Green etherification of bioglycerol with 1-phenyl ethanol over supported heteropolyacid

ORIGINAL PAPER

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**Ganapati D. Yadav · Payal A. Chandan ·
Nirupama Gopalaswami**

Abstract Escalating demand for biodiesel production has generated surplus glycerol. Therefore, the consumption of glycerol for valuable conversions has become a global challenge. In an effort to convert glycerol, we have etherified it to make a biologically active component, 3-(1-phenylethoxy) propane-1,2-diol. Etherification of glycerol with 1-phenyl ethanol was carried out by using heterogeneous acid catalysts. The process is green and clean. Different types of heteropolyacids (HPAs) supported on hexagonal mesoporous silica (HMS) and K-10 clay were prepared by incipient-wetness technique and screened to get high selectivity towards monoether of glycerol. 20% w/w *dodeca*-tungstophosphoric acid (DTP)/HMS was found to be the best. The effects of various reaction parameters such as speed of agitation, catalyst loading, mole ratio of reactants and temperature were evaluated systematically to prove that the reaction obeys Langmuir–Hinshelwood–Hougen–Watson (LHHW) type of mechanism. It was also observed that the reaction was free from any external mass transfer as well as intra-particle diffusion limitations and was intrinsically kinetically controlled. An overall second order kinetic equation was used to fit the experimental data, under the assumption that all the species are weakly adsorbed on the catalytic sites. Apparent activation energy was estimated as 27.0 kcal/mol. Solvent-free condition for this reaction has also added the green chemistry perception to the reaction.

Abbreviations

a_p	Solid–liquid interfacial area (cm^2/cm^3 of liquid phase)
A	Reactant species A—1-phenyl ethanol
AS	Chemisorbed A
B	Reactant species B—Glycerol
BS	Chemisorbed B
P	Monoether of glyceryl ether (product)
PS	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 at solid (catalyst) surface (mol/g cat)
C_{PS}, C_{WS}	Concentration of P and W at solid (catalyst) surface (mol/g cat)
C_S	Concentration of vacant sites (mol/g cat)
C_t	Total concentration of the sites (mol/g cat)
C_{WP}	Weisz–Prater constant
D_P	Diameter of catalyst particle (m)
D_{AB}	Diffusion coefficient of A in B (m^2/s)
D_{BA}	Diffusion coefficient of B in A (m^2/s)
D_e	Effective diffusivity (cm^2/s)
R_p	Radius of catalyst particle (m)
$-r_A$	Rate of disappearance of A ($cm^3/gmol\ s$)
k_{SLA}, k_{SLB}	Solid–liquid mass transfer coefficients (m/s)
K_A	Equilibrium constant for adsorption of A on catalyst surface (l mol^{-1} min^{-1})
K_B	Equilibrium constant for adsorption of B on catalyst surface (l mol^{-1} min^{-1})

G. D. Yadav (✉) · P. A. Chandan · N. Gopalaswami
Department of Chemical Engineering, Institute of Chemical
Technology (ICT), Matunga, Mumbai 400 019, India
e-mail: gdyadav@yahoo.com; gd.yadav@ictmumbai.edu.in

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k_{SR}	Surface reaction rate constant for forward reaction (l mol^{-1} min^{-1})
$k_{SR'}$	Surface reaction rate constant for reverse reaction (l mol^{-1} min^{-1})
K_P	Equilibrium constant for adsorption of P on catalyst surface (min^{-1})
K_W	Equilibrium constant for adsorption of W on catalyst surface (min^{-1})
r_{obs}	Observed rate of reaction (mol/g cat/s)
S	Vacant site
Sh	Sherwood number
t	Time (min)
w	Catalyst loading (g/cm^3 of liquid phase)
X_A	Fractional conversion of A

Greek letters

| ϵ	Porosity
ρ_p	Density of catalyst particle (g/cm^3)
τ	Tortuosity (-)
μ	Viscosity of reaction mixture (kg/m.s)

Introduction

Heterogeneous catalysis by heteropoly acids has recently emerged as an innovative method for green chemistry practices. Heteropoly acids (HPAs), their salts and polyoxometalates (POMs) are attractive since they are low in toxicity, highly stable towards humidity, recyclable and air stable. Heteropoly acids are more active catalysts than conventional inorganic and organic acids for various reactions in solutions (Kozhevnikov 2002; Nakato et al. 1997, Yadav 2005). The use of HPAs in non-polar solvents improves product selectivity and also provides their easy separation from the reaction mixture. Today, catalysis by heteropoly acids (HPAs) is a potential area due to its economic and green benefits (Yadav and Kirthivasan 1995, 1997; Yadav and Bokade 1996; Kozhevnikov 2007). A variety of organic reactions that are catalysed by Bronsted acids such as H$_2$SO$_4$, HCl and other protonic acids or Lewis acids such as AlCl$_3$, FeCl$_3$, etc. proceed in the presence of heteropoly acids or polyoxometalates, more efficiently, under milder conditions, with greater selectivity, better yields and shorter reaction time. Supported heteropolyacid catalysts have been employed for both alkylation and acylation (Mizuno and Misono 1998; Miyaji et al. 2003; Kamiya et al. 2007; Kamiya et al. 2008). It has been demonstrated that the acidic cesium salts of HPAs are highly water-tolerant catalysts for hydration of olefins (Kimura et al. 1997) and hydrolysis of esters (Nakato et al. 1998).

Amongst many other solid acid systems, HPAs having Keggin anion structures are most active due to their superacidity and redox nature. However, HPAs in the bulk form offer poor efficiency due to low surface area, rapid deactivation and relatively poor stability. Attempts have been made to improve the efficiency and stability of HPAs by using various supports including mesoporous silica, mesoporous aluminosilicates, alumina, carbon and zirconia (Ren et al. 2010). Our laboratory has been investigating different aspects of green processes with benign solid acid catalysts, which have direct industrial relevance in refineries, petrochemicals, pharmaceuticals, rubber chemicals, dyestuff, agrochemicals, perfumery and flavour chemicals. Also, we have pioneered the use of supported heteropolyacids for a variety of reactions (Yadav 2005; Yadav et al. 2003; Yadav and George 2009; Yadav and Bokade 1996; Yadav and Kamble 2009; Yadav and Kirthivasan 1995, 1997; Yadav and Nair, 1999a, b). Synergetic combinations of various heteropoly acids with inorganic supports as nano-catalysts have been successfully developed and evaluated in a number of industrially important reactions (Bokade and Yadav 2009; Yadav and Asthana 2003; Yadav and Doshi 2000, 2002,2003; Yadav et al. 2003, 2004; Yadav and Salgaonkar 2005, 2009). Use of supported HPAs as heterogeneous catalysts, amongst others, in transformation of renewable feedstocks into value-added chemicals will assume greater importance as the fossil fuels stock gets consumed.

