

Acetalization of ketones on K-10 clay and rare earth exchanged HFAU-Y zeolites: A mild and facile procedure for the synthesis of dimethylacetals

Bejoy Thomas · S. Sugunan

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Abstract Dimethylacetals of ketones; cyclohexanone, acetophenone, and benzophenone have been prepared by reacting ketones with methanol under mild reaction conditions. Large pore zeolites (H-Y and its rare earth metal, Ce^{3+} , La^{3+} , and RE^{3+} modified forms), and mesoporous clay (K-10 montmorillonite and its cerium exchanged counterpart) with regular pore structure, silica and silica-alumina have been used as catalysts. Clay catalysts are found to be much more active than zeolites, thanks to slightly bigger pore size. The nature of the pores of the solid acid catalysts determine acetalization efficiency of a particular catalyst. As evidenced by the reaction time studies, the catalyst decay is greater over the zeolites than over the clays. Carrying out the reaction with ketones of different molecular sizes it is shown that K-10 clays and rare earth exchanged H-Y zeolites are promising environmentally friendly catalysts for their use in the production fine chemicals.

Keywords Acetalization · Dimethylacetal · K-10 montmorillonite clay · Ce-montmorillonite clay · Rare earth exchanged H-Y zeolite

1. Introduction

Acetalization is one of the most widely used synthetic method for protecting aldehydes and ketones in the course

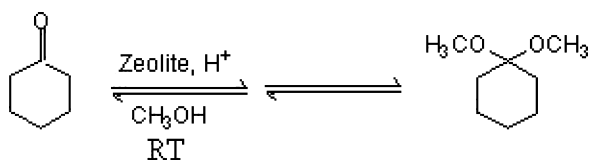
of preparation of a variety of multifunctional complex organic molecules since dimethyl acetals display higher stability towards strong bases, Grignard reagent, lithium aluminium hydride, strong oxidants, and esterification reagents than their parent carbonyl compounds [1]. Besides the interest of acetal as protecting groups, many of them have found direct application as fragrances, in cosmetics, food and beverage additives, in pharmaceuticals, in detergents, in lacquer industry, and polymer chemistry [2, 3–7]. Also, the reaction is widely used for the synthesis of enantiomerically pure compounds [8]. Generally, these reactions are carried out by treatment of the carbonyl compound with alcohol and/or the corresponding orthoester in the presence of an acid catalyst.

Various kinds of acids are well known to catalyze the reaction in homogeneous phase, including HCl, H_2SO_4 , $FeCl_3$ and Lewis acidic diphosphine complexes of Pt and Pd etc [1, 9]. Several problems, however remains to be solved. For example, the reaction in homogeneous phase is frequently carried out using trimethyl orthoformate as the reagent, but the use of methanol for the reaction is to be desired. In the case of a typical HCl/methanol system many kinds of undesired products are often formed, due to the strong acidity of HCl. In all the above methods, the reagents are irreversibly lost leading to low overall *atom efficiency* and high *E-factor*. Hence the choice of the catalyst is of prime importance in these environmentally conscious days. Solid acid catalysts are the best alternative. Solid acid catalysts reported for this reaction include; montmorillonite clay [10, 11], mesoporous aluminosilicate [12], Ce-mont [13], sulphated metal oxides [14], cation exchanged resins [15], and acidic zeolites [2, 6]. There are other protocols available for the protection of carbonyl compounds. Velusamy et al. reported the chemo selective synthesis of acetals from aldehydes using Co(II) catalysts [17]. Banik and co-workers recently reported the

