Praise Worthy Prize

Solid Acid Catalyzed Solventless Highly Selective, Effective and Reusable Method for Synthesis of 1, 4-dioxanol Using Glycerol and Cyclohexanone

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Abstract – *Selective transformation of glycerol into value added products remains a challenging task due to its polyfunctional nature. Acetalization of glycerol to 5-membered [1, 3] dioxan-4-yl)-methanol was efficiently catalyzed by cesium doped dodecatungstophosphoric acid supported on clay K10. 100% selectivity toward desired product was achieved. The influence of solid-liquid mass transfer resistance and absence of the intra-particle diffusion resistance was calculated to ascertain the kinetic aspect of the reaction. The effect of various parameters such as speed of agitation, catalyst loading, mole ratio and temperature on selectivity and conversion of glycerol was investigated in detail. Suitable kinetic model was developed and reaction was found to follow pseudo first order regime with energy of activation 11.64kcal/mol. Catalyst was found to be active and reusability was studied up to four runs. The result clearly shows effectiveness of catalyst for selective synthesis of [1, 3] dioxan-4-yl)-methanol for an environmentally benign process.* **Copyright © 2012 Praise Worthy Prize S.r.l. - All rights reserved.**

Keywords: Acetalization, Solid Acids, Selectivity, Cyclic Acetal, Pseudo First Order

Nomenclature

UDCaT-5	University Department of Chemical Technology catalyst -5
MUICaT-5	Mumbai University Institute of Chemical Technology Catalyst-5
FRSZ	Fuel reach sulfated zirconia
Cs-DTP/K10	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on montmorillonite acid treated clay K-10
DTP/HMS	Dodecatungstophosphoric acid supported on Hexogonal mesoporous silica

I. Introduction

Increasing global warming due to excessive use of fossil fuel and amplification in environmental pollution, results in global alarm toward development of green and sustainable technology [1]. Therefore quest for renewable feed stocks that able to solve energy requirements and production of novel chemicals of industrial importance with producing no environmental risk is the need of modern chemical industry[2]-[4]. Glycerol is a primary byproduct in the biodiesel production from transesterification of fatty acids with methanol. Every three mole production of fatty methyl ester produces one mole of glycerol. In other words we can say that 100kg of glycerol is being produced for every 1000kg of biodiesel [5], [6]. Glycerol is extremely functionalized molecule and promising chemical intermediate for the production of several valuable

oxygenates [7]. Recently various papers have been published to explain the importance of glycerol chemistry and its selective transformation into value added products [8]-[10]. Due to presence of amenable functionalities it is very difficult to get selective transformation of glycerol into desired form. Therefore in order to develop novel uses of glycerol different catalytic processes such as hydrogenolysis, oxidation, etherification, esterification, reforming and acetalization have been developed [11]-[19]. One of the most important reactions of glycerol is the acetalization with aldehyde and ketone as novel intermediates. Six membered cyclic acetals are potential precursors for the production of green platform chemicals like 1, 3-dihydroxyacetone and 1, 3-propanediol [20]. Protection of carbonyl functionality for its selective transformation into desired moiety is always remained center of attraction for chemical industries. It is well known that dioxanols are generally stable to bases, Grignard reagent, metal hydride oxidants and esterification reagents. Many of the acetals have direct applications in cosmetics, food and beverage additives, pharmaceuticals, in detergents, diesel fuels, in lacquer industries and as bases for surfactants[10], [22]-[25]. Acetalization of glycerol was traditionally done by homogeneous acid catalysis, which leads to formation of undesired inorganic salts; hence process cost increases and methodology become environmentally hazardous [26]-[30]. Attention is being paid toward development of green and sustainable process for selective modification of glycerol. H. Serafim and co-workers has described acetalization of glycerol

with benzaldehyde over a range of zeolites [31]. Acetalization of acetone was demonstrated by J. Deutsch and co-workers, which requires long reaction time, low conversion and use of chlorinated solvent [32]. Silica supported molybdenum trioxide was prepared using sol-gel method and demonstrated as efficient catalyst for acetalization of various aldehydes by S. B. Umbarkar et. al [7]. Use of protic acids such as silica supported heteropolyacids [19], ion exchange resins [32], montmorillonite [33], zeolites [34], mesoporous aluminosilicates [35]-[36] were reported in literature. It is well reported that acetalization of ketone require stronger conventional acids which seems to be undesirable for environmentally cautious modern industrial processes [7]. Recently Crotti et al. has shown use of organoiridium derivative as promising catalyst for acetalization of aldehydes and ketones, but that too suffers from low conversion of ketones into preferred product and preparation of organoiridium catalyst requires environmentally objectionable components [37]. Recently Paolo P. Pescarmona et al. has described an efficient method for conversion of glycerol to solketal using mesoporous substituted silicates as catalyst, but it suffers from long reaction time for catalyst preparation as well as use environmentally detrimental chemicals [38]. Nevertheless, all reported procedures use expensive reagents, tedious workup procedure and generation of undesired waste.

