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Synthesis and performance evaluation of silica-supported copper chromite catalyst for glycerol dehydration to acetol

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Abstract. Sol-gel technique was used to prepare silica-supported copper chromite catalyst from acid hydrolysis of sodium silicate. The catalyst was characterized by BET surface area, FESEM, XRD, H₂-TPR and pyridine adsorption by FTIR. The catalyst was activated in a hydrogen atmosphere based on H₂-TPR result. The surface acidity of the catalyst was evaluated by NH₃-TPD and pyridine adsorption. XRD result of reduced catalyst showed the presence of Cu⁰, Cu¹⁺ and Cr₂O₃ in the catalyst. Glycerol dehydration was carried out at different temperature (180 °C to 240 °C) from aqueous glycerol solution with the reduced catalyst in a batch reactor. The glycerol conversion was reached 100% with maximum acetol selectivity of 70% for highest Copper chromite loaded (40 wt%) on silica at 220 °C in atmospheric pressure. The distilled liquid product was analyzed by high-performance liquid chromatography. Oxidized catalyst and spent catalyst showed lower glycerol conversion with low acetol selectivity than the reduced form of the catalyst. This is due to the cuprous ion in the reduced form of the catalyst, which acts as Lewis acid sites in glycerol dehydration.

Keywords. Glycerol; copper chromite; acetol; pyridine-FTIR; H₂-TPR; XRD.

1. Introduction

Biodiesel has shown potentials to act as the supplement of fossil diesel since it is a renewable and environment-friendly source of energy. But the major obstruction to use biodiesel is the high cost of production. Biodiesel significantly reduces engine emissions such as sulfur dioxide (100%), unburned hydrocarbons (68%) and polycyclic aromatic hydrocarbons (80-90%)² To produce 9 kg of biodiesel, about 1 kg of crude glycerol is formed as a by-product. Most of the biodiesel producers refine glycerol for sale as a commodity in the glycerol market. Several steps (acid and alkali treatment followed by distillation) are used to purify glycerol from the crude solution to 80-85% glycerol. Further purification to produce pure glycerol increases the overall price, which is not costeffective. However, an increase in the production of biodiesel is expected to reduce the price of glycerol, and also, the glycerol conversion to other consumer products is much more desirable. The spectrum of glycerol utilization has also grown such that presently it has over 1500 known end uses. The conversion of glycerol to other value-added commodity products are mainly based on processes like heterogeneous catalysis of hydrogenolysis, dehydration, etherification, etc.^{3–5} Mario and Pagliaro⁶ summarize twenty-two different possible ways to convert glycerol into valueadded products like polyhydroxylalkanoates, citricacid, hydrogen, 2'2-dimethyl-1'3-dioxolan-4-methylacetate, monoglyceride, etc.

Glycerol dehydration primarily results in two different products. One is acrolein, and the other is hydroxyacetone (HA) or acetol which can be further converted into 1,2 and 1,3-propanediol through hydrogenation.^{7,8} Acetol plays a very important role in organic synthesis and intermediates. Also, it is used in industries like food, dyes and additives.⁹ The price of acetol is high and it is produced industrially from petroleum resources. Crude petroleum reserves are depleting day by day and hence a bio-based source of acetol is an obvious choice of research. In the literature, several transition metal catalysts have been tested for glycerol dehydration. Copper is well known for the lower ability to cleave the C-C bonds of a glycerol molecule, resulting in undesirable degradation products.¹⁰ Huang et al.,¹¹ have prepared silica-supported

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CuO catalyst by gel precipitation technique due to strong copper/support interaction, and this catalyst proves to be much more active. They have reported that the conversion of glycerol is 73%. This is due to high copper dispersion and small metal particle size. Kim et al.,¹² have used chromium to promote the activity of copper. They have done co-precipitation of chromium with copper which dramatically increases the activity of glycerol, converts 87% to 1,2propanediol with 84% selectivity. Because of the synergistic effect of Cu and Cr the activity of copper chromite catalyst is higher than an individual catalyst.^{13,14} Copper increases the intrinsic catalyst activity but is easily sintered. In the catalyst, chromium acts as a stabiliser to reduce the sintering rate. Sato *et al.*,¹⁵ have shown that basic support (MgO, CaO, ZnO) effectively shows low acetol selectivity but acidic support (SiO₂, Al₂O₃, ZrO₂, Fe₂O₃) effectively promotes acetol selectively. Copper chromite is one of the efficient catalysts for converting glycerol to acetol.^{16,17} In addition, the low oxidation state of copper species in the cubic spinal form is very important for a catalytic application. Vasiliadou and Lemonidou¹⁸ have used copper supported on mesoporous silica for glycerol hydrogenolysis reaction. They observed that strong deactivation for this catalyst is due to copper particle sintering and strongly adsorbed carbonaceous deposit in the mesoporous structures. Depending on the catalyst and the operating conditions, the reaction of glycerol hydrogenolysis proceeds through two mechanisms.^{9,19,20} In one of the mechanism, dehydration of glycerol to form acetol on acid sites was followed by hydrogenation step on metal sides. Another mechanism is where dehydrogenation of glycerol to glyceraldehydes over basic site was followed by dehydration to acetol and finally hydrogenation to propylene glycol. Since hydrogenation requires high hydrogen pressure so side reaction occurs to form several by-products including ethylene glycol, lactic acid, propionic acid, etc.9,21,22