B. Thomas
NMR Research Center, Indian Institute of Science, Bangalore 560
012, India

S. Sugunan (✉) · B. Thomas
Department of Applied Chemistry, Cochin University of Science
and Technology, Kochi-682 022, Kerala, India
e-mail: ssg@cusat.ac.in

iodine-catalyzed protection of carbonyl compounds [18]. We have used K-10 clay, Ce-mont, and rare earth exchanged H-Y zeolites for the efficient acetalization of three ketones; cyclohexanone, acetophenone, and benzophenone. It will be shown that by tailoring the textural properties of zeolites and K-10 clay, it is possible to obtain highly active and highly selective solid acid catalyst for the dimethyl acetal synthesis. Also, the effect of molecular size of ketones on the acetalization efficiency is discussed. A simple, efficient and highly eco-friendly protocol is described for the substrate selective acetalization of ketones with methanol over these solid acid catalysts. The chemical reaction scheme for the acetalization of cyclohexanone can be depicted as;



Ketones in presence of acid catalysts reacts with methanol under well optimized reaction conditions at ambient temperatures to produce dimethyl acetal.

2. Experimental section

The general method of ion exchange was adopted from that of Kuhl [19]. Rare earth exchanged H-Y zeolites were obtained by contacting 2 g H-Y (*Sud-Chemie (India) Ltd.*, Si/Al = 1.5) with 100 mL of 0.5 M rare earth nitrate (obtained from *Indian Rare Earths Ltd.*, Udyogamandal, Kerala) solutions at 353 K for 24 h [20, 21]. K-10 montmorillonite clay (Si/Al = 2.7) was procured from *Aldrich Chemical Company*, USA. SiO₂ 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). Silica-alumina was prepared by well-known chemical routes [22, 23]. K-10 montmorillonite clay (Si/Al ratio 2.7) was ion exchanged directly with 0.5 M cerium nitrate in aqueous acetone for 24 h (obtained from *Indian Rare Earths Ltd.*, Udyogamandal, Kerala; 0.025 mole nitrate per gram clay) at 353 K for 24 h to prepare cerium-exchanged montmorillonite [24] (designated as Ce-mont. in the present study).

The percentage of metal ion exchanged and framework Si/Al ratio were determined by Energy Dispersive X-ray analysis using a *JEOL JSM-840 A* (Oxford make model 16211 with a resolution of 1.3 eV). The crystalline nature of the materials was established by X-ray diffraction studies performed using a *Rigaku D-max C* X-ray diffrac-

tometer with Ni-filtered Cu K α radiation. Infrared induced vibration was studied using a *Nicolet Impact 400FT IR* spectrometer. ²⁹Si solid-state NMR experiments were carried out in the magic angle-spinning mode using a *Bruker DSX-300* spectrometer at a resonance frequency of 59.63 MHz. For the experiment a standard 4 mm double-bearing *Bruker MAS* probe was used. A sample rotation frequency of 7 kHz with a single pulse excitation corresponding to $\pi/2$ flip angle was applied for the studies. The pulse length for the experiment was 4 μ s, whereas the pulse delay was 5 sec.

Acid structural properties were estimated using temperature programmed desorption (NH₃-TPD) of ammonia with a 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 internal diameter. It was then activated at 573 K under constant nitrogen flow for half an hour. After cooling to room temperature, the sample was saturated with ammonia in the absence of carrier gas (N₂) and the system was allowed to attain equilibrium. Nitrogen flow was restarted to flush out excess and physisorbed ammonia. The temperature was then raised from 100 K to 873 K in a stepwise manner (kept for half an hour at each 100 K intervals) 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 *Micromeritics Gemini* surface area analyzer using N₂ adsorption technique at liquid nitrogen temperature.

We have employed a molecular modeling program *CERIUS2* (MSI, USA) using COMPASS force field calculation for molecular size and volume determination. The molecular sizes are 0.75, 1.03, and 1.19 nm respectively for cyclohexanone, acetophenone and benzophenone. The corresponding volumes were 38.351, 47.538, and 59.494 nm³.

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 with 250 mg of pre-activated (at 773 K) catalyst 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 GCMS 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 323–533 K with a heating rate of 10 K/minute, injector: 513 K and detector: 563 K).

