

ACETALIZATION OF CYCLOHEXANONE

<i>Contents</i>	5.1 <i>Introduction</i>
	5.2 <i>Acetalization of Ketones</i>
	5.3 <i>Reaction Procedure</i>
	5.4 <i>Optimization of Reaction Conditions</i>
	5.5 <i>Catalytic Activity of Prepared Samples</i>
	5.6 <i>De-protection Reaction (Hydrolysis of Dimethoxy Cyclohexanone)</i>
	5.7 <i>Catalytic Activity of Prepared Samples in Deacetalization of Acetals</i>
	5.8 <i>Conclusion</i>
	5.9 <i>References</i>

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The synthesis of dimethyl acetals of carbonyl compound such as cyclohexanone has successfully been carried out by the reaction between cyclohexanone and methanol using different solid acid catalysts. The strong influence of the textural properties of the catalysts such as acid amount and adsorption properties (surface area and pore volume) determine the catalytic activity.

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5.1 Introduction

Acids are the catalysts which are used most in industry, including the fields of oil refining, petrochemicals and chemicals. They are responsible for producing more than 1×10^8 mt/year of products. Among the first acid catalysts, the most commonly used were HF, H₂SO₄, HClO₄ and H₃PO₄ (in liquid form or supported on Keiselguhr). Solid acids have many advantages such as simplicity in handling, decreasing reactor and plant corrosion problems, and environmentally safe disposal [1]. Also, wastes and by-products can be minimized or avoided by developing cleaner synthesis routes [2]. On the other hand, any reduction in the amount of sulphuric acid needed and/or any simplification in handling procedures is required for risk reduction, economic advantage and environment protection. In addition, there is current research and general interest in heterogeneous systems because of the importance of such systems in industry and in developing technologies [3]. Very recently, many others have demonstrated that heterogeneous reagent systems have many advantages such as simple experimental procedures, mild reaction conditions and minimization of chemical wastes as compared to the liquid phase counterparts [4]. The acetalization reaction is a process that is widely used in organic synthesis to protect the carbonyl group of aldehydes and ketones [5]. Afterward, acetals became important reactants for synthesis of enantiomerically pure compounds which were widely used as steroids, pharmaceuticals, and fragrances [6]. The title reaction is many times a requirement to protect carbonyl groups specifically during the manipulation of multifunctional 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 [5]. 1, 2-Diacetals are efficient protecting groups for vicinal 1, 2-diol units in carbohydrates [7, 8]. In particular, protection of monosaccharide units as cyclohexane 1, 2-diacetals (CDA) offers rapid access to important building blocks for oligosaccharide synthesis [9]. S.V. Ley, Grice and co-workers reported the preparation, structure, and derivatization and NMR data of cyclohexane 1, 2-diacetal protected carbohydrates [7a, 10]. Previously, the catalysts used in the acetalization reactions were generally proton acids, Lewis acids, and a number of transitional metal complexes including Rh, Pd and Pt [11]. Although good results were obtained, the separation of the products from the catalyst system after the reaction was still difficult to overcome and the noble metal catalysts used were quite expensive and usually unstable [12]. Although many efficient and reliable reactions for the conversion of carbonyl compounds to their corresponding acetals have been reported, there are, however, some drawbacks such as long reaction times, tedious work-up and separation of catalyst, toxic metal waste, unwanted side reaction and nonselectivity regarding these methods. Therefore, design and synthesis of a catalytic system that may be stable, easily separable, and reusable has long been pursued. Furthermore, the basic requirements for achieving high catalytic activity, as it was reported in previous literature, were the presence of sufficient acidity and the existence of two adjacent acid sites to have the reactants in a mutually cis position [12] and all these studies offered us the possibility of designing suitable catalysts for this reaction. Zeolites, clays, sulphated metal oxides, and mesoporous materials provide a convenient catalytic route for protecting the carbonyl groups during organic synthesis.

Besides the interest of acetals as protecting groups of carbonyl compounds during organic synthesis, many of them have found direct

applications as fragrances in cosmetics, food and beverage additives, pharmaceuticals, and polymer chemistry, medicinal and drug design chemistry. This reaction is extensively used in the synthesis of enantiomerically pure compounds [13] which find practical application in the fields of synthetic carbohydrates, food and beverage additives [14] steroids [15], pharmaceuticals and fragrances [16] among others. The methyl and ethyl acetals of n-octanal and n-decanal, for example, find widespread applications in perfume and flavour industries [17]. Sometimes, several acetals named as 'potential fragrances' are introduced into the different formulations and, at the time of contact with the skin, the products are hydrolysed and odorous compounds are released. The conversion of a carbonyl compound to its acetal alters its vapour pressure, solubility and aroma characteristics, and often results in flavour attenuation. For example, the propylene dioxy derivative of vanillin is commonly used as a vanilla flavour since it causes flavour attenuation [18].

