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Selectivity engineering of solid base catalyzed O-methylation of 2-naphthol with dimethyl carbonate to 2-methoxynaphthalene

Ganapati D. Yadav*, Jeetendra Y. Salunke

Department of Chemical Engineering, Institute of Chemical Technology, Matunga, Mumbai 400019, India

A R T I C L E I N F O

ABSTRACT

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Keywords: Solid base Hydrotalcite 2-Naphthol Hexagonal mesoporous silica Green chemistry 2-Methoxynaphthalene Dimethyl carbonate 2-Methoxynaphthalene is an important intermediate used in the production of naproxen which is widely used as a non-steroidal, anti-inflammatory, analgesic and antipyretic drug. In the current work, catalytic methylation of 2-naphthol was studied by using dimethyl carbonate as a greener agent vis-à-vis methyl halides and dimethyl sulfate. Catalysts based on calcined-hydrotalcite (CHT) supported on hexagonal mesoporous silica (HMS) were synthesized. Effect of CHT loading on HMS was systematically studied including full characterization. The activity and selectivity of CHT/HMS was examined by studying the effects of different operating parameters to deduce mechanism and kinet-ics. Conversion of 2-naphthol at 463 K and autogenous pressure was 92% with 90% selectivity toward 2-methoxynaphthalene on 20% (w/w) CHT/HMS. The catalyst was easily recovered and reused without any significant loss in activity. A kinetic model was developed. It follows zero order kinetics based on Langmuir–Hinshelwood–Hougen–Watson mechanism with strong adsorption of reactants. The apparent activation energy is 32.3 kcal/mol.

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1. Introduction

Naphthalene derivatives find various applications in pharmaceutical, dyestuff, fine chemicals and perfumery industries. 2-Methoxynaphthalene is an important intermediate used in the production of naproxen. It is widely used a non-steroidal anti-inflammatory, analgesic and antipyretic drug [1–5], 2-Methoxynaphthalene is also a very important ingredient for perfumery and food industry and known as yara yara; it is usually manufactured from 2-naphthol and methanol in the presence of homogeneous catalysts such sulfuric acid or *p*-toluenesulfonic acid. In the production of fine chemicals, many non-catalytic or homogeneous catalyzed processes are employed. The homogeneous catalysts are difficult to recover and reuse and generally neutralized. The aqueous effluent containing dissolved solids is discharged creating load on the environment. Selectivity in homogeneous catalyzed reactions is also not tunable. Due to the drawbacks of homogeneous acids such as corrosion, safety, hazards, and separation problems; solid acids have been used to develop green processes [2,3]. Solid catalysts are easily separable and recyclable [5]. O-Alkylation of 2-naphthol with alkanols such as methanol, ethanol, n-propanol, 2-propanol and n-butanol has been studied in detail by using various solid acid catalysts [2].

Solid acids and superacids as catalysts have been extensively used for industrial processes [6–16]. However, in contrast with solid acids, comparatively a few studies have been reported on the use of solid bases as industrial catalysts [6,17–21]. Base catalyzed reactions include alkylation, isomerization, Michael addition, and aldol, Knoevenagel and Claisen–Schmidt condensations, which are employed for the production of several bulk chemicals, fine chemicals, pharmaceuticals, perfumes and flavors. More than 2 million tonnes of bulk chemicals are produced annually via processes catalyzed by alkalies such as NaOH, KOH and Ca(OH)₂. After the reaction, the alkaline medium is neutralized with acids, which contributes to \sim 30% of the production cost, resulting from product separation, purification and waste-water treatment [17–21].

Dimethyl carbonate (DMC) is an attractive reagent whose potential in a variety of reactions is being probed by different groups. DMC can act as a methylating or carboxymethylating reagent [3,22,23]. It is produced in bulk from renewable resources and is biodegradable. Hence, it can be employed as an alternative to existing reagents such as diazomethane, dimethyl sulfate or methanol [2,24]. As a methylating agent, it is environmentally safe and also prolongs the catalyst life. The co-products of the reaction can be recycled to make DMC in industrial processes [25–29].

Traditionally the synthesis of 2-methoxynaphthalene is accomplished by using dimethyl sulfate or diazomethane [4,24], methanol and concentrated sulfuric acid [4,25] or methyl halides, which

^{*} Corresponding author. Tel.: +91 22 3361 1001/1111/2222; fax: +91 22 3361 1002/1020.

E-mail addresses: gd.yadav@ictmumbai.edu.in, gdyadav@yahoo.com, gdyadav@gmail.com (G.D. Yadav).