3. Results and discussion

3.1. Physicochemical characteristics

Chemical composition of the parent and different rare earth exchanged zeolites are seen in Table-1. Results were reproducible within an error limit of 4%. The cerium content of Ce-mont clay is found to be 7.2%. X-ray diffraction and infrared spectral studies confirm that the zeolite framework remains intact even after ion exchange at moderately high temperatures. Consistent with the earlier reports, the parent as well as rare earth exchanged zeolites crystallizes into cubic unit cell with F3dm space group. Major shift in the framework vibrational band positions in infrared spectroscopy is shown in Table 1. Details are reported elsewhere [25].

High-resolution solid-state silicon-29 NMR spectroscopy is a powerful tool for investigating the structure and nature of bonding characteristics in zeolites [26, 27]. MAS NMR spectra of pure H-Y and rare earth exchanged LaH-Y zeolites are shown in Fig. 1. The spectra pure H-Y and the rare earth exchanged zeolites show two main peaks correspond, from left to right, with Si (2Al) and Si (1Al) ordering of the aluminate and silicate tetrahedra, though the intensity ratio is not very clear. There are also small humps corresponding to a small concentration of Si (3Al) and Si (0Al) structural unites. Lippmaa and co-workers have already demonstrated the regular dependence of the ^{29}Si chemical shifts on the number of alumina tetrahedra linked via oxygen bridges, to each SiO_4^{4-} tetrahedron [28]. The peaks were centered at -99.7 ppm in the case of H-Y and -97.8 ppm in the case of LaH-Y zeolites. However, for the mixed rare earth exchanged zeolite the

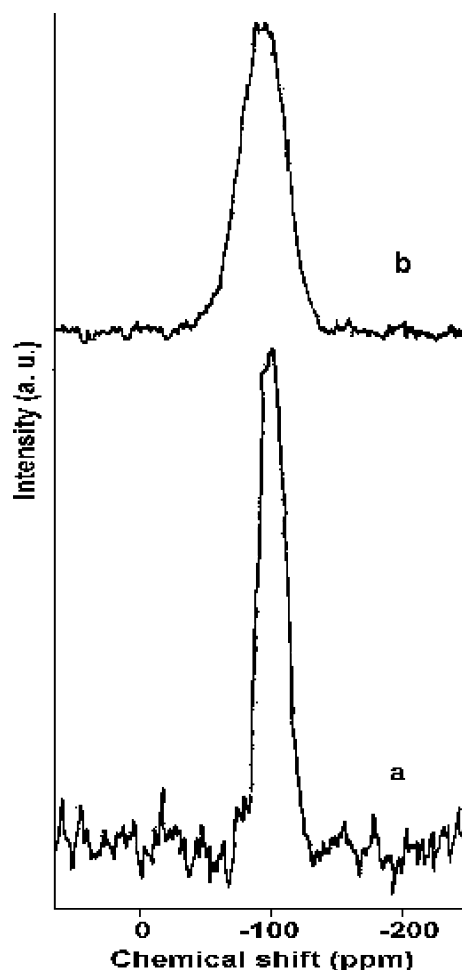


Fig. 1 ^{29}Si MAS NMR spectra of parent zeolite H-Y (a) and rare earth exchanged LaH-Y (b) zeolites recorded at a resonance frequency of 59.63 MHz with sample spinning speed of 7 kHz

