

Hydrogenolysis of Glycerol using Fe-Fe/Al₂O₃ Complex Catalyst

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Macrocytic complex catalyst Fe-FeL₁ complex of L₁ (L₁ = C₂₄H₂₆O₂N₄) was synthesized and studied in the hydrogenolysis reaction of glycerol reaction in a high pressure batch reactor. The catalyst was well characterized *i.e.* FTIR, XRD, TGA and BET surface area. The study of hydrogenolysis was found that the selectivity of 1,2-propane diol 80 % at 220 °C temperature and 0.35 MPa pressure in presence of hydrogen gas and Fe-Fe/Al₂O₃ and 30 % glycerol concentration in water gives 1,2-propane diol as the only product and conversion was 36 % at 220 °C. It is further seen that if the concentration of glycerol in water is increased beyond 40 % there is a decrease in the total conversion and carbon is produced as coke during the reaction.

Keywords: Complex catalysts, Hydrogenolysis, Bimetallic complex, Fe-FeL₁/Al₂O₃.

INTRODUCTION

Hydrogenolysis is a chemical reaction where a carbon-carbon or carbon-heteroatom (for example carbon-hydroxyl, carbon-nitrogen or carbon-sulphur, =C=O, ≡C-N≡, ≡C-S-) bonds are cleaved by hydrogen. The heteroatom may vary but they are usually oxygen, nitrogen, or sulfur. A related reaction is hydrogenation, where hydrogen is added to the molecule by cleaving of the bond. In hydrogenolysis, one requires hydrogen and is carried out in presence of catalyst [1,2]. Alkane hydrogenolysis has been carried out in presence of hydrogen and raw materials have usually been ethane, propane, butane or heptanes [3]. Other molecules studied are aromatics, alcohols and carboxylic esters. The catalyst used for alkanes are usually silica supported molybdenum, ruthenium supported alumina and Ni-Mo on alumina, Pd on alumina, Pt on Mg-Al, *etc.* Through hydrogenolysis of higher polyols (glycerine, sorbitol and xylitol), wide range of value added chemicals like 1,2-propylene glycol, 1,3-propylene glycol, ethylene glycol, ethanol, *etc.* can be catalytically synthesized. This route of synthesis is of immense industrial importance and, of late, has been a part of several laboratory scale studies. One of the several routes for the production of oxygenated chemicals such as ethylene glycol, propylene glycol and lactic acid [4,5] is through the hydrogenolysis of glycerol. The product ethylene glycol [4] is used in the production of polymers, resins, functional fluids (antifreeze, de-icing), foods and cosmetics. 1,2-Propylene glycol [5] is used as antifreeze, aircraft de-icer and lubricant. 1,3-Propylene glycol [6] is copolymerized with terephthalic

acid to produce polyesters, which is used for manufacturing carpet and textile fibres exhibiting strong chemical and light resistance. Lactic acid and lactate salts [4] are also important for the food and beverage industry. However, lactic acid is mostly utilized for the production of polylactic acid (PLA). Several catalysts reported in literature for hydrogenolysis of glycerol are Ru/C, Pt/C, Ru/C+Pt/C, Ru/C+Au/C, PtRu/C, AuRu/C, *etc.* Catalysts in presence of base NaOH and CaO, Ru/CsPW, Rh/CsPW, Pt/WO₃/ZrO₂ [7], ruthenium based bimetallic catalysts [8], Cu-ZnO catalysts [9]. Hydrogenolysis over copper chromite catalyst [10] in vapour phase with no hydrogen addition in the reaction gives propylene glycol and in liquid phase [11], with hydrogen introduced, it forms acetol. With addition of sulfur to ruthenium based catalysts, propylene glycol is produced with increased selectivity [12,13]. The hydrogenolysis of glycerol (solvent water, sulfolane or dioxane was used under 80 bar of hydrogen at 180 °C) using heterogeneous Cu, Pd and Rh catalysts supported on ZnO, C and alumina in the presence of tungstic acid as a modifier improves the selectivity towards 1,3-propanediol [14]. Hydrogenolysis over raney nickel catalyst in presence of phosphonium salt forms 1,2-propanediol [15]. Co/MgO was also used as a catalyst system where MgO acts as the basic component and supports cobalt nanoparticles [16]. The role of noble metals has been examined on the conversion of glycerol to propanediols [17-19]. It has been reported that H₂WO₄ is effective in enhancing the glycerol conversion [20] and ruthenium supported on carbon along with Amberlyst (a cation exchange resin) was reported [19,21] to exhibit a higher activity under mild conditions than