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Nomenclature

HMS	hexagonal mesoporous silica			
CHT	calcined hydrotalcite			
DMC	dimethyl carbonate			
А	reactant species, 2-naphthol			
В	reactant species, dimethyl carbonate			
A _S ,	chemisorbed A			
BSa	chemisorbed B			
C_{S_1}	chemisorbed C			
M _{Sa}	chemisorbed M			
C, Ĕ, F	2-methoxynaphthalene, methanol, carbondioxide,			
	respectively			
CA	concentration of A (mol/cm ³)			
$C_{\rm B}$	concentration of B (mol/cm ³)			
C _E	concentration of E (mol/cm ³)			
C _W	concentration of W (mol/cm ³)			
$C_{\rm V}$	concentration of V (mol/cm ³)			
C_{AS_1}	concentration of A at solid (catalyst) surface			
1	(mol/cm ³)			
$C_{\rm BS_2}$	concentration of B at solid (catalyst) surface			
2	(mol/cm ³)			
C_{ES_1}	concentration of C at solid (catalyst) surface			
-	(mol/cm ³)			
C_{VS_2}	concentration of V at solid (catalyst) surface			
	(mol/cm ³)			
C_{WS_2}	concentration of W at solid (catalyst) surface			
	(mol/cm ³)			
C _{S1} and	$1 C_{S_2}$ concentration of vacant sites (mol/cm ³)			
C_{T}	total concentration of the sites (mol/cm ³)			
C_{T_1}	total concentration of the sites of type T_1 (mol/cm ³)			
C_{T_2}	total concentration of the sites of type T_2 (mol/cm ³)			
$K_{\rm A}, K_{\rm B}$	A, K_B adsorption equilibrium constants for A and B			
(cm ³ /mol)				
$K_{\rm E}, K_{\rm M}, F$	K_V desorption equilibrium constants for E, W, and V			
1.	(cm ³ /mol)			
κ_1	torward reaction rate constant for surface reaction			
K'_1	backward reaction rate constant for surface reaction			
к	zero order rate constant (mol/g _{cat} s)			
W	catalyst loading (g/cm ²)			
XA	Iractional conversion of A			

are corrosive and toxic. Thus, synthesis of high quality 2methoxynaphthalene from 2-naphthol and dimethyl carbonate (DMC) by using solid bases as catalysts appeared to be an attractive process [23].

Solid bases in supported forms would be more beneficial. Several metal oxides, carbon and mesoporous silica have been used as supports for acids and metals but their use for bases is limited. Mesoporous materials are of great interest because they extend the range of molecular-sieve materials into the very large pore regime. Their properties such as high thermal stability (up to 1198 K), larger surface area (above $1000 \text{ m}^2/\text{g}$), uniform sized pores and adsorption capacity for aromatic organic molecules render mesoporous materials to be exploited for a variety of applications in catalysis [30–32]. Hydrotalcites are mixed oxides having high surface area, phase purity, tunable basicity and structural stability [21,23]. They have numerous uses such as antacids, ion exchangers, absorbers, catalysts and supports [33]. Hydrotalcites, with a positively charged layered-brucite type of structure, are uncommon in nature but they can be easily synthesized. Positive charges are created in the hydrotalcite structure, through replacement of Mg by Al, which are neutralized by interlayer anions such as carbonate, nitrate, hydroxide and chloride. The interlayer anions can also be replaced by other With the foregoing prelude, the current studies were focused on the O-alkylation of 2-naphthol with dimethyl carbonate to produce 2-methoxynapththalene using hexagonal mesoporous silica (HMS) supported hydrotalcite. Thus, a novel catalyst calcinedhydrotalcite (CHT) supported on hexagonal mesoporous silica (HMS) was synthesized. Effect of CHT loading on HMS was systematically studied including full characterization. The activity and selectivity of CHT/HMS was examined by studying the effects of different operating parameters to deduce mechanism and kinetics. The results are novel.

2. Experimental methods

2.1. Chemicals and catalysts

The following chemicals were obtained from firms of repute and used without further purification: 2-naphthol (Merck, Mumbai, India), dimethyl carbonate, ethanol (AR), sodium hydroxide, 2-methoxy naphthalene (all from M/s S.D. Fine Chemical Ltd., Mumbai), hexadecyl amine (Otto Chemical-Biochemica Reagent, Mumbai), tetraethyl orthosilicate (Sigma–Aldrich, USA), magnesium nitrate hexahydrate, aluminum nitrate nonahydrate (all from Thomas Baker Chemicals, Mumbai), sodium carbonate (Himedia Laboratories Pvt. Ltd., Mumbai). Ordered hexagonal mesoporous silica (HMS) was prepared according to our earlier work [37–41]. The following catalysts were prepared by well-developed procedures and characterized in the laboratory: (a) CHT, (b) 10% (w/w) CHT/HMS, and (c) 20% (w/w) CHT/HMS [21,23].