Biodiesel processes via transesterification produce 10% w/w of glycerol as the co-product. The production of glycerol in 2009 was 1.72 MMTA worldwide and the production of biodiesel will be economically viable if the co-product glycerol is converted into several value-added products. Glycerol finds applications in a plethora of areas from personal care to technical applications (Aresta et al. 2005; Zhou et al. 2008; Behr et al. 2008; Pagliaro et al. 2007; Jerome et al. 2008). There is a significant market for polymers, ethers and other compounds. Glycerol can be converted into variety of valuable products by reactions such as hydrogenolysis, dehydration, esterification, etherification, oxidation, etc. (Scheme 1). The volume of products such as epichlorohydrin, propanediols, acrolein/acrylic acid and Fisher–Tropsch products, which are currently produced by petrochemical routes is huge and glycerol as a renewable source will be very attractive in coming years. Taken together, all these chemicals have huge demand and since the source is renewable, these catalytic processes will be very attractive commercially.

Etherification of glycerol with alkanols is commercially attractive to provide value-added monoalkyl glyceryl ether (MAGE). Since glycerol has three hydroxyl groups with similar pKa values, the control of the regioselectivity is the main key of the process to minimise waste and by-products production. MAGEs resulting from these transformations are highly valuable chemicals since they exhibit a wide spectrum of biological activities such as anti-inflammatory
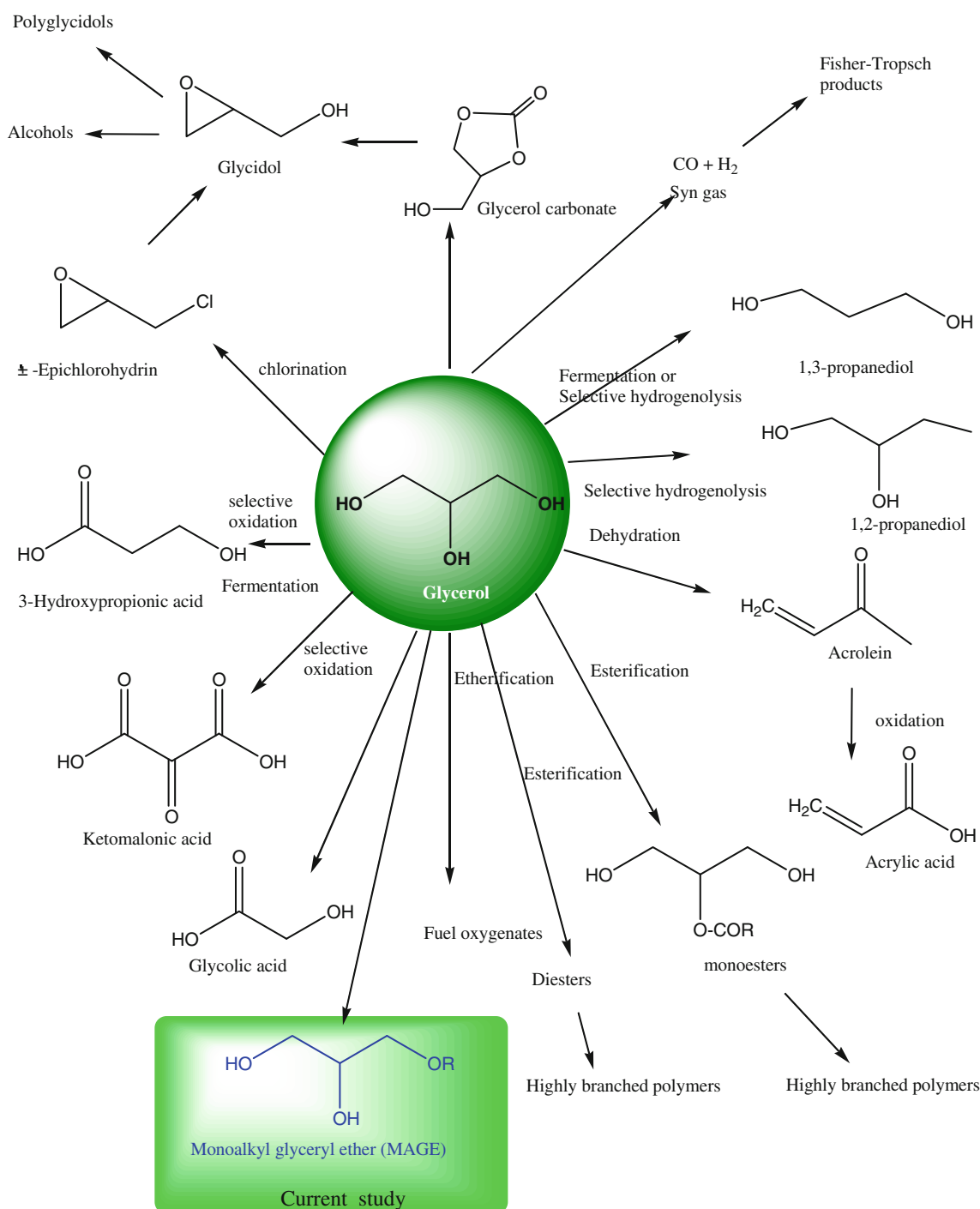
Scheme 1 Value-added chemicals which could be derived from bioglycerol using different catalytic processes

(Chalmers et al. 1996), antibacterial, antifungal (Haynes et al. 1994; Boeryd et al. 1971), immunological stimulation (Brohult et al. 1986) and anti-tumour properties (Mori and Kabata 1998; Weber 1988). They are also important precursors for the preparation of 1,3-dioxolan-2-ones (Horibe et al. 2000; Okutsu and Kitsuki 2004) and bis(sodium

sulphonate ester) type cleavable surfactants (Ono et al. 1998). Glycerol ethers also have many potential uses, such as fuel additives, solvents (Queste et al. 2006) and cryogenics (Koshchii 2002). There is a dearth of literature on the etherification of glycerol to value-added MAGEs. The production of MAGEs from glycerol was investigated

using alkyl chlorides (Wessendorf 1995). Gu et al. (2008) have reported etherification reactions between benzyl, propargyl and allyl alcohols, olefins and dibenzyl ethers with glycerol to give the corresponding MAGEs in moderate to excellent yields. Reactions of glycerol with iso-butene (Klepacova et al. 2005) or *tert*-butanol with acid catalysts afford *tert*-butyl-glycerol ethers, which have potential for blending with diesel (Wessendorf 1995). Recently, catalytic reductive alkylation for the synthesis of linear 1-*O*-alkyl mono-and di-glycerol ethers in one step has also been reported (Shi et al. 2009). A range of transformations of glycerol under microwave conditions using Starbon-derived materials is also known (Luque et al. 2008).

Most of the available literature for the conversion of glycerol to glycerol ethers is limited to synthesis of alkyl ethers (e.g. *t*-butyl ether of glycerol). A few of the described processes use sulphuric acid, phosphoric acid or *p*-toluene sulphonic acid as a catalyst which are homogeneous. The reaction mass is neutralised at the end of the reaction leading to effluent containing dissolved salts. The acids are corrosive and need special material of construction and not viable to use on industrial scale.

