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Selective acetalization of ethylene glycol with methyl 2-napthyl ketone over solid acids: Efficacy of acidic clay supported $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

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ABSTRACT

Catalytic conversion of biomass to value added products is relevant with regard to several industries. Biomass derived ethylene glycol has many applications. Acetalization is used to synthesize valuable chemicals and also occasionally to protect carbonyl groups of aromatic molecules in organic transformations. Acetalization of ethylene glycol to cyclic dioxolane has many applications in fragrance, cosmetics, food and beverage additives, pharmaceuticals, detergents, and lacquer industries. The current work reports synthesis of 2-methyl-2-napthyl-1,3-dioxolane by acetalization of ethylene glycol with methyl 2-napthyl ketone using several heterogeneous solid acid catalysts including 20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 (Cs-DTP/K-10), UDCaT-4, UDCaT-5 and K-10 clay. Among them, 20% (w/w) Cs-DTP/K-10 catalyst was found to be the most efficient catalyst giving 87% conversion of methyl 2-napthyl ketone with 100% selectivity toward 2-methyl-2-napthyl-1,3-dioxolane. Effects of several reaction parameters were studied and optimized. The optimum reaction conditions were: 110 °C, molar ratio of methyl 2-naphthyl ketone to ethylene glycol 1:2, catalyst loading 0.02 g/cm^3, speed of agitation 800 rpm, and time 3 h. Reaction mechanism and kinetic model were developed. The methodology was extended to different substrates, and catalyst reusability was also studied. The catalyst was well characterized by various techniques such as XRD, BET, FTIR, TPD and SEM. It is robust and recyclable.

1. Introduction

The defuctionalization of biomass and subsequent conversion to various platform molecules is highly desirable to develop sustainable chemical industry. Such feedstock could be generated through syngas (Fischer Tropsch) synthesis, fermentation and extraction of biomass. Among these routes sugars, HMF, glycerol, ethanol, butanol, ethylene glycol, etc. are promising feedstocks to make a variety of value added chemicals. Acetalization is a general process that is usually used as a protecting method for carbonyl compounds such as aldehydes and ketones in the presence of other functional groups in reactions of multifunctional organic molecules [1,2]. However, in fragrance and flavor industries, acetals and ketals are very widely used in formulations because of the type of 'notes' they create, whereas some of these compounds are used as oxygenated fuel additives having tremendous scope. Glycerol and other glycols can be thus valorized through acetalization and ketalization which are acid catalyzed reactions. Common method for the synthesis of acetals and ketals of glycerol or other glycols is through reaction with aldehyde or ketone in the presence of an acid catalyst [3,4]. The most commonly used acids catalysts are homogeneous such as sulfuric acid, phosphoric acid, hydrochloric acid, and *p*-toluenesulfonic acid (PTSA) [5–7], and also heterogeneous ion-exchange resins [8–11] and zeolites [12]. Acetals and ketals of glycerol comprise valuable constituents for the formulation of gasoline, diesel and biodiesel fuels. These oxygenated compounds, when included into standard diesel fuel, lead to emissions with substantial decrease in particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes [5,9]. Similarly, these products can act as cold flow improvers for use in biodiesel and also reducing its viscosity [5]. This issue is of significant importance due to the growing demand for new additives specifically for biodiesel that are biodegradable, non-toxic and renewable. Addition of acetals and ketals to biodiesel improves its viscosity and also meets the conventional requirements of flash point and oxidation stability [7].

The propylene glycol acetal of methyl naphthyl ketone is a flavoring material with blossom orange note, which involves the acetalization of the methyl naphthyl ketone with propylene

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Nomenclature

A	reactant species A–ethylene glycol
AS	chemisorbed A
B	reactant species B–methyl 2-naphthyl ketone
BS	chemisorbed B
E	product, 2-methyl-2-naphthyl-1, 3-dioxolane
ES	chemisorbed product
W	water
C_A, C_B	concentration of A and B (mol/cm^3)
C_{A0}, C_{B0}	initial concentration of A and B (mol/cm^3)
C_{AS}, C_{BS}	concentration of A and B on solid catalyst surface (mol/g-cat)
C_{ES}, C_{WS}	concentration of E and W at solid catalyst surface (mol/g-cat)
C_S	concentration of vacant sites (mol/g-cat)
C_t	total concentration of sites (mol/g-cat)
$-r_A$	rate of disappearance of A (mol/cm^3 s)
K_A	equilibrium constant for adsorption of A on catalyst surface (cm^3/mol)
K_B	equilibrium constant for adsorption of B on catalyst surface (cm^3/mol)
k	surface reaction rate constant for forward reaction (cm^6 mol^{-1} min^{-1} g-cat^{-1})
K_P	equilibrium constant for adsorption of P on catalyst surface (cm^3/mol)
K_W	equilibrium constant for adsorption of W on catalyst surface (cm^3/mol)
S	vacant site
t	time
w	catalyst loading (g/cm^3 of liquid phase)
X_A	fractional conversion of A

glycol [3]. The commercial process for acetals is catalyzed by strong acids such as *p*-toluenesulfonic acid. The acetalization of ethylene glycol with methyl 2-napthyl ketone to synthesize 2-methyl-2-napthyl-1,3-dioxolane is industrially important and has blossom orange fragrance. However, the process is normally carried out using homogeneous acid catalysts which need to be replaced. The use of heteropolyacids [13–17] and their modified forms with in situ generation of nano-catalysts [18–21] including different supports such clays [13–21] and hexagonal mesoporous silica [22], their characterization and applications have been deliberated in some of our publications.

The current investigation deals with efficacy of different solid acid catalysts for acetalization of ethylene glycol with methyl 2-napthyl ketone to synthesize 2-methyl-2-napthyl-1,3-dioxolane. A variety of catalysts were evaluated for their activity and selectivity. Use of modified heteropolyacid supported on acid treated K-10 clay as the most active and selective catalyst is discussed. Reaction mechanism and kinetics are established.

2. Experimental

2.1. Chemicals and catalysts

The sources of various chemicals were as follows: dodecatungstophosphoric acid (DTP), cesium chloride, methanol, *n*-decane, zirconium oxychloride, aluminum nitrate, ammonium persulfate, ethanol (M/s s.d. Fine Chem. Ltd., Mumbai, India); montmorillonite K-10 clay, tetraethyl orthosilicate (M/s. Fluka Chemicals, Germany);ethylene glycol, methyl 2-napthyl ketone, benzophenone, acetophenone, propylene glycol, toluene (M/s. Sigma Aldrich, Mumbai, India); dodecyl amine, chlorosulfonic acid (Spectrochem Ltd., Mumbai, India).

2.2. Catalyst synthesis

20% (w/w) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 (designated as Cs-DTP/K-10) was prepared by incipient wetness technique developed in our lab [19–21] including UDCaT-4 [23–25] and UDCaT-5 [25,26].