2.1.1. Preparation of CHT

Hydrotalcite was synthesized by a standard aqueous preparation and heat crystallization process [21,23]. A solution of magnesium nitrate [Mg(NO₃)₂·6H₂O, 1 mol] and aluminum nitrate [Al(NO₃)₃·6H₂O, 0.5 mol] was prepared by dissolving the corresponding salts in distilled water. The solution was then co-precipitated by adding it to a solution of 50% aqueous solution of NaOH (3.5 mol) and Na₂CO₃ (anhydrous 0.94 mol) in distilled water. The addition was done slowly over 4 h under vigorous agitation at room temperature. During the addition, the pH of the solution was maintained between 9 and 10. The slurry was filtered and washed with deionized water until the pH of wash water was 7. After drying at 373 K for 24 h, the solids were calcined at 723 K for 12 h [42].

2.1.2. Preparation of 10% and 20% (w/w) CHT/HMS

HMS (10 g) was added to 10 ml aqueous solution containing magnesium nitrate $[Mg(NO_3)_2.6H_2O, 1 mol]$ and aluminum nitrate $[Al(NO_3)_3.6H_2O, 0.5 mol]$. It was stirred vigorously for 30 min at 333 K to form a suspension. The solution was then co-precipitated by adding 50% aqueous solution of NaOH (3.5 mol) and Na₂CO₃ (anhydrous 0.94 mol) in 10 ml distilled water. The addition took about 4 h and was carried out with vigorous agitation at room temperature. During the addition, the pH of the solution was maintained between 9 and 10. The slurry was cooled to room temperature, filtered and washed with deionized water until the pH of the solution was 7. After drying at 373 K for 24 h the solids were calcined at 723 K for 12 h. The molar ratio of Mg to Al was 2:1, and

mass ratio of CHT to HMS was either 1/10 or 2/10 for 10% and 20 wt% depending on the catalyst recipe.

2.2. Catalyst characterization

Mg–Al–O mixed oxide was characterized by Scanning Electron Micrographs (SEM) and Energy Dispersive X-ray Spectroscopy (EDXS) (JEOL JSM 6380LA Analytical scanning Microscope) using a 10 kV voltage at a counting rate 519 cps and energy range of 0–20 keV. The surface area, pore volume and pore size distribution were measured by nitrogen BET by using Micromeritics ASAP 2020 instrument. Basic and acidic site densities were measured by temperature programmed desorption of CO₂ and NH₃, respectively. Powder X-ray diffraction (XRD) patterns were obtained using Bruker AXS diffractometer D8 Cu-K α radiation (λ = 1.540562). Samples were step scanned from 10.0 to 99.9° in a stepping time of 17.7 s.

2.3. Reaction procedure

A typical procedure for methylation 2-naphthol with dimethyl carbonate is given below.

The reaction was carried in an autoclave (Amar Equipments, Mumbai) of 100 ml capacity. It was equipped with a 45° inclined-four-bladed-pitched-turbine impeller, temperature controller (\pm 1 °C), pressure indicator, and speed regulator (\pm 5 rpm). 2-Naphthol (0.0155 mol) and DMC (0.467 mol) and 0.035 g/cm³ of the catalyst were charged to the autoclave. The total liquid phase volume of the reaction mass was 40 cm³ which was allowed to reach the desired temperature, and an initial sample was collected. Agitation was then started at a known speed. Samples were withdrawn periodically for analysis.

2.4. Method of analysis

The analysis was carried out by GC (Chemito model 1000, FID detector) using a BPX-50 capillary column (0.22 mm \times 30 m). The product conformation was done by using GC–MS (QP-2010 GCMS, Shimadzu restek, phase: Rtx-wax, length 30 m, 0.25 mm I.D., 0.25 μ m).

3. Results and discussion

3.1. Catalyst characterization

Although all materials were characterized, the most active and selective catalyst, namely, 20% (w/w) CHT/HMS was chosen for further study. Therefore, the characterization of this material is presented here.

3.1.1. X-ray diffraction studies (XRD)

The X-ray diffraction pattern of authentic HMS as well as 20% (w/w) CHT/HMS was recorded using a Bruker AXS powder diffractometer D8 with Cu-K α (1.54 Å) radiation (Fig. 1). The XRD patterns of these materials do not contain any sharp reflection but only a broad diffuse band similar to that of amorphous materials. The XRD patterns for CHT supported on silica were similar to those of corresponding HMS. In particular, no crystalline phase could be detected in the case of CHT supported on silica. CHT particles were too small to show any XRD pattern. The pores of HMS were blocked by in situ formed Al–Mg mixed oxides, or by the walls of HMS were partially destroyed. Therefore there was a decrease in reflections at low 2θ in the XRD pattern of CHT/HMS. It is completely amorphous without any long range order.



Fig. 1. XRD of 20% CHT/HMS catalyst.