Solid acid catalyst has given great contribution toward development of environmentally viable methodology for vital industrial reactions. Our laboratory has been investigating different aspects of green processes with benign novel solid acid catalysts, which have direct relevance to industry. The activity and selectivity of different solid catalysts such as acid treated clay[39]-[41], sulfated zirconia[42]-[47], modified heteropolyacids [48]-[53] and UDCaT series of super acidic catalyst have been explored by our laboratory for green esterification, trans-esterification, acylation, alkylation, condensation, cyclization, rearrangement and many more acid catalyzed reactions[54]-[59]. Till date no literature is available on detailed study of glycerol based ketal formation using solid acid catalyst, its kinetic study and mechanistic investigation. In course of our studies on solid acid catalyzed reactions we would like to demonstrate same with ambient reaction condition, high selectivity and conversion toward desired molecule, simple reaction workup and reusable methodology.

II. Materials and Methods

II.1. Chemicals and Catalysts

All the chemicals were procured from reputed firm and used without further purification glycerol, cesium chloride, dodecatungstophosphoric acid, methanol, n-heptanes (S.D. fine chem. Ltd. Mumbai). K10 clay (Fluka Germany), cyclohexanone (Aldrich, USA). Amberlyst-15, Indion 130, duolite-297 were procured

from s.d.fine.

II.2. Preparation of 20% $Cs_{2.5}H_{0.5}PW_{12}O_{40}K/10$

Approximately 0.001kg of K-10 was dried in an oven to 120ºC for 1h of which $8x10^{-3}$kg was weighed accurately. 0.2808×10^{-3}(1.671×10^{-3} mol) of CsCl was weighed accurately and dissolved in $10\times10^{-6}m^3$ of methanol. This volume of solvent used was approximately equal to the pore volume of the catalyst. The solution was added to the previously dried and accurately weighed 8×10^{-3}kg of K-10 clay to form slurry. The slurry was stirred vigorously and air-dried. The resulted material was then dried in an oven at 120ºC for 2 h. This was then further subjected to impregnation by an alcoholic solution of 2×10^{-3}kg (6.688×10^{-4} mol) of DTP in $10\times10^{-6}m^3$ of methanol. The solution was added to the previously treated K-10 clay with CsCl again to form slurry. The slurry was stirred vigorously and air-dried. The preformed catalyst was dried in an oven at 120 ºC for 2 h and then calcined at 300ºC for 3h [12], [48]-[50].

II.3. Catalyst Characterization

Infrared spectra of the samples pressed in KBr pellets were obtained at a resolution of $200m^{-1}$ between $4x10^5$ and $4x10^4m^{-1}$. The spectra were collected with a Perkin-Elmer instrument and in each case the sample was referenced against a blank KBr pellet. Surface area measurements and pore size distributions analysis were done by nitrogen adsorption on Micromeritics ASAP 2010 instrument at an adsorption temperature 77K, after pretreating the sample under high vacuum at 300°C for 4hr. powder XRD patterns were obtained using (Bruker AXS, D8 Discover, USA) Cu Ka radiation. Samples were step scanned from 5 to 45 in 0.045steps with stepping time of 0.5s. The elemental composition was obtained by Energy Dispersive X-ray Spectroscopy (EDXS) on KEVEX X-ray spectrometer. SEM of catalyst was taken on camera SU-30 microscope. The ammonia-TPD data were recorded for K10, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ by using AutoChem 11 2920 TPD/TPR instrument (Micromeritics, USA) by using 10% ammonia in Helium.

II.4. Experimental Set up and Analysis

All reactions were carried out in a $50\times10^{-6}m^3$ stainless glass reactor with an internal diameter of 0.005m. A standard four pitched blade turbine impeller was used for agitation. The temperature was maintained at ±1 ºC of the desired value. In a typical solvent less reaction, 0.0075mol of glycerol and 0.15mol of cyclohexanone were taken. Dodecane was used as an internal standard (2×10^{-4}kg) with a catalyst loading of 6.4kg/m³. The reaction was carried out without solvent. The catalysts were dried at 50ºC for 2h before use. The reaction mixture was allowed to reach t he desired temperature and the initial sample was collected. Agitation was then

commenced at a known speed. Samples were withdrawn at periodic intervals up to 2 h.

II.5. Method of Analysis

Clear liquid samples were withdrawn from the reaction mass periodically and they were analyzed by gas chromatography on a Chemito 8610 model, OV-17 stainless steel packed column. The conversion was based on decrease in concentration of limiting reactant glycerol. All the reaction products were confirmed by GC-MS.