other metal-acid bifunctional catalyst systems. In spite of several research efforts, drawbacks of existing technologies for production of 1,2-propane diol have been limited to the laboratory scale only. The hydrogenolysis of dilute solutions of glycerol (10-30 % w/w) has been carried out in a pressure range of 10-32 MPa and temperature range of 200-350 °C and the reaction gave low selectivity towards propylene glycol. High selectivity towards ethylene glycol and other byproducts like lactic acid, acetol, acrolein and degradation products like propanol, ethanol, methanol and methane is reported in the literature. Among the metals used as catalyst, copper has been effective in reducing the reaction temperature and pressure. Dasari *et al.* [10] found Raney Ni with copper to be an efficient catalyst. They also suggested that high concentration of glycerol in feed gives higher conversion of glycerol and higher yield of 1,2-propanediol. Miyazawa *et al.* [12] have shown that higher concentration of glycerol in feed would give more waste products and smaller conversion of glycerol on hydrogenolysis over Ru/C. The literature suggested that the following metals are of prime importance *viz.*, nickel, copper, platinum, palladium and ruthenium. Platinum, palladium and ruthenium being noble metals, their use would greatly alter the economics of the process, hence in this, work homonuclear bimetallic complex catalyst Fe-Fe/L₁ was prepared and catalytically tested.

EXPERIMENTAL

The chemicals sodium dichromate, *p*-cresol, 4-toluene sulfonyl chloride, sodium azide, benzene, benzoyl chloride, anhydrous diammonium hydrogen orthophosphate and *m*-phenylene diamine were purchased from Loba Chemie, Mumbai. Sodium hydroxide, sodium chloride, toluene, isopropanol, glycerol, methanol, formaldehyde, N,N-dimethyl formamide and 1,2-dichloroethane were procured from Qualigens Fine Chemicals, Mumbai. Analytical grade of anhydrous ammonium molybdate [(NH₄)₂Mo₇O₂₄·4H₂O] was purchased from Samir Tech-Chem Pvt. Ltd., Vadodara, ferric nitrate [Fe(NO₃)₃] from Ranbaxy Fine Chemicals Ltd.

Preparation of 2,6-diformyl-4-methylphenol: About 33 % NaOH solution is prepared by dissolving 100 g of NaOH in 400 mL water and 126 g (2 mol) of *p*-cresol is added which forms a golden yellow coloured product. A 37 % formaldehyde solution is added to this mixture and stirred for 0.5 h and left for 24 h at ambient temperature (35 °C). This mixture is filtered by vacuum filtration and the filtrate obtained is washed with saturated solution of sodium chloride. The product obtained is 2,6-dimethylol-4-methyl phenol. A 1300 mL water and 130 mL of 33 % NaOH are added to 2,6-dimethylol-4-methyl phenol taken in a round-bottomed flask and stirred. A 494 g (2.6 mol) of *p*-toluene sulfonyl chloride dissolved in toluene is added to the above and stirred for 20 h at room temperature. An aqueous and emulsified phase is formed. This mixture is kept in an ice bath and toluene is added till solids are formed. A white solid is called tosylated phenol is formed which is separated by vacuum filtration and washed with toluene and dried, forming 272 g of product (m.w. 338).

The tosylated phenol (272 g, 0.8 mol) is now oxidized with sodium dichromate (208 g, 0.69 mol) and acetic acid

(645 mL). 160 mL acetic acid is taken in a 3-necked reactor vessel of 2 L volume, which is equipped with a stirrer, an addition funnel and a water-cooled reflux condenser. The sodium dichromate is dissolved in remaining acetic acid (485 mL) and introduced through the addition funnel drop wise with stirring for about 40 min at 110 °C. The reaction mixture is cooled, filtered and washed with water to get green coloured crystals of tosylated dialdehyde.