3.1.2. TGA

TGA analysis of the prepared catalyst showed that the material was stable beyond 300 °C. A mass loss of about 8.8% was observed up to 294.8 °C due to moisture present in the catalyst and removal of CO₂ from the carbonate species used in the preparation. The first weight loss observed below 200 °C was due to the loss of interlayer water and physically absorbed moisture. The next loss of weight, above 300°C, was due to the loss of CO₂ from interlayer carbonate anions and also hydroxy groups from the brucite-like (Mg(OH)₂) layers [21,23] (Fig. 2). The hydrotalcite is Mg₆Al₂(OH)₁₆CO₃·4H₂O and on calcination it gives Mg₆Al₂O₈(OH)₂. Hydrotalcites are stable up to 400 °C. At 200 °C, water molecules are lost and anhydrous hydrotalcite is obtained. At higher temperatures, CO₃²⁻ (carbonate) is removed and solids are partially hydroxylated; and Mg₆Al₂O₈(OH)₂ is formed. If calcined at temperatures higher than 450 °C and up to 900 °C, MgO (periclase) and the spinel MgAl₂O₄ are irreversibly obtained. But, if calcined at around 500 °C, Mg₆Al₂O₈(OH)₂ is formed and, in the presence of water and carbonates, the original hydrotalcite is recovered [21,43,44].



Fig. 2. TGA of 20% CHT/HMS catalyst.



Fig. 3. FT-IR spectra of 20% CHT/HMS catalyst.

The above analysis showed that the catalyst possessed high stability with intact morphological behavior up to 800 °C.

3.1.3. FT-IR spectra

FT-IR spectra were recorded using Perkin-Elmer instrument spectrum 100 series. Spectra of 20% (w/w) CHT/HMS with Mg:Al ratio of 2:1 showed absorption at 1069 cm⁻¹ which indicated the asymmetric stretching of Si–O–Si. The peak at around 480 cm⁻¹ and 803 cm⁻¹ was given by internal bands of SiO₄ tetrahedra. A broad absorption band at 3407 cm⁻¹ was attributed to stretching of hydrogen bonded hydroxyl group and water molecules and the corresponding deformation mode appeared at 1634 cm⁻¹ (Fig. 3).

 Table 1

 Basicity and acidity of 20% CHT/HMS.

Catalyst	Basicity by CO ₂ TPD (mmol/g)	Acidity by NH ₃ –He (mmol/g)
20% CHT/HMS	0.68	0.53

Table 2

Clamontal	analyzic	of 20%	CUIT	/IIN/C	catal	ret
пенненнаг	diidivsis	0120/6	UT L		CdldIV	/51

-		
Element	Weight (%)	Atomic (%)
0	49.08	62.34
Mg	6.11	5.11
Al	4.08	3.07
Si	40.74	29.48
Total	100.00	100.00

3.1.4. Temperature programmed desorption (TPD)

TPD was performed in an Autochem II 2920 TPD/TPR instrument (Micromeritics, USA) equipped with TCD detector. The basicity of catalyst was studied by using TPD with 10% CO₂–He (Fig. 4a). A broad peak with a maximum at 130 °C corresponded to desorption of physisorbed CO₂. It suggested the presence of weak basic sites on catalyst surface. The generation of acidic sites in CHT was confirmed by conducting TPD with 10% NH₃–He (Fig. 4b). A broad peak with a maximum at 130 °C corresponded to desorption of physisorbed NH₃. This indicated the presence of weak acidic sites on the catalyst. This is also in tune with our earlier findings [21,23] (Table 1).

3.1.5. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDXS)

SEM (Scanning Electron Microscope) micrographs and Electron Dispersive Scanning (EDS) data for the catalysts were obtained on a JEOL JSM 6380LA instrument SEM (Fig. 5). TEM images for 20% (w/w) CHT/HMS show that Mg–Al oxides are uniformly dispersed on HMS and the CHT loading does not disturb the hexagonal structure of HMS (Fig. 6). It also confirms that CHT particles are located on surface of HMS. The particle size was in the range of $0.1-2 \,\mu$ m. EDXS analysis shows the incorporation of CHT in HMS (Table 2).



Fig. 4. Temperature programmed desorption of 20% CHT/HMS catalyst. (a) TPD of 20% CHT/HMS with 10% CO₂-He and (b) TPD of 20% CHT/HMS with 10% NH₃-He.



Fig. 5. SEM images of 20% CHT/HMS catalyst at different magnification.