III. Results and Discussion

III.1. Catalyst Characterization

The preservation of Keggin structure was confirmed by using FTIR. Bulk DTP($H_3PW_{12}O_{40}$) and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ show the characteristic IR bands at $108 \times 10^3 m^{-1}$(P-O) in central tetrahedral, $984 \times 10^2 m^{-1}$(terminal W=O) $897 \times 10^2 m^{-1}$(W-O-W) associated with the asymmetric vibrations in the Keggin polyanion. However $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is characterized by a split in the W=O band, suggesting the existence of direct interaction between the polyanion and Cs^+. FTIR Cs-DTP/K10 indicates that the primary Keggin structure is preserved in both cases on K-10 support. The bands in the region of $(1631-1642) \times 10^2 m^{-1}$ are attributed to –OH bending frequency of water molecules present in catalysts [48]-[50], [60]. The scanning electron micrograph reveals that both K-10 and 20%DTP/K10 samples possesses rough surfaces. Whereas 20% $Cs_{2.5}H_{0.5}PW_{12}O_{40}$K/10 shows a smoother surface because of the layer of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ over the external surface of K-10.Ammonia TPD was carried out by dehydrating 0.2×10^{-3}kg of the catalyst sample at 573K in dry air for 1hr and then purged with helium for 0.5h. The temperature was decreased to 398K under the flow of helium and then $0.5 \times 10^{-3} m^3$ of NH_3 pulses were supplied to the samples until no more uptake of NH_3 was observed. The Powder XRD pattern of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K10 and DTP reveals that DTP is crystalline while K-10 is amorphous in nature. Even though some lose in crystallinity of observed when it was supported on K-10, but the Keggin structure of DTP remained intact.

The comparison of the fresh and reused catalyst does show any change that means the catalyst structure remained same even after four cycles. The surface area analysis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K10 and K-10 indicates that BET surface area of previous one is less as compare to the later. The pore size of K-10 and its modified catalysts are in the range of 50-75A°, suggesting that pore sizes lie in the mesoporous range. The adsorption-desorption isotherm for support and catalyst indicates that they form type isotherm with the hysteresis loop of H-3, which characteristic of mesoporous solid [48]-[50], [60].

III.2. Efficacy of Various Catalysts

Various solid acid catalysts were employed to assess their efficacy and selectivity for product of interest in reaction shown in Scheme 1. A 6.4kg/m³ loading of catalyst based on the volume of reaction mixture was employed at 50°C and a speed of agitation 66000rps. Table I gives activity and selectivity of various Lewis as well as Bronsted acid catalyst.

The reaction revealed in scheme 1 proceeds through protonation of ketone followed by attack of one of the hydroxyl group of glycerol, which leads to removal of water molecule from ketone.
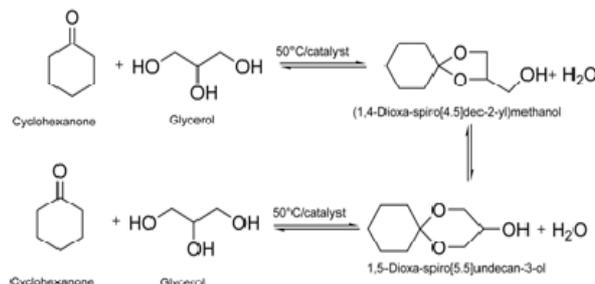
Scheme 1

The generated carbonation either attacked by primary or secondary hydroxyl group of glycerol giving (1, 5-Dioxa-spiro [4.5] undecan-3-ol or (1, 4-Dioxa-spiro [4.5] dec-2-yl) methanol.

Modified sulfated zirconia UDCaT-5, a super acidic catalyst gives 96% conversion with 94% selectivity toward 1,4-dioxolane, whereas FRSZ a sulfated zirconia catalyst shows very low conversion and selectivity for the reaction. Commercial ion exchange resins Indion-120 and DTP/HMS prepared by Yadav and co-workers gives 100% conversion with good selectivity but both face the dilemma of reusability.

TABLE I
CATALYST SCREENING

Sr. No	Catalyst	Conversion %	Selectivity (1:4 - 1:5)
1	K-10	80	84:16
2	Cs-DTP/K10	100	100
3	MUICaT-5	9	100
4	UDCaT-5	96	94:6
5	DTP/HMS	100	100
6	FRSZ	46	88:12
7	Indion-120	100	95:5
8	Duolite	48.7	93:7

Reaction conditions: glycerol 0.0075mol, cyclohexanone 0.15mol, $0.2 \times 10^{-6} m^3$ dodecane as internal standard, catalyst loading 6.4kg/m³, speed of agitation 66000rps, temperature 50°C.

Montmorilionite K-10 gives 80% conversion but with low selectivity, on the other hand when K 10 was treated with Cs-DTP its reactivity as well as selectivity toward product of concern is excellent as compared to other catalysts. Due to high selectivity, reactivity and reusability of Cs-DTP/K10 it is selected for further investigation.

III.3. Effect of Speed of Agitation

The effect of speed of agitation on the conversion of glycerol in the reaction with cyclohexanone was studied in the range of 54000-78000rps under otherwise similar conditions.

