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Effect of pore size on the catalytic activities of K-10 clay and H-zeolites for the acetalization of ketones with methanol

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Abstract

One-pot acetalizations of cyclohexanone, acetophenone and benzophenone were carried out using methanol over H-montmorillonite clay (a mesoporous material), silica, alumina, and different zeolites such as HFAU-Y, HBeta, H-ZSM-5, and H-mordenite. In all the cases, a single product—the corresponding dimethylacetal—was obtained in high yields. Hemiacetal formation was not observed with any catalyst. A comparison of catalytic activity indicated that montmorillonite K-10 is the most active catalyst for the reaction. As evidenced by the reaction time studies, the catalyst decay is greater over the zeolite catalyst than over the clay.

Keywords: Acetalization; Clays; Diffusional properties; Dimethylacetal; Molecular size effect; Zeolites

1. Introduction

Zeolites have attracted great deal of attention among researchers in the field of heterogeneous catalysis due to their very high activity, high selectivity, and relatively high surface area and better reusability. It is generally observed that almost all reactions catalyzed by concentrated sulphuric acid are catalyzed by zeolites also. Zeolites have the additional advantages of higher product selectivity and better reusability over H_2SO_4. Many applications of zeolites in commercially important reactions like fluid catalytic cracking (FCC) [1], isomerization [2], alkylation [3], and Beckmann rearrangement reaction of cyclohexanone oxime to caprolactam [4] and in the synthesis of linear alkyl benzenes (LABs) [5] by the alkylation of benzene with long chain alkenes are reported. Zeolites are non-corrosive and they produce no harmful degradation products. Thus, they are eco-friendly catalysts holding tremendous potential in the development and adaptation of green processes.

1,2-Diacetals are efficient protecting groups for 1,2-diol units in carbohydrates [6–8]. In particular, monosaccharide units protected as cyclohexanone 1,2-diacetal (CDA) offer rapid access to important building blocks for oligosaccharide synthesis [8,9]. Grice et al. have reported the preparation, structure, derivatization and NMR data of CDA-protected carbohydrates [10,11]. The assembly of large, complex oligosaccharides presents a significant challenge to synthetic chemistry. Currently the routes to these molecules often employ large number of steps owing to unavoidable protecting group manipulation and activation protocols. Cheung et al. reported that tuning the reactivity of glycosyl doners by selective introduction of different protecting and leaving groups, in conjunction with the principle of orthogonal activation, enabled highly efficient oligosaccharide synthesis [12]. One-pot sequential glycosidation of four or five components gave tetrasacchrides and pentasaccharides, respectively. Acetalization reactions also find extensive applications in the synthesis of enantiometrically pure compounds [12,13], which find practical application in the fields of synthetic carbohydrates [14,15], steroids [16], pharmaceuticals, and fragrance [17,18] and polymer chemistry [19].

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Thus, development of efficient reagents for acetalization reaction is of considerable interest.

Traditionally, acetalizations of aldehydes and ketones are performed using trimethyl orthofomate in the presence of an acid catalyst such as HCl, H_2SO_4, *p*-toluenesulphonic acid, or iron(III) chloride [20,21]. Eco-friendly solid acid catalysts such as SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2 [22], Ce-exchanged montmorillonite [23], acidic zeolites [18,24,25], and siliceous mesoporous material [26] have also been reported to be active for the acetalization reactions. The Lewis acidity of complexes such as $[(dppe)M(H_2O)_2]$, where M is Pt or Pd (dppe is 1,2-bis(diphenylphosphino)ethane) is also utilized for acetalization reactions in a homogeneous reaction medium [27,28]. In this paper, we report the room temperature, single-pot acetalization of cyclohexanone, acetophenone, and benzophenone with methanol for the preparation of the corresponding dimethylacetals. The effects of temperature, molar ratio of ketones and methanol and amount of catalyst on the acetalization process were investigated in some detail. We focused our attention on the wide difference in the activity of various zeolites, some common metal oxides, and montmorillonite K-10 clay. We conclude that the pore size of the catalyst system has a remarkable influence on the catalytic activity.