The most general method for the synthesis of acetals is the reaction of carbonyl compounds with an alcohol or an ortho ester in the presence of acid catalysts [19]. The synthesis of dimethyl acetals of carbonyl compound cyclohexanone has successfully been carried out by the reaction between cyclohexanone and methanol using different solid acid catalysts. The commonly used acid catalysts include corrosive protic acids such as HCl, H₂SO₄ and Lewis acids such as ZnCl₂ and FeCl₃ [20, 21]. Homogeneous acid catalysts ranging from Mg (ClO₄)₂ [22], p-toluene sulphonic acid [23], and a series of cationic diphosphine Lewis acidic complexes of Pt (II), Pd (II), and Rh (III) [12a, 24] etc. have also been employed successfully for the generation of acetals. Gorla and Venanzi have described the basic structural requirements to achieve high activity of the catalysts [25].

However, acetalization procedures mentioned above require expensive reagents, tedious work-up procedure and neutralization of the strongly acidic media leading to the production of harmful wastes. Hence, these methods suffer limitations derived from high E-factors and low atom utilization as the catalysts are irreversibly lost. Furthermore, the formation of dimethyl acetals in homogeneous phase is often carried out by using trimethyl ortho formate as the reagent. Methanol is more desirable for this reaction. The choice of the catalyst is of prime importance in these environmentally conscious days. Green chemistry demands the replacement of highly corrosive, hazardous and polluting acid catalysts with eco-friendly and renewable solid acid catalysts. The use of heterogeneous solid catalysts in the organic synthesis and industrial manufacture of chemicals is interesting and important, since they provide green alternatives to homogeneous catalysts. This is particularly important in acid catalysis where solid acids are not only safe alternatives to hazardous and corrosive liquid acids, but also have many advantages, such as simplicity in handling, decreasing reactor and plant corrosion problems and environmentally safe disposal. Also, wastes and by-products can be minimized or avoided by developing cleaner synthesis routes. Any reduction in the required quantity of liquid acids and/or any simplification in treatment procedures are necessary for to reduce risk, create economic advantage and protect the environment. Environmentally benign solid acid catalysts such as various rare earths-exchanged Mg–Y zeolites, CeMg– Y and Ce-montmorillonite were revealed to be the most efficient catalysts for the acetalization reactions. Although significant progress has been achieved in improving the catalytic activity, selectivity, and reagent scope, in many cases, however, they require a high catalyst loading and suffer from catalytic activity losses during reuse. Therefore, there is still a need for a low

loading, more economic, and environmentally benign solid catalysts [26]. Previously, the catalysts used in the acetalization reactions were generally proton acids, Lewis acids, and a number of transitional metal complexes including Rh, Pd, and Pt [11]. Although good results were obtained, the separation of the products from the catalyst system after the reaction was still difficult to overcome and the noble metal catalysts used were quite expensive and usually unstable [12a]. Therefore, to design and synthesize a catalytic system that may be stable, easily separable, and reusable has long been pursued. Furthermore, the basic requirements for achieving high catalytic activity, as it was reported in previous literature, were the presence of sufficient acidity and the existence of two adjacent acid sites to have the reactants in a mutually cis position [12a] and all these studies offered us the possibility of designing suitable catalysts for this reaction. Acetalization of cyclohexanone reached equilibrium within 60 min and the yields of acetal were 66.7% with CeMg–Y zeolite and 69.8% with Ce^{3+} cation. Cyclohexanone reacted smoothly in methanol at room temperature with solid acid catalysts.

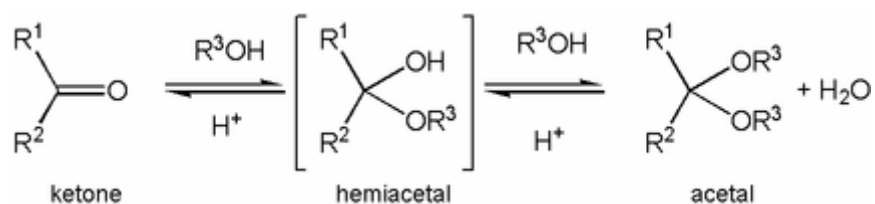


Fig. 5.1 Pathways of acetalization of cyclohexanone

5.2 Acetalization of ketones

Acetal or ketal formation is a reversible reaction, which proceeds by a two-step mechanism. Their formation is strongly affected by electronic and steric factors (12b).