2.3. Catalyst characterization

X-ray powder diffraction (XRD) was performed using a Bruker AXS powder diffractometer D8 instrument, with Cu-Kα (1.54 Å) radiation, to analyze the crystallinity, textural patterns of the catalyst and the phase purity of synthesized catalysts. The XRD patterns were recorded by scanning the catalyst sample within the 2θ range of 10–80°. The specific surface area, pore volume and pore diameter of each sample were obtained from nitrogen adsorption–desorption isotherms measured in Micromeritics ASAP 2010 automated instrument and specific surface area, pore volume and pore diameter of all prepared catalysts were calculated by using the BET model. Fourier transform infrared (FTIR) spectra in the range of 400–4000 cm^{-1} were collected on a Perkin Elmer Spectrophotometer using a sample disk of 5% catalyst weight in KBr powder. Surface morphology of the catalyst was captured by SEM (SU 30 microscope, JEOL, Japan). The sample was dried and mounted on specimen studs and sputter coated with a thin film of platinum to make the surface conducting. Temperature programmed desorption (TPD) was performed by using ammonia as a probe molecule in Micromeritics AutoChem 2920 instrument. It was carried out by heating 0.2 g of the catalyst at 573 K in dry air for 1 h and then purging it with helium for 0.5 h. The temperature was decreased to 398 K under the flow of helium and then 0.5 ml NH_3 pulses were supplied to the sample until no more uptake of NH_3 was observed. NH_3 was then desorbed in helium flow by increasing the temperature to 573 K, with a heating rate of 10 K/min, and NH_3 desorption was measured using a TCD detector.

2.4. Reaction procedure and analytical methods

A typical acetalization reaction of methyl napthyl ketone with ethylene glycol was carried out in a 100-ml glass reactor (5 cm diam.) fitted with a Dean-Stark apparatus for continuous removal of water during reaction with overhead stirring and water condenser (Fig. 1). The reactor was charged with methyl napthyl ketone (0.10 mol), ethylene glycol (0.20 mol), toluene as solvent, and *n*-decane as internal standard. A known catalyst loading was used (0.02 g/cm^3) in control experiments. The reaction mixture was vigorously stirred at different reaction temperatures. The reaction was continued until maximum conversion was obtained. The analysis of reaction products was carried out using GC (Chemito 1000) equipped with a BPX-50 capillary column (length: 30 m, ID: 0.25 mm) and with FID detector. Confirmation of reaction products was achieved by GC–MS (Perkin Elmer, Clarus 500) using the same capillary column.

3. Results and discussion

Preliminary experiments suggested that the best catalyst was 20% (w/w) Cs-DTP/K-10 and its characterization is briefly presented here including the used catalyst.

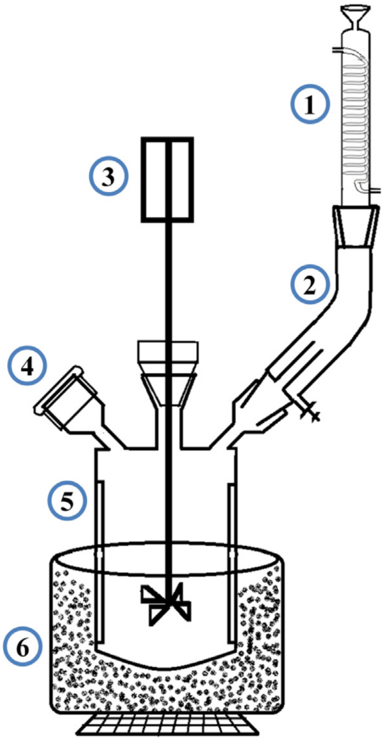


Fig. 1. Schematic diagram of the glass reactor assembly with modified Dean Stark apparatus. 1. water condenser, 2. Dean Stark apparatus, 3. overhead stirrer, 4. sample port, 5. oil bath, 6. thermostatic oil bath.

3.1. Catalyst characterization

3.1.1. X-ray powder diffraction (XRD)

From the background XRD reflection for K-10, it was found that K-10 was amorphous in nature. The XRD patterns for K-10 reveal one peak at $2\theta = 28.1^\circ$, which is due to quartz, and there is no effect on the 2θ value of quartz even after supporting K-10 clay either with dodeca-tungstophosphoric acid (DTP) or with Cs-DTP. Bulk DTP is crystalline in nature, but it was observed that while loading DTP on K-10, some of its crystallinity was lost. XRD patterns of 20% (w/w) Cs-DTP/K-10 showed that there was no change in textural pattern and crystallinity thereby confirming the stability of the catalyst (Fig. 2).

3.1.2. BET surface area analysis (nitrogen adsorption)

The specific surface area of K-10 clay (240 m^2/g) was found to decrease with 20% Cs-DTP loading on K-10 clay (193 m^2/g) (Table 1). This may be due to the blockages of pores by particles Cs-DTP generated in situ on K-10 clay. The pore size distribution suggested that the average pore size for catalysts was in the range of 5.0–6.5 nm (mesoporous region). The adsorption–desorption isotherms for K-10 and 20% Cs-DTP/K-10 showed that they have form of Type IV isotherm with the hysteresis loop of type H_3, which is a characteristic of mesoporous solid (Fig. 3a and b).

3.1.3. Fourier transform infrared (FTIR) spectroscopy

Primary structures of supported DTP and Cs-DTP were identified by comparing their FTIR absorbance bands to those of bulk DTP, Cs-DTP salt alone and 20% Cs-DTP/K-10 which showed characteristic IR bands at approximately 1080 cm^{-1} (P—O in central tetrahedral), 984 cm^{-1} (terminal W=O), 897 cm^{-1} and 812 cm^{-1} (W—O—W) associated with the asymmetric vibrations in the Keggin polyanion. However, Cs-DTP is characterized by the split in the W=O band, suggesting the direct interaction between the poly anion and Cs^+. FTIR spectra of 20% (w/w) DTP/K-10 and 20% (w/w) Cs-DTP/K-10 indicated that the primary Keggin structure was preserved in both the cases on K-10 support. When the characteristic peaks of unsupported HPA and K-10 were superimposed, the peaks for the supported catalysts appeared without any shift in the peak position. Sharp peak at 1631 cm^{-1} indicated the presence of H_3O^+ (Bronsted acidity). In DTP, water was present as water of crystallization while in the case of Cs-DTP/K-10 it indicated the presence of partial H^+ ion directly attached to the polyanion (···O—H) and was present in K-10 and possibly as H_3O^+ (Fig. 4).

3.1.4. Scanning electron microscope (SEM)

SEM images of K-10 clay and 20% (w/w) Cs-DTP/K-10 show almost similar morphological properties and no change in catalyst surface morphology was observed (Fig. 5a and b).

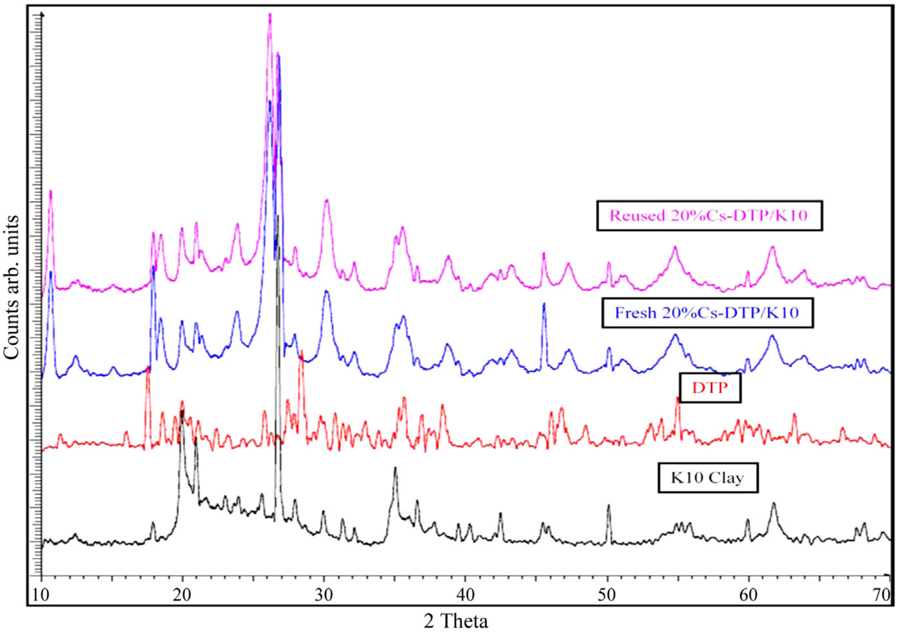


Fig. 2. XRD of catalysts.

