

Efficacy of a novel mesoporous solid acid catalyst UDCaT-4 in liquid phase benzylation of naphthalene

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Abstract

Friedel-Crafts alkylations are important class of reactions in the production of chemicals of industrial relevance. In the current work, selective monobenzylation of naphthalene with benzyl chloride was achieved at 80 °C by using a novel mesoporous solid acid catalyst UDCaT-4 which is a hexagonal mesoporous silica incorporating persulfated alumina and zirconia. It is found that UDCaT-4 exhibit superior catalytic activity than persulfated alumina and zirconia. The catalyst is reusable. The reaction was 100% selective towards monobenzylation of naphthalene without any dibenzylation. The Langmuir-Hinshelwood model with weak adsorption of reactants and products was found to validate the kinetics. The energy of activation is 26.0 kcal/mol.

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1. Introduction

Friedel-Crafts alkylation and acylation are ubiquitous for the production of intermediates and fine chemicals and these reactions are carried out industrially by employing Lewis acid such as AlCl_3 , BF_3 , TiCl_4 , or Bronsted acids such as H_2SO_4 , HF as catalysts [1,2]. The homogeneously catalyzed reactions require high catalyst concentration; often the amounts being more than stoichiometric. Since the catalysts are not recovered but neutralized, these processes are heavily polluting [1–4]. A considerable progress has been achieved in recent years through the developments in solid acid catalysts as replacements for traditionally polluting catalysts [3–5]. There are a large number of well studied solid acids, amongst which catalysts based on acid-treated clays and metal oxides, zeolites, sulfated zirconia, ion exchange resins, etc., are excellent alternatives in view of their ease of handling, robustness, activity. Zeolites provide a remarkable shape selectivity but slow diffusion of reactants through micropores of zeolites makes them relatively poor catalysts in

reactions involving bigger molecules like naphthalene and other polyaromatic ring derivatives [6–13]. Besides, the stability of zeolites in reactions where acids are produced as co-products is questionable and their rapid deactivation due to coke formation at high temperatures is problematic. All these technological challenges have led to upsurge in development of mesoporous acid catalysts. The current work delineates the benzylation of naphthalene with benzyl chloride on a novel mesoporous solid superacid called UDCaT-4. UDCaT is an acronym to a series of novel catalysts developed by us and it stands for University Department of Chemical Technology (UDCT) by which the authors institute was popularly known until very recently. Some of this series included mesoporous catalysts UDCaT-1 [14–16], UDCaT-4 [15–18], UDCaT-5 [19–21] and UDCaT-6 [13,22] and were used in alkylation using alkyl halides, alcohols and ethers; acylations with acid chlorides and anhydrides; esterification and cracking reactions using large molecules. All of these catalysts are modified versions of sulfated zirconia, whereas UDCaT-2, the shape sieving sulfated zirconia based catalyst [22,23] was used in condensation, nitration and benzylation reactions. It was thus thought to study the efficacy of some of the newly developed catalysts in our laboratory.

Alkylation of naphthalene with a variety of olefins and alkyl and aralkyl halides is commercially relevant and is typically

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catalyzed by strong homogeneous acids. Benzyl naphthalenes are useful as intermediates for organic syntheses in the field of additives for lubricants, dyes and antioxidants. Monobenzylated naphthalene was synthesized from naphthalene by using $\text{RuCl}_3 \cdot \text{XH}_2\text{O}$ as catalyst and benzyl bromide as a benzylating agent [24]. Benzylation of naphthalene with benzyl alcohol has been studied using various catalysts such as complexed $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ and $\text{AlCl}_3\text{-PhNO}_2$ and K-10 clay but no details are provided [25,26]. Schmerling [27] prepared isomers of benzyl naphthalene using CuCl_2 and AlCl_3 or ZnCl_2 as a catalyst in equimolar amounts. Grignard reagent prepared from magnesium and 1-naphthyl bromide has been used to react with benzyl chloride to get 1-benzyl naphthalene [28]. A reversible isomerization of benzyl and substituted benzyl naphthalenes is reported using AlCl_3 or *p*-toluene sulphonic acid [29]. Beltrame et al. [30] have reported benzylation using benzyl chloride and MCM-41 as a catalyst which also gives several polyalkylated products and they have also employed Nafion–silica composite as a catalyst with benzyl alcohol as benzylating agent [31]. Benzylation of benzene and substituted benzenes has been studied using benzyl chloride by InCl_3 , GaCl_3 , FeCl_3 and ZnCl_2 supported on clays Si-MCM-41 [32] and zeolites [33,34].