The conversion of glycerol was found to be practically the same in all the cases, which indicated the absence of external solid-liquid mass-transfer resistance for the transfer of reactants and products (Fig. 1). Thus, agitation speeds beyond 66000rps ensured that external mass-transfer effects did not influence the reaction. Hence, all further reactions were conducted at 66000rps.
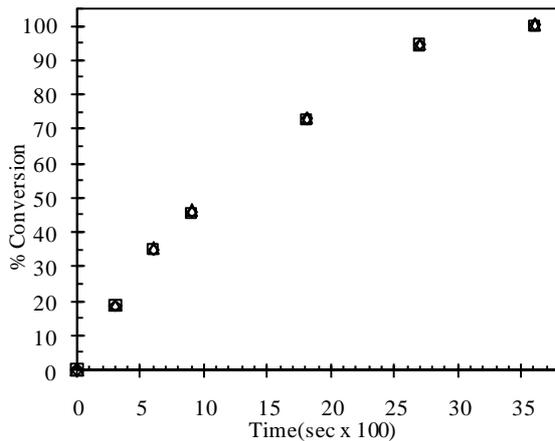
Fig. 1. Effect of speed of agitation on conversion of glycerol.
Reaction conditions: glycerol 0.0075mol, cyclohexanone 0.15mol, $0.2 \times 10^{-6} m^3$ dodecane as internal standard, catalyst loading $6.4 kg/m^3$, temperature 50°C. (□ 54000rps, ◇ 66000rps, △ 78000rps)

Theoretical calculations were also done to establish that there was absence of external mass transfer resistance. A complete theory is given elsewhere by us and a typical calculation is presented here for the sake of brevity [50], [60].

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 liquid phase diffusivity values D_{AB} (glycerol in cyclohexanone) and D_{BA} (cyclohexanone in glycerol) were calculated by using Wilke–Chang equation [61]. The values of D_{AB} and D_{BA} at 323K were calculated as 1.445×10^{-9} and 1.724×10^{-9} m^2/s, respectively. The values of solid–liquid mass transfer coefficients k_{SL-A} and k_{SL-B} were calculated by the Sherwood number correlation as 0.4982 and 0.5944 m/s, 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. The surface area of particles per unit liquid volume (a_p) was calculated for $58 \times 10^{-10} m$ particle size (average) at a catalyst loading of $6.4 kg/m^3$. Thus the values of mass transfer rates of glycerol ($= k_{SL-A}a_P C_{Ao}$) and cyclohexanone ($= k_{SL-B}a_P C_{Bo}$) from the bulk liquid of the external surface of the catalyst, were found to be 7.734×10^2 and 1.84×10^4 $mol/m^3 s$, respectively at mole

ratio of 1:20. The initial observed rate of the reaction was found to be 5.4×10^{-6} kg/m^3. Substuting these values in following equation:

$$\frac{1}{r_{obs}} \gg \frac{1}{k_{SL-A} a_p [A_o]}$$

i.e. $1.85 \times 10^5 \gg 1.29 \times 10^{-3}$ and:

$$\frac{1}{r_{obs}} \gg \frac{1}{k_{SL-B} a_p [B_o]}$$

i. e. $1.85 \times 10^5 \gg 5.42 \times 10^{-5}$

The above inequality demonstrates that there is an absence of resistance due to the solid-liquid external mass transfer for both the species A and B and the rate may be either surface reaction controlled or intra-particle diffusion controlled. Therefore, the effects of catalyst loading at a fixed particle size and temperature were studied to evaluate the influence of intra-particle resistance.

III.4. Effect of Catalyst Loading

The effect of catalyst loading was studied over range of $3.2 kg/m^3$–$9.6 kg/m^3$ (Fig. 2). In the absence of external mass transfer resistance, the rate of reaction was directly proportional to catalyst loading based on the entire liquid phase volume. This indicates that as the catalyst loading increased the conversion of glycerol increases, which is due to proportional increase in the number of active sites.
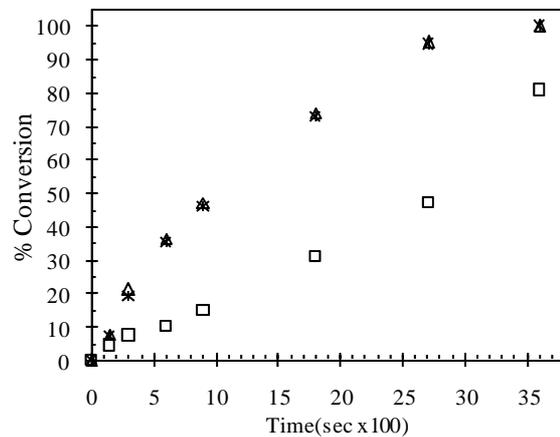
Fig. 2. Effect of catalyst loading on conversion of glycerol.
Reaction conditions: glycerol 0.0075mol, cyclohexanone 0.15mol, $0.2 \times 10^{-6} m^3$ dodecane as internal standard, temperature 50°C, speed of agitation 66000rps (Catalyst loading: □ $3.2 kg/m^3$, △ $6.4 kg/m^3$, ✻ $9.6 kg/m^3$)