Table 1
Textural properties and acidities of catalysts.

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Total acidity (mmol/g)	(Acidity/area) × 10^4 mmol/m^2
K-10 clay	240	0.38	6.36	0.139	5.8
20% Cs-DTP/K-10	193	0.29	6.21	0.405	21.0
UDCaT-4	232	0.20	3.10	0.560	24.1
UDCaT-5	84	0.21	3.00	0.582	69.2

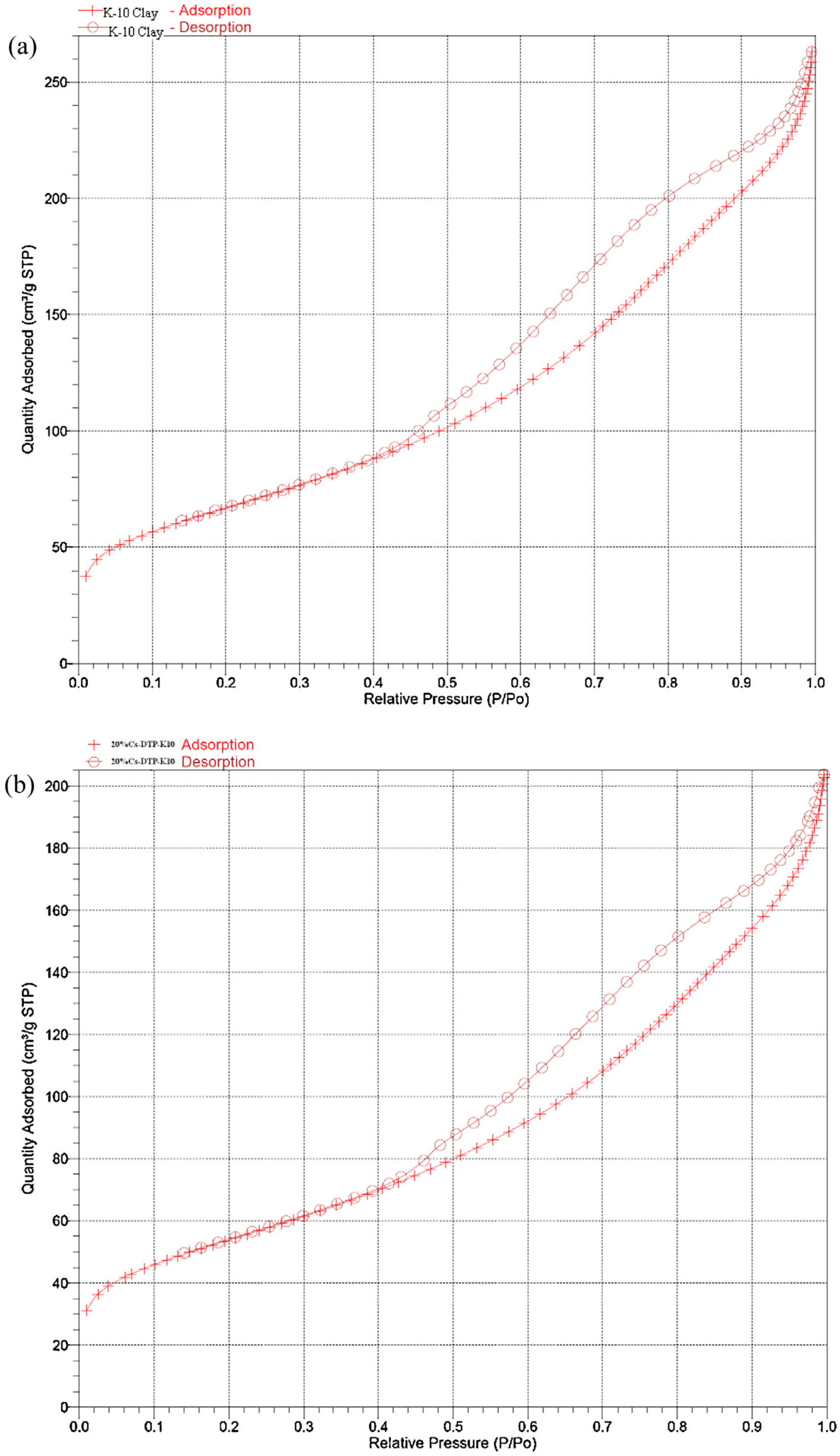


Fig. 3. (a) BET of K-10 clay. (b) BET of 20%Cs-DTP/K-10.

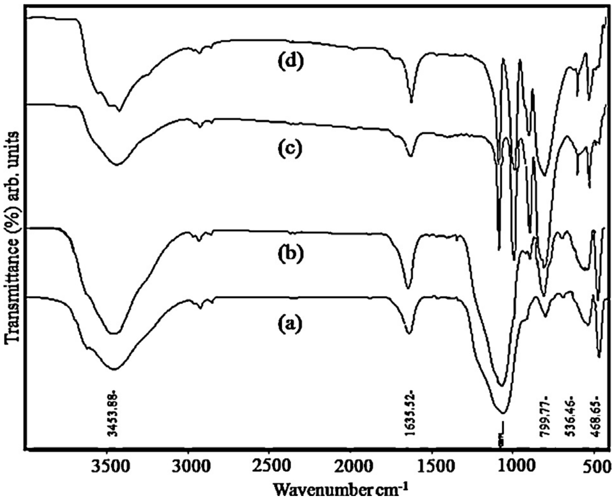


Fig. 4. FTIR spectra of catalyst. (a) Fresh 20% Cs-DTP/K-10, (b) reused 20% Cs-DTP/K-10, (c) Cs-DTP salt, (d) pure DTP.

3.1.5. *Temperature programmed desorption (TPD)*

TPD using ammonia as a probe was employed for the measurement of the total acidity and acid strength and details regarding total acidity of the catalysts are given in Table 1. These catalysts are superacids having high site density.