The first step is the formation of hemiacetal, followed by the removal of a molecule of water. Formation of a cation from the protonated hemiacetal is the rate determining step of acetalization reactions. However, the protonation of hemiacetal is also a slow step and the reaction medium has to be sufficiently acidic to promote efficient protonation of hemiacetal. Also, the reaction medium must be polar enough to stabilize of the cation intermediate formed from hemiacetal.

In the mechanism presented below, cyclohexanone is first protonated by the Brönsted acid sites (H^+ ions of the catalyst) to produce the intermediate (2) which then combine with methanol to form the hemiacetal (4). Protonation of (4) leads to intermediate (5) which undergoes subsequent dehydration to give (6). Reaction of (6) with a molecule of methanol gives intermediate (7). Removal of a proton from (7) leads to the formation of the acetal (8).

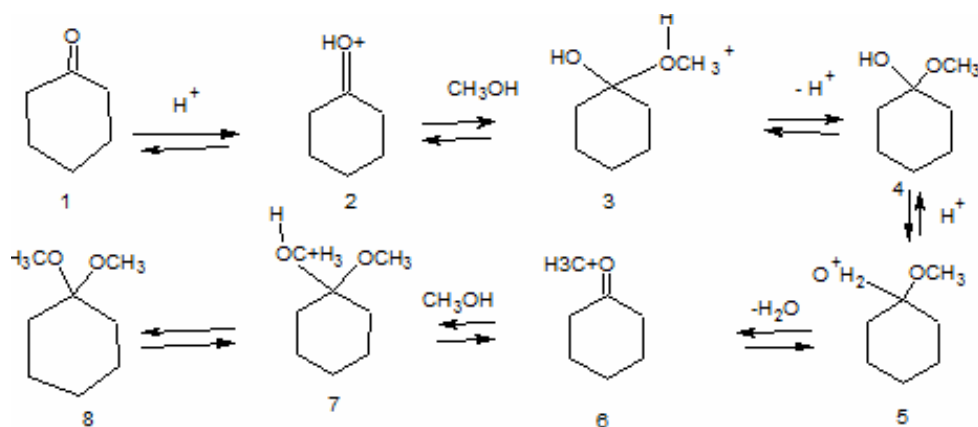


Fig. 5.2 Mechanism of acetalization of cyclohexanone

5.3 Reaction Procedure

In order to explore the influence of the modified mesoporous ceria catalyst on reaction, the reaction of cyclohexanone with methanol was

chosen as a model reaction. Initially, the reaction was performed under catalyst free condition and no product formation was observed. Then, to obtain optimized reaction conditions, the acetalization reaction was performed with cyclohexanone and methanol using different amounts of modified mesoporous ceria catalyst at different temperatures. Cyclohexanone, purchased from Aldrich Chemical Company, USA and commercial-grade methanol (available from S. D. 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. Samples were withdrawn every 30 minutes and at the end of the reaction 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 and 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% phenyl methyl silicone.

5.4 Optimization of Reaction Conditions

The reaction conditions play an important role in deciding the catalytic activity. The factors influencing the activity of catalyst in the reaction were studied by varying the reaction temperature, weight of the catalyst, molar ratio of cyclohexanone to methanol and time of reaction. The parameters were optimized and the best conditions were found.

5.4.1 Effect of Volume of methanol on cyclohexanone conversion

Fig.5.3. shows the effect of molar ratio of cyclohexanone to methanol on cyclohexanone conversion. A number of experiments were done to

study the effect of molar ratio of cyclohexanone to methanol. Molar ratio of the reactants plays a major role in the rate of reaction. The conversion of cyclohexanone increases with the increase in the molar volume of methanol. When volume of methanol is 10 ml conversion is maximum and then it is getting decreased. The conversion changes from 29% to 60.2 % when the molar ratio changes from 1: 05 to 1:10. Further increase in molar ratio causes a decrease in the conversion