3.1.6. Nitrogen sorption

The N₂ adsorption/desorption isotherm was obtained by using TriStar II 3020 (Micromeritics, USA) instrument at liquid N2 temperature. The sample was degassed at 90 °C for 1 h and then at 300 °C for 1 h under nitrogen atmosphere (Fig. 7). It is type-IV isotherm, as defined by the IUPAC, with well defined steps in N₂ adsorption and desorption isotherm and there was hysteresis in the adsorption isotherm at relative pressure (p/p_0) in the range of 0.4–0.8. In this curve, three well-defined stages can be identified, (i) a slow increase in nitrogen uptake at low relative pressures, corresponding to monolayer-multilayer adsorption on the pore walls, (ii) a sharp step at intermediate relative pressures indicative of capillary condensation in mesopores and (iii) a plateau at high relative pressures associated with multilayer adsorption on the external surface [36]. The reduction in the BET surface area and pore volume of CHT/HMS indicating the nano-particles of magnesium and aluminum mixed oxides are generated on HMS through hydrotalcite calcinations and some large particles can block a few pore junctions there by reducing accessibility of some channels of the support (Fig. 8). During the synthesis of CHT/HMS, growth of crystalline magnesium-aluminum oxides is very unlikely, as evidenced by the XRD analysis and BET surface area measurement, which indicate that the characteristic hexagonal structure of the HMS and mesoporosity are not perturbed even after HMS is converted to CHT/HMS, thus indicating its framework stability [21]. HMS retains its mesoporosity even after it has been converted to CHT/HMS and this explanation is in accordance with the IUPAC classification [45]. Some of the textural characteristics of these catalytic samples are given in Table 3.

3.2. Efficacy of various catalysts

Scheme 1 depicts that reaction. The effect of various parameters such as speed of agitation, catalyst loading, mole ratio of reactants, and temperature of reaction was studied for obtaining kinetics of the reaction. All the experiments were conducted for 270 min. The mole ratio of 2-naphthol: DMC was varied and optimum was 1:30 at 463 K. Formation of small amount of byproducts 2-methoxy-1-methylnaphthalene and 2-methoxy-1,6,7-trimethylnaphthalene was noticed. The second byproduct 2-methoxy-1,6,7-trimethylnaphthalene was due to the sequential reaction of 2-methoxy-1-methylnaphthalene and it could be controlled through reaction time.

The effect of different amounts of CHT were loaded on hexagonal mesoporous silica (HMS) was studied. With increase in CHT loading from 10 to 20% (w/w) of HMS, the conversion of 2-naphthol



Fig. 6. TEM images of 20% CHT/HMS.

Table 3Textural characteristics of 20% CHT/HMS.

Sample	Single point surface area (m²/g)	BET surface area (m²/g)	BJH adsorption cumulative pore volume (cm ³ /g)	Average pore diameter (4V/A) (Å)
20% CHT/HMS	480.48	496.46	0.67 cm ³ /g	47.45



Scheme 1. O-alkylation of 2-naphthol with DMC over CHT/HMS.



Fig. 7. N₂ isotherm of 20% CHT/HMS at 77 K. (+) Adsorption; (-+) desorption.



Fig. 8. Pore size distribution of 20% CHT/HMS.

increased. Unsupported CHT was also used for this reaction and taken in the proportion as percent loading on HMS. Since 20% (w/w) CHT/HMS was the best catalyst, the effect of various parameters on conversion and selectivity was studied by using this catalyst (Table 4). A small amount of 2-naphthol conversion was observed for uncatalyzed reaction after 270 min due to the activation of C–O bond of DMC by mesomeric effect at 463 K temperature. At this temperature DMC favors the methylation by reacting with 2-naphthol of dissociation constant (p K_a = 9.51).

3.3. Development of kinetic model and mechanism of reaction

The possible reaction mechanism for the methylation of 2naphthol with dimethyl carbonate is shown in Scheme 2.

In the absence of both external mass transfer and intra-particle diffusion resistances, it is possible to develop a kinetic model. It is assumed that 2-naphthol (A) and dimethyl carbonate (B) adsorb on catalytic sites S_1 and S_2 , respectively according to the Langmuir–Hinshelwood–Hougen–Watson (LWHW) mechanism to

Table 4

Effect of various catalysts on O-methylation of 2-naphthol.

Catalyst	Conversion (%)	Selectivity (%)		
		2-Methoxynaphthalene	2-Methoxy-1- methylnaphthalene	2-Methoxy-1,6,7- trimethylnaphthalene
CHT	84.1	91.64	4.82	2.92
10% CHT/HMS	53.7	92.26	5.43	2.41
20% CHT/HMS	91.5	90.10	6.43	3.47
Nil	13.1	99.52	0.48	0.0



Scheme 2. Catalytic cycle.

produce 2-methoxynaphthalene (E), methanol (W) and CO_2 (V). Here S_1 and S_2 are basic and acidic sites, respectively.