3.2. *Acetalization of ethylene glycol with methyl 2-naphthyl ketone*

3.2.1. *Catalyst screening*

For acetalization of ethylene glycol with methyl 2-naphthyl ketone, solid acid catalysts including, 20% (w/w) Cs-DTP/K-10, UDCaT-4, UDCaT-5, and K-10 clay were screened. The reaction without catalyst (blank) was also studied by using identical reaction parameters: temperature 110 °C, methyl 2-naphthyl ketone:ethylene glycol mole ratio of 1:2, speed of agitation 800 rpm, catalyst loading 0.02 g cm^{-3}, 3 h reaction time. Toluene was used as solvent and *n*-decane as internal standard. Efficacy of these catalysts was found as follows: 20% (w/w) Cs-DTP/K-10 > UDCaT-4 > UDCaT-5 > clay K-10 > blank (Fig. 6). Out of them 20% (w/w) Cs-DTP/K-10 catalyst gave the highest methyl 2-naphthyl ketone conversion of 86.8%, followed by UDCaT-4, UDCaT-5 and K-10 clay gives 79.5, 74.9, 30.2%, respectively with 100% product selectivity (Table 2). Since water was removed continuously, the reaction was irreversible. Without catalyst (blank) reaction gives conversion of 10% (Fig. 6). This is not surprising since in acetalization reactions at high temperature, self-catalysis due to protons from glycol can also take place. The surface areas and acidity of catalysts are given in (Table 1). In all studied catalysts 100% selectivity toward 2-methyl-2-naphthyl-1,3-dioxolane was observed (Table 2). 20% (w/w) Cs-DTP/K-10 catalyst shows the highest conversion of methyl 2-naphthyl ketone, the limiting reactant due to its Bronsted acidic sites having acidity of 0.405 mmol/g and high surface area of 193 m^2/g as compared to clay K-10. Even though the surface area of clay K-10 is high 240 m^2/g, its acidity of 0.139 mmol/g is less. The complete characterization of UDCaT-4 and UDCaT-5 has been reported earlier [23–26]. These catalysts are superacids with distribution of Bronsted and Lewis acidity which has been discussed in detail. Their activity can be explained in terms of Bronsted acid and acidity per unit surface area and average pore sizes which are responsible for activity (Tables 1 and 2). The pore sizes of UDCaT-4, UDCaT-5 and Cs-DTP/K-10 are 3.10, 3.0 and 6.21 nm with corresponding conversions of 79.5, 74.9 and 86.8%, respectively. The accessibility of active sites by the reactants ethylene glycol with methyl 2-napthyl ketone in all three catalysts would not pose any problem but the product 2-methyl-2-napthyl-1,3-dioxolane being bulky would have intraparticle diffusion limitation

Table 2
Product selectivity in acetalization of methyl 2-naphthyl ketone with ethylene glycol using different catalysts.

Catalyst	Conversion (%)	Selectivity (%) 2-methyl-2-naphthyl-1,3-dioxolane
20% Cs-DTP/K-10	86.8	100
UDCaT-4	79.5	100
UDCaT-5	74.9	100
K-10 clay	30.2	100
Blank	10.4	100

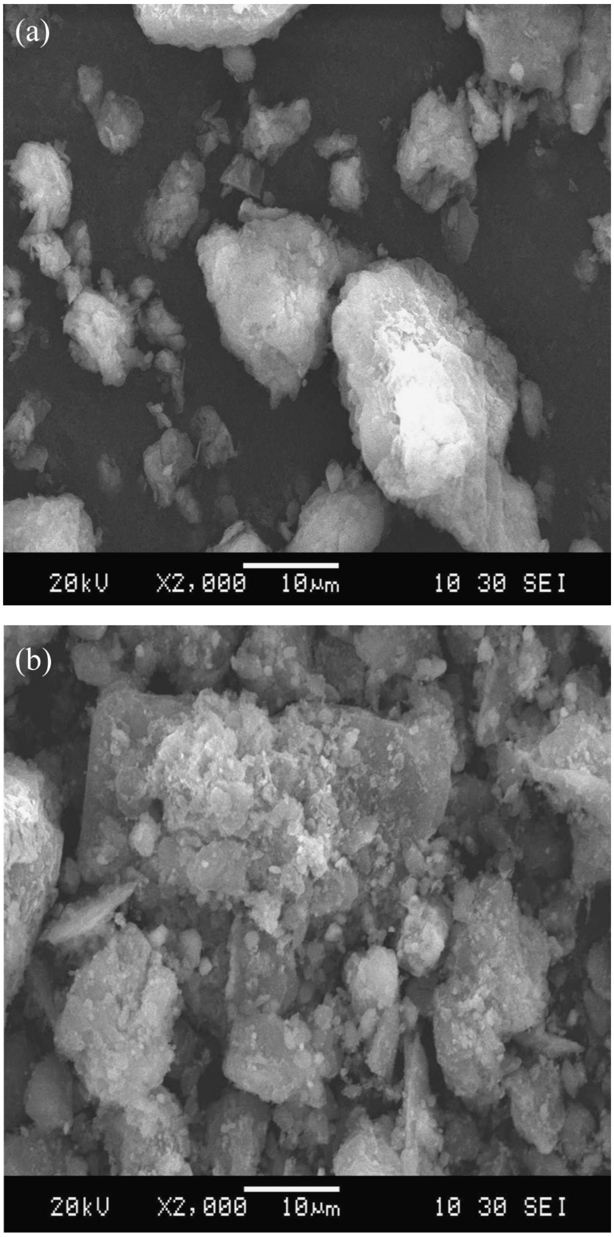
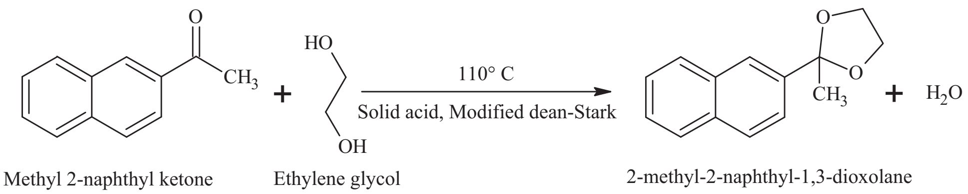


Fig. 5. (a) SEM of K-10 clay. (b) SEM of 20% Cs-DTP/K-10.



Scheme 1. Acetalization of ethylene glycol with methyl 2-naphthyl ketone.

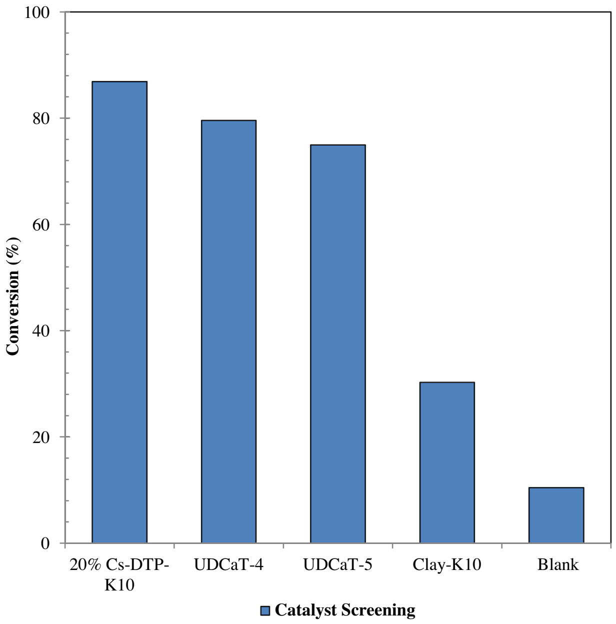


Fig. 6. Catalyst screening of acetalization of ethylene glycol. Methyl 2-naphthyl ketone conversion (■). Reaction conditions: temperature 110 °C, molar ratio of methyl 2-naphthyl ketone to ethylene glycol is 1:2, catalyst loading 0.02 g cm^{-3}, speed of agitation 800 rpm, reaction time of 3 h.