2. Materials and methods

Pure HFAU-Y zeolite was supplied by Sud-Chemie Ltd. (India) H-ZSM-5 and H-BEA (H-β) were supplied by National Chemical Laboratories (NCL) India. H-Mordenite was supplied by Zeolyst International, New York, USA. Montmorillonite K-10 was procured from Aldrich Chemical Company. SiO_2 was prepared by the acidification of an aqueous solution of sodium silicate. The gelatinous precipitate obtained was washed free of electrolytes using de-ionized water. It was dried at 383 K overnight in an air oven and dehydrated by calcining to 773 K at a heating rate of 20 K/min under a constant flow of air over the sample (60 mL/min). Aluminium oxide was prepared by the addition of ammonia to a boiling solution of aluminium nitrate. The hydrated oxide was washed free of electrolytes using de-ionized water and dried at 383 K in an air oven overnight. It was then calcined to 773 K at a heating rate of 20 K/min under a constant flow of air over the sample (60 mL/min) [29,30].

The crystalline nature of the materials was established by X-ray diffraction studies performed using a Rigaku D-max C X-ray diffractometer with Ni-filtered Cu Kα radiation. Acid structural properties were estimated using temperature programmed desorption (TPD) of ammonia with conventional equipment. Pelletized catalyst (500 mg) was activated at 773 K in a muffle furnace and loaded in a steel reactor of 15 cm length and 0.5 cm i.d. It was then activated at 573 K under constant nitrogen flow for 0.5 h. After cooling to room temperature, the sample was saturated with ammonia in the absence of carrier gas (N_2) and the system was allowed to attain equilibrium. Nitrogen flow was restarted to flush out excess and physisorbed ammonia. The temperature was then raised in a stepwise manner at a linear heating rate of 20 K/min. The ammonia desorbed from 373 to 873 K was monitored using a conventional TPD analyzer. BET surface area and pore volume measurements were performed using a Macromeritics Gemini surface area analyzer using N_2 adsorption technique at liquid nitrogen temperature.

Cyclohexanone, acetophenone, and benzophenone were purchased from Aldrich Chemical Company, USA and commercial-grade methanol (available from SD Fine Chemicals, India) were used as received. One-pot acetalization reactions of carbonyl compounds were carried out in a 50 mL glass batch reactor equipped with a magnetic stirrer, thermometer, water condenser and temperature controller. All the experiments were performed under nitrogen. In a typical run, 10 mL of a 1:10 mixture of ketone and methanol was stirred for 10 h under a slow flow of moisture-free nitrogen. Samples were withdrawn every 2 h and at the end of the reaction (after 10 h) and were analyzed with a Chemito GC1000 gas chromatograph equipped with a SE-30 capillary column (oven temperature 353–503 K, injector temperature 373 K, detector temperature 373 K). The products were further analyzed by GC–MS using a Shimadzu-5050 instrument provided with a 30 m HP-30 capillary column of cross linked 5% phenylmethylsilicone. The MS detector voltage was 1 kV. The *m/z* values and relative intensity (%) are indicated for the significant peaks (conditions: column temperature was adjusted between 323 and 533 K with a heating rate of 10 K/min; injector: 513 K; detector: 563 K).

3. Results

The surface area (S_{BET}), the micro-pore volume (V_{micro}) and other general features of the zeolites are presented in Table 1. For each zeolite, the values of surface area and pore volume match well with reported values [31]. It is seen that the adsorption–desorption nitrogen isotherm shapes of the sample showed a hysterisis loop attributable to the presence of mesopores. Comparatively large amounts of mesopores are found in HFAU-Y and HBeta zeolites. This portion is much lower in the mordenite.