There is no report on the synthesis of 3-(1-phenyleth-oxy) propane-1,2-diol from glycerol and 1-phenylethanol using heterogeneous catalysis. This is a biologically active compound with uses as anti-inflammatory, antibacterial, antifungal, immunological stimulation and anti-tumor properties. The selectivity of this reaction towards mono-etherification of the terminal –OH group in glycerol is challenging. A reasonable estimate of demand for such a valuable chemical could be about 500 TPA and as its properties get evaluated and its availability on a commercial scale increases, its market share will also increase substantially.

The combination of all the processes will result in the utilisation of massive volume of waste glycerol generated in bio-diesel process. Eventually, this product adds to the family of glycerol platform. Some of these products could be manufactured using the same battery of reactors and separators in a multi-product industry.

We have developed a green and clean process embracing solvent less, single step and easy approach using a heterogeneous catalyst within shorter reaction times. Since supported heteropolyacids have been extensively studied in our laboratory as nano-catalysts, it was thought worthwhile to employ them in the current work and study the kinetics also (Scheme 2). There is no report on modelling and kinetics.

The main reaction is the mono etherification of glycerol at primary OH group. This product on further addition of 1-phenyl ethanol generates di-ether which is a minor reaction. Etherification at secondary OH group is also a minor side reaction. The current work gives high selectivity towards monoether product in short reaction duration.

Experimental

Chemicals

The following chemicals were procured from firms of repute and used without further purification: 1-phenyl ethanol (Merck, Germany), glycerol (Merck, Germany), *N*-methyl pyrollidone (S.D. Fine chem. Ltd., Mumbai), dodecatungstophosphoric acid (Sisco research labs, Mumbai), tetraethylorthosilicate (Merck, Germany), hexadecyl-amine (Spectrochem Ltd., Mumbai, India), ethanol (S.D. Fine chem. Ltd., Mumbai) and methanol (S.D. Fine chem. Ltd., Mumbai).

Screening of various catalysts

Various heteropoly solid acid catalysts like *dodeca*-tung-stophosphoric acid supported on hexagonal mesoporous silica (DTP/HMS), *dodeca*-tungstophosphoric acid supported on montmorrilonite clay (DTP/K-10), *dodeca*-molybdophosphoric acid supported on hexagonal meso-porous silica (DMP/HMS), *dodeca*-molybdophosphoric acid supported on montmorrilonite clay (DMP/K-10), caesium-incorporated *dodeca*-tungstophosphoric acid (Cs-DTP/k-10) and caesium-incorporated *dodeca*-molybdophosphoric acid (Cs-DMP/K-10) were prepared by incipient-wetness technique and screened for the reaction of glycerol with 1-phenyl ethanol. 20% w/w DTP/HMS gave the highest conversion of about 94% in 2 h with selectivity of 75% to the desired mono ether product (Fig. 1).

Catalyst synthesis

HMS was synthesised by the following method: 5 g hexadecyl amine was dissolved in 41.8 g of ethanol and 29.6 g of distilled water. To this, 20.8 g of tetraethyl orthosilicate was added under vigorous stirring. The addition of ethanol improved the solubility of the template. The mixture was aged for 18 h at 30°C. The clear liquid above the white coloured precipitate was decanted and the precipitate HMS was dried on a glass plate. The template was removed by calcining the resulting material at 550°C in air for 3 h. 20% w/w DTP-HMS was freshly synthesised by the wet impregnation technique by dissolving 2 g of *dodeca*-tungstophosphoric acid in 20 cm^3 methanol. The solution was added slowly drop wise to 8 g of hexagonal mesoporous silica under constant stirring till a thick paste was formed. This thick paste was kneaded until fine powder was obtained. The mixture was further dried in oven at
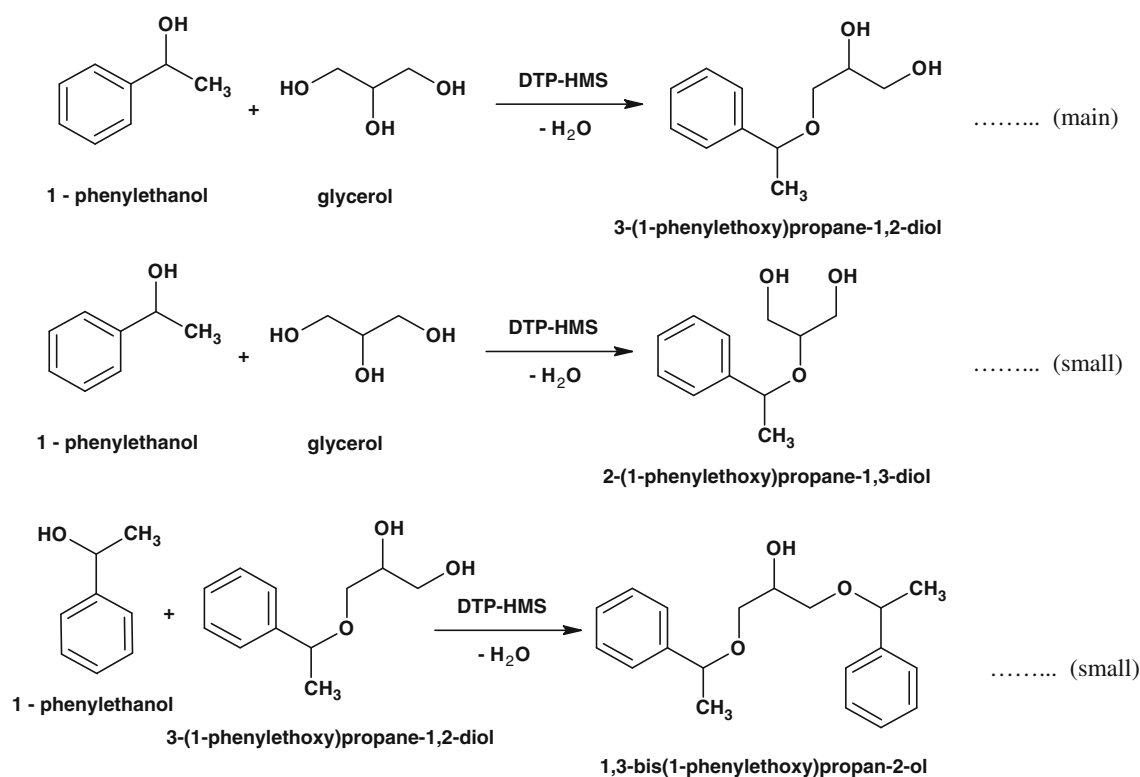
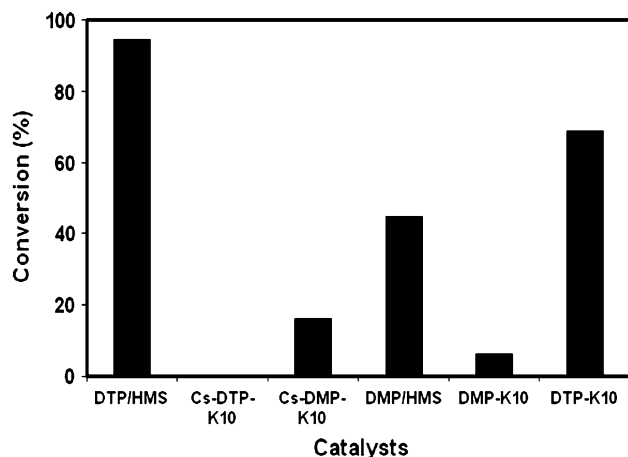Scheme 2 Etherification of glycerol with 1-phenyl ethanol over solid acid catalyst