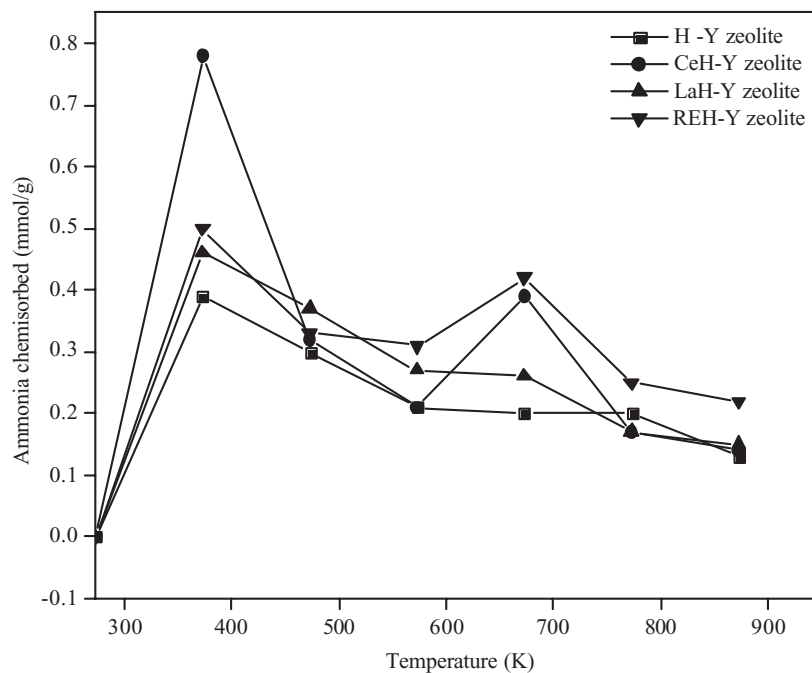
chemical shift is -98.7 ppm (not shown in the figure). The strain induced by the bulky and heavily charged lanthanum cations in the extra-framework cation locations is responsible for this down field shift in the peak position. The repulsive

Table 1 Chemical composition and framework vibrational band shifts ($400\text{--}1300\text{ cm}^{-1}$) as observed by infrared spectral studies on pure H-Y and different rare earth zeolites; CeH-Y, LaH-Y and REH-Y

Zeolite	Chemical composition ^a	Assymmetric stretch (cm^{-1}) EL or IT ^b	Symmetric stretch (cm^{-1}) EL or IT ^b	Double ring ^c (cm^{-1})	T-O bend ^d (cm^{-1})
H-Y	$\text{H}_{76.5}\text{Al}_{76.5}\text{Si}_{115.5}\text{O}_{384}$	1050	771	570	457
CeH-Y	$\text{Ce}_{14.06}\text{H}_{34.07}\text{Al}_{76.25}\text{Si}_{115.57}\text{O}_{384}$	1083	790	574	480
LaH-Y	$\text{La}_{15.44}\text{H}_{29.23}\text{Al}_{76.25}\text{Si}_{115.75}\text{O}_{384}$	1061	771	572	463
REH-Y ^e	$\text{La}_{9.01}\text{Ce}_{1.68}\text{Pr}_{3.91}\text{Nd}_{4.28}\text{H}_{18.78}\text{Al}_{75.42}\text{Si}_{116.58}\text{O}_{384}$	1072	772	573	469

^aAs determined by Energy Dispersive X-ray analysis. ^bEL, External linkage; IT, internal tetrahedra. ^c D₆R double ring units. ^d T= Si, Al. ^eRENa-Y is a mixed rare earth exchanged zeolite with La^{3+} as the main counter cation and small amounts of Ce^{3+} , Pr^{3+} and Nd^{3+} .

Fig. 2 Temperature dependence of chemisorption of ammonia on pure H-Y and various rare earth exchanged forms



interactions of protons and lanthanum enhance the migration of La^{3+} cations from super cage cation position to small cage cation locations. Migration also may affect the position of the peak. This is strongly supported by the fact that REH-Y zeolite with lanthanum as the main rare earth cation shows a similar trend as LaH-Y. Migration of counter and residual cations reduces the number of accessible Brønsted acid sites (BAS) on rare earth zeolites [29, 30]. This indicates that the ^{29}Si NMR peaks are influenced by the counter cations in the extra-framework cation locations.