But it was observed that from catalyst loading of $6.4 kg/m^3$ to $9.6 kg/m^3$ there is no significant change in the conversion and the selectivity toward desired product that means the more than desired number of catalyst sites were available for the reaction, hence $6.4 kg/m^3$ catalyst

loading was selected as optimum and further it was selected for the investigations. Theoretical calculation was done by using Wiesz-Prater criterion to assess the influence of intraparticle resistance. According to Weisz-Prater criterion, C_{wp} can be evaluated from the observed rate of reaction, particle radius (Rp), effective diffusibility of the limiting reactant (D_e) and concentration of reactant on the surface of the particle[61], [62]. The effective diffusivity of glycerol (D_{e-A}) inside the pores of the catalyst was obtained from the bulk diffusivity (D_{AB}), porosity (ε) and tortuosity (τ) as 1.92×10^{-10} m^2/s. In the present case, the value of C_{wp} was calculated as 2.65×10^{-3} for the initial observed rate which is much less than 1 and therefore the reaction is intrinsically kinetically controlled. A further proof of the absence of the intra-particle diffusion resistance was obtained through the study of the effect of temperature and it will be discussed later.

III.5. Effect of Mole Ratio

The effect of mole ratio of glycerol to cyclohexanone was studied from 1:10 to 1:25, keeping the total volume of the reaction mass constant at 15.5×10^{-6} m^3 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$/K-10 clay as the catalyst (Fig. 3). The catalyst concentration was kept at 6.4kg/m^3. There was a sharp increase in conversion from mole ratio of 1:10 to 1:25. Not much difference was seen in the final conversion when mole ratio varied from 1:20 to 1:25. Therefore the mole ratio was kept at 1:20 for the remaining experiments. At a mole ratio of 1:20, the conversion obtained was 100% with more than 99% selectivity toward the 1, 4-dioxanol. It was observed that changing the mole ratio has very high impact on selectivity and conversion. When glycerol was taken in excess, the reaction was very sluggish.
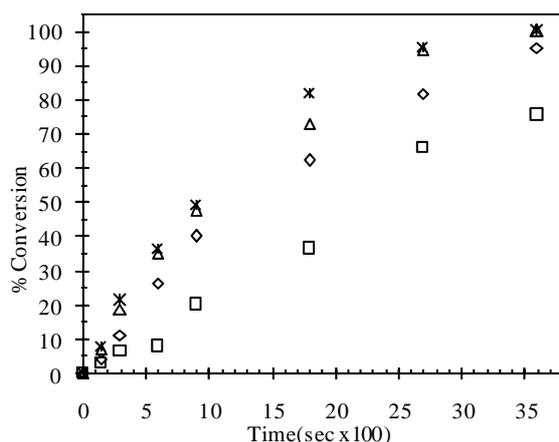
Fig. 3. Effect of mole ratio of glycerol to cyclohexanone.
Reaction conditions: 0.2×10^{-6} m^3 dodecane as internal standard, catalyst loading 6.4kg/m^3, speed of agitation 66000rps, temperature 50°C
(□ 1:10, ◇ 1:15, △ 1:20, ✳ 1:25)

III.6. Effect of Temperature

The effect of temperature on the rate of reaction

between cyclohexanone and glycerol was studied under otherwise similar conditions. The temperature was varied from 30°C to 60 °C. The conversion of glycerol to selective product was observed to increase with an increase in the reaction temperature. The effect of temperature on the conversion of glycerol is given in (Fig. 4). The conversions were linear with time at all temperatures. These observations show that the reaction is pseudo first order in substrate concentration and the model is validated at different temperatures. The Arrhenius plot was made to determine the energy of activation (Fig. 6). The energy of activation has been found to be 11.64 kcal/mol.
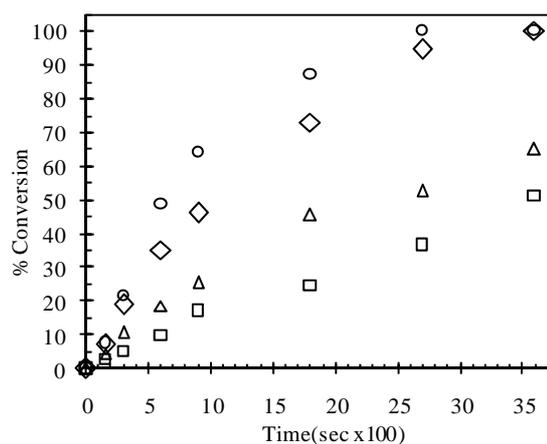
Fig. 4. Effect of temperature on conversion of glycerol.
Reaction conditions: glycerol 0.0075mol, cyclohexanone 0.15mol, 0.2×10^{-6} m^3 dodecane as internal standard, catalyst loading 6.4kg/m^3, speed of agitation 66000rps (□ 30°C, △ 40°C, ◇ 50°C, ○ 60°C)

III.7. Reaction Mechanism and Kinetics

From the value of energy of activation it is evident that intraparticle diffusion resistance was absent. Thus, the reaction could be controlled by one of the following steps, namely adsorption, surface reaction or desorption (Scheme 2). Therefore, for development of model, the actual mechanism was undertaken. It is assumed that glycerol (A) and cyclohexanone (B) adsorb weakly on catalytic surface. It is cyclohexanone from liquid phase that reacts with chemisorbed AS, accordingly to power law type of mechanism.