Fig. 1 Catalysts screening for etherification of glycerol with 1-phenyl ethanol. Reaction conditions: 1-phenyl ethanol 0.05 mol, glycerol 0.2 mol, 0.024 gm/cm³ catalyst, 25 cm³ total reaction volume, 1.0 cm³ N-methyl pyrrolidone as internal standard, speed of agitation 1,000 rpm, temperature 120°C

George 2009; Yadav and Manyar 2003). The salient features of the characteristic results are mentioned here. In FT-IR, the broad band stretching from 1000 to 1200 cm^{-1} was due to Si–O stretching vibration of HMS. The peak around 1626 cm^{-1} indicated presence of bronsted acidic sites, 895 and 812 cm^{-1} showed W–O–W asymmetric vibrations associated with Keggin ion. A smoother surface layer was clearly seen from the SEM micrographs with particle size in the range of 4–8 μm. The acidity of the catalyst was determined by ammonia TPD. A broad peak with a maximum between 100 and 140°C corresponding to desorption of weakly held physisorbed ammonia showed the presence of acidic sites in the catalyst. The adsorption desorption isotherms for the catalyst showed type IV isotherm with the hysteresis loop of type H_3, which is a characteristic of mesoporous solids. Characteristic nitrogen BET surface area obtained was very high around 600 m^2/g and pore size was in the mesoporous region.

Reaction procedure

The reactions were carried out in a 50 cm³ capacity glass reactor of 4.8 cm i.d equipped with four equally spaced baffles and six bladed turbine impeller. The reaction temperature was maintained by means of a thermostatic oil bath, which was maintained at a desired temperature with an accuracy of ±1°C, in which the reaction assembly was
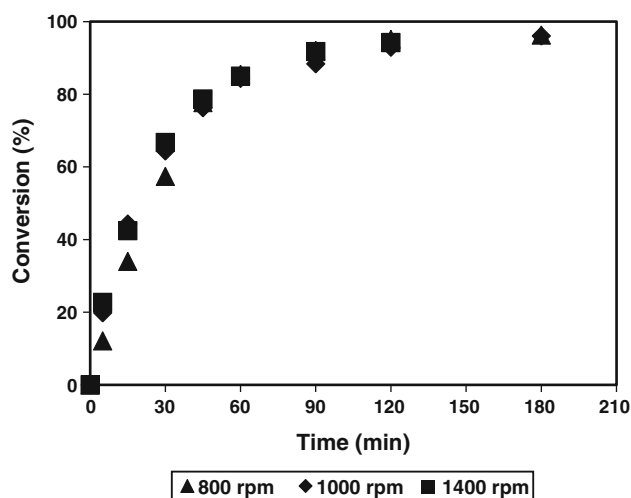
120°C and calcined at 285°C for 4 h to get the active solid acid catalyst.

Catalyst characterisation

20% w/w DTP-HMS catalyst was characterised by various techniques reported by our group earlier (Yadav and

Fig. 2 Effect of speed of agitation on conversion of 1-phenyl ethanol. Reaction conditions: 1-phenyl ethanol 0.05 mol, glycerol 0.2 mol, 0.024 gm/cm^3 DTP-HMS catalyst, 1.0 cm^3 N-methyl pyrrolidone as internal standard, 25 cm^3 total reaction volume, temperature 120°C

immersed. Standard experiments were carried out by taking 1-phenyl ethanol 0.05 mol, glycerol 0.2 mol, N-methyl pyrrolidone 0.5 cm^3 as an internal standard which makes the total volume of the reaction mixture as 25 cm^3. 0.024 g/cm^3 20% w/w DTP-HMS catalyst was added at 120°C. The reaction mixture was allowed to reach the desired temperature and the initial sample was collected. Agitation was then commenced at a known speed.

Method of analysis

Clear liquid samples were withdrawn at regular time intervals by reducing the speed of agitation momentarily to zero and allowing the catalyst to settle at the bottom of the reactor. Typically, glycerol was taken excess in the reaction solution and the conversions were based on the limiting reactant, 1-phenyl ethanol. Analysis of the reaction mixture was performed on GC (Chemito, model 1000) by using FID and a capillary wax column BP-20 (0.25 mm diameter and 30 m length). The product was confirmed by GC–MS (Perkin Elmer instrument, Clarus 500) with BP-1 capillary column (0.25 mm i.d., 30 m length) and EI mode of MS.

Results and discussions

Effect of speed of agitation

The effect of speed of agitation was studied in the range of 800–1400 rpm with 0.024 g/cm^3 catalyst loading at 120°C (Fig. 2). The mole ratio of glycerol to 1-phenyl ethanol was

kept at 4:1. There was no change in the rate and conversion patterns, which was indicative of the absence of any resistance to external mass transfer of 1-phenyl ethanol to the external surface of the catalysts. However, all further reactions were carried out at a speed of 1000 rpm. Theoretical calculations were also done verify the absence of external mass transfer resistance. We have given the theoretical development in some of our earlier work (Yadav and Manyar 2003; Kozhenikov et al. 1996); for instance, a typical calculation is presented here.