The important physicochemical characteristics of different zeolites employed in the present study are summarized in Table 2. The table describes the distribution of acidity in three temperature regions of 373–473 K (weak acid sites), 473–673 K (medium acid strength) and 673–873 K (strong

acid sites). The data on the chemisorption of ammonia in zeolites at different temperatures as obtained from step-wise thermal desorption is presented in Fig. 2. For pure H-Y and lanthanum-exchanged zeolites the amount of ammonia desorbed decrease gradually as the temperature increase. For CeH-Y and REH-Y zeolites there is increase in the amount of ammonia chemisorbed at 673 K. All zeolites invariably show higher desorption at low temperatures. This is due to the interaction of ammonia with non-acidic sites in zeolites. The low temperature ammonia desorption is more in the case of rare earth exchanged zeolites and is already reported in the case of mordenite zeolite [31]. Hence the number of acid sites measured by ammonia chemisorption at lower temperature can be taken only as an upper limit of the acid sites in the zeolites. However, at higher temperatures (>623 K) the

Table 2 Textural and acid structural properties of different zeolites

Catalyst	Amount of ammonia (mmol/g^{-1}) desorbed within certain temperature range K				Textural properties	
	W ^{a,b}	M ^a	S ^a	Total	Surface area (m^2/g)	Pore volume ^c (cc/g)
H-Y	0.69	0.41	0.33	1.43	398	0.266
CeH-Y	1.10	0.60	0.31	2.02	511	0.340
LaH-Y	0.51	0.71	0.46	1.68	464	0.288
REH-Y	0.68	0.86	0.49	2.03	483	0.301
K-10-Mont.	0.55	0.24	0.13	0.92	183	0.204
Ce-mont.	0.56	0.28	0.18	1.02	198	0.207
SiO_2	0.59	0.11	0.07	0.77	155	0.172
$\text{SiO}_2\text{-Al}_2\text{O}_3$	0.55	0.18	0.10	0.83	168	0.179

^a The ammonia desorbed in the temperature range 373–473 K might contain small amounts of physisorbed ammonia too. ^bW, M, and S stand for weak (373–473 K), medium (474–673 K), and strong (674–873 K) acid sites. ^c Total pore volume measured at 0.9976 P/P_0 .

non-acidic ammonia interactions are weak and hence the sites measured by chemisorption of ammonia are expected to be acidic ones. This part is considerably larger in the case of all the rare earth exchanged zeolites compared to pure H-Y. This supports the enhancement the acid structural properties upon rare earth exchange.

Catanach and co-workers identified three desorption peaks for Y type zeolites located at 463, 513 and 673 K which corresponds to the loss of about 45 (49.45%), 28 (30.77%) and 18 (19.78%) molecules of ammonia per unit cell [32]. Dehydroxylation occurs only at 963 K. Lok and colleagues proposed for high silica to alumina ratio zeolites, the first NH_3 -TPD (below 473 K) peak is associated largely with weakly chemisorbed NH_3 molecules rather than physically adsorbed NH_3 molecules. The second peak (between 473–673 K) is associated with NH_3 molecules adsorbed on zeolite hydroxyl groups (the Brønsted acid sites) and the third NH_3 -TPD peak (between 673–873) is desorption from very strong BAS or LAS [33]. The first and second desorption peaks usually account for most of the ammonia adsorbed and the third peak is usually very small in absolute amount. All the as-exchanged zeolites show steady observation for the above statements and produce typically three desorption peaks in the stipulated temperature ranges (see desorption pattern in Fig. 2). Details are reported in our previous communications [25]. K-10 Mont. clay is rather weakly acidic (0.92 mmol/g) and the cumulative acid amount increases slightly on cerium exchange (1.02 mmol/g). In general, ammonia TPD studies shows that zeolites are far more acidic compared to K-10 clays.

Surface area and pore volume increase invariably on exchange with rare earth cations (Table 2). The increase of surface area might be due to the decrease in the crystallite size and improvement in the microporous nature on exchange of hydrogen in H-Y zeolite with rare earth cations. Montmorillonite clay is a layered alumino-silicate with a dioctahedral layer sandwiched between two tetrahedral layers. Unlike zeolites used, this does not have a regular pore structure [34]. The pore size > 1.0 nm 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). Pure silica and silica-alumina are porous solid without regular pores. These have surface area and pore volume far less compared to zeolites.