Let A= Glycerol, B= Cyclohexanone, IS= intermediate carbocation, CS= 1, 4-dioxolane, DS=1, 5-dioxane, AS= chemisorbed glycerol, BS= chemisorbed cyclohexanone, WS= water, S= vacant sites.

Adsorption:

Adsorption of glycerol on vacant site S

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

Adsorption of cyclohexanone on vacant site S

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

Surface reaction:

Surface reaction between AS and BS in vicinity of active site leads to formation of intermediate carbocation which, undergo further reaction to give adsorbed product CS and DS:

$$BS + AS \underset{k_1^1}{\overset{k_1}{\rightleftharpoons}} IS + S \qquad (3)$$

$$IS + S \underset{k_2^1}{\overset{k_2}{\rightleftharpoons}} CS + WS \qquad (4)$$

$$IS + S \underset{k_3^1}{\overset{k_3}{\rightleftharpoons}} DS + WS \qquad (5)$$

$$CS \underset{k_4^1}{\overset{k_4}{\rightleftharpoons}} DS \qquad (6)$$
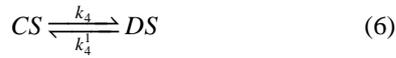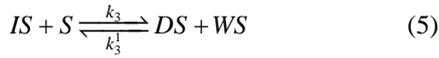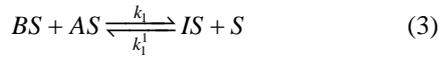
where k_1, k_2, k_3, k_4 are surface reaction rate constant for forward reaction and $k_1^1, k_2^1, k_3^1, k_4^1$ Surface reaction rate constant for reverse reactions respectively.

Desorption:

Desorption of adsorbed products and water molecule:

$$CS \overset{\frac{1}{K_C}}{\rightleftharpoons} C + S \qquad (7)$$

$$DS \overset{\frac{1}{K_D}}{\rightleftharpoons} D + S \qquad (8)$$

$$WS \overset{\frac{1}{K_W}}{\rightleftharpoons} W + S \qquad (9)$$
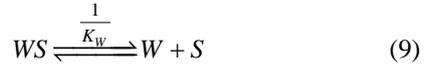
Because isomerization C to D does not occurs at 50°C, therefore this step can be neglected.

The total concentration of the active sites, C_T expressed in mol/g of catalyst given by:

$$C_T = C_S + C_{AS} + C_{BS} + C_{CS} + C_{DS} + C_{WS} \qquad (10)$$
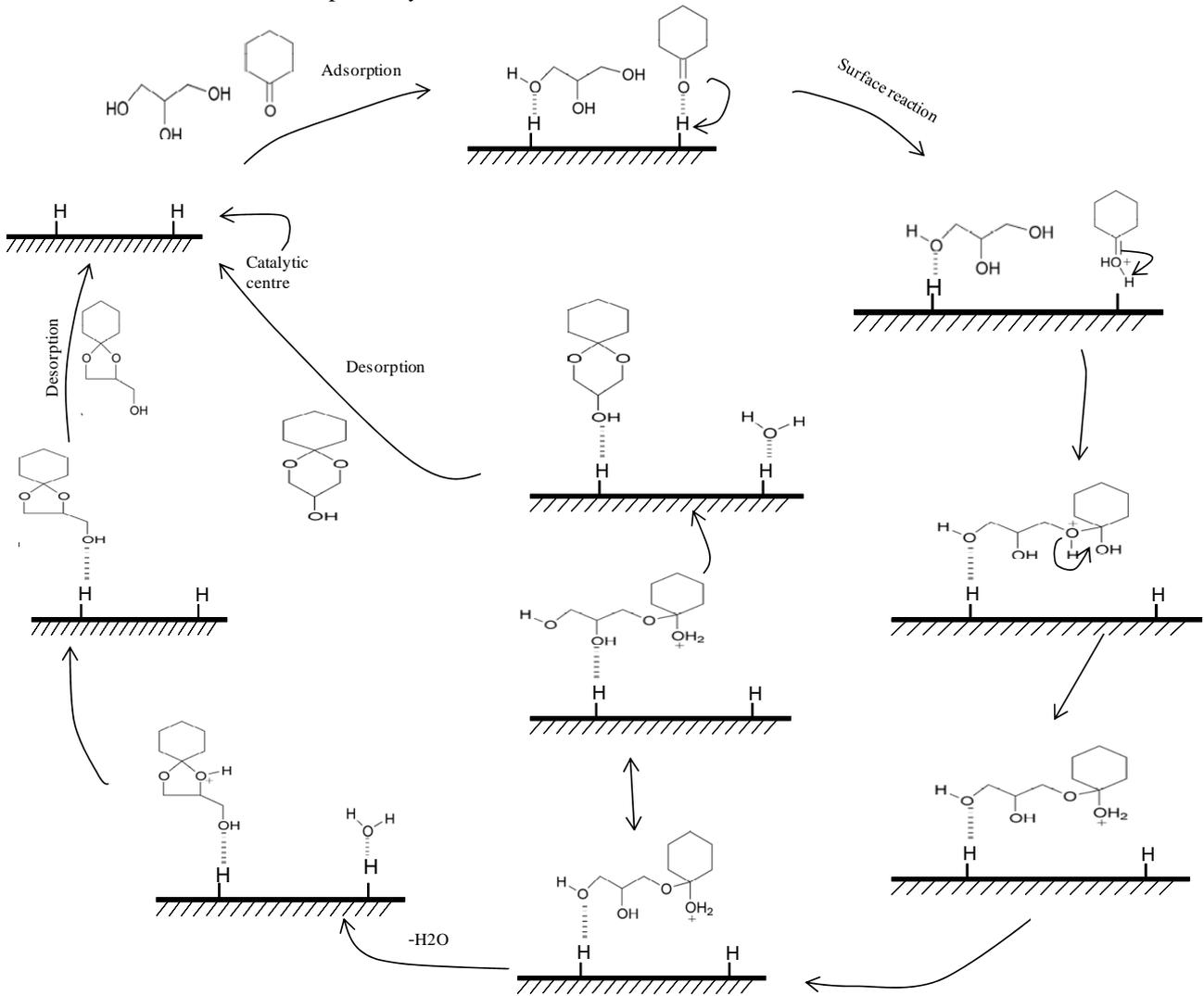
Scheme 2. Plausible reaction mechanism