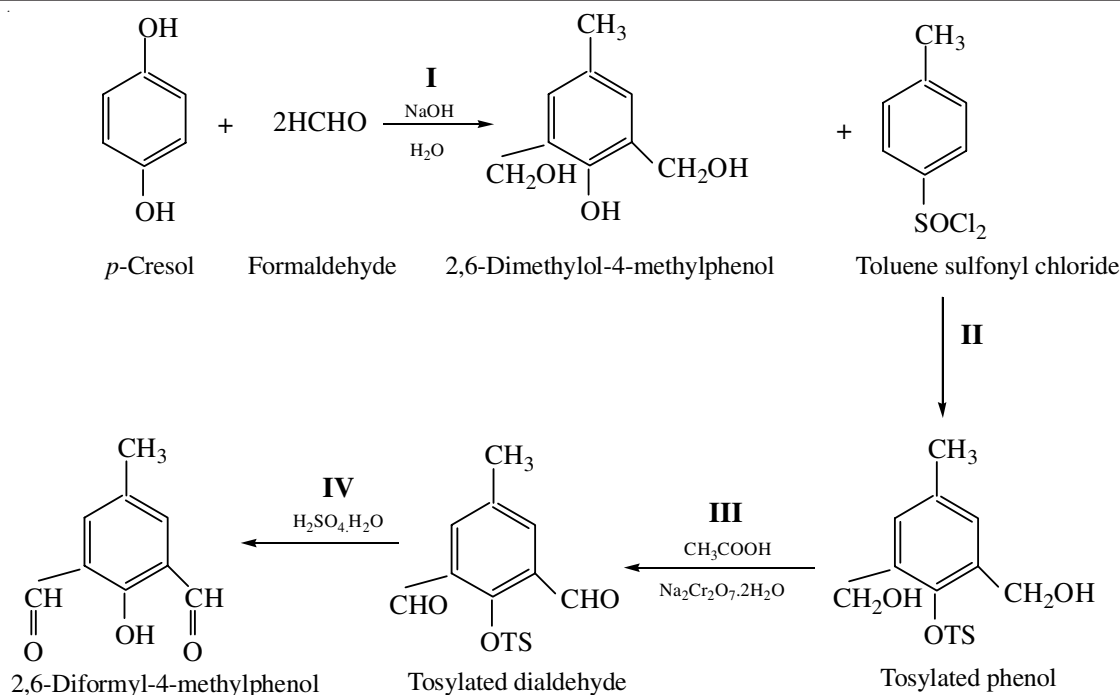
Tosylated dialdehyde (250 g) is taken in a 5 L beaker and 900 mL of H₂SO₄ is added. This mixture is stirred for 1 h and ice-water slurry is added till the volume becomes 4 L. The precipitated material is collected by vacuum filtration, washed with water and dried. This is dissolved in toluene and the liquid is recrystallized which yields brownish yellow coloured needle like crystals (**Scheme-I**). The product obtained is 2,6-diformyl-4-methylphenol. The melting point of this compound was determined to be 130 °C.

Synthesis of Fe-Fe complex: The complex is synthesized in three steps. In the first step, in a 250 mL conical flask 2,6-diformyl-4-methylphenol (0.95 g, 0.012 mol) and N,N-dimethyl formamide (50 mL) are taken in a 250 mL conical flask and 1,2-phenylenediamine (0.65 g, 0.006 mol) is added. To this solution ferric nitrate (0.65 g, 0.006 mol) is added and the solution is stirred till the entire ferric nitrate dissolves completely. The solution is kept for 1 h and diethyl ether is added later in it. Precipitation begins and the precipitate is filtered and dried. In the second step, this dried material (2.14 g, 0.005 mol) and cupric acetate (1.597 g, 0.008 mol) are taken in a 250 mL conical flask and dissolved in 20 mL methanol. The solution is stirred for 0.5 h and crystals of complex appear. These are collected by filtration and washed with diethyl ether and dried. The dried material (1.871 g, 0.0036 mol) is then dissolved in 30 mL methanol and 1,2-phenylenediamine (0.336 g, 0.336 mol) is added to it. A brown precipitate is formed which is washed with diethyl ether and dried in a vacuum desiccator (**Scheme-II**).