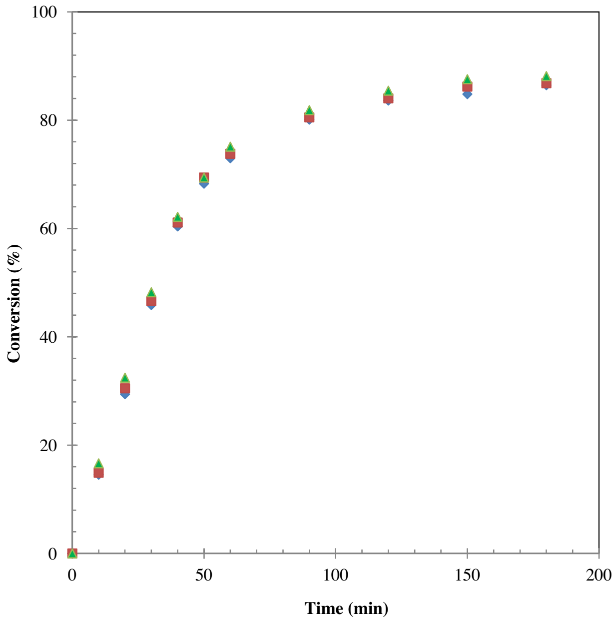


Fig. 7. Effect of speed of agitation of acetalization of ethylene glycol. Reaction conditions: temperature 110 °C, molar ratio of methyl 2-naphthyl ketone to ethylene glycol is 1:2, catalyst loading 0.02 g cm^{-3}, reaction time of 3 h. (◆) 600 rpm; (■) 800 rpm; (▲) 1000 rpm.

to some extent in UDCaT-4 and UDCaT-5 and thus the conversion is less in these two catalysts. UDCaT-4 (persulfated alumina and zirconia on hexagonal mesoporous silica (HMS) catalyst had Lewis acidic sites of 0.582 mmol/g, and the support used is hexagonal mesoporous silica (HMS). It is reported in the literature that K-10 clay is the better support for acetalization, esterification and etherification reactions [27]. K-10 clay is better support because it adsorbs the water molecules generated in the reaction and shifts the reaction equilibrium toward the product. UDCaT-4 (persulfated alumina and zirconia on hexagonal mesoporous silica (HMS) and UDCaT-5 (super acidic modified sulfated zirconia based catalysts) showed slightly less conversion 79.5 and 74.9%, respectively as compared to 20% (w/w) Cs-DTP/K-10. This is because of these catalysts having Lewis acidic sites of 0.582 and 0.560 mmol/g respectively and lower surface area (84 m^2/g) in case of UDCaT-5. Hence catalyst plays a significant role in this study and 20% (w/w) Cs-DTP/K-10 catalyst was found robust catalyst and used for further study (Scheme 1).

3.2.2. *Effect of speed of agitation*

The effect of speed of agitation was studied in the range of 600–1000 rpm with 20% (w/w) Cs-DTP/K-10 (Fig. 7). It was observed that there was very marginal increase in conversion of methyl 2-naphthyl ketone when speed of agitation was increased from 600 to 1000 rpm. At 600 rpm the initial rate of reaction was almost the same as that at 800 and 1000 rpm. Hence, further reactions were carried out at 800 rpm to ensure that external mass transfer effects did not influence the rate of reaction. Theoretical calculations were also done as delineated earlier [23] to find that a speed of 800 rpm was indeed sufficient to ensure absence of external mass transfer resistance. That confirms the absence of resistance to external mass transfer of methyl 2-naphthyl ketone to the external surface of the solid acid catalyst.

3.2.3. *Effect of mole ratio*

Effect of methyl 2-naphthyl ketone to ethylene glycol mole ratio was studied at 1:1, 1:2, and 1:3, on methyl 2-naphthyl ketone conversion was studied over 20% (w/w) Cs-DTP/K-10 catalyst (Fig. 8). It was observed that methyl 2-naphthyl ketone conversion increased with increasing mole ratio from 1:1 to 1:2 with final conversions of 71 to 87%, respectively. At 1:2 mole ratio the conversion was 87% but with further increasing molar ratio at 1:3, the final conversion was slightly lower (84%). Further, it is also likely because there is competitive adsorption between methyl 2-naphthyl ketone and ethylene glycol molecules on the catalytic sites and more of ethylene glycol was adsorbed. Hence 1:2 molar ratio was found to be the optimum and therefore further reactions were carried out using 1:2 molar ratio.

3.2.4. *Effect of catalyst loading*

The effect of 20% (w/w) Cs-DTP/K-10 loading on the conversion of methyl 2-naphthyl ketone was studied by varying the amount from 0.01 to 0.03 g cm^{-3} of total reaction mixture at 110 °C for 3 h.

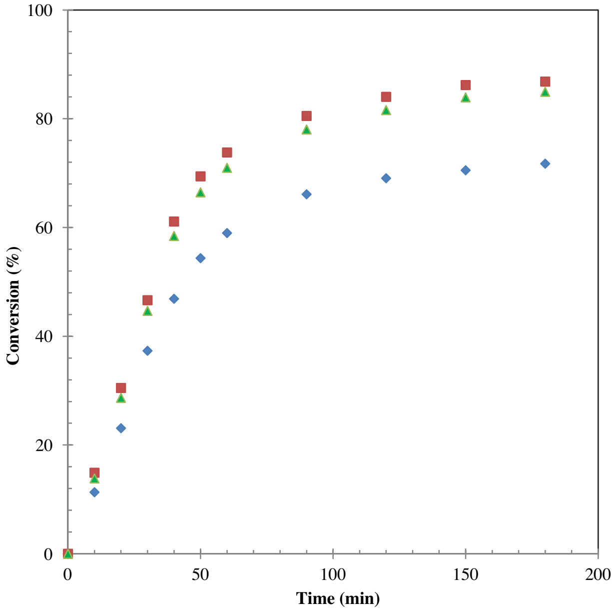


Fig. 8. Effect of mole ratio of acetalization of ethylene glycol. Reaction conditions: temperature 110 °C, speed of agitation 800 rpm, catalyst loading 0.02 g cm^{-3}, reaction time of 3 h. (◆) 1:1; (🟥) 1:2; (▲) 1:3.

It was observed that with increase in catalyst loading the conversion of methyl 2-naphthyl ketone was increased; it was due to the increase in number of active sites and availability of large surface area and pore dimension of the catalyst. And in the absence of external mass transfer resistance, the rate of reaction was directly proportional to the amount of catalyst loading. Hence with increase in catalyst loading from 0.01 to 0.03 g cm^{-3}, the conversion of methyl 2-naphthyl ketone was increased from 71 to 92%. The initial rate of reaction, given as change in fractional conversion with respect to time (dX_A/dt) was directly proportional to catalyst loading (Fig. 9).

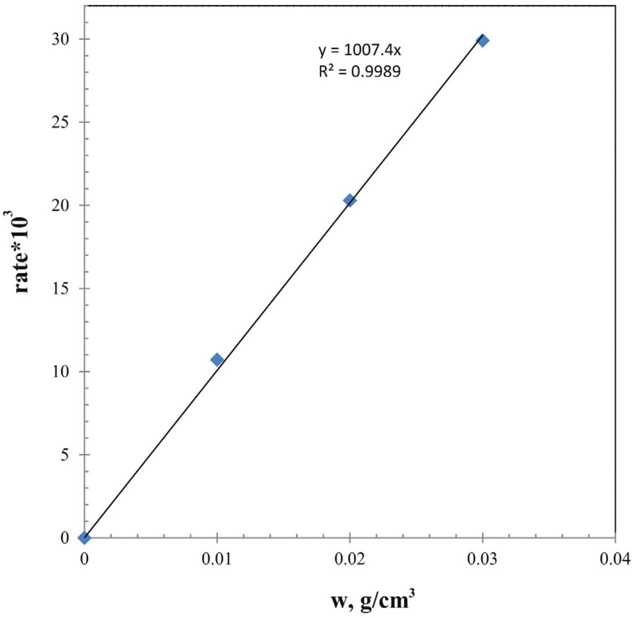


Fig. 9. Plot of initial rate of reaction vs. catalyst loading.