The acid structural properties of the samples were determined by thermodesorption of chemisorbed ammonia (NH_3-TPD). This method provides general information on the number and distribution of acid strength of the active sites. The amounts of ammonia desorbed were formally divided into three temperature ranges to denote three types of acid sites: (1) weak acid sites, ranging from 373 to 473 K; (2) moderate acid strength, ranging from 473 to 673 K; (3) high acid strength, ranging from 673 to 873 K as shown in Table 2. It was observed that ammonia desorption from acid

Table 1
General features of zeolites and montmorillonite K-10 clay used in the liquid phase acetalization reaction of ketones

Zeolite/clay	Si/Al[a]	S_{BET} ($m^2 g^{-1}$)	Pore volume[b] ($cm^3 g^{-1}$)	General features				
				Dimensionality	Pore size (nm)	Point group[c]	Crystal face[c]	Crystal size[c] (μm)
HFAU-Y1.5[32]	1.5	398	0.266	3D	Super cage: 1.18; window: 0.74 × 0.74	*Fdm*	Cubic	0.90
HZSM-540[33]	40	413	0.163	3D	0.53 × 0.56	*P*$_n$*ma*	Orthorhombic	0.40
HBeta26[34]	26	745	0.232	3D	0.66 × 0.67	*P*4$_1$22	Tetragonal	0.51
HMOR19[35]	19	552	0.188	2D	0.26 × 0.57	*Cmcm*	Orthorhombic	0.92
Montmorillonite K-10[36]	2.7	183	0.204	2D	Average pore size > 1.0 nm	–	–	≈1.0

[a] As determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.
[b] Total pore volume measured at 0.9976 P/P_0.
[c] As determined by powder X-ray diffraction studies.

Table 2
TPD of ammonia from different zeolites HFAU-Y, HZSM-5, HBeta, HMOR and other materials used in the acetalyzation reaction

Catalyst	Amount of ammonia (mmol/g^{-1}) desorbed within certain temperature range (K)				
	373–473[a] (w)	473–673 (m)	673–873 (s)	373–873 (cumulative)	*s*/*w* + *m*
HFAU-Y1.5	0.69	0.41	0.33	1.43	0.30
HZSM-540	0.65	0.34	0.29	1.28	0.29
HBeta26	0.52	0.70	0.51	1.73	0.42
HMOR19	0.63	0.56	0.73	1.92	0.61
Montmorillonite K-10	0.55	0.24	0.13	0.92	0.16
SiO_2	0.59	0.11	0.07	0.77	0.10
γ-Al_2O_3	0.56	0.19	0.13	0.88	0.17

[a] Ammonia desorbed in the temperature range 373–473 K might contain small amount physisorbed ammonia too.

sites occurred mainly at relatively low temperatures for HZSM-5 and HFAU-Y zeolites, at the intermediate temperatures for the beta sample, and in the high temperature domain for MOR zeolite sample. The overall amount of ammonia desorbed enables one to evaluate the concentration of accessible acid sites. For different zeolites, the acidity values follow the order: HMOR19 > HBeta26 > HFAU-Y1.5 > HZSM-540.

Acetalization of all the three ketones with methanol produced the corresponding diacetals as the only product. Montmorillonite clay was found to be the most active catalyst with any ketone. Zeolites are far less active compared to the mesoporous clay. Among different zeolites, mordenite was found to be the most active towards the reaction and H-Y the least active. Silica and alumina exhibited negligible activity for the reaction. There was no predominant increase in the percentage conversion with increase of reaction time. It appears that the acetalyzation products themselves adsorb to the catalysts and thereby block the pores and/or the active sites leading to the loss of catalytic activity. This is more pronounced in the case of zeolites. Among different ketones, cyclohexanone is the most active and benzophenone the least. Montmorillonite shows a conversion of 71.7% in 2 h with cyclohexanone, 13.8% with acetophenone and 2.8% with benzophenone, whereas with mordenite the conversion is 64.9, 9.8 and 2.2%, respectively. Silica and alumina do not initiate any conversion. Reaction time studies show that the catalyst loses activity during the formation of acetals. This is more pronounced in the case of zeolites (see Table 3) than in the case of montmorillonite K-10. There is apparently not much change on the yield of acetals after 10 h in the case of zeolites.

4. Discussion

Liquid phase acetalization of ketones over montmorillonite K-10 clay is much more efficient than over zeolites or common metal oxides used in catalysis such as silica and alumina. The activity difference could be due to two important properties: acid structural properties (total acidity and strength of the acidic sites) and diffusional properties, which are determined by the pore structure of the materials.