External mass transfer resistance

The rate of mass transfer could be calculated from the knowledge of mass transfer coefficients for both the reactants, which were obtained from their bulk liquid phase diffusivities. The inter-particle mass transfer resistance was calculated using the Wilke–Chang equation and Sherwood number. The diffusivity D_{AB} and D_{BA} was calculated from Wilke–Chang equation given by $D_{AB} = 117.3 \times 10^{-18} \times (\psi \cdot M_B)^{0.5} T/(\mu \times Va^{0.6})$ where $\psi = 1$ (the association factor for glycerol), M_B molecular weight of glycerol, T reaction temperature, μ viscosity of reaction mixture, V_a molar volume of 1-phenyl ethanol. The value of D_{AB} was found to be 5.96×10^{-10} m^2/s. Similarly the value of D_{BA} was found to be 9.28×10^{-10} m^2/s. The value of solid to liquid phase mass tranfer co-efficients k_{SLA} and k_{SLB} was calculated from Sherwood number $Sh = k_{SL} \times D_p/D_{AB}$ and the values were found to be 0.58 and 0.89, respectively. To be on the safer side, the limiting value of the Sherwood number was taken as 2. The actual value is so far greater than 2 due to intense agitation (Yadav and Manyar 2003; Kozhenikov et al. 1996). The effect of mass transfer resistance due to A and B is given by $1/(k_{SLA} \times a_p)$ and $1/(k_{SLB} \times a_p)$ where a_p represents the solid–liquid interfacial area and the values obtained are 2.87×10^{-3} and 1.85×10^{-3} m^3/kg, respectively. The initial rate (r_{Ai}) was calculated from standard reaction and was found to be 0.17 from which $1/r_{Ai}$ was calculated to 5.8 and it was very much greater than by $1/(k_{SLA} \times a_p)$ and $1/(k_{SLB} \times a_p)$. It confirms that the mass transfer rates were much higher than rates of reaction and hence speed of agitation had no influence on reaction rate.

Effect of catalyst loading

The effect of catalyst loading was studied over the range of 0.01–0.032 g/cm^3 (Fig. 3). In the absence of external mass transfer resistance, the rate of reaction was directly proportional to the catalyst loading based on the entire liquid phase volume, which is due to the proportional increase in the number of active sites. Further reactions were carried out with 0.024 g/cm^3 catalyst loading.
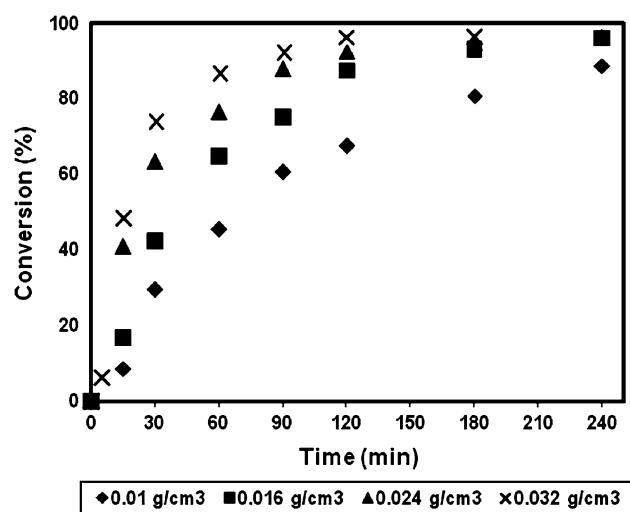
Fig. 3 Effect of catalyst loading on conversion of 1-phenyl ethanol. Reaction conditions: 1-phenyl ethanol 0.05 mol, glycerol 0.2 mol, 1.0 cm^3 *N*-methyl pyrrolidone as internal standard, 25 cm^3 total reaction volume, speed of agitation 1000 rpm, temperature 120°C

Fig. 4 Effect of mole ratio of 1-phenylethanol: glycerol on conversion of 1-phenyl ethanol. Reaction conditions: 1.0 cm^3 *N*-methyl pyrrolidone as internal standard, Speed of agitation 1000 rpm, 25 cm^3 total reaction volume, catalyst loading 0.024 gm/cm^3, temperature 120°C

This catalyst is robust as has been proved in our earlier work (Yadav and Manyar 2003). The catalyst could be recovered and reused several times. It was recovered by filtration of the reaction mixture. The filtered catalyst was washed with methanol, dried in the oven at 120°C for 10 h and reused.

Effect of intra-particle diffusion resistance

The Weisz–Prater criterion was employed to assess the influence of intra-particle diffusion resistance. According to Weisz–Prater criterion, the dimensionless parameter $\{C_{WP} = r_{obs} Rp^2/D_e [C_{AS}]\}$ which represents the ratio of the intrinsic reaction rate to the intra-particle diffusion rate, can be evaluated from the observed rate of reaction, the particle radius (R_p), effective diffusivity of the limiting reactant (D_e) and [C_{AS}] concentration of the reactant at the external surface of the particle. The effective diffusivity of 1-phenyl ethanol ($D_e - A$) inside the pores of the catalyst was obtained from the bulk diffusivity (D_{AB}), porosity (ε) and tortuosity (τ) as 7.95×10^{-9} m^2/s where $D_e - B = D_{AB} \cdot \varepsilon/\tau$. The average values of porosity and tortuosity were taken as 0.4 and 3, respectively, as a conservative estimate. In the present case, the value of C_{WP} was calculated as 4.23×10^{-6}, which is less than 1. Hence, there was no intra-particle diffusion resistance.

Effect of mole ratio

Under solvent-less conditions, with excess of glycerol, the reaction mixture becomes highly viscous. The effect of
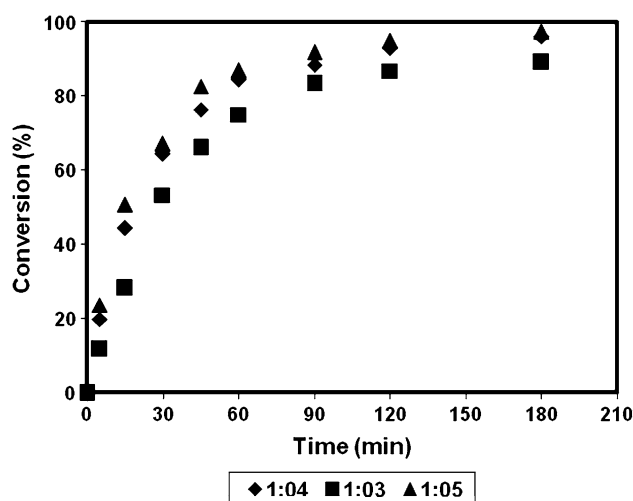
1-phenyl ethanol to glycerol ratio was studied at 1:3, 1:4 and 1:5 under otherwise similar conditions (Fig. 4). The rate of conversion of 1-phenyl ethanol was found to increase with the increase in the amount of glycerol. Below 1:3 ratio, glycerol and 1-phenyl ethanol becomes immiscible with each other and above 1:5 ratio the reaction mixture becomes highly viscous. Therefore, further reactions were carried out with 1:4 mol ratio.

Effect of temperature

The effect of temperature on conversion was studied between 100 and 140°C. It was observed that the rate of reaction increases with increase in temperature (Fig. 5). This would suggest a kinetically controlled mechanism. Above 120°C, the reaction occurs very fast and the kinetics would be difficult to predict. Therefore, 120°C was taken as optimum for the reaction.