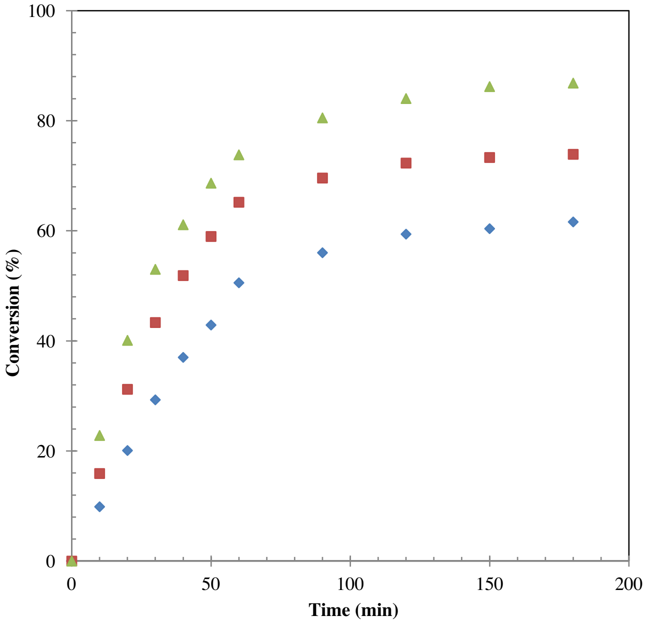


Fig. 10. Effect of reaction temperature of acetalization of ethylene glycol. Reaction conditions: molar ratio of methyl 2-naphthyl ketone to ethylene glycol is 1:2, catalyst loading 0.02 g cm^{-3}, speed of agitation 800 rpm, reaction time of 3 h. (◆) 90 °C; (🟥) 100 °C; (▲) 110 °C.

3.2.5. Effect of reaction temperature

Methyl 2-naphthyl ketone conversion as a function of temperature was studied in the range of 90–110 °C; conversion of methyl 2-naphthyl ketone increased with increasing temperature from 90 to 110 °C (Fig. 10). At 90 °C the conversion was 61% which increased up to 87% at 110 °C. Initial rates of reaction were calculated and it was found that the rate increased substantially with increasing temperature.

3.2.6. Reaction mechanism and kinetics

Scheme 2 depicts the mechanism. 20% (w/w) Cs-DTP/K-10 is a strong solid acid catalyst which can donate a proton to the hydroxyl group of the ethylene glycol which leads to the formation of an oxonium ion. These are Bronsted acid sites. The carbonyl of the methyl 2-naphthyl ketone could attack the carbon bearing the oxonium ion on the ethylene glycol to form an intermediate which then releases water to form the five-member ring product. The initial rate data could be analyzed on the basis of Langmuir–Hinshelwood–Hougen–Watson (LHHW) mechanism.

Weak adsorption of ethylene glycol (A) on a vacant site S is given by

$$\mathrm{A} + \mathrm{S} \overset{K_A}{\rightleftharpoons} \mathrm{AS} \tag{1}$$

Similarly, adsorption of methyl 2-naphthyl ketone (B) on the vacant site is represented as

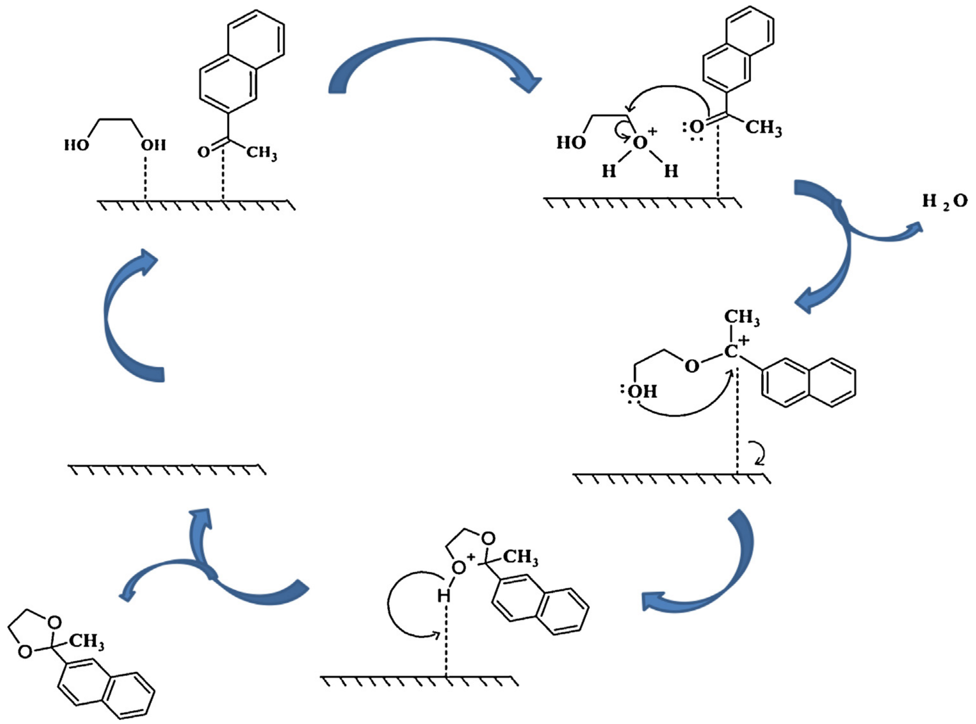
$$\mathrm{B} + \mathrm{S} \overset{K_B}{\rightleftharpoons} \mathrm{BS} \tag{2}$$

Surface reaction of AS with BS on the adjacent sites leads to formation of 2-methyl-2-naphthyl-1, 3-dioxolane (ES) and water (WS) on the catalytic sites

$$\mathrm{AS} + \mathrm{BS} \overset{K_2}{\rightleftharpoons} \mathrm{ES} + \mathrm{WS} \tag{3}$$

Desorption of 2-methyl-2-naphthyl-1, 3-dioxolane and water is shown as

$$\mathrm{ES} \overset{1/K_E}{\rightleftharpoons} \mathrm{E} + \mathrm{S} \tag{4}$$



Scheme 2. Possible reaction mechanism of acetalization of ethylene glycol with methyl 2-naphthyl ketone forming 2-methyl-2-naphthyl-1,3-dioxolane.

$$\mathrm{WS} \overset{1/K_W}{\rightleftharpoons} \mathrm{W} + \mathrm{S} \tag{5}$$

Now the total concentration of the sites, C_t is expressed as

$$C_t = C_S + C_{AS} + C_{BS} + C_{ES} + C_{WS} \tag{6}$$

This can also be expressed as:

$$C_t = K_A C_A C_S + K_B C_B C_S + K_E C_E C_S + K_W C_W C_S \tag{7}$$

Or, the concentration of vacant sites as

$$C_S = \frac{C_t}{1 + K_A C_A + K_B C_B + K_E C_E + K_W C_W} \tag{8}$$

If the surface reaction (C) is controlling the rate of reaction, then the rate of reaction of A is given by the equation

$$-r_A = -\frac{dC_A}{dt} = k_2 C_{AS} C_{BS} - k_2' C_{ES} C_{WS} \tag{9}$$

$$-\frac{dC_A}{dt} = \frac{k_2\{K_A K_B C_A C_B - (K_E K_W C_E C_W)/K_2\} C_t^2}{(1 + K_A K_C + K_B C_B + K_E C_E + K_W C_W)^2} \tag{10}$$