The foregoing suggests that there is tremendous scope to study the benzylation of naphthalene using new catalysts.

Among many solid acids other than zeolites, incorporation of superacidity into metal oxide has received considerable attention. Especially sulfated zirconia is the most extensively studied catalyst due to its superacidity [35–42]. However, some of the major problems associated with sulfated zirconia in its bulk form are its low efficiency due to low surface area ($\sim 100 \text{ m}^2/\text{g}$), rapid deactivation and relatively poor stability in reactions where water is generated as a co-product. Incorporation of different transition metals has been attempted to improve the acidity of zirconia but it still suffers from deactivation at high temperatures and there is an inherent lack of ordered mesoporosity. The activity and stability of sulfated zirconia can be improved by incorporating alumina and further treatment with ammonium persulfate (e.g. isomerization of *n*-butane) [43]. However, the surface area of persulfated alumina and zirconia (PAZ) is lower than that of sulfated zirconia. Thus, new catalysts with superacidity, greater stability, high surface area and ordered mesoporosity need to be designed to minimize the diffusion resistance for the reaction of bulky molecules. Considerable progress has been made in designing new solid acid catalysts in UDCaT series in our laboratory. Hexagonal mesoporous silica (HMS) is an excellent mesoporous support and thus it was identified as a support for persulfated alumina and zirconia in order to synthesize a new catalyst called UDCaT-4 possessing high surface area ($364 \text{ m}^2/\text{g}$) and ordered mesoporosity. The stability and robustness of the catalyst has been ascertained in the presence of HCl and water, respectively, formed as co-products in these reactions [11,17,18].

The current work discusses the superior activity of a new solid acid catalyst UDCaT-4 in the monobenylation of naphthalene with benzyl chloride. A new kinetic model is also developed based on experimental data.

2. Experimental

2.1. Chemicals

Zirconium oxychloride, aluminum nitrate (AR grade), aqueous ammonia solution, ammonium persulfate (AR grade), naphthalene, benzyl chloride, cyclohexane, 95% commercial grade ethanol were procured from M/s. s.d. fine Chemicals Ltd., Mumbai, India. Tetraethyl orthosilicate (TEOS) (Fluka) was taken as the neutral silica source and hexadecyl amine (Spectrochem Ltd.) as the neutral amine as template.

2.2. Catalyst preparation

Persulfated modified alumina and zirconia (PAZ) was prepared by sol–gel method from aluminum nitrate and zirconium oxychloride solution according to the method described elsewhere [11]. The ordered Hexagonal Mesoporous Silica (abbreviated as HMS) was prepared as per described procedure [17,18].

Desired quantities of zirconium oxychloride and aluminum nitrate was dissolved in known volume of distilled water and added to precalcined HMS by incipient wetness technique. After addition the solid was dried in an oven at 120°C for 3 h. The dried material was then hydrolyzed by ammonia gas at room temperature and washed with distilled water till no chlorine ion was detected and then dried at oven for 2 h at 120°C . The persulfation was carried out by immersing above solid material in to 1N ammonium persulfate solution and then calcined at 650°C for 3 h to get UDCaT-4.

2.3. Experimental procedure

All the reactions were carried out in a 5 cm i.d. fully baffled mechanically agitated glass reactor of 100 cm^3 total capacity which was equipped with a six blade-pitched turbine impeller (2 cm diameter) and a reflux condenser. The impeller was located at a distance of 2 cm from the bottom. The assembly was kept in an isothermal bath at the desired temperature and mechanically stirred at a known speed with an electrical motor. Predetermined quantities of reactants and solvent were added to the reactor and the temperature was increased to the desired value. The catalyst was added when the temperature reached the set value.