Development of kinetic model

The above results were used to build a kinetic model. From the calculated values of mass transfer rates of A and B and the initial rate it was evident that the reaction was devoid of inter and intra-particle diffusion resistances. The reaction involves two reactants namely 1-phenyl ethanol (A) and glycerol (B) to give the desired product monoether of glyceryl ether (P) and water (W). A dual site reaction mechanism was proposed for this reaction. Thus, the reaction may be controlled by any of these 3 steps namely (1) adsorption, (2) surface reaction (3) desorption. It was
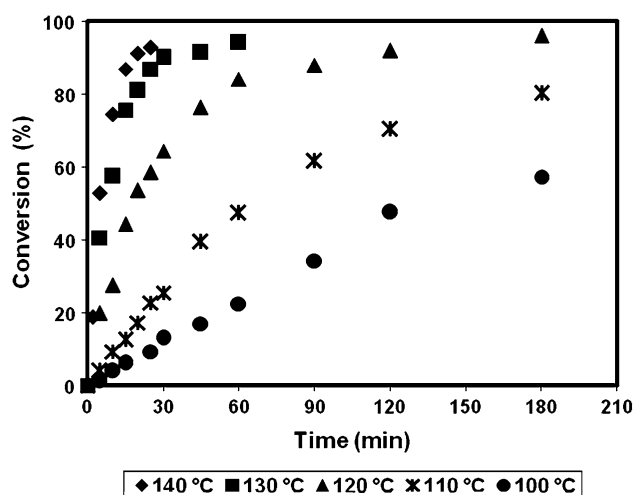
Fig. 5 Effect of temperature on conversion of 1-phenyl ethanol. Reaction conditions: 1-phenyl ethanol 0.05 mol, glycerol 0.2 mol, 1.0 cm^3 N-methyl pyrrolidone as internal standard, 25 cm^3 total reaction volume, speed of agitation 1000 rpm, catalyst loading 0.024 gm/cm^3

assumed that, reactants 1-phenyl ethanol and glycerol were weekly adsorbed on the catalyst.

Adsorption of 1-phenyl ethanol (A) on vacant site was given by

$$A + S \overset{K_A}{\leftrightarrow} AS \qquad (1)$$

Adsorption of glycerol (B) on vacant site was given by

$$B + S \overset{K_B}{\leftrightarrow} BS \qquad (2)$$

Surface reaction of AS and BS leading to the formation of monoalkyl glyceryl ether (PS) on the site

$$AS + BS \overset{K_{SR}}{\leftrightarrow} PS + WS \qquad (3)$$

Desorption of monoalklyl glyceryl ether (PS) and water (WS) is given by

$$PS \overset{1/K_P}{\leftrightarrow} P + S \qquad (4)$$

$$WS \overset{1/K_W}{\leftrightarrow} W + S \qquad (5)$$

The total concentration of the sites, C_t expressed as

$$C_t = C_S + C_{AS} + C_{BS} + C_{PS} + C_{WS} \qquad (6)$$

Or

$$C_t = C_S + K_A C_A C_S + K_B C_B C_S + K_P C_P C_S + K_W C_W C_S \qquad (7)$$

The concentration of vacant sites,

$$C_S = \frac{C_t}{1 + K_A C_A + K_B C_B + K_P C_P + K_W C_W} \qquad (8)$$

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

$$-r_A = -\frac{dC_A}{dt} = k_{SR} C_{AS} C_{BS} - k'_{SR} C_{PS} C_{WS} \qquad (9)$$

$$-\frac{dC_A}{dt} = \frac{k_{SR}\{K_A K_B C_A C_B - (K_P K_W C_P C_W / k_{SR})\} C_t^2}{(1 + K_A C_A + K_B C_B + K_P C_P + K_W C_W)^2} \qquad (10)$$

When the reaction is far away from equilibrium,

$$-\frac{dC_A}{dt} = \frac{k_{SR} K_A K_B C_A C_B C_t^2}{(1 + \sum K_i C_i)^2} \qquad (11)$$

$$= \frac{k_r w C_A C_B}{(1 + \sum K_i C_i)^2} \qquad (12)$$

where $k_r w = k_{SR} K_A K_B C t^2$; w is catalyst loading. If the adsorption constants are very small, then the above equation reduces to

$$-\frac{dC_A}{dt} = k_r C_A C_B w \qquad (13)$$

Let $C_{B0}/C_{A0} = M$, the molar ratio of 1-phenyl ethanol to glycerol at time $t = 0$. Then, Eq. 13 can be written in terms of fractional conversion as

$$\frac{dX_A}{dt} = k_r C_{A0} w (1 - X_A)(M - X_A) \qquad (14)$$

This upon integration leads to:

$$\ln\left\{\frac{M - X_A}{M(1 - X_A)}\right\} = k_1 C_{A0}(M - 1)t \qquad (15)$$

where

$$k_1 = k_r w \qquad (16)$$

Thus a plot of $\ln(M - X_A)/M(1 - X_A)$ against time at different temperatures gave an excellent fit, thereby validating the model (Fig. 6) indicating that the reaction is an overall second order. The values of the rate constants
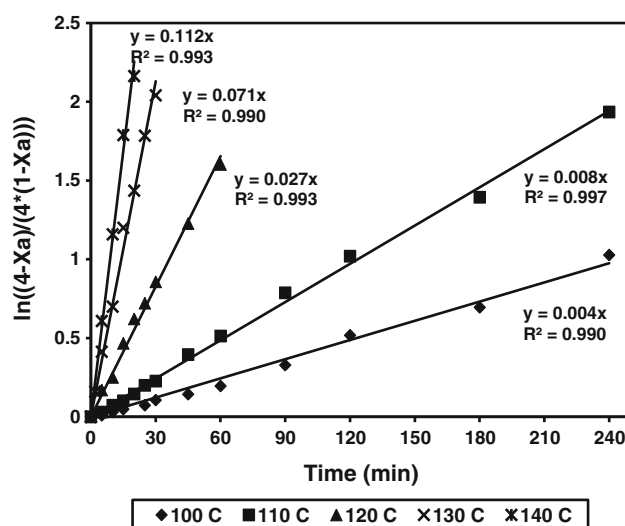

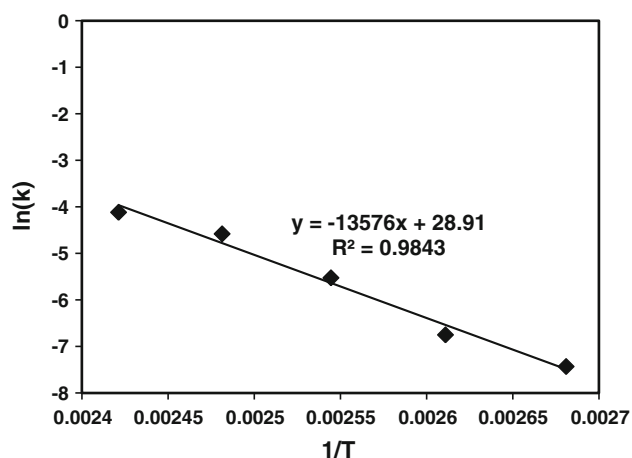Fig. 6 Plot of $\ln(M - X_A)/M(1 - X_A)$ against time

Fig. 7 Arrhenius plot

at different temperatures were calculated and an Arrhenius plot was used to estimate the apparent activation energy of the reaction (Fig. 7). The apparent activation energy was found to be 27 kcal/mol, which indicates intrinsic kinetically controlled reaction.