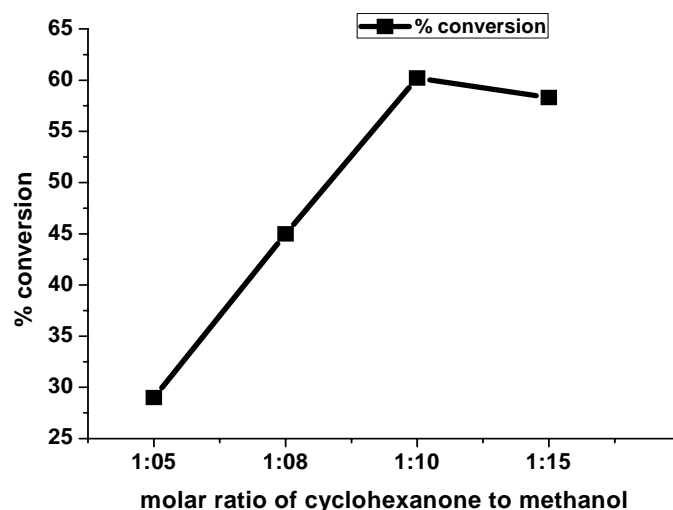


Fig.5.3 Effect of molar ratio on conversion of cyclohexanone

Reaction conditions: Catalyst-0.05g CeFe (10%), Temperature-70°C, Time -30min.

5.4.2 Temperature

The conversion of cyclohexanone depends very much on temperature. At room temperature there was no reaction. As the temperature is increased and reached 70°C the conversion became appreciable. Further increase in temperature caused an increase in the conversion and it reaches maximum at 80°C but the boiling of methanol takes place. Beyond 80°C the rate of reaction was decreased. So the temperature for the reaction was selected as

70°C. At all temperatures the sole product was dimethyl acetal. The result of the study of temperature dependence of the reaction is shown in Fig 5.4.

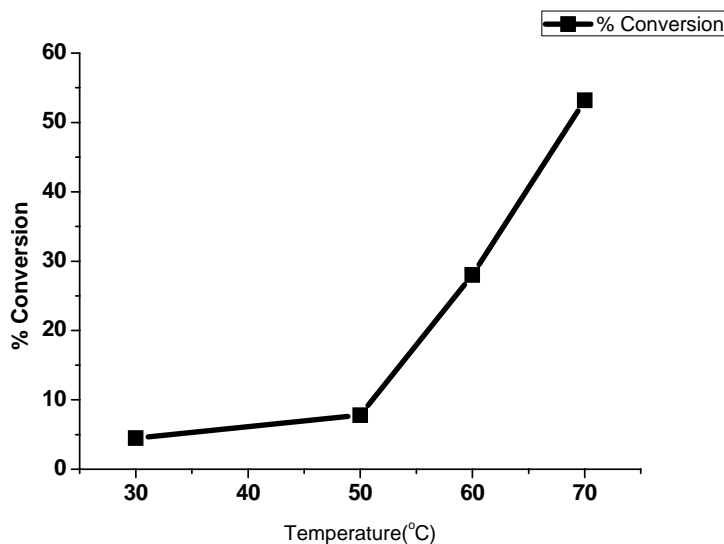


Fig.5.4 Effect of Temperature on conversion of cyclohexanone

Reaction conditions: Catalyst-0.05 g CeFe (10%), Time -30min

5.4.3 Weight of the catalyst

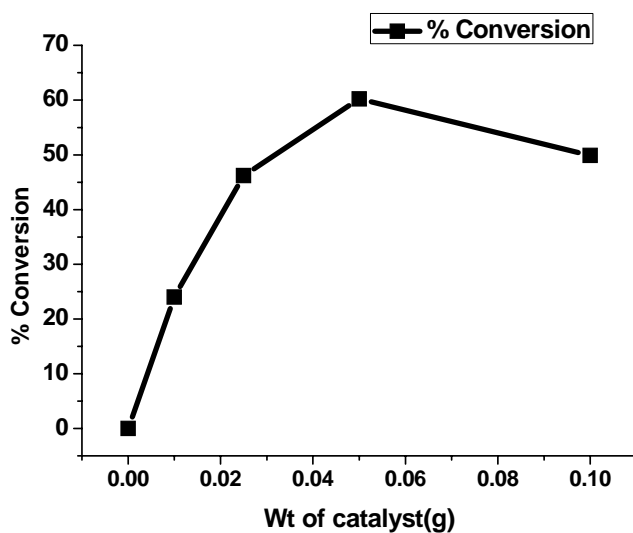


Fig.5.5 Effect of wt. of catalyst on conversion of cyclohexanone

*Reaction conditions: Volume of methanol-10ml,
Catalyst- CeFe (10%), Temperature- 70°C, Time -30min.*