In this study, acetol production was optimized with the help of silica-supported copper chromite catalyst. The catalyst was synthesized from acid hydrolysis of sodium silicate. The active component copper chromite was added during the synthesis of silica. The catalyst was activated in a hydrogen atmosphere before glycerol dehydration. The catalyst was characterized by BET surface area, FESEM, XRD, TGA, H₂-TPR, NH₃-TPD, pyridine FTIR. The reaction was carried out with different catalytic system by varying reaction conditions. Based on the reaction products a mechanism have been proposed for getting high selectivity of acetol.

2. Experimental

2.1 Materials

Glycerol (AR grade) was purchased from (Nice chemical Pvt. Ltd.) for dehydration studies. Acetol (Sigma-Aldrich) was used as a reference for HPLC calibration. Sodium silicate (Na₂SiO₃.9H₂O, Loba Chemie), Polyvinyl alcohol (PVA, Mol. wt. 85000–124000, S. D. Fine Chem. Ltd.) were used for silica support preparations. Phenol (AR grade) was used to increase the porosity of the silica matrix. The active compound copper chromite (CuO.CuCr₂O₄) was purchased from Spectrochem India.

2.2 Catalyst preparation

Silica supported copper chromite catalyst was prepared from acid hydrolysis of sodium silicate (Na₂SiO₃) by sol-gel technique.²³ Polyvinyl alcohol (PVA) was added as a stabilizer to get regular particle sizes. A small quantity of phenol was added to increase the porosity in the silica matrix. During hydrolysis stoichiometric amount of copper, chromite was added to incorporate into the silica matrix. A typical reaction scheme was as follows. 2 gm of PVA was dissolved in 100 mL of distilled water and the required quantity of sodium silicate solution was added to it. The mixture was heated till 60 °C, under agitated condition using magnetic stirrer and 10 gm of phenol was added into the mixture. 2 N HCl solution was added dropwise into the mixture in heating and stirring condition to make the solution acidic. The addition of acid was continued up to initiation of cloud formation. Then desired amount of copper chromite powder (pass through 75 micron mesh size) was added into the solution. The pH of the mixture was adjusted to 1–2 by the addition of 2 N HCl solution till the end. The heating and stirring were continued for another 2 h. The reaction mixture was left for 24 h. Then the precipitate was filtered and washed with distilled water several times until the removal of free acid. The precipitate was dried in an air oven at 100 °C until constant weight. Then it was grounded and calcined in a muffle furnace at 500 °C for 4 h. The catalyst was activated in a tubular furnace at 350 °C for 4 h in a hydrogen atmosphere. The yield of the blank silica was 10 g for the typical compositions and the loading level was calculated based on the atomic weight % of copper as per molecular formula $(CuO.CuCr_2O_4)$ provided by the supplier to maintain the (Cu:SiO₂) mass ratio. The composition of the different catalyst system and nomenclature were given in Table 1.

2.3 Characterization of catalyst

Nitrogen adsorption-desorption isotherms measured at 77 K with a multipoint method using Quantachrome Nova touch surface area and a pore size analyzer. The catalyst samples were degassed at 200 $^{\circ}$ C for 4 h under vacuum.

| Serial No. | Sodium silicate (g) | Copper Chromite (g) | Cu : SiO ₂ Mass ratio | Nomenclature |
|------------|---------------------|---------------------|-------------------------------------|------------------|
| 1 | 47 | _ | 0:10 | SiO ₂ |
| 2 | 42.6 | 2.4 | 1:9 | SiCuCr10 |
| 3 | 37.8 | 4.8 | 2:8 | SiCuCr20 |
| 4 | 33.1 | 7.4 | 3:7 | SiCuCr30 |
| 5 | 28.4 | 9.8 | 4:6 | SiCuCr40 |

 Table 1.
 Compositions and nomenclature of the catalyst.

The images of surface morphology and the elemental mapping of the catalyst were determined by Field Emission Scanning Electron Microscopy (FESEM) using Sigma 300 with EDAX (Ametek) at different magnification level. The powder was gold-coated before FESEM studies and elemental mapping.

X-ray diffraction (XRD) patterns of catalysts were obtained at room temperature using a Rigaku, Japan Diffractometer (Smart Lab, 9 kW) equipped with a vertical goniometer. The scans were collected in the range of $2\theta = 10-80$ using copper (CuK α 1 radiation, $\lambda = 1.54056$ nm, 45 KV and 200 mA) at the scanning speed of $0.05^{\circ}(2\theta)$ /s. The diffractograms of the experiment were compared with the ICDD powder diffraction file database.