When the reaction is far away from the equilibrium

$$-\frac{dC_A}{dt} = \frac{k_2 C_t^2 K_A K_B C_A C_B}{\left(1 + \sum K_i C_i\right)^2} \tag{11}$$

$$= \frac{kw C_A C_B}{(1 + K_i C_i)^2} \tag{12}$$

where $kw = k_2 C_t^2 K_A K_B$ and w is catalyst loading. If the adsorption constants are very small, then above equation reduces to

$$-\frac{dC_A}{dt} = kw C_A C_B \tag{13}$$

Let $C_{B0}/C_{A0} = M$, the molar ratio of methyl-2-naphthyl ketone to ethylene glycol at time $t = 0$. Then, Eq. (13) can be written in terms of fractional conversion as

$$\frac{dX_A}{dt} = kw C_{A0}(1 - X_A)(M - X_A) \tag{14}$$

Upon integration this leads to:

$$\ln\left(\frac{M - X_A}{M(1 - X_A)}\right) = k_1 (M - 1) t \tag{15}$$

where $k_1 = kw C_{A0}(M - 1)$

Thus, in consonance with Eq. (15) a plot of $\ln((M - X_A)/(M(1 - X_A)))$ vs. t at different catalyst loading (w) to get straight lines passing through origin, the slopes of each line divided by $C_{A0}(M - 1)$ gives the average k values and gave an excellent fit (Fig. 11). The rate of reaction is proportional to the number of active sites present on the surface. It would therefore

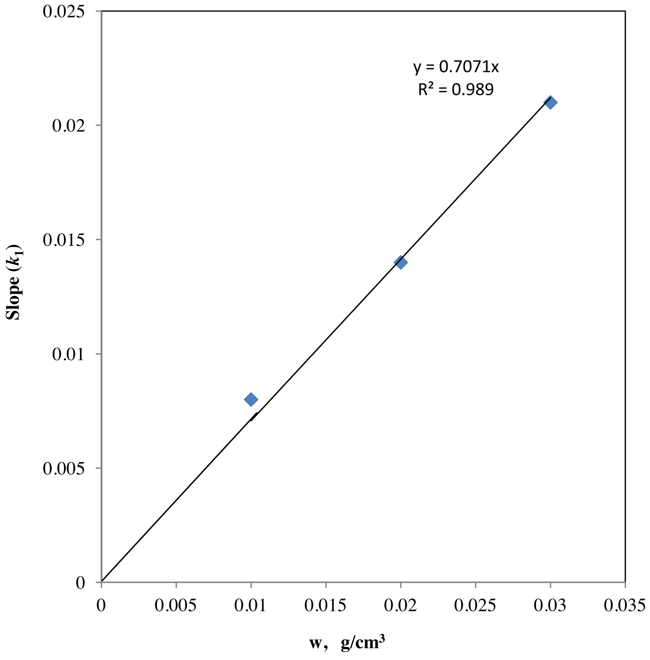


Fig. 11. Slope k_1 vs. catalyst loading (w) (g/cm^3).

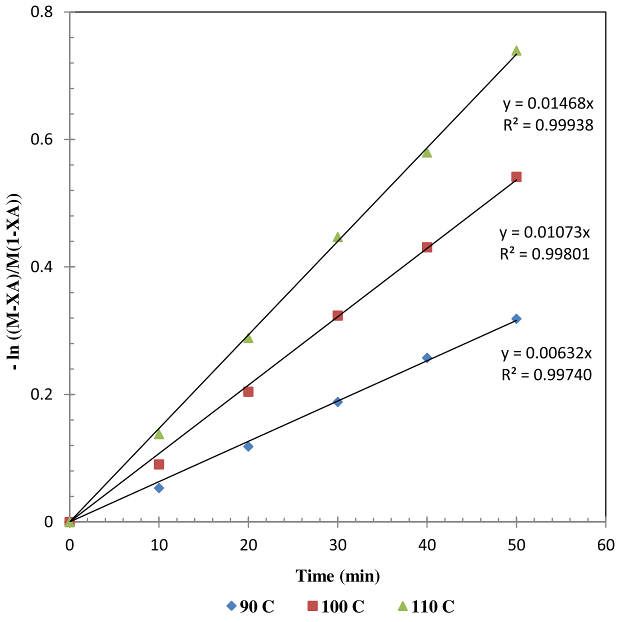


Fig. 12. Second order plot of $-\ln\{(M-X_A)/[M(1-X_A)]\}$.

mean that the reaction mechanism is LHHW type with very weak adsorption of both the reactants in the absence of any diffusional resistance. The values of k_1 were also found at the different temperatures at the same w and M (Fig. 12). The Arrhenius plot of $\ln k_1$ vs. $1/T$ is shown in (Fig. 13), from which the activation energy was calculated and found to be 11.66 kcal/mol. The high value of activation energy also supported the fact that the overall rate of reaction is not influenced by external mass transfer or intraparticle diffusion resistance and it is intrinsically kinetically controlled reaction on active sites.

3.2.7. *Catalyst reusability study*

Catalyst reusability study was carried out by performing the reaction under the optimized reaction conditions: temperature 110 °C, molar ratio of methyl 2-naphthyl ketone to ethylene glycol 1:2, catalyst loading 0.02 g cm^{-3}, speed of agitation 800 rpm, reaction time of 3 h (Fig. 14). After completion of the reaction, the catalyst was recovered by filtration and washed with methanol several times to remove the adsorbed materials from the surface of the catalyst. There was some loss of catalyst during filtration and handling (~4–5%). Further there was no loss or leaching of the active component Cs-DTP in the liquid phase which was confirmed by the ascorbic acid test [17]. Since the product is bulkier, it was thought desirable to activate the catalyst. The catalyst was calcined at 300 °C for 3 h, in the flowing air for re-activation. It was characterized again. BET surface area of the used catalyst was very marginally reduced from 193 to 189 m^2/g which is within experimental error. The XRD and FTIR studies of the used catalysts are given in Figs. 2 and 4 which show that the catalyst has retained its fidelity during reuse. This catalyst showed practically the same activity and selectivity of desired products even after three catalytic cycles. The nano-particles of Cs-DTP on K-10 surface are robust as has been found out in other studies [28].

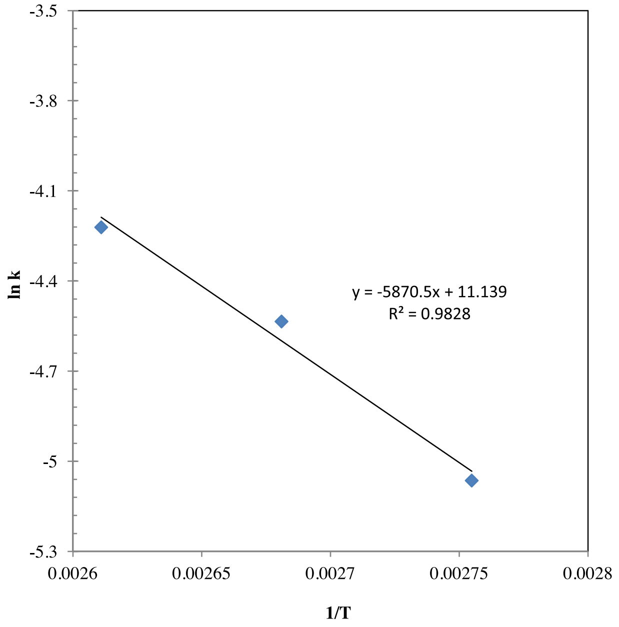


Fig. 13. Arrhenius plot.