Since acetalization is an acid-catalyzed reaction, it is logical to correlate the acid structural properties of the materials as obtained from the temperature programmed desorption of ammonia with activity. According to the TPD ammonia results, HMOR was the most acidic catalyst and had the highest *s*/*w* + *m* ratio, which means it possesses the strongest acid sites. Also, zeolites have more strong acid sites than the clay (montmorillonite K-10) or oxides

Table 3
Acetalization of cyclohexanone, acetophenone, and benzophenone: variation of catalyst

Catalyst	Percentage conversion of ketones					
	Cyclohexanone[a]		Acetophenone[b]		Benzophenone[b]	
	2 h	10 h	2 h	10 h	2 h	10 h
HFAU-Y1.5	43.6	49.9	4.4	7.6	1.2	2.4
HZSM-540	62.4	66.9	5.1	8.3	1.6	3.8
HBeta26	63.5	69.5	5.1	8.8	1.8	4.1
HMOR19	64.9	84.0	9.8	12.9	2.2	5.7
Montmorillonite K-10	71.7	88.2	13.8	21.2	2.8	5.8
SiO_2	0	0	0.9	1.2	0	0
γ-Al_2O_3	2.8	4.9	1.1	1.9	0	0
None[c]	0	0	0	0	0	0
Filtrate[d]	0	0	0	0	0	0

Experimental conditions: ketone:methanol molar ratio, 1:10; reaction temperature, ambient temperatures; catalyst amount: 250 mg; gentle flow of inert nitrogen.

[a] Reactions were carried out at room temperature under atmospheric pressure.

[b] Reactions were carried out at ambient temperature and atmospheric pressure.

[c] Without using catalyst.

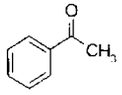
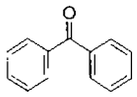
[d] After the reaction over HMOR19, the catalyst was removed by filtration and the filtrate obtained was used to examine the catalytic activity of the possible dissolved components of the catalyst.

(see Table 2). However, the clay is a much superior catalyst compared to zeolites. This is not entirely surprising since catalytic activity of a catalyst towards the acetalization reaction does not require strong acidity. Based on these results, we concluded that the acid properties of these materials do not have a major role in deciding catalytic activity. Hence, other properties of these materials have a more decisive role in determining their catalytic activity.

HMOR has a bi-directional pore system with parallel circular 12-ring channels (0.65 nm × 0.70 nm) and elliptical 8-ring channels (0.26 nm × 0.57 nm). However, it practically functions as a unidirectional pore system since the 8-ring channels do not allow the passage of all but small molecules. H-Beta has a three-dimensional interconnecting pore system with pores of 0.55 nm × 0.55 nm and 0.76 nm × 0.64 nm and HFAU-Y has a 3D interconnecting pore systems with super cages of 1.18 nm connected by circular 12-ring 0.74 nm windows. The ZSM-5 zeolite contains a zigzag channel system intersecting a straight 10-ring channel (medium pore) to produce the three-dimensional pore system of 0.51 nm × 0.55 nm and 0.53 nm × 0.56 nm (straight channels) [32–35]. SiO_2 and Al_2O_3 do not have a regular pore structure.

The shape selectivity associated with the zeolites has its origin in the well-defined pore structure which could be manipulated to some extent. With larger substrates, diffusional restriction leading to lose of catalytic activity is often encountered in the case of zeolites. So, the quest for other materials having large pore dimensions has been the subject of intense research. Montmorillonite clay is a layered alumino-silicate with a dioctahedral layer sandwiched between two tetrahedral layers. Unlike any other zeolites used, this does not have a regular pore structure [36]. The pore size given in Table 1 is an average value. The structure of the clay is constituted of both micropores and mesopores. The amount of mesopores is less when compared to the amount of micropores. This explains its reduced surface area and pore volume when compared to zeolites (Table 2). However, the average pore size is greater than that of zeolites (>1.0 nm).