In heterogeneous catalysis weight of the catalyst plays an important role in influencing the rate of a reaction. The acetalization of cyclohexanone was repeated with different weights of CeFe (10%) catalyst at 70°C, using 10 ml of methanol, to optimize the catalyst weight. The reaction was conducted for 30 minutes and the product collected was analysed. Without the catalyst, reaction was at a negligible rate. As the weight of catalyst is increased the reaction rate is also increased. Conversion is maximum with 0.05 g of the catalyst and then it is decreased. So 0.05g of catalyst was used for further reaction. The Fig. 5.5 shows that there was no conversion in the absence of catalyst. As the amount of catalyst increases, the rate of reaction also increases. It is very much noticeable that very small amount of the mesoporous ceria based catalyst is enough the reaction rate to increase from zero to 60%. With 0.05g catalyst the rate reaches maximum but after that there is a small decrease when the weight of the catalyst is doubled to 0.1g. So the weight was optimized as 0.05g.

5.4.4 Time of reaction.

To study the effect of reaction time on the reaction rate the reaction was done for 2 hours at 70°C with 0.05g of CeCr (10%) using 1:10 molar ratio of cyclohexanone to methanol.

Fig. 5.6 shows that at 15 minutes the conversion of cyclohexanone was very low (48.5%). At 30 minutes it is increased to 53.5 %. Then it decreases till 1 hour then it remains almost constant. Decrease in the catalytic activity after 30 minutes may be due to high adsorption of bulky reaction products and remain constant may be because of the lower diffusion rate of these bulky groups. The products may be adsorbed by the

catalyst resulting in blocking of the pores or active sites leading to the loss of catalytic activity.

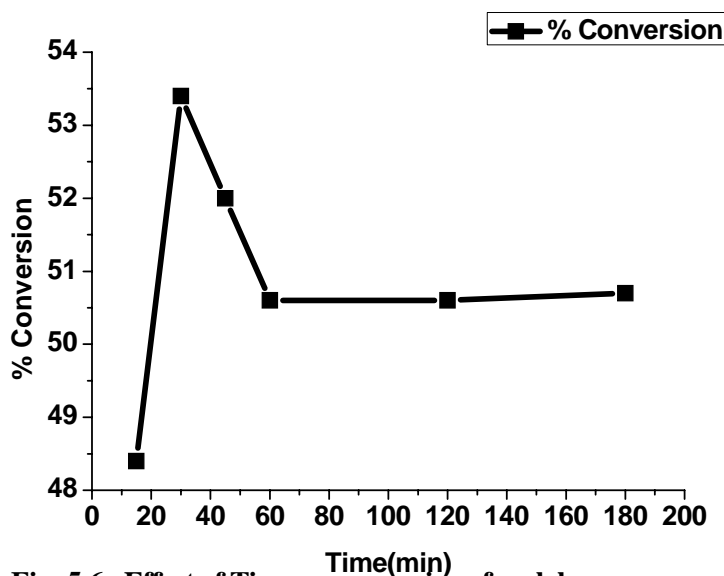


Fig. 5.6 Effect of Time on conversion of cyclohexanone

Reaction conditions: Volume of methanol-10ml, Catalyst-0.05g CeFe (10%), Temperature- 70°C.

5.4.5 Leaching Test and Recycling

Metal leaching studies give the information about the nature of reaction. To test the heterogeneity of the catalytic system, the leaching test was performed. For this the catalyst was removed from the reaction mixture by filtration after a small interval after the reaction has proceeded. Then the reaction was allowed to proceed again without the catalyst and the % conversion of cyclohexanone before and after the filtration was analysed using GC. The reaction was carried out at 70°C, using CeCr (10%) keeping the molar ratio of cyclohexanone to methanol 1:10 for 15 minutes. Then the catalyst is filtered off and again the reaction mixture was allowed to proceed under the same condition for 15 more minutes. It was found that after filtration of the catalyst, the filtration liquor reacted much more slowly

and at a similar rate to the reaction taking place in the absence of the catalyst (Table 5.1, Entry 2), indicating that no leaching of the active catalytic species occurred during the reaction.

After filtration, the catalyst was washed with methanol and dried before the next cycle. The catalyst was found to be reusable for consecutive cycles without any significant loss of activity. The conversion was analysed. The result is given in the Table 5.3.