where C_S is the concentration of vacant sites, kmol/m³ of catalyst, C_{AS}, C_{BS}, C_{CS}, C_{DS} and C_{WS} are concentration of vacant site, A, B, C, D and W on solid surface in mol/m³ respectively. Substituting the concentration of surface species in above equation i.e. put:

$$C_{AS} = K_A C_A C_S, C_{CS} = K_C C_C C_S, C_{DS} = K_D C_D C_S$$
$$C_{WS} = K_W C_W C_S, C_{IS} = K_I C_I C_S \quad (11)$$

C_A, C_B, C_C, C_D, C_I and C_W are concentration of species A, B, C, D, I and W in the reaction medium likewise. After substituting equation (11) in equation (10) we get:

$$C_S = \frac{C_T}{\left(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D + K_W C_W\right)} \quad (12)$$

where K_A, K_C, K_D, and K_W are adsorption equilibrium constants. Replacing the total concentration (C_T) of sites by w, the catalyst loading in kg/m³ of liquid phase, where $C_T \propto$ w, therefore:

$$C_S = \frac{k_1 w}{\left(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D + K_W C_W\right)} \quad (13)$$

Surface reaction controlled model:

If the surface reaction between chemisorbed AS and B from the liquid phase leading to all parallel reactions, is rate controlling then overall rate of reaction (r_o) in kg mol m⁶s⁻¹ of B with AS = sum of all net rates of various surface complexes given by equation:

$$r_0 = k_1 C_{BS} C_{AS} - k_1^1 C_{IS} C_S + k_2 C_{IS} C_S + \\ -k_2^1 C_{CS} C_{WS} + k_3 C_{IS} C_S - k_3^1 C_{DS} C_{WS} \quad (14)$$

Putting equation (11) in (14) and using equation (13) we will get:

$$-r_0 = -\frac{dC_A}{dt} =$$
$$= \frac{\left[\begin{array}{c} k_1 K_A K_B C_A C_B - k_1\left(k_2 + k_3 - k_1^1\right)C_I + \\ -K_W\left(k_2^1 K_C C_C + k_3^1 K_D C_D\right)C_W \end{array}\right] C_T^2}{\left(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D\right)^2} \quad (15)$$

Equation (15) suggests that the relative values of the rate constants, equilibrium constants and the concentrations of the various species will govern the overall rate of chemisorbed glycerol (AS) with cyclohexanone (B) from the liquid phase.

Assuming weak adsorption of all species and negligible reversible reactions, Eq. (15) is converted into:

$$-\frac{dC_A}{dt} = \frac{k_1 C_T^2 K_A K_B C_A C_B}{\left(1 + \sum K_i C_i\right)^2} \quad (16)$$

Let:

$$k_{R_2} w = k_1 C_T^2 K_A K_B \quad (17)$$

Therefore:

$$-\frac{dC_A}{dt} = k_{R_2} C_A C_B w \quad (18)$$

where w is catalyst loading and k_{R2} reaction rate constant, if the adsorption constants are small, then the above equation reduces to:

$$-\frac{dC_A}{dt} = k_{R_2} w C_{A_0}\left(1 - X_A\right)C_{B_0} \quad (19)$$

C_{Ao} and C_{Bo} are initial concentration of A and B, because cyclohexanone was taken molar excess over glycerol ($C_{B_0} \gg C_{A_0}$), therefore it becomes a pseudo first order equation which can be integrated as follows:

$$-ln\left(1 - X_A\right) = k_1 wt \quad (20)$$

where, k_1 is the pseudo-first order constant.