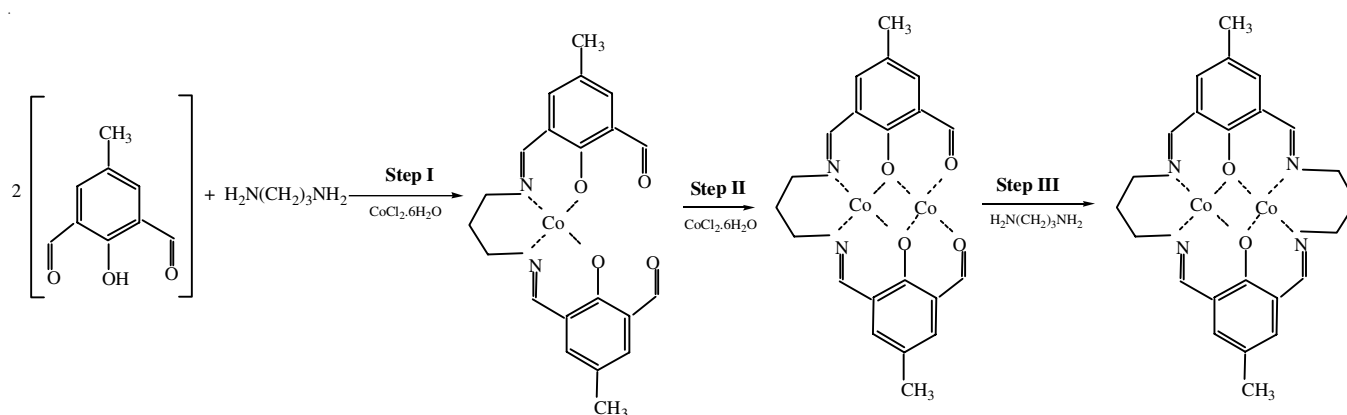
Loading of Fe-Fe complex on alumina: The aluminum oxide (approximately) 9 g is dissolved in 20 mL of deionized water. 1 g of powdered catalyst is then mixed with the resulting aqueous alumina solution and is stirred in magnetic stirrer at 80 °C for 0.5 h. The resulting mixture is then dried at 160 °C in oven for 4 h, followed by calcinations at 320 °C for 3 h.

Reaction procedures: A high pressure batch reactor made of stainless steel (300 mL) is used for carrying out the hydrogenolysis reactions. The reactor is equipped with a pressure gauge, a thermocouple, gas delivery system and provision for sampling. An on/off controller is used for controlling the temperature with a chrome alloy thermocouple for temperature sensing. The reactor was operated in batch wise mode with initial feeding of glycerol solution, hydrogen gas and the catalyst before heating is started.

The reactor is initially charged with 200 mL of aqueous glycerol and 2 g of catalyst. It is then pressurized with 0.35 MPa of hydrogen gas and then heated to the required temperature for the desired reaction time. Every reaction is carried out for 8 h. The product samples are withdrawn at regular intervals of 0.5 h by means of a needle valve. The quantity withdrawn is less than 1 mL so that the total change in volume can be



Scheme-I: Preparation of 2,6-diformyl-4-methylphenol starting from *p*-cresol and formaldehyde



Scheme-II: Synthesis of homodinuclear macrocyclic Fe-Fe complex of ligand L

neglected. The products obtained after reaction are analyzed by gas chromatography using a Chromosorb 101 S. S. column of 62 length, O. D. 1/822 and I. D. 2mm. The flame ionization detector was used and the oven temperature was kept at 210 °C and operated in the isothermal mode.