Economics of the process

In the usual homogeneously catalysed *trans*-esterification of bio-oils, it also contains variable amounts of excess alcohol, water, NaOH, and a mixture of soaps, unreacted fats and oils. The glycerol phase which is heavier than aqueous phase, settles at the bottom. It is subjected to neutralisation with acid, foam breaking and distillation. This impure glycerol is subjected to vacuum distillation. However, with reference to green chemistry, heterogeneous catalysis would be most advantages and we have shown independently how solid acids can give excellent yield of biodiesel and glycerol which do not produce soaps and other impurities (for instance, supported heteropolyacids; Bokade and Yadav 2009). Therefore, such good quality glycerol will be further used for 3-(1-phenylethoxyl) propane-1,2-diol.

Since it is a heterogeneous catalysed reaction, the quality of the product is superior with absence of any inorganic contaminants. The process gives 98% conversion with 75% selectivity to the mono *O*-alkyl product. The product can be separated easily.

Since the prices of glycerol are fluctuating, a rudimentary cost of production with recycles of methanol and unreacted starting materials can be arrived at. By taking the cost as: glycerol US $ 0.80/kg, 1-phenylethanol $ 4.50/kg, catalyst $ 0.10/kg and processing cost of 30% of the raw materials, with recycle of unreacted reagents, the approximate cost of production 3-(1-phenylethoxy) propane-1,2-diol is $6.22/kg.

Since this is a fine chemical, the cost of this product in the market is approximately $ 8–10/kg, depending on volume. Therefore, the process will be green, clean and economical.

Conclusion

Heterogeneous acid catalysis by supported heteropoly acids offers substantial economic and environmental benefits. The etherification of glycerol with 1-phenyl ethanol was studied using a variety of catalysts amongst which 20% w/w DTP-HMS as the catalyst. This catalyst was found to be highly active and selective giving 75% selectivity towards mono ether product. The effects of various parameters on the rates of the reactions were discussed. A second order rate equation for the reaction mechanism was successfully developed and validated. The apparent activation energy 27.0 kcal/mol was estimated. This method has contributed substantially to the conversion of glycerol to more value-added chemicals.

References

Aresta M, Dibenedetto A, Carone M, Colonna T, Fragale C (2005) Production of biodiesel from macroalgae by supercritical CO_2 extraction and thermochemical liquification. Environ Chem Lett 3:136–139. doi:10.1007/s10311-005-0020-3

Behr A, Eilting J, Irawadi K, Leschinski J, Lindner F (2008) Improved utilisation of renewable resources: new important derivatives of glycerol. Green Chem 10(1):13–30. doi:10.1039/b710561d

Boeryd B, Hallgren B, Stallberg G (1971) Studies on the effect of methoxy-substituted glycerol ethers on tumour growth and metastasis formation. Br J Exp Pathol 52:221–230

Bokade VV, Yadav GD (2009) Transesterification of edible and non-edible vegetable oils with alcohols over heteropolyacids supported on acid treated clay. Ind Eng Chem Res 48:9408–9415

Brohult A, Brohult J, Brohult S, Joelsson I (1986) Reduced mortality in cancer patients after administration of alkoxyglycerols. Acta Obstet Gynecol Scand 65:779–785

Chalmers W, Wood AC, Shaw AJ, Majnarich JJ (1996) Treatment of inflammatory diseases. Eversharp Inc. US3294639

Gu Y, Azzouzi A, Pouilloux Y, Jerome F, Barrault J (2008) Heterogeneously catalyzed etherification of glycerol: new pathways for transformation of glycerol to more valuable chemicals. Green Chem 10:164–167. doi:10.1039/b715802e

Haynes MP, Buckley HR, Higgins ML, Pieringer RA (1994) Synergism between the antifungal agents amphotericin B and alkyl glycerol ethers. Antimicrob Agents Chemother 38(7):1523–1529

Horibe M, Suzuki K, Ogura E, Yamamoto N (2000) Production of 1,3-dioxolan-2-one derivative. Lion Corp. JP239271

Jerome F, Pouilloux Y, Barrault J (2008) Rational design of solid catalyst for the selective use of glycerol as a natural organic building block. ChemSusChem 1(7):586–613. doi:10.1002/cssc.200800069

Kamiya Y, Ooka Y, Ohnishi R, Fujita T, Kurata Y, Tsuji K, Nakajo T, Okuhara T (2007) Alkylation-acylation of p-xylene with γ-butyrolactone or vinylacetic acid catalyzed by heteropolyacid supported on silica. J Mol Catal A 262(1-2):77–85. doi:10.1016/j.molcata.2006.08.055

Kamiya Y, Okuhara T, Misono M, Miyaji A, Tsuji K, Nakajo T (2008) Catalytic chemistry of supported heteropolyacids and their applications as solid acids to industrial processes. Catal Surv Asia 12(2):101–113. doi:10.1007/s10563-008-9043-7

Kimura M, Nakato T, Okuhara T (1997) Water tolerent solid acid catalysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for hydrolysis of esters in the presence of excess water. Appl Catal A Gen 165(1):227–240. doi:10.1016/s0926-860X(97)00204-4

Klepacova K, Mravec D, Bajus M (2005) tert-Butylation of glycerol catalyzed by ion-exchange resins. Appl Catal A 294(2):141–147. doi:10.1016/j.apcata.2005.06.027

Koshchii SV (2002) Optimization of synthesis of mono-O-methylglycerol isomers. Russ J Appl Chem 75:1434–1437. doi:10.1023/A:1022224828164

Kozhenikov IV, Kloetstra KR, Sinne A, Zandbergen HW, van Bekkum H (1996) Synthesis of catalysts comprising heteropoly acid $H_3PW_{12}O_{40}$ supported on MCM-41 molecular sieve and amorphous silica. J Mol Catal A Chem 114:287–298. doi:10.1016/S1381-1169(96)00328-7

Kozhevnikov IV (2002) Catalysts for fine chemicals: catalysis by polyoxometalates, vol 2. Wiley, Chichester

Kozhevnikov IV (2007) Sustainable heterogeneous acid catalysis by heteropoly acids. J Mol Cat A Chem 262:86–92. doi:10.1016/j.molcata.2006.08.072

Luque R, Budarin V, Clark JH, Macquarrie DJ (2008) Glycol transformations on polysaccharide derived mesoporous materials. App Catal B Environ 82:157–162. doi:10.1016/j.ap.catb.2008.01.015

Miyaji A, Echizen T, Nagata K, Yoshinaga Y, Okuhara T (2003) Selective hydroisomerization of n-pentane to isopentane over highly dispersed $Pd-H_4SiW_{12}O_{40}/SiO_2$. J Mol Catal A 201:145–153. doi:10.1016/s1381-1169(03)00129-8