A plot of $-\ln(1-X_A)$ versus time was made as different temperatures (Fig. 5). It is seen that the data fits well and hence validates the model. Arrhenius plot of was made (Fig. 6) to get the energy activation as 11.64kcal/mol which shows that the reaction is intrinsically kinetically controlled.
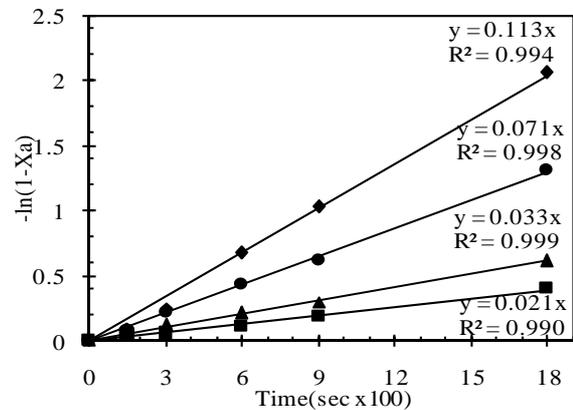
Fig. 5. Plot of –ln (1-Xa) against time

III.8. Reusability Study

The reusability of the catalyst was studied by filtering the catalyst at the end of the reaction. Reusability of 20% Cs-DTP/K-10 was tested by conducting four runs. After each reaction the catalyst was filtered and then refluxed with (3×50×10⁻⁶m³) of cyclohexanone for 2 h in order to remove any adsorbed material from catalyst surface and pores and dried at 110°C for 2 h after every use. There were losses during handling since the particle size was

very small and typically about 5% catalyst would be lost. Catalyst was found to have excellent reusability for four cycles after fresh use (Fig. 7).
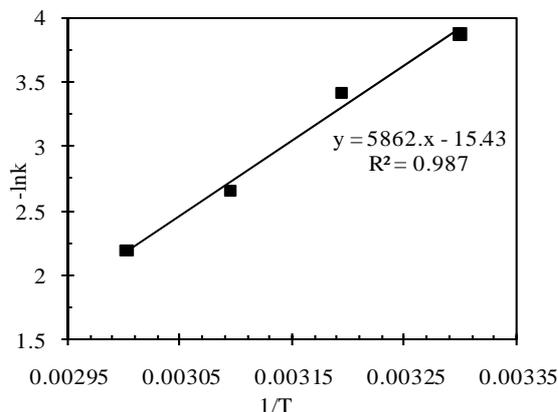
Fig. 6. Arrhenius plot
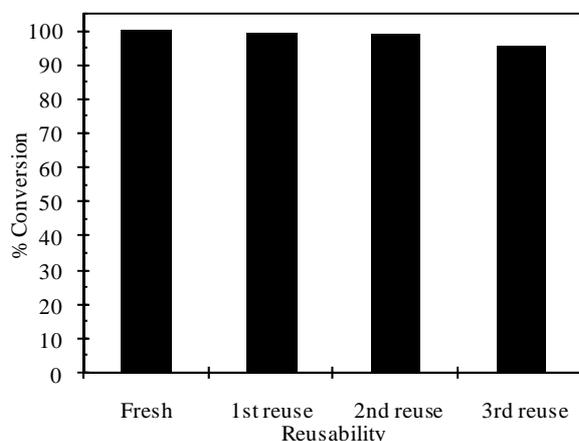
Fig. 7. Reusability of catalyst for conversion of glycerol.
Reaction conditions: glycerol 0.0075mol, cyclohexanone 0.15mol,
$0.2 \times 10^{-6} m^3$ dodecane as internal standard, catalyst loading $6.4 kg/m^3$,
speed of agitation 66000rps, temperature 50°C

IV. Conclusion

Solventless acetylation of glycerol with cyclohexanone was efficiently catalyzed by Cs-DTP/K10.

In all reactions more than 99% of selectivity toward 1, 4-dioxanol was observed. The effect of various parameters like speed of agitation, catalyst loading, mole ratio and temperature was demonstrated in detail. The reaction follows pseudo first order regime and energy of activation was calculated on the basis of Arrhenius plot which is found to be 11.64kcal/mol. The selective conversion of glycerol into valuable oxygenated products via catalytic route provides an excellent methodology for utilization of biomass.

In conclusion we have developed a highly selective, efficient and reusable solid acid catalyzed method for synthesis of 1, 4-dioxanol.

Acknowledgements

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