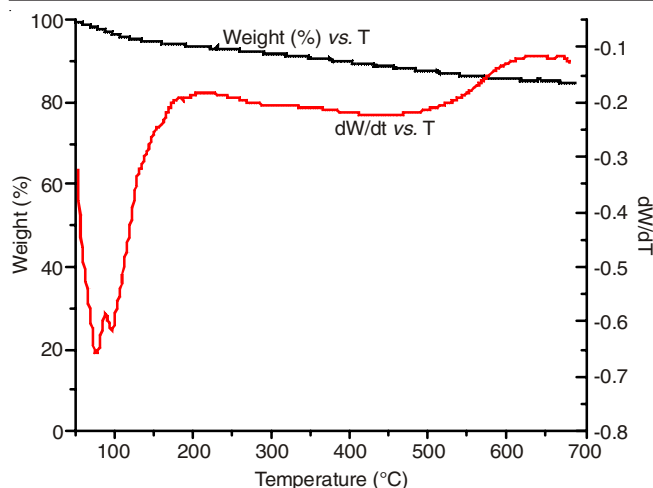
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RESULTS AND DISCUSSION

FTIR analysis of the complex: The FTIR analysis was carried out on a Bruker Vector 22 instrument in the 4000-400 cm^{-1} wavenumber range. The sample were ground with KBr and Pressed to 1-mm thick film. The bands due to the C=N (1541 cm^{-1} in step I, 1540 cm^{-1} in step II and 1532 cm^{-1} in step III) and C=O bond. The latter bond frequency in the final step when the complex Fe-FeL' is reacted with 1,3-diaminopropane.

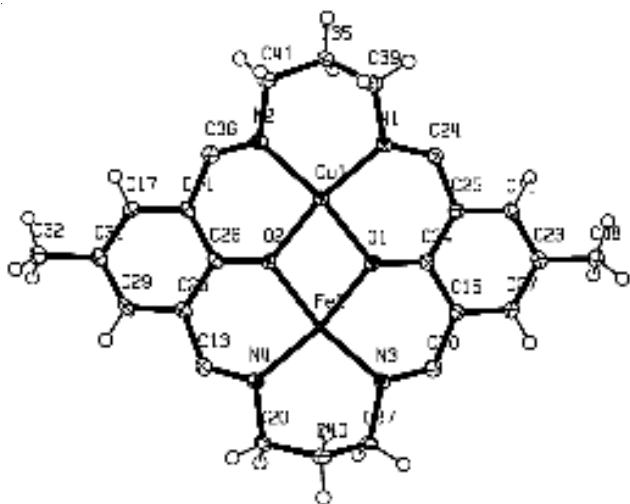
CHN analysis of Fe-Fe macrocyclic complex: The CHN analysis was carried out on a CE-440 elemental analyzer (Leeman Labs Inc., USA) helium was used as the carrier gas and 4-5 mg of the sample was required. The experimental % weights of 37.937 % carbon, 6.05 % hydrogen, 14.402 % nitrogen and heteroatom's (halogens, sulfur) of a sample. Theoretical values of carbon, hydrogen, nitrogen were calculated as 38.29 %, 3.45 % and 14.89 % respectively. The molecular formula of the complex is found to be Fe-FeL·2H₂O [L = C₂₄H₂₆O₂N₄].

Thermal stability of complex and final catalyst: Thermogravimetric analysis of complex and the final catalyst was carried out using a Perkin-Elmer instrument in N₂ atmosphere. The Fe-Fe complex was heated from 35 to 700 °C at the rate of 10 °C/min and it was found that the complex was stable upto 220 °C (Fig. 1). A total weight loss of 98 % was observed when the complex was heated till 700 °C. Similarly the TGA of the final catalyst was carried out by heating it from 40 to 800 °C at the rate of 10 °C/min and it was found that the final catalyst was stable till 600 °C.

Fig. 1. Thermogravimetric analysis of Fe-Fe-L/Al₂O₃ catalyst

Single crystal X-ray analysis of the Fe-Fe complex:

Single crystal of the 1,3-diamino propane complex of Fe-Fe has been isolated by dissolving the complex in methanol and then slowly evaporating the solvent at room temperature (28 °C). In a preliminary attempt, ferric chloride as a metal salt was used and the complex showed an empty cavity (no Fe atom) in the single crystal structure obtained shown in Fig. 2.