3.2. Acetalization of ketones

We have used five classes of solid acid catalysts in this work for the acetalizations of ketones. They include; (1) rare earth exchanged H-Y zeolites, (2) K-10 montmorillonite clay, (3) Ce-montmorillonite clay, (4) silica, and (5) silica-alumina. Three ketones with different molecu-

lar sizes, cyclohexanone, acetophenone, and benzophenone were reacted with methanol to produce the corresponding dimethylacetals.

Acetalizations of ketones produce corresponding dimethylacetal. Hemiacetal formation was not detected in the reaction mixture even after 50 h of reaction. There was no byproducts for the reaction. The results of the studies are illustrated in Table 3. In general, clays are found to be the more active catalyst with all ketones. Pure H-Y, various as-exchanged rare earth H-Y zeolites are less active compared to mesoporous K-10 clay. Among different zeolites, CeH-Y is found to be the most active towards the acetalization reactions and H-Y the least. Silica exhibits negligible activity for the reaction. There was no predominant increase in the percentage conversion with reaction time. Among different ketones cyclohexanone is the most active and benzophenone the least. K-10 Mont. shows a conversion of 71.7 % in 2 h with cyclohexanone, 13.8% with acetophenone and 2.8% with benzophenone whereas; with CeH-Y it is 69.8, 11.9, and 2.6% respectively. Silica-alumina and pure silica were near inefficient as an acetalization catalyst. Nevertheless, SiO_2 - Al_2O_3 initiates acetalization of cyclohexanone (3.8% in 2 h) and acetophenone (1.3% in 2 h) to a limited extent. No conversion was observed while blank run (without catalyst).

Table 2 shows that zeolites are far more acidic compared to K-10 clay. If we consider the acid structural properties (see Table 2), zeolites must be far more active than K-10 clay. According to TPD studies, REH-Y was the most acidic and has the highest number acid sites (2.03 mmol/g) among the catalysts. However, it produced lower acetal in 2 h. K-10 clay has an acid amount far inferior (cumulative; 0.92 mmol g^{-1}) to any rare earth exchanged zeolites. However, it produces more acetal with any ketones than REH-Y. The catalytically active sites involved in the reaction were thought to be bridging hydroxyl groups. The bridging hydroxyl groups present in much larger amounts in zeolites than clays and must have higher intrinsic activity than clays which have weaker acid sites related to silanol groups. Thus, we conclude that it is not only the acidic structure of the catalysts that determine the acetalization ability to a greater extent. It is reported that the catalytic activity of catalyst towards the reaction does not require strong acidic sites [35]. As pointed out by Corma and co-workers the pore diffusion limitation imposed by larger molecular sizes of the reactant played an important role during the reaction using zeolite catalysts [16, 35].

As pointed out earlier the pore diffusion limitation induced by the large molecular size of the reactant played an important role during the acetalization reaction using zeolite catalyst [2, 35]. Therefore only a fraction of the acid sites on the outer surface of the zeolites are available for reactants and slightly higher product yield could only be

Table 3 Results obtained in the acetalization of cyclohexanone, acetophenone, and benzophenone with methanol over different solid acid catalysts

Catalyst	Percentage conversion of ketones					
	Cyclohexanone ^a		Acetophenone ^b		Benzophenone ^b	
	2 h	10 h	2 h	10 h	2 h	10 h
H-Y	43.6	49.9	4.4	7.6	1.2	2.4
CeH-Y	69.9	75.5	11.9	19.7	2.6	4.9
LaH-Y	58.5	64.3	7.6	10.3	2.1	3.6
REH-Y	64.4	69.7	8.9	13.3	2.3	4.1
K-10 Mont.	71.7	88.2	13.8	21.2	2.8	5.8
Ce-mont.	78.9	96.8	21.2	28.6	4.1	7.2
SiO ₂ -Al ₂ O ₃	3.8	4.9	1.3	1.6	0	0
SiO ₂	0	0	<1	1.2	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 dry nitrogen. ^aReactions were carried out at room temperature under atmospheric pressure. ^bReactions were carried out at ambient temperature (353 K) and atmospheric pressure. ^cWithout using catalyst. ^dAfter the reaction over CeH-Y zeolite, 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.