Table 5.1 Influence of metal leaching in acetalization of cyclohexanone with methanol

Time (min)	Conversion (%)
15	48.4
30*	49

Catalyst: 0.05g CeCr (10%), Temperature: 70°C, Cyclohexanone to methanol molar ratio: 1:10

*After filtration

Table 5.2 Optimized Reaction conditions for acetalization of cyclohexanone

Parameters	Optimized conditions
Temperature	70°C
Cyclohexanone-Methanol Ratio	1:10
Catalyst Amount	0.05g
Time	30 min

5.5 Catalytic Activity of prepared samples

Table 5.3 Catalytic activities of different prepared catalysts

Catalyst	Conversion of cy. hexanone (%)	TON ^a	TOF ^b
CeO ₂	12	-	-
w.c	4	-	-
CeFe (2%)	56.4	318.5	637
CeFe (4%)	57	160.9	321.8
CeFe (10%)	64	72.3	144.6
CeCr (2%)	28	141.5	283
CeCr (4%)	33.7	85.1	170.2
CeCr (10%)	53.4	53.9	107.8
CeMn (2%)	38.5	205.3	410.6
CeMn (4%)	20.7	55.2	110.4
CeMn (10%)	29.4	31.3	62.6
CeCo (2%)	39.6	223.6	447.6
CeCo (4%)	29.1	82.2	164.4
CeCo (10%)	34.5	26.4	52.8
CeNi (2%)	33.3	188	376
CeNi (4%)	32.5	91.8	183.6
CeNi (10%)	33.2	37.5	75
CeCu (2%)	36	230.4	460.8
CeCu (4%)	38.1	121.9	243.8
CeCu (10%)	35.7	45.7	91.4

a- $TON = (\text{mmoles of reagent reacted} / \text{mmoles of metal added}) \times 100$

b- $TOF = TON / \text{time (h)}$

Acetalization of cyclohexanone was carried out over all the prepared catalyst systems using methanol under the optimized conditions. In all the cases the corresponding diacetal was obtained as a single product with high

yield. In a typical run, 10 ml of 1:10 mixture of ketone and methanol was stirred with 50 mg of pre-activated catalyst, at 70°C for 30 minutes.

For a comparison of catalytic activity of mesoporous ceria modified by different transition metals as catalyst for acetalization of cyclohexanone, reaction was studied both in presence of catalysts and without catalyst. A comparative evaluation result obtained is given in the Table 5.3.

It is noticeable that a negligible conversion was obtained for blank reaction. Pure Mesoporous ceria gave very low conversion under the specified reaction conditions. Modification with different transition metals increases the activity in acetalization reaction. All the modified ceria catalysts produced dimethyl acetal as the only product during the reaction. The highest activity was shown by 10% iron incorporated mesoporous ceria system.

From the reaction mechanism, it appears that the reaction proceeds with the formation of very bulky intermediates and a microporous material like zeolite may be less reactive in comparison to a mesoporous material. It is not only the acidic structure of the catalysts which determine the acetalization ability to a greater extent but also the diffusional properties of the catalytic systems are the deciding factor in the acetalization reaction of ketones. The activity of catalyst towards the acetalization reaction does not require strong acidic sites [16a]. As pointed out by Corma and co-workers the pore diffusion limitation imposed by larger molecular sizes (0.75nm for cyclohexanone as determined by the energy minimization program) of the reactant played an important role during the acetalization reaction using solid acid catalysts [1, 27]. 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 nm³ [28]. Enhancement in catalytic activity could be explained in terms of improvement in textural and structural properties. Enhancement in the total pore volume could provide a better diffusional pathway for the bulky acetals. It appears that the acid structural properties and the diffusional properties of the catalytic systems are the deciding factor in the acetalization reaction of ketones.

The enhancement in catalytic activity could be explained in terms of improvement in textural and structural properties. Enhancement in the total pore volume could provide a better diffusional pathway for the bulky acetals. The enhanced formation of acetal over transition metal modified mesoporous ceria could also be explained as follows. In general transition metal modified mesoporous ceria possess much more amounts of weak plus medium acid sites and an assembly of these weak acid sites may act as an effective/strong acid site. A reasonable hypothesis is that all the surface hydroxyl groups on the pore wall of the catalyst point to the centre of each pore, and thus they could work as a group. Such an assembly might induce efficient catalysis despite the low acidity of each -OH group [29]. In the case of modified samples, the surface hydroxyl groups provide most of the weak acid sites. The bigger pore size of catalyst samples over zeolites promotes the rate of diffusion of the bulky products through the channels. The rate determining step of acetalization is the formation of a cation from the protonated hemiacetal. Lin and co-workers proposed that the bulkiness of hemiacetal of acetophenone might prevent the bulky CH⁺ (OCH₃) from attacking its carbonyl carbon shifting the rate determining step during the acetalization with tri methoxy ortho formate [30]. Hence, we conclude that