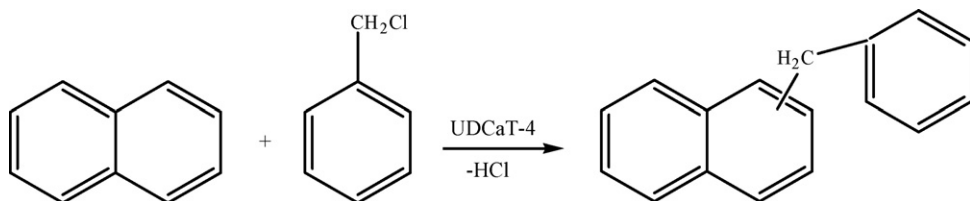
Standard reaction was carried out by dissolving 0.0585 mol naphthalene in cyclohexane as a solvent and 0.0195 mol benzyl chloride was added to it. The total volume of reaction mixture was made up to 45 cm^3 . The reaction mixture was then transferred into the glass reactor fitted with a reflux condenser. The reaction was started at the set temperature after the addition of the catalyst. A typical catalyst loading of $0.022 \text{ g}/\text{cm}^3$ liquid phase volume was used.

2.4. Analysis

Analysis was performed on GC (Chemito Gas Chromatograph, model 8510) by using a $4 \text{ m} \times 3.8 \text{ mm}$ stainless steel column packed with 10% OV-17 on Chromosorb WHP, cou-

pled with a flame ionization detector and N₂ as carrier gas. The product was confirmed by GC–MS.

2.5. Reaction scheme



3. Results and discussion

3.1. Catalyst characterization

UDCaT-4 is completely characterized by XRD, BET surface area, FTIR, SEM and EDAX and the details were published recently by us [11,17]. Only a few salient features are reported here.

XRD, BET surface area and pore size analysis provided an explanation for entrapment of nanoparticles of PAZ (<3.6 nm) in mesoporous of HMS. XRD data of UDCaT-4 suggested that the structural integrity of HMS is retained even after converting it into UDCaT-4. The diffractogram of UDCaT-4 further revealed that the introduction of small amount of alumina (0.16%, w/w) and sulfate ion (1.17%, w/w) stabilized the tetragonal phase of the zirconia, which is an ideal phase conducive for superacidity in sulfated zirconia, into the pores of HMS. Furthermore, the pore volume of UDCaT-4 (0.21 cm⁻³ g⁻¹) is much less than that of pure HMS (0.78 cm⁻³ g⁻¹) indicating that large amount of crystalline zirconia (9.01%, w/w), and alumina must be present inside pores of UDCaT-4. FTIR spectroscopy and EDAX analysis further support the assumption drawn on introduction of sulfate ion in UDCaT-4. The sulfur Ka1 and zirconium La1 distribution spectra determined by EDAX analysis shows the incorporation and homogeneous distribution of zirconia and sulfur atoms in UDCaT-4.

The TPD profiles of PAZ and UDCaT-4 show that although UDCaT-4 possesses weak and medium acid sites and the total acid sites of UDCaT-4 (0.56 mmol/g) are greater than those of PAZ (0.09 mmol/g).

SEM of UDCaT-4 revealed that similar to the morphology of HMS, UDCaT-4 is made up of sub-micrometer sized free standing or aggregated sphere shaped particles. SEM analyses further supports the argument that active centers of the PAZ are successfully embedded in HMS and the structural integrity of HMS is unaltered even after it is converted to UDCaT-4.

3.2. Catalytic activity of UDCaT-4

UDCaT-4 was compared with persulphated alumina zirconia without support under otherwise similar reaction conditions at a speed of agitation of 1000 rpm. UDCaT-4 showed much higher activity than persulphated alumina zirconia (PAZ) without support due larger surface area provided by inactive HMS. Therefore, UDCaT-4 showed a greater turnover number of 416 as

compared to 74 of PAZ (Table 1). There was no effect of speed of agitation on the conversion in the range of 800–1200 rpm, which suggested that the reaction was free from external mass transfer resistance.