Adsorption:

Adsorption of A on a vacant site S₁ is given by:

 $A + S_1 \stackrel{K_A}{\longleftrightarrow} AS_1 \tag{1}$

Adsorption of B on a vacant site S₂ is given by:

$$B + S_2 \longleftrightarrow BS_2 \tag{2}$$

Surface reaction:

Surface reaction of AS_1 and BS_2 leads to the formation of ES and WS on the active sites as given by

$$AS_1 + BS_2 \longleftrightarrow ES_1 + WS_2 + V$$
(3)

It is assumed that $\text{CO}_2(V)$ occupies an adjacent basic site S_2 to produce VS_2 .

Desorption:

Desorption of 2-methoxynaphthalene (ES_1) and methanol (WS_2) is given by:

 $\mathrm{ES}_1 \stackrel{1/K_\mathrm{E}}{\longleftrightarrow} \mathrm{E} + \mathrm{S}_1 \tag{4}$

 $WS_2 \stackrel{1/K_W}{\longleftrightarrow} W + S_2$ (5)

 $VS_2 \stackrel{1/K_V}{\longleftrightarrow} V + S_2$ (5a)

The total concentration of the sites, *C*_T expressed as,

 $C_{T_1} = C_{S_1} + C_{AS_1} + C_{ES_1} \tag{6a}$

 $C_{\rm T_2} = C_{\rm S_2} + C_{\rm BS_2} + C_{\rm WS_2} + C_{\rm VS_2} \tag{6b}$

$$C_{\rm T} = C_{\rm T_1} + C_{\rm T_2} \tag{6c}$$

 $C_{T_1} = C_{S_1} + K_A C_A C_{S_1} + K_E C_E C_{S_1}$ (7a)

$$C_{T_2} = C_{S_1} + K_B C_B C_{S_2} + K_W C_W C_{S_2} + K_V C_V C_{S_2}$$
(7b)

When the adsorption and desorption steps are assumed to be in equilibrium, the concentration of vacant sites can be written as,

$$C_{S_1} = \frac{C_{T_1}}{1 + K_A C_A + K_E C_E}$$
(8a)

$$C_{S_2} = \frac{C_{T_2}}{1 + K_B C_B + K_W C_W + K_V C_V}$$
(8b)

If the surface reaction controls the rate of reaction, then the rate of reaction of A is given by

$$-r_{\rm A} = -\frac{dC_{\rm A}}{dt} = k_2 C_{\rm AS_1} C_{\rm BS_2} - k_{2'} C_{\rm ES_1} C_{\rm WS_2} C_{\rm VS_2}$$
(9)

$$-\frac{dC_A}{dt} = \frac{k_2(K_A K_B C_A C_B - ((K_E K_W K_V C_E C_W C_V)/K_2))C_{T_1} C_{T_2}}{(1 + K_A C_A + K_E C_E)(1 + K_B C_B + K_W C_W)}$$
(10)

When the reaction is far away from equilibrium

$$-\frac{dC_{\rm A}}{dt} = \frac{k_2 C_{\rm T_1} C_{\rm T_2} K_{\rm A} K_{\rm B} C_{\rm A} C_{\rm B}}{\left(1 + \sum K_i C_i\right) \left(1 + \sum K_j C_j\right)}$$
(11)

$$-\frac{dC_{\rm A}}{dt} = \frac{k_{\rm R_2} w K_{\rm B} C_{\rm A} C_{\rm B}}{\left(1 + \sum K_i C_i\right) \left(1 + \sum K_j C_j\right)} \tag{12}$$

where $k_{R_2}w = k_2C_{T_1}C_{T_2}K_AK_B$ where, *w* is catalyst loading. If the adsorption constants are small; where $k_{R_2}w = k_2C_{T_1}C_{T_2}K_AK_B$ where, *w* is catalyst loading. If the adsorption constants are small, then the above equation reduces to:

$$-\frac{dC_{\rm A}}{dt} = k_{\rm R_2} w K_{\rm B} C_{\rm A} C_{\rm B} \tag{13}$$

Let $C_{B_0}/C_{A_0} = M$ be the molar ratio at time t=0. Then Eq. (13) can be written in terms of fractional conversion as

$$\frac{dX_{\rm A}}{dt} = k_{\rm R_2} w C_{\rm A_0} (1 - X_{\rm A}) (M - X_{\rm A}) = k_1 C_{\rm A_0} (1 - X_{\rm A}) (M - X_{\rm A})$$
(14)

This upon integration, it leads to:

$$\ln\left\{\frac{M-X_{\rm A}}{M(1-X_{\rm A})}\right\} = k_1 C_{\rm A_0}(M-1)t \tag{15}$$

When $M \gg 1$, then the above Eq. (13) as a pseudo-first order equation,

$$-\ln(1 - X_{\rm A}) = k_1 t \tag{16}$$

where

$$k_1 = k_{\rm R_2} w K_{\rm B} C_{\rm B_0} \tag{17}$$

When $K_A C_A \gg 1$ and $K_B C_B \gg 1$

$$-\frac{dC_{\rm A}}{dt} = kw \tag{18}$$

Eq. (18) is a typical zero order equation which is written in terms of the fractional conversion, X_A , leads to the following.