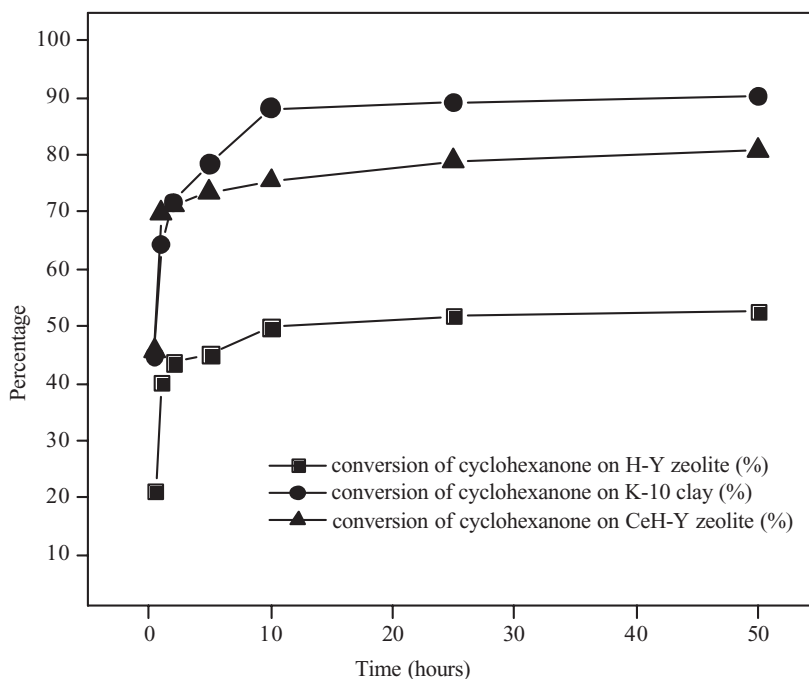
attained with larger time on stream of the reaction. K-10 clay is a mesoporous materials and the effect pore diffusion is not as critical as in the case of zeolites. This explains the comparative low activity of as-exchanged zeolites (conversion range from 58.5 to 69.9% in 2 h with cyclohexanone) than low acidic mesoporous K-10 montmorillonite and cerium-exchanged clays (conversion is 71.7 and 78.8% respectively in 2 h). The greater pore size of clays ease the rate of diffusion of the bulky products through the channels.

Cerium exchanged materials; both CeH-Y and Ce-mont produce comparatively larger amounts of acetals than other rare earth exchanged zeolites or K-10 montmorillonite clay. Tateiwa and co-workers reported the acetalization of carbonyl compounds with methanol in presence of different cation exchanged montmorillonite clay (M^{n+} -mont; $M^{n+} = Ce^{3+}, Zr^{4+}, Fe^{3+}, Al^{3+}, Zn^{3+}, H^{+},$ and Na^{+}) [12]. Ce-mont was found to be the most effective catalysts for the substrate-selective acetalization. REH-Y zeolite yields comparatively larger amounts of acetal with all ketones than LaH-Y. Presence of small amounts of cerium (see Table 1) might be the reason for the enhanced production of acetal over REH-Y. Proper acid amount as well as suitable drying ability of CeH-Y zeolite and Ce-mont seems to work well in shifting the equilibrium in favor of the product (12). Also, a Ce^{3+} ion act as a Lewis acid site and activate the carbonyl group by coordination, in the order of 1 kJmol^{-1} [13].