3.3. Effect of catalyst loading

The effect of catalyst loading was studied in the range of 0.011–0.033 g/cm³ under otherwise similar reaction conditions. As the catalyst loading was increased from 0.011 to 0.022 g/cm³, the reaction rate increased substantially while further increase in catalyst loading to 0.033 g/cm³, there was a slight increase in the conversion (Fig. 1). Further increase in the catalyst loading did not result in the increase in conversion.

3.4. Effect of mole ratio

In order to study the effect of mole ratio on the conversion of benzyl chloride other parameters like temperature, catalyst loading were kept constant. The mole ratio of benzyl chloride:naphthalene was varied from 2:1, 1:1 to 1:3; it was found that with increase in the concentration of naphthalene the reaction rate increased (Fig. 2). Maximum conversion was obtained for the mole ratio of 1:3 (benzyl chloride:naphthalene), so it was selected for further studies.

Table 1
Comparison of catalytic activity

Parameters	HMS	PAZ	UDCaT-4
BET surface area (m ² /g)	833	81	233
Pore volume (cm ⁻³ g ⁻¹)	0.78	0.11	0.21
Turnover number	0	74	416

Turnover number = moles of product/moles of zirconium.

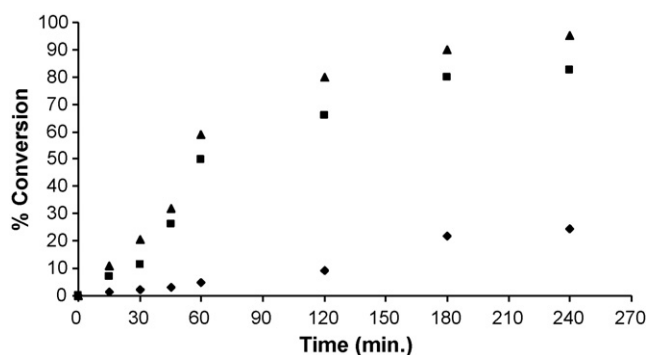


Fig. 1. Effect of catalyst loading. Temperature: 80 °C; solvent: cyclohexane (45 cm³). Benzyl chloride: 0.019 mol; naphthalene: 0.058 mol; speed of agitation: 1000 rpm, time: 4 h. (◆) 0.011 g/cm³; (■) 0.022 g/cm³; (▲) 0.033 g/cm³.

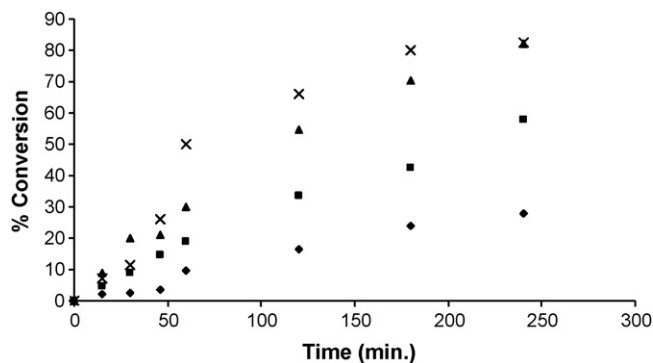


Fig. 2. Effect of mole ratio. Temperature: 80 °C; solvent: cyclohexane (45 cm³). Catalyst loading: 0.022 g/cm³; speed of agitation: 1000 rpm, time: 4 h. (◆) 2:1, (■) 1:1, (▲) 1:2 and (×) 1:3 (benzyl chloride:naphthalene).

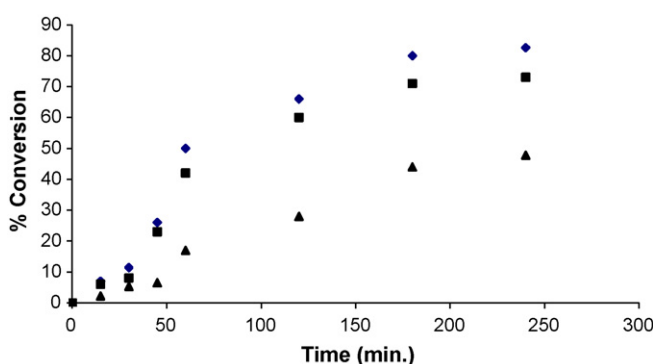


Fig. 3. Effect of temperature. Catalyst loading: 0.022 g/cm³; solvent: cyclohexane (45 cm³). Benzyl chloride: 0.019 mol, naphthalene: 0.058 mol; speed of agitation: 1000 rpm. (◆) 80 °C, (■) 75 °C and (▲) 70 °C.