$$\frac{dX_{\rm A}}{dt} = \frac{kw}{C_{\rm A_0}} \tag{19}$$

which on integration gives the following:

$$X_{\rm A} = \left(\frac{kw}{C_{\rm A_0}}\right)t\tag{20}$$

3.4. Effect of speed of agitation

The effect speed of agitation was studied in the range of 800–1200 rpm to determine the influence of mass transfer resistance for the transfer of reactants from the bulk liquid phase to the exterior surface of the catalyst particle (Fig. 9). The conversion of 2-naphthol was unaffected by speed in the entire range of 800–1200 rpm confirming that there was no mass transfer resistance. Thus, further experiments were carried out at 1000 rpm.



Fig. 9. Effect of speed of agitation on conversion of 2-naphthol. Reaction condition: 2-naphthol−0.0155 mol; dimethyl carbonate−0.467 mol; catalyst−0.035 g/cm³; temperature−463 K; total volume−40 cm³; reaction time−270 min. (♦) 800 rpm; (■) 1000 rpm; (▲) 1200 rpm.

3.5. Effect of catalyst loading

In the absence of external mass-transfer resistance and intraparticle diffusion resistance, the rate of reaction is directly proportional to catalyst loading based on the entire volume of liquid-phase. The catalyst loading was varied from 0.01 to 0.04 g/cm³ (Fig. 10). There was no significant difference in conversion when the loading was increased from 0.035 to 0.04 g/cm³ catalyst loading. This would suggest that the number of active sites available for reaction was greater than required and hence additional loading was of no consequence. The plot of initial rate of reaction as function of catalyst loading showed that the rate of reaction increased linearly with the catalyst loading (Fig. 11). In this figure the rate of change of fractional conversion at constant initial concentrations versus time is plotted. Fig. 12 shows the conversion and



Fig. 10. Effect of catalyst loading on conversion of 2-naphthol. Reaction condition: 2-naphthol-0.0155 mol; dimethyl carbonate-0.467 mol; speed of agitation-1000 rpm; temperature-463 K; total volume-40 cm³; reaction time-270 min. (\bullet) 0.01 g/cm³; (\blacksquare) 0.03 g/cm³; (\blacktriangle) 0.035 g/cm³; (\bigstar) 0.04 g/cm³.



Fig. 11. Plot of initial rate of reaction against catalyst loading. Reaction condition: 2-naphthol–0.0155 mol; dimethyl carbonate–0.467 mol; speed of agitation–1000 rpm; temperature–463 K; total volume–40 cm³; reaction time–270 min.

selectivity of 2-methoxy naphthalene for different catalyst loading. Further, Fig. 10 suggests that the conversion is linear with respect to time giving zero order kinetics, which validates the above model.

3.6. Effect of mole ratio

The effect of mole ratio of 2-naphthol to DMC was studied by varying it in the range of 1:10–1:40 (Fig. 13). Once again it shows a zero order kinetics. The conversion was found to increase with decreasing the concentration of 2-naphthol. Decreasing the concentration of 2-naphthol leads to more availability of catalyst sites for 2-naphthol to adsorb on catalyst, as it was taken as limiting



Fig. 12. Effect of catalyst loading on conversion and selectivity of 2-naphthol. Reaction condition: 2-naphthol–0.0155 mol; dimethyl carbonate–0.467 mol; speed of agitation–1000 rpm; temperature–463 K; total volume–40 cm³; reaction time–270 min. () Conversion (%); () selectivity (%).



Fig. 13. Effect of mole ratio on conversion of 2-naphthol. Reaction condition: catalyst -0.035 g/cm^3 ; speed of agitation-1000 rpm; temperature-463 K; total volume -40 cm^3 ; reaction time-270 min. (\bigcirc) 1:10; (\bigcirc) 1:20; (\blacktriangle) 1:30; (\diamondsuit) 1:40.

reactant. After the mole ratio 1:40 though the rate of reaction increases the selectivity of desired product goes on decreasing because more of DMC occupies the sites (Fig. 14). Hence 1:30 mole ratio was taken as optimum for further studies.

