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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.

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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.

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