higher than that of 2-ethyl hexanal. The initial rates in mmol-mg^{-1}-min^{-1} are 3.5×10^{-5} and 2.3×10^{-5} for hexanal and 2-ethyl hexanal, respectively.

A similar difference in adsorption rates was found between hexahydrobenzaldehyde and 2-ethyl hexanal, the former showing a higher rate of adsorption.

Since 2-ethyl hexanal was found not to react even though it gets adsorbed, we thought it would be interesting to study the adsorption kinetics of the acetal of 2-ethyl hexanal. Figure 4 compares the individual adsorptions (not from a mixture) of the acetals of hexanal and 2-ethyl hexanal. It may be observed that while the dimethyl acetal of hexanal adsorbs, the adsorption of acetal of 2-ethyl hexanal is very little. The small

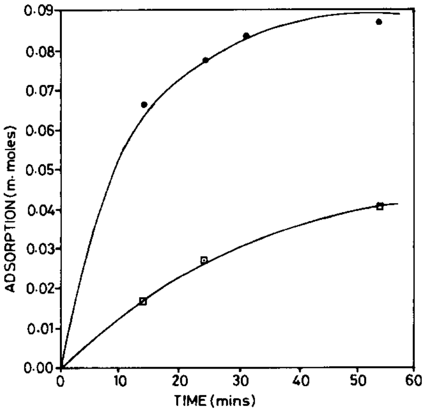

FIG. 2. Kinetics of competitive adsorption of hexanal and hexahydrobenzaldehyde; (○) hexanal, (□) hexahydrobenzaldehyde. Conditions: $T = 26°C$, 0.1 mmol each of aldehydes in 1 ml of carbon tetrachloride; H-ZSM-5: 200 mg.

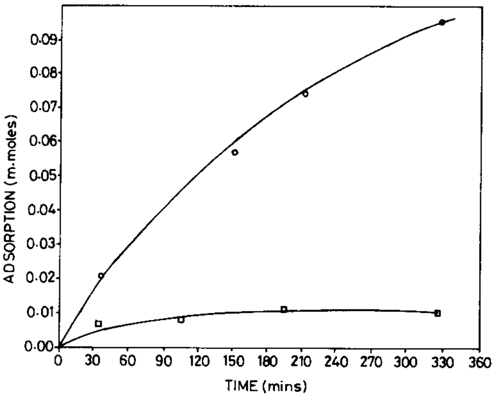

FIG. 4. Kinetics of adsorption of acetals of hexanal and 2-ethyl hexanal; (○) acetal of hexanal, (□) acetal of 2-ethyl hexanal. Conditions: $T = 26°C$, 0.1 mmol of the acetal in 1 ml of carbon tetrachloride; H-ZSM-5: 200 mg.

amount adsorbed (approximately 1% by weight of H-ZSM-5 taken) corresponds to adsorption on external sites. Thus, it appears that the dimethyl acetal of 2-ethyl hexanal cannot diffuse through the channels of H-ZSM-5.

The competitive adsorption studies with benzaldehyde and hexahydrobenzaldehyde indicated that the former adsorbed at a significantly faster rate than the latter.

DISCUSSION

Let us first consider the aromatic aldehydes. They react at a much faster rate than the aliphatic aldehydes (See Table 1). It was also found that benzaldehyde adsorption occurs at a faster rate compared to hexahydrobenzaldehyde. Thus, benzaldehyde must be reacting inside as well as outside the zeolite channels. This is perhaps true of the other aromatic aldehydes as well (*ortho*- and *para*-tolualdehyde). The higher reaction rate of the aromatic aldehydes may be the result of higher diffusion and adsorption rate as well as higher inherent reactivity with respect to alipahtic aldehydes (*10*).

Shape Selectivity of Aliphatic Aldehydes

The adsorption rates that we have computed for the various absorbates are really the diffusion rates. Thus, hexanal diffuses at a faster rate than hexahydrobenzaldehyde and also gives a higher rate of acetalisation. Evidently, this is a shape selective effect.

Further evidence for shape-selective effects with aliphatic aldehydes comes from the results on 2-ethyl hexanal. Interestingly, 2-ethyl hexanal does diffuse into the 5.5 Å size ZSM-5 channels and adsorb. However, the acetal does not show any adsorption. 2-Ethyl hexanal adsorbs in the channel and might be reacting to form the product dimethyl acetal, which cannot, however, diffuse out of the channels of the zeolites ZSM-5. This explains why H-ZSM-5 does not catalyse acetalisation of 2-ethyl hexanal. The effect is similar to that of the product selectivity observed on zeolites for hydrocarbon transformations (*11*).

Interestingly, in presence of 2-ethyl hexanal, the conversions of hexanal and hexahydrobenzaldehyde fall. This may be due to the adsorption of 2-ethyl hexanal inside the zeolite channel, partially denying access to the other reactant.

The behaviour of tungstosilicic acid (which catalyses the acetalisation of 2-ethyl hexanal in a mixture) lends additional support to the operation of shape selective effect on H-ZSM-5. The higher reaction rate for 2-ethyl hexanal relative to that of hexanal on the heteropolyacid is in accordance with the expected reactivity pattern. In 2-ethyl hexanal the electron-releasing alkyl group adjacent to the aldehyde would polarise the carbonyl facilitating protonation by acids (*10*).

The lower activity of HY zeolite relative to H-ZSM-5 for acetalisation of benzaldehyde (in spite of a higher number of acidic sites in the former) may be attributed to the strength of acid sites. It should be noted that the reactions are carried out at room temperature. It appears that the room temperature acidity (proton mobility) for H-ZSM-5 is significantly higher (than that for HY) which more than compensates for the fewer number of acidic sites. More work, however, needs to be done to explore shape-selective acetalisation by HY zeolites.

Synthetic Utility of Shape Selective Acetalisation

In synthetic organic chemistry, ketones are selectively reduced by sodium borohydride in presence of aldehydes by initially protecting the latter (by conventional acid catalysis) as acetal before the addition of sodium borohydride (*9*). Since H-ZSM-5 could differentiate between two aldehydes towards acetalisation reaction depending on size and shape, the shape-selective acetalisation reactions could be utilised for selective reduction of one aldehyde over the other in a mixture. For example, using H-ZSM-5, it should be possible to initially acetalise hexanal in presence of 2-ethyl hexanal and then add sodium borohydride to reduce only 2-ethyl hexanal to 2-ethyl hexanol. In a similar manner it should be possible to reduce hexahydrobenzaldehyde selectively in presence of hexanal. Such examples of selective reductions of one aldehyde in the presence of the other (when both are more or less equally reactive) are not known in the literature to the best of our knowledge.

ACKNOWLEDGMENTS

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