Fig. 2. Molecular structure of Fe-Fe-L/Al₂O₃

BET analysis: The surface area of the samples was measured employing single point BET method using nitrogen gas for adsorption. The apparatus used is a bench top COULTER SA 3100. Brunauer-Emmett-Teller (BET) method is widely used for evaluation of the surface area from physisorption isotherm data. The surface area of unmodified alumina and the prepared catalyst was determined using the BET method. The surface area of unmodified alumina (dried alumina before any reaction) was 218.45 m²/g and after loading the complex (final step of catalyst preparation), it reduced to 142.02 m²/g (a decrease of about 35 %). This indicates that the complexes are covalently bonded mostly within the pores and because of this bonding it shows a high level of interaction equivalent to the bond energy of the carbamate group. After loading the Fe-Fe complex, there was a decrease in surface area and the observed surface area of [Fe-Fe]/Al₂O₃ catalyst is 100.48 m²/g, respectively.

Scanning electron microscopy (SEM) analysis: The SEM analyses of the complexes and the catalysts have been taken on a JEOL JSM-840A and the presence of the metal on the catalyst has been confirmed. The sample is powdered and gold coated under vacuum to make it conducting for electrons, the observed morphological structure of a catalyst is a result of a systematic alignment of aggregated nanoparticles and random self assembly of cubic like structure which consequently reduce high surface energy (Fig. 3).

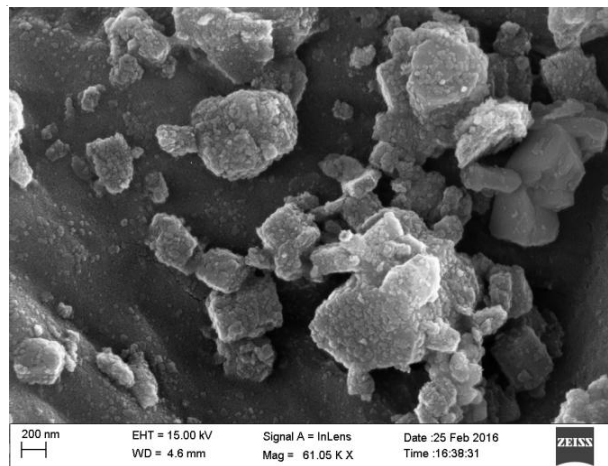


Fig. 3. SEM image of Fe-Fe/alumina

Hydrogenolysis of glycerol: When the complex catalyst (Fe-Fe supported on alumina) was used in the temperature range of 165–240 °C, there was substantial conversion. The reaction was also studied for different concentrations of glycerol in aqueous medium. Fig. 4 shows the overall per cent conversion of aqueous solution of 30 % glycerol as a function of time for different reaction temperatures. In this figure, induction time was found to be absent for all temperatures upto 220 °C and the conversion attained an equilibrium value. The overall conversion of glycerol increased from 2 to 36 % when the temperature is increased from 180 to 220 °C. The GC analysis of the liquid

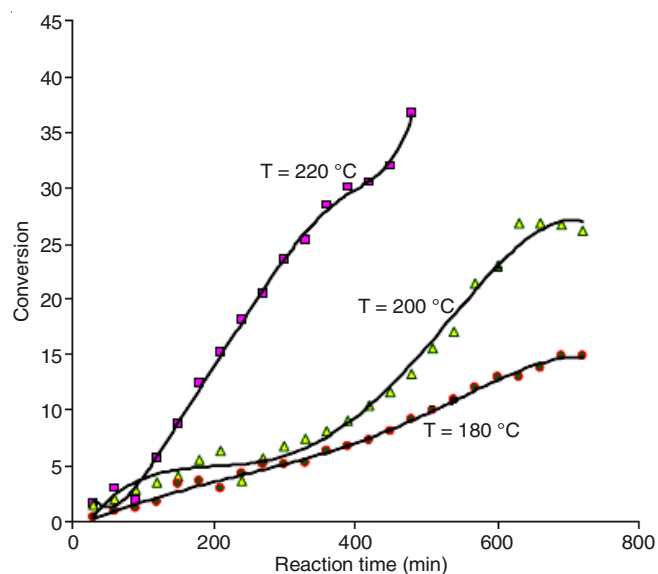


Fig. 4. Variation of conversion with time at different temperatures of 30 % glycerol (by wt) in aqueous medium using Fe-FeL/alumina catalyst