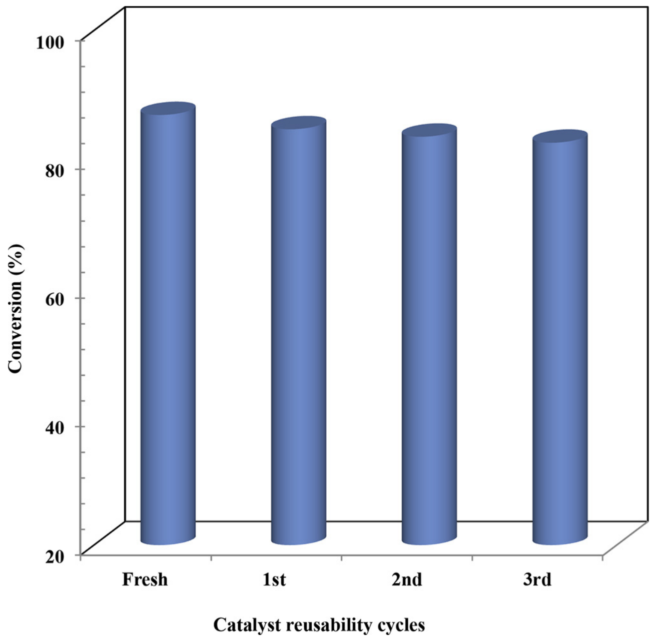
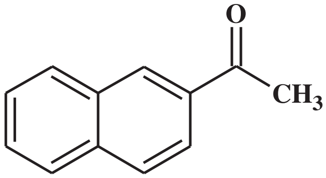
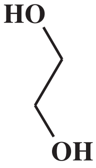
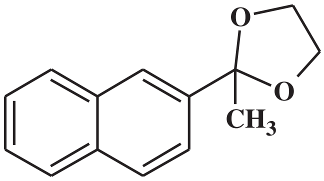
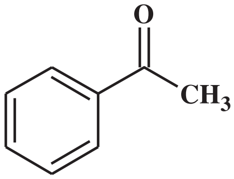
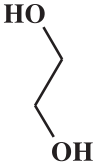
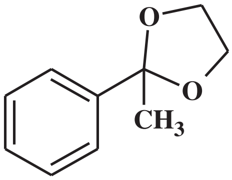
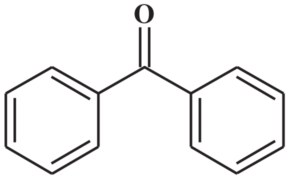
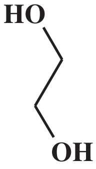
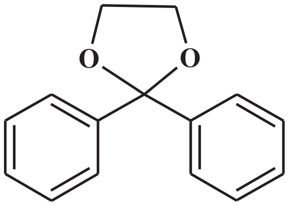
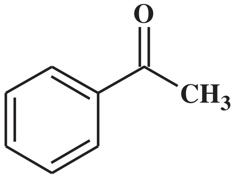
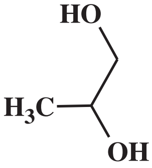
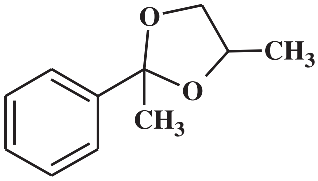
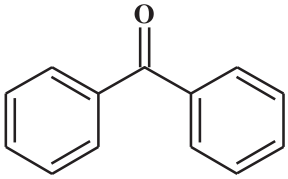
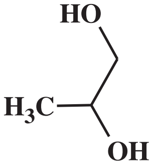
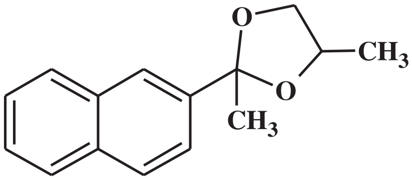


Fig. 14. Reusability study of acetalization of ethylene glycol. Methyl 2-naphthyl ketone conversion (■). Reaction conditions: temperature 110 °C, molar ratio of methyl 2-naphthyl ketone to ethylene glycol is 1:2, catalyst loading 0.02 g cm^{-3}, speed of agitation 800 rpm, reaction time of 3 h.

3.2.8. *Substrate study*

1,2-Propylene glycol and ethylene glycol were used along with other substrates over 20% Cs-DTP/K-10 catalyst as given (Table 3) at identical reaction parameters. In all substrates 100% selectivity of 1,3-dioxolane of glycols was obtained. The conversion and selectivity to the 1,3-dioxolane were influenced by the size of ketones used. In the case of ethylene glycol, other ketones were tested under similar reaction conditions, including acetophenone and benzophenone and conversion of acetophenone and benzophenone obtained was 72 and 69% respectively. Benzophenone is a bulky ketone and leads to lower conversion. In the case of 1,2-propylene glycol, acetalization with ketones including acetophenone and methyl 2-naphthyl ketone were studied. The conversion of acetophenone and methyl 2-naphthyl ketone was obtained of 60 and 56%, respectively. Methyl 2-naphthyl ketone gave lower conversion with 1,2-propylene glycol as compared to ethylene glycol because of the bulkiness of the product and its steric hindrance. In any of these substrates, no by-product was formed.

Table 3
Substrate study for acetalization of glycols with different ketone using 20% (w/w) Cs-DTP/K-10 catalyst.

Limiting reactant	Execs reactant	Product	Conversion (%)
			87
			72
			69
			60
			56

Reaction conditions: temperature 110 °C, molar ratio of ketone to glycol is 1:2, catalyst loading 0.02 g cm^{-3}, speed of agitation 800 rpm, reaction time of 3 h. Selectivity 100% in each case.

4. Conclusions

Acetalization of ethylene glycol with methyl 2-naphthyl ketone was studied using a number of catalysts to synthesize 2-methyl-2-naphthyl-1,3-dioxolane, amongst which 20% (w/w) Cs-DTP/K-10 was the best catalyst. The process gives 87% methyl 2-naphthyl ketone conversion with 100% selectivity of 2-methyl-2-naphthyl-1,3-dioxolane at 110 °C. Various reaction parameters were studied to fix the optimized reaction conditions. Various substrates like as 1,2 propylene glycol, and different ketones were studied at identical reaction conditions to get 100% selectively toward 1,3-dioxolane of different glycols. Reaction mechanism and kinetic model were well fitted and the apparent activation energy was calculated. The catalyst was regenerated after the reaction and showed very good reusability. The catalyst 20% (w/w) Cs-DTP/K-10 was fully characterized both before and after use to understand its superior properties and reusability. The XRD patterns showed that there was no change in textural pattern and crystallinity thereby confirming the stability of the catalyst. The pore size distribution suggested that the average pore size for catalysts was in the range of 5.0–6.5 nm (mesoporous region). FTIR spectra indicated that the primary Keggin structure was preserved on K-10 support. Sharp peak at 1631 cm^{-1} indicated the presence of Bronsted acidity. SEM images of K-10 clay and 20% (w/w) Cs-DTP/K-10 show almost similar morphological properties and no change in catalyst surface morphology was observed. NH_3-TPD showed the catalyst was superacidic in nature having high site density.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

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