As pointed out earlier, the pore diffusion limitation induced by the large molecular size of the reactants played an important role on the acetalization reaction using zeolite catalyst [18,24,25,37]. Only the acid sites on the outer surface of the zeolites are available to reactants and higher product yield could only be attained after longer reaction time. This will explain the comparatively lower activity of zeolites over common mesoporous materials of lower acidity such as montmorillonite K-10. Montmorillonite K-10 is a mesoporous material and in effect reactants can easily access all the acidic sites available for the reaction. Hence, it is concluded that the effect of pore diffusion was not as critical for the clay as in the case of zeolites. Even though the concentration of mesopores is low, it will be enough for the acetalization reaction. The presence of these mesopores must be responsible for the greater activity of montmorillonite. The wide variation in the activity is further confirmed by our studies on some common metal oxides such as alumina and silica (both prepared by usual chemical routes). Alumina and silica which do not possess enough acid centers exhibit very low or no activity for the acetalization reaction. All zeolites, even through they have a regular microporous structure, do not show same activity. Mordenite with large straight pores allows diffusion of the product easily and hence will have the highest overall activity among the zeolites. HFAU-Y has a 3D cage structure and the diffusion of the products is hampered by the complicated pore system, which explains its low activity. Lack of sufficiently large pores and very low acidity might be the reasons for the extremely low activity of silica and

0.51+0.14+0.1 nm
volume: 38.351 cubic nm

0.79+0.14+0.1 nm
volume: 47.538 cubic nm

0.95+0.14+0.1 nm
volume: 59.494 cubic nm

Scheme 1. Molecular sizes and the corresponding volumes of different ketones.

alumina. Reaction time studies show that the catalyst decays during the formation of acetals. This is more pronounced in the case of zeolites. The decay on zeolites is probably due to the higher adsorption of the reactants and lower rate of desorption of products. Over the clay, the rate of desorption is comparatively higher and consequently there is less decay. Mordenite (like the clay) exhibits a low rate of decay mostly due to the unidirectional pore system (see above discussion).

The diffusion of the reactants through a given pore size is a factor of the molecular size of the ketones. The reactivity of the ketones decreases in the order cyclohexanone > acetophenone > benzophenone (Table 3). The difference in the acetalization activity among different ketones could be correlated to their molecular sizes and volumes. Scheme 1 depicts the molecular sizes of the ketones examined by us and their corresponding volumes.

In the case of cyclohexanone; the distance between oxygen and the most distant hydrogen is 0.51 nm; the van der Waals radius of oxygen is 0.14, and that of hydrogen is 0.1 nm leading to an effective end-to-end distance of 0.75 nm. Its volume is estimated at 38.351 nm^3. Applying similar strategy, the molecular sizes of acetophenone and benzophenone were found to be 1.03 nm (volume 43.578 nm^3) and 1.19 nm (volume 59.494 nm^3). It is seen from the above molecular size and volume calculation that both follow the order cyclohexanone < acetophenone < benzophenone. The efficiency of acetalization of the three ketones over different catalysts follows the reverse order. But we cannot overemphasize the role of molecular size on reactivity since it is known that cyclohexanone is more reactive towards nucleophiles than both acetophenone and benzophenone (taken in that order) [38].

5. Conclusions

We have established that the zeolites and H-montmorillonite clay are active and selective catalysts for the acetalization of ketones. The reaction requires active sites with low acid strength. However, rather than acid structure it is the pore sizes and their distribution in the catalyst that are more critical. This is further confirmed from our studies on zeolites, silica, alumina, and montmorillonite clay. Montmorillonite is a far better a catalyst with any ketone. Working with small ketones (cyclohexanone) as reactants, these materials are moderately active. However, these materials are less effective with ketones of larger size (acetophenone and benzophenone). Hence, when reactants with molecular size greater then 0.75 nm (cyclohexanone; 0.75 nm) are used, geometrical constraints do not allow the reactants to diffuse inside the pores of the zeolites and only the external surfaces of these materials become available for the reactants. Reaction time studies show the catalyst decay during the formation of acetals, which is larger on zeolites than montmorillonite K-10 due to the larger adsorption and lower diffusion rates on the former.

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