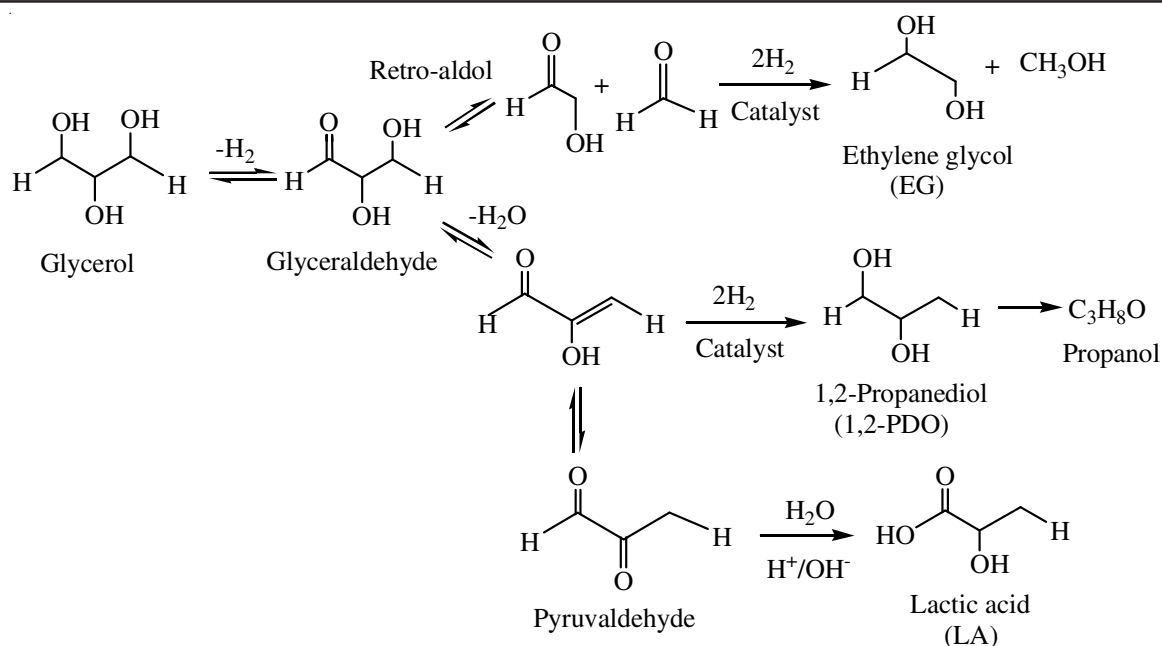


Fig. 5. Mechanism of hydrogenolysis of glycerol

phase showed the formation of 1,2-propanediol, ethylene glycol. The major product was 1,2-propanediol and ethylene glycol was formed in small amount.

Mechanism of the reaction: The reduction of glycerol is known to give several chemicals and has been discussed by Miyazawa *et al.* [12,13]. The overall reaction has been shown to form gases (such as CO and CO_2) as well as liquid products such as ethylene glycol and 1,2-propanediol based on the products formed. The reactions 1 and 2 give rise to dehydroxylation of CO bond whereas reaction 3 and 4 are dehydroxylation by H_2O (or adsorbed OH groups on the catalyst). In the presence of metallic catalyst and hydrogen, glycerol can form 1,2-propanediol, 1,3-propanediol and ethylene glycol (Fig. 5).

Conclusion

In the present work, a heterodinuclear Fe-Fe complex macrocyclic complex supported on alumina has been prepared for the hydrogenolysis of aqueous glycerol (10, 20, 30, 40 % glycerol by weight in water). The reaction was performed in the temperature range of 180–220 °C and the initial hydrogen pressure of 0.35 MPa was used. It was shown that in this temperature range, there was no gas formation and there was an increase in the overall conversion with increase in water content. The catalyst was found to be efficient at low hydrogen pressure and 1,2-propanediol was formed with 80 % selectivity (and 36 % conversion) when 20 % aqueous glycerol was used as feed. Based on the mechanism proposed in the literature, reaction mechanism was written by eliminating steps, which gave rise to gaseous components. Macrocyclic complex was synthesized and it was molecularly bonded to support alumina.

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