Mizuno N, Misono M (1998) Heterogeneous catalysis. Chem Rev 98(1):199–218. doi:10.1021/cr960401q

Mori R, Kabata Y (1998) Production of alklyglyceryl ether. Nihon surfactant Kogyo, Nikko chemicals. JP63077833

Nakato S, Kimura M, Okuhara T (1997) Hydration of olefins in excess water catalysed by cesium hydrogen salt of dodecatungstophosphoric acid. Chem Lett 26(80):839–840. doi:10.1246/cl.1997.839

Nakato T, Kimura M, Nakato S, Okuhara T (1998) Changes of surface properties and water-tolerant catalytic activity of solid acid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in water. Langmuir 14(2):319–325. doi:10.1021/la970867j

Okutsu M, Kitsuki T (2004) Method of manufacturing cyclic carbonate. Kao Corp. JP168674

Ono D, Yamamura S, Magamura M, Takeda J (1998) Synthesis and properties of bis(sodium sulfonated ester) types of cleavable surfactants derived from 1-O-alkylglycerols. J Surfactants Deterg 1:201–206. doi:10.1007/s11743-998-0020-8

Pagliaro M, Ciriminna R, Kimura H, Rossi M, Pina CD (2007) From glycerol to value added products. Angew Chem Int Ed 46(24):4434–4440. doi:10.1002/anie.200604694

Queste JS, Bauduin P, Touraud D, Kunz W, Aubry JM (2006) Short chain glycerol 1-monoethers-a new class of green solvo-surfactants. Green Chem 8:822–830. doi:10.1039/b603973a

Ren Y, Yue B, Gu M, He H (2010) Progress of the application of mesoporous silica-supported heteropolyacids in heterogeneous catalysis and preparation of nanostructured metal oxides. Materials 3(2):764–785. doi:10.3390/ma3020764

Shi Y, Dayoub W, Favre-Reguillon A, Chen G, Lemaire M (2009) Straightforward selective synthesis of linear 1-O-alkyl glycerol and di-glycerol monoethers. Tetrahedron Lett 50(49):6891–6893. doi:10.1016/j.tetlet.2009.09.134

Weber N (1988) Biological effects of alkylglycerols. In: Braquet P, Mangold HK, Vargaftig NN (eds) Progress in biochemical pharmacology, vol 22. Karger, Basel, pp 48–57

Wessendorf R (1995) Erdoel and Kohle, Erdgas. Petrochemie 48:138–1142

Yadav GD (2005) Synergism of clay and heteropoly acids as naocatalysts for development of green processes with potential industrial applications. Catal Surv Asia 9(2):117–137. doi:10.1007/s10563-005-5997-X

Yadav GD, Asthana NS (2003) Selective decomposition of cumene hydroperoxide into phenol and acetone by a novel cesium substituted heteropolyacid on clay. Appl Catal A Gen 244:341–357. doi:10.1016/S0926-860X(02)00605-1

Yadav GD, Bokade VV (1996) Novelties of heteropoly acid supported on clay: adsorption controlled etherification of phenethyl alcohol with alkanols. Appl Cat A Gen 147(2):299–315. doi:10.1016/S0926-860X(96)00206-2

Yadav GD, Doshi NS (2000) Alkylation of hydroquinone with methyl-tert-butyl-ether and tert-butanol. Catal Today 60(3–4):263–273. doi:10.1016/S0920-5861(00)00343-6

Yadav GD, Doshi NS (2002) Synthesis of linear phenyldodecanes by the alkylation of benzene with 1-dodecene over non-zeolitic catalysts. Org Proc Res Dev 6:263–272. doi:10.1021/op000044s

Yadav GD, Doshi NS (2003) Alkylation of aniline with methyl-tert-butyl ether (MTBE) and tert-butanol over solid acids: product distribution and kinetics. J Mol Catal A Chem 194(1-2):195–209. doi:10.1016/S1381-1169(02)00526-5

Yadav GD, George G (2009) Monoalkylation of biphenyl over modified heteropoly acid: novelties of cesium substituted dodecatungstophosphoric acid supported on hexagonal mesoporous silica. Catal Today 141:130–137. doi:10.1016/j.cattod.2008.04.013

Yadav GD, Kamble SB (2009) Alkylation of xylenes with isopropyl alcohol over acidic clay supported catalysts: efficacy of 20% w/w $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 clay. Ind Eng Chem Res 48:9383–9393. doi:10.1021/ie800737v

Yadav GD, Kirthivasan N (1995) Single pot synthesis of methyl-tert-butyl ether (MTBE) from tert-butanol and methanol: dodecatungstophosphoric acid supported on clay as an efficient catalyst. J Chem Soc Chem Commun 203–204. doi:10.1039/C3995000203

Yadav GD, Kirthivasan N (1997) Synthesis of bisphenol-A: comparison of efficacy of ion exchange resin catalysts vis-à-vis heteropolyacid supported on clay and kinetic modeling. Appl Catal A 154(1-2):29–53. doi:10.1016/s0926-860X(96)00364-X

Yadav GD, Manyar HG (2003) Novelties of synthesis of acetoveratrrone using heteropoly acid supported on hexagonal mesoporous silica. Microporous Mesoporous Mater 63:85–96. doi:10.1016/S1387-181(03)00434-7

Yadav GD, Nair JJ (1999a) Selectivity engineering in the nitration of chlorobenzene using eclectically engineered sulfated zirconia and carbon molecular sieve catalysts. Catal Lett 62:49–52. doi:10.1023/A:1019066131736

Yadav GD, Nair JJ (1999b) Sulfated zirconia and its modified versions as promising catalysts for industrial processes. Microporous Mesoporous Mater 33:1–48. doi:10.1016/S1387-1811(99)00147-X

Yadav GD, Salgaonkar SS (2005) Selectivity engineering of 2,6-diisopropylphenol in isopropylation of phenol over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 clay. Ind Eng Chem Res 44:1706–1715. doi:10.1021/ie049141q

Yadav GD, Salgaonkar SS (2009) Loss prevention and waste minimization with cascade engineered green synthesis of bisphenol-A from cumene hydroperoxide and phenol using heteropoly acid supported clay catalysts. Org Proc Res Dev 13:501–509. doi:10.1021/op800262u

Yadav GD, Asthana NS, Kamble VS (2003) Cesium-substituted dodecatungstophosphoric acid on K-10 clay for benzoylation of anisole with benzoyl chloride. J Catal 217(1):88–96. doi:10.1016/s00219517(02)00175-6

Yadav GD, Asthana NS, Salgaonkar SS (2004) Regioselective benzoylation of xylenes over caesium modified heteropolyacid supported on K-10 clay. Clean Tech Environ Policy 6:105–113. doi:10.1007/s10098-003-0197-8

Zhou CH, Beltramini JN, Fan YX, Lu GQ (2008) Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. Chem Soc Rev 37:527–549. doi:10.1039/b707343g