Comparing H-Y and different as-exchanged zeolites, it is seen that the rare earth exchanged zeolites yield more acetal than pure H-Y zeolite. H-Y produces 43.6%, 4.4% and 1.2% acetal with cyclohexanone, acetophenone and benzophenone respectively whereas, the as-exchanged CeH-Y produce 69.9%, 11.9% and 2.6% of respective acetals in 2 h. This enhancement in the catalytic activity could be explained in terms of the improvement in the acid amount as well as surface area and pore volume data (Table 1). The improvement in total pore volume could provide a better diffusional probability for the bulky acetals. Also, the proper acid amount as well as suitable drying ability of rare earth zeolites seems to work well in shifting the equilibrium in favour of the product. This is more pronounced in the case of CeH-Y due to special influence of cerium cation. Tateiwa et al. reported in similar lines in the case of Ce-mont catalyst [12].

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 2). It is seen from the molecular size calculation that the sizes follow the order cyclohexanone < acetophenone < benzophenone. 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) [36].

Fig. 3 Effect of reaction time on the formation of dimethoxy cyclohexane with methanol over H-Y and CeH-Y zeolites and K-10 montmorillonite clay. Reaction temperature; RT, molar ratio of cyclohexanone and methanol; 1:10, amount of catalyst; 0.25 g, and gentle flow of dry nitrogen



3.3. Effect of reaction time

Acetalization of cyclohexanone was measured on H-Y, CeH-Y zeolites and K-10 montmorillonite clay as a function of reaction time. No product other than acetal was detected by careful GC and GC-MS analysis of the reaction mixture even after 50 h of reaction. Results of the studies are presented Fig. 3. Once the reaction attains equilibrium in one hour, the formation of acetal remains almost constant over H-Y and CeH-Y zeolites (52.1 and 80.8% in 50 h). On the other hand, K-10 montmorillonite clay having slightly higher initial activities (64.3% in one hour), can achieve a final larger conversions (90.2% in 50 h). This can be a clear indication that the large products formed can adsorb in zeolite-Y blocking the pores and/or the active sites leading to a loss of catalytic activity. The adsorption of products on the large pores of K-10 clay is only to a very limited extent and a corresponding increase in the yield of dimethoxy cyclohexane with time.

We have found that the deactivated catalysts can be almost fully regenerated by continuous solvent extraction to remove most of the “heavy” products. These as-extracted samples show only 40, 52 and 51% of activity respectively for the reaction. These samples then were regenerated by activating at 773 K for 5 h under constant flow of nitrogen [37, 38–39]. They were again employed as catalysts in the third experimental and no substantial loss of activity were found. H-Y and CeH-Y zeolites produce 39.5 and 68.1% acetal respectively in one hour and K-10 montmorillonite produces 69.1%. The catalyst deactivation studies indicate while zeolite and K-10 have slightly different initial activity, zeolite

deactivate much more rapidly than K-10 clay owing to the larger adsorption and lower diffusion rates of the products in the microporous structure.

We have conducted experiments to obtain clear evidence for the stability and true heterogeneity of the catalysts towards the reaction. After the reaction over CeH-Y zeolite and Ce-mont clay, the catalysts were removed by filtration and the filtrate obtained was used to examine the catalytic activity of the possible dissolved components of the catalyst (see Table 3; filtrate). Furthermore, no aluminium was detected in the reaction mixture by the SEM-EDX. No aluminium was detected while qualitative analysis of the mixture also. These results strongly suggest against the possible aluminium leaching during the reaction.

4. Conclusion

A simple, efficient and highly eco-friendly protocol is described for the substrate selective acetalization of ketones with methanol over rare earth exchanged H-Y zeolites, K-10 montmorillonite, Ce-mont clays, $\text{SiO}_2\text{-Al}_2\text{O}_3$ and silica. K-10 and cerium exchanged montmorillonite clays were found to be more active than zeolites. It appears that when working with ketones of different molecular sizes as reactants, the reactivity of ketones decrease in the order cyclohexanone > acetophenone > benzophenone, which is the reverse order of molecular size. 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. The catalysts

can be recycled without loss of activity. Removal of water is not warranted in these reactions.

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