3.5. Effect of temperature

To study the effect of temperature, catalyst loading and mole ratio were kept constant while temperature was varied from 70 to 80 °C (Fig. 3). It was observed that as the temperature was raised above 70 °C, the reaction rate increased, but above 75 °C, there was not much enhancement in the reaction rate. This is likely due to intra-particle diffusion limitation.

3.6. Reusability of catalyst

After the fresh run reaction mixture was filtered to separate catalyst. It was observed that there was a drastic reduction in the activity of the catalyst when it was filtered and used as such due to pore blocking by solidous mono-benzylated naphthalene isomers. Therefore, the catalyst after the run was over was filtered and washed with copious quantities of methanol and toluene sequentially and dried at 120 °C for 3 h and then recalcined at 500 °C. This restored its activity. To compensate the minor losses, fresh catalyst was added to maintain the same catalyst loading. Catalyst activity was tested for three runs. Catalyst was found to be reusable (Table 2).

Table 2
Reusability of catalyst

Run	Conversion % after 4 h
Fresh	82
First	82
Second	80

4. Mechanism and kinetic model

In the absence of both external mass transfer resistance and intra-particle diffusion resistance, it is possible to develop a kinetic model. Several models were tried and the following was observed to fit the data very well.

Chemisorption of benzyl chloride (A) and naphthalene (B) takes place on two adjacent vacant surface (S) according to Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism to produce the monobenzylated naphthalenes and HCl (D), which are all parallel reactions leading to different monobenzylated naphthalenes. For the sake of simplicity, all of them are shown as (C).



The reaction on the catalyst surface is given by:



The adsorption of C and D is given by:



The concentration of total sites, C_t (mol/g-cat) including that of vacant sites S is:

$$\begin{aligned} C_t &= C_S + C_A + C_B + C_C + C_D \\ &= C_S(1 + K_A + K_B + K_C + K_D) \end{aligned} \quad (6)$$

Thus,

$$C_S = \frac{C_t}{1 + \sum K_i C_i} \quad (7)$$

C_t can be substituted by w , the catalyst loading in g/cm³ without the loss of generality, and when the surface reaction is controlling the overall rate, the rate of reaction of A is given by:

$$-r_A = \frac{-dC_A}{dt} = \frac{k_2 K_A K_B w C_A C_B}{(1 + K_i C_i)^2} \quad (8)$$

If the adsorption of all reactant and product species is weak, then the above equation reduces to the typical second order equation:

$$-r_A = \frac{-dC_A}{dt} = k'_2 w C_A C_B \quad (9)$$

In terms, $M = C_{B_0}/C_{A_0}$ initial moles of naphthalene to benzyl chloride, X_A , the fractional conversion of A, the above equation

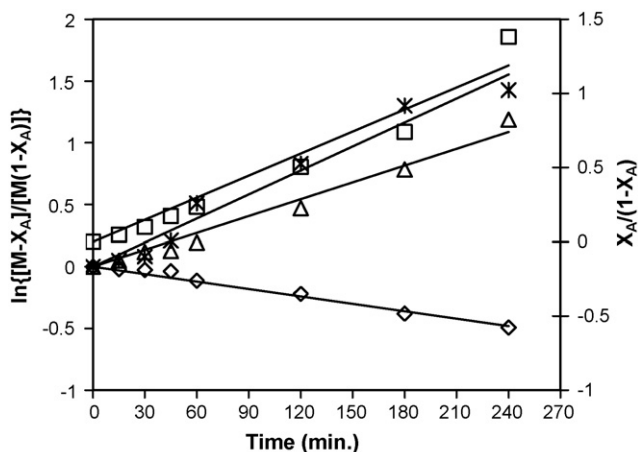


Fig. 4. Validation of model for all values of mol ratios (M). The right hand side Y-axis for $M=1$, the lower line is for $M=0.5$. (\diamond) 0.5, (Δ) 2, (\times) 3 and (\square) 1.