the comparative low activity of acetophenone and benzophenone might be due to two reasons: (1) the bulkiness of hemiacetal might prevent the attack of the CH₃OH on the carbonyl carbon atom there by effecting a change in the rate-determining step (2). The electron withdrawing power of phenyl group reduces the easy release of the pair of electron on the carbonyl carbon during the reaction. But we cannot over emphasize the role of molecular size on reactivity since it is known that cyclohexanone is more reactive. The method developed by us does not involve additives and the catalysts can be recycled without loss of activity. Removal of water is not warranted in these reactions.

We have prepared 19 different catalyst samples. For the comparison of catalyst composition, from the product yield and considering the reaction as pseudo unimolecular, the intrinsic rate constants in the units of min⁻¹m⁻² was determined for each catalyst sample using the formula,

$$k(\text{min}^{-1} \text{m}^{-2}) = \frac{2.303}{twA} \log \frac{100}{100-\% \text{ yield}}$$

Where

t: Time of the reaction in minutes,

w: Weight of the catalyst (g), and

A: BET surface area of the catalyst (m²/g).

The rate constants of different samples are given in the Table 5.4.

Table 5.4 Rate constants of acetalization of cyclohexanone using different catalyst systems

Catalyst	Rate constant $\times 10^{-3}$ ($\text{min}^{-1}\text{m}^{-2}$)
Ce	0.05
CeFe (2%)	2.96
CeFe (4%)	3.32
CeFe (10%)	7.5
CeCr (2%)	1.77
CeCr (4%)	2.29
CeCr (10%)	4.37
CeMn (2%)	2.34
CeMn (4%)	1.28
CeMn (10%)	2.12
CeCo (2%)	2.48
CeCo (4%)	1.8
CeCo (10%)	2.59
CeNi (2%)	2.62
CeNi (4%)	2.89
CeNi (10%)	3.15
CeCu (2%)	3.62
CeCu (4%)	3.99
CeCu (10%)	4.08

The data reveal that the effect of modification of ceria with transition metals enhances its catalytic activity to a large extent. But the effect on catalytic activity by different metals is not alike. Different metals show different trend in the enhancement of catalytic activity. From the table it is evident that on incorporation of successive amounts of iron, chromium, copper and nickel the activity increases in a similar manner. For manganese

and cobalt there is a decrease in activity initially upon loading then it is increased.

5.5.1 Correlation between acidity and cyclohexanone conversion

Acetalization reaction being an acid catalysed reaction, the difference in the activities of the catalysts can be attributed to their difference in the acidity values. Fig.5.7. shows that the conversion of cyclohexanone upon acetalization, using different systems are in agreement with sum of weak and medium acidity as measured by ammonia TPD studies. The strong influence of textural properties of the catalysts such as acid amount and adsorption properties (surface area and pore volume) determine the catalytic activity. The reaction requires active sites with considerable acid strength. In addition to the acid strength, the pore volume, pore sizes and their distribution in the catalyst are responsible for their activity in the reaction.

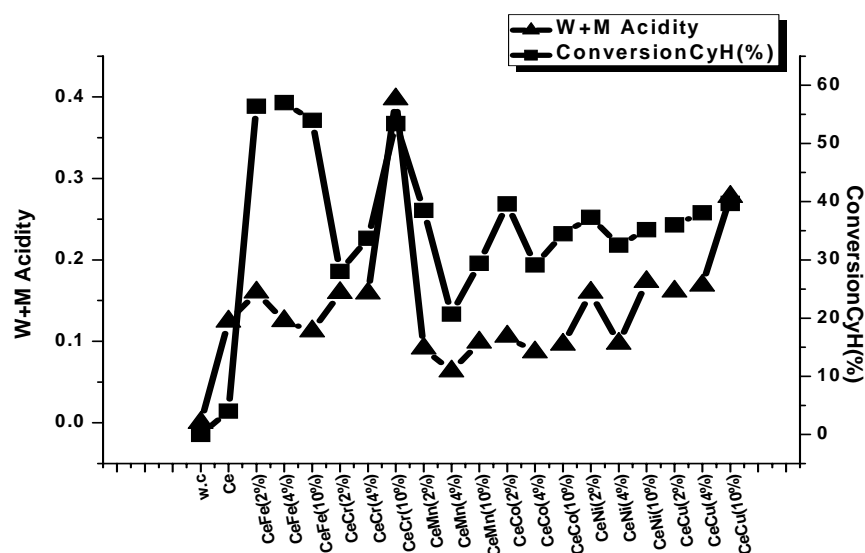


Fig.5.7 Catalytic activity correlated with sum of weak and medium acid sites obtained from TPD of ammonia