3.7. Effect of temperature

The effect of temperature on rate of reaction was studied under otherwise similar conditions at 453, 458, 463, and 468 K, respectively. The conversion of 2-naphthol was observed to increase with increase in temperature (Fig. 15). It shows zero order kinetics at all temperatures. Fig. 16 shows that as the temperature increases the conversion increases but the selectivity to desired product decreases due to the formation of alkylated product of sequential reaction, 2-methoxy-1-methyl-naphthalene and 2-methoxy-1,6,7trimethyl-naphthalene. The Arrhenius plot was made to determine



Fig. 14. Effect of mole ratio on conversion and selectivity of 2-naphthol. Reaction condition: catalyst–0.035 g/cm³; speed of agitation–1000 rpm; temperature–463 K; total volume–40 cm³; reaction time–270 min. (



Fig. 15. Effect of temperature on conversion of 2-naphthol. Reaction condition: 2-naphthol-0.0155 mol; dimethyl carbonate-0.467 mol; catalyst-0.035 g/cm³; speed of agitation-1000 rpm; total volume-40 cm³; reaction time-270 min. (\blacklozenge) 453 K; (\blacksquare) 458 K; (\bigstar) 468 K.

the energy of activation as 32.29 kcal/mol (Fig. 17). This value also exhibits that the reaction is kinetically controlled.

3.8. Reusability of catalyst

The reusability of catalyst was studied without any make up with fresh catalyst. After completion of reaction the catalyst was recovered and washed with methanol for two to three times. Then it was refluxed with methanol for 1 h, filtered and dried in an oven at 383 K overnight. This process was repeated for every reuse of catalyst. In catalyst reusability study, there was no fresh catalyst



Fig. 16. Effect of temperature on conversion and selectivity of 2-naphthol. Reaction condition: 2-naphthol–0.0155 mol; dimethyl carbonate–0.467 mol; catalyst–0.035 g/cm³; speed of agitation–1000 rpm; total volume–40 cm³; reaction time–270 min. (

Table 5	
Catalyst reusability	۰.

Reusability	Conversion (%)	Selectivity (%)		
		2-Methoxynaphthalene	2-Methoxy-1- methylnaphthalene	2-Methoxy-1,6,7- trimethylnaphthalene
Fresh	91.52	90.10	6.43	3.47
1st	91.24	89.90	7.22	2.89
2nd	90.99	89.17	7.62	3.22
3rd	87.50	89.28	7.9	2.83



Fig. 17. Arrhenius plot for methylation of 2-naphthol.

added into the reaction mixture. The actual amount of catalyst used (g/cm^3) for the next batch was almost 5% less than the previous batch. However, the batch volume was reduced so as to maintain the same catalyst loading as the fresh batch and also same mole ratio of reactants. It was observed that there is no significant loss in conversion and selectivity (Table 5). The little loss in conversion after second reuse was found due to the adsorption of molecule on the catalyst surface.

3.9. Statistical validation

In order to test the confidence of the results, linear regression has been carried out in Polymath for the zero order kinetics. The following model has been used,

$$X_{\rm A} = \frac{k_0 \, \exp(-E_a/RT) w \cdot t}{C_{\rm A_0}} \tag{21}$$

Which is modified to:

$$\ln\left(\frac{X_{A}C_{A_{0}}}{wt}\right) = \left(-\frac{E_{a}}{RT}\right) + \ln k_{0}$$
(22)

Linear regression was carried for this equation using all available data treating $\ln(X_A C_{A_0}/wt)$ as the dependent variable and 1/T as the independent variable. The parameters E_a and k_0 were estimated and the 95% confidence intervals for the same were obtained.



Fig. 18. Statistical validation of model.

Thus, $E_a = 33.348 \pm 6.19$ and $k_0 = 2.18 \times 10^{11} \pm -854$. It can be seen that the errors in the parameters are much smaller than the actual values of the parameters indicating the model provides a good description of the experimental results.

Further, the residuals for X_A were plotted against X_A , initial concentration, catalyst loading and temperature. There was no systematic pattern in the residual plot indicating that there were no systematic experimental errors. For sake of brevity, only one plot is shown in Fig. 18. Previously for the calculations of activation energy, i.e. Arrhenius plot we are not using significant number of digit. We take more significant number of digit and plotted a new Arrhenius plot; from this plot we calculate the activation energy 32.29 kcal/mol. Thus, the model is valid.

4. Conclusion

2-Methoxynaphthalene was prepared by catalytic methylation of 2-naphthol using dimethyl carbonate as a greener alternative. A novel catalyst calcined-hydrotalcite (CHT) supported on hexagonal mesoporous silica (HMS) was developed. Effects of various parameters on conversion and selectivity were systematically studied in a batch autoclave. 20% (w/w) CHT/HMS was the best catalyst which was fully characterized. Conversion of 2-naphthol was 92% with 90% selectivity toward 2-methoxynaphthalene. The catalyst was easily recovered and reused without any significant loss in activity. A kinetic model was developed for this reaction. The reaction follows zero order kinetics based on Langmuir–Hinshelwood–Hougen–Watson mechanism with strong adsorption of reactants. The activation energy for the reaction is 32.29 kcal/mol indicates that the reaction is intrinsically kinetically controlled.

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