can be integrated to get the following:

$$\ln \left[\frac{M - X_A}{M(1 - X_A)} \right] = (M - 1)k_2'wC_{A_0}t \quad \text{for } M \neq 1 \quad (10)$$

$$\frac{X_A}{1 - X_A} = k_2' C_{A_0} w t \quad \text{for } M = 1 \quad (11)$$

Thus, a plot of $\ln[(M - X_A)/(M(1 - X_A))]$ against t is shown in Fig. 4 for different values of M . It is seen that the data fits very well. The values of rate constants at different temperatures were calculated (Fig. 5) for the same value of M , which once again shows an excellent fit. An Arrhenius plot was used to estimate energy of activation (Fig. 6). The apparent activation energy was determined as 26.00 kcal/mol. This activation energy also supported the fact that the overall rate of reaction is not influenced by either external mass transfer or intra-particle diffusion resistance and it is an intrinsically kinetically controlled reaction on active sites.

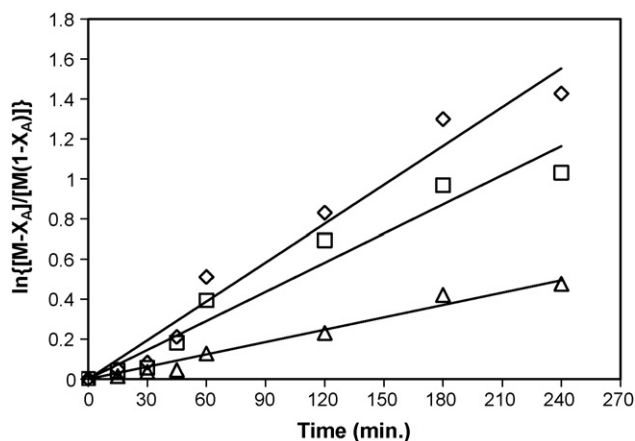


Fig. 5. Validation of model for different temperatures for the same value of M . (\diamond) 353 K, (\square) 347 K and (Δ) 343 K.

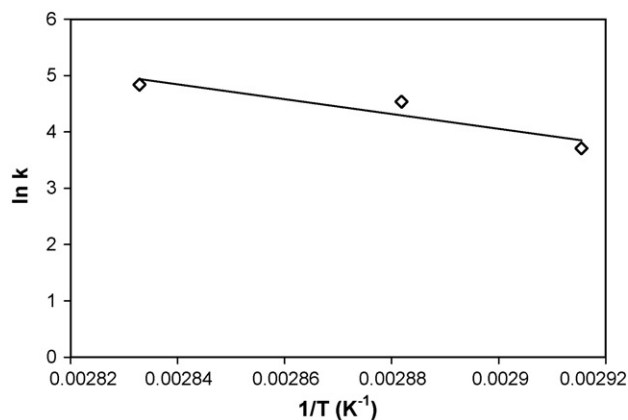


Fig. 6. Arrhenius plot.

5. Conclusion

UDCaT-4, synthesized by generating persulfated alumina and zirconia in hexagonal mesoporous silica, exhibits a perfect blend of superacidic centers, high surface area of 364 m²/g and ordered mesoporosity. Because of these characteristics, UDCaT-4 exhibits excellent catalytic activity for the alkylation of bulky molecules like naphthalene. Benzoylation of naphthalene was studied by using a mesoporous solid superacid UDCaT-4, which was a modified version of persulfated alumina zirconia catalyst on hexagonal mesoporous silica. The catalyst was more active than PAZ. It can be reused without loss of activity. The reaction was 100% selective towards monobenzylated naphthalene without any dibenzoylation. The Langmuir-Hinshelwood model with weak adsorption of reactants and products was found to fit the kinetic equation.

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