5.6 De-protection reaction (Hydrolysis of dimethoxy cyclohexanone)

The introduction and removal of protecting groups can play an important role in organic and natural product synthesis [31]. A major challenge in a multistep synthesis is to protect a carbonyl group from nucleophilic attack until its electrophilic properties of carbonyl can be exploited. Thus, regeneration of the parent carbonyl compound is a key step in such reactions. A number of acidic aqueous media, [32] acidic non-aqueous media [33] and non-acidic [34] methods have been reported for oxidative cleavage of acetals and ketals to the respective carbonyl compounds. However, some of the methods have limitations including severe reaction conditions, low yields of the products, unavailability and instability of the reagents, the requirement for aqueous reaction conditions and tedious work-up. Therefore, introduction of new methods and inexpensive reagents for such transformation is still in demand. De-protection is often performed by acid-catalyzed trans acetalization in acetone (in excess or as solvent), or hydrolysis in wet solvents or in aqueous acid. A convenient de-protection of acyclic and cyclic o, o -acetals and o, o -ketals is achieved in excellent yields within minutes under neutral conditions in the presence of a catalytic amount of iodine [35]. The electrophilicity of the carbonyl group is a dominant feature of its extensive chemistry. A major challenge in multistep synthesis is to shield a carbonyl from nucleophilic attack until its electrophilic properties can be exploited. For this reason the protection and deprotection of the carbonyl functional group remain crucial challenges to organic chemists. Experience shows that the critical parameters are generally the stability and the cleavage of the protecting group rather than its introduction. As with most of the protecting groups, many methods are available for the deprotection of acetals and ketals [36]. Now we wish to report a convenient method for deprotection of

acetals or ketals. Hydrolysis of acetal was performed at 70°C in the presence acetone-water mixture in the ratio 20:1. The reaction was conducted for 30 minutes by adding 10 ml of the acetone – water mixture.

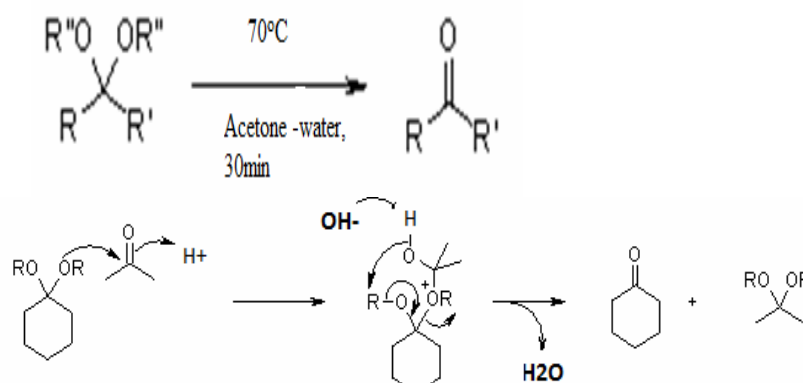


Fig.5.8 Mechanism of hydrolysis of dimethoxy cyclohexanone

5.7 Catalytic Activity of prepared samples in deacetalization of acetals

Catalyst	%Deacetalization
CeFe (2%)	100
CeFe (4%)	100
CeFe (10%)	100
CeCr (2%)	100
CeCr (4%)	98
CeCr (10%)	98.2
CeMn (2%)	98.3
CeMn (4%)	100
CeMn (10%)	98.9
CeCo (2%)	100
CeCo (4%)	100
CeCo (10%)	100
CeNi (2%)	100
CeNi (4%)	100
CeNi (10%)	100
CeCu (2%)	100
CeCu (4%)	100
CeCu (10%)	100

A cheap and easy procedure for the effective conversion of acetals and ketals to their corresponding carbonyl derivatives has been achieved here. The low cost and availability of the reagents, easy procedure and work-up make this method attractive for the large-scale operation. The high yields, the observed selectivity, the very gentle reaction conditions, and the almost neutral pH make this procedure particularly attractive for multistep synthesis.

5.8 Conclusion

In conclusion, we introduced a mild and selective reagent for the oxidative cleavage of acetals under aqueous and heterogeneous conditions. The stability, simple work-up and high yields of the products are among the advantages of this procedure which make it an attractive supplement to the present reported methods.

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