The thermal stabilities of the catalysts were determined by thermogravimetric analysis (TGA) using a SHIMADZU thermogravimetric analyzer DTG 60 model. The catalyst sample was heated in a platinum pan from room temperature to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Temperature programmed reduction (H₂-TPR) of silicasupported copper chromite catalyst was performed in Quantachrome ChemBet Pulsur chemisorption flow analyzer equipped with thermal conductivity detector (TCD). The reduction experiment was carried out in a U-shaped quartz reactor. Exactly 0.1 g of powdered sample was placed in the reactor. Prior to the reduction, the catalyst was pre-treated to 200 °C at the heating rate of 10 °C/min in helium gas flow of 80 mL/min. After 30 min at 200 °C the catalyst was cooled down to room temperature in Helium (He) atmosphere. For reduction, a reducing gas (5% H₂ in Ar) was used at the flow rate of 80 mL/min. The temperature was gradually increased from ambient temperature to 750 °C at the heating rate of 10 °C/min. H₂ consumption was monitored by the thermal conductivity detector (TCD) continuously.

To determine the number of acid sites of the catalyst' ammonia (NH₃) temperature-programmed desorption (TPD) was performed in the above instrument. Before carrying out the TPD experiment of the catalyst, about 0.1 g of sample was pre-treated in Helium flow (80 mL/min) at 200 °C at heating rate 10°/min for the 30 min. After cooling the catalyst in a helium atmosphere to 40 °C the helium ammonia gas mixture (5% NH₃–95% He) flow was started and continued up to 30 min. Then pure helium gas flow was started at room temperature for 30 min to remove any ammonia gas present

in the system. Thermal treatment was performed and the temperature rose from 50 °C to 750 °C at 10°/min. In order to determine the acidity of the catalyst from NH_3 -TPD profiles' areas under the curves were integrated by Gaussian deconvolution of the peaks and amount of acidity was expressed in micromoles per gram of the catalyst.

To determine the nature of acid and strength of acid sites pyridine adsorbed FTIR was done (Shimadzu Corpn., Japan; IR-Prestige 21). Before recording analysis, all reduced catalyst samples and pyridine were taken in a separate Petri dish, and kept in a vacuum oven (500 mm Hg) overnight to reach equilibrium. Before analysis, the samples were taken out from vacuum oven and the spectrums were recorded in DRS mode.

2.4 Catalytic performance evaluation

Dehydration of glycerol was carried out in a stainless steel batch reactor of 500 mL capacity (Amar Equipment, India) equipped with an electrical temperature controller and a mechanical stirrer. The reaction was carried out at various temperatures at atmospheric pressure. 20% aqueous glycerol solution was fed into the reactor vessel and 1 g reduced catalyst was added into the reactor.²⁴ The glycerol and catalyst mixture was agitated at a speed of 700 rpm to create a slurry reaction mixture. The distilled product was condensed by passing the vapour through a water condenser in which chilled water at 10 °C was circulated. Initial fraction (from room temperature to 100 °C) of the distilled product was discarded as it is considered that the dehydration reaction starts above 100 °C. The distilled product was collected after reaching the desired temperature (180 °C, 200 °C, 220 °C, 240 °C) and analyzed by HPLC (high-pressure liquid chromatography). The reaction was continued up to 3 h at the reaction temperature. The distilled products were collected, sealed and stored for analysis. The residue in the reactor was collected and after weighing it was washed with methanol followed by filtration and air drying to separate the spent catalyst.

2.5 HPLC analysis of distillates

To quantify the products obtained from the catalytic dehydration of glycerol high-performance liquid

chromatography (HPLC) from waters was used.²⁵ The HPLC system was equipped with two pumps (waters 515 HPLC pump) and UV/Vis detector (water 2487 dual λ absorbance detector). Acetonitrile and water mixture were used as the mobile phase at the volume ratio 40:60 in isocratic mode. The flow rate of the mobile phase was fixed at 0.1 mL/min. C-18 column was used in this study.²⁶ The injection volume was 20 μ L. The terms of conversion and selectivity were defined by the following expression.

$$= \frac{\text{Initial mass of glycerol and catalyst} - \text{Residue after reaction}}{\text{Initial mass of glycerol}} \\ \times 100$$

The selectivity of the products (acetol, acetaldehyde and acetic acid, etc.) was calculated based on the formula:

Product selectivity
$$\% = \frac{\text{Mass of specific product}}{\text{Mass of all liquid products}} \times 100$$
(2)

3. Results and Discussion

Silica-supported copper chromite catalyst are prepared by acid hydrolysis of sodium silicate and copper chromite is added during the preparation of silica. The precipitated material is washed and dried in air oven followed by calcination at 500 °C for 4 h in a muffle furnace. The properties of the synthesized catalyst are evaluated by BET specific surface area, FESEM, XRD, TGA, H₂-TPR, NH₃-TPD and pyridine FTIR.

3.1 Catalyst characterization results

3.1a *BET surface area*: The surface area and pore volume of silica-supported copper chromite are given in Table 2. The surface area and pore volume are highest for 30 wt% copper chromite containing silica followed by SiCuCr40. The BJH pore diameter is similar for 30 wt% and 40 wt% sample. Literature reported that the catalyst prepared by precipitation gel technique is stable due to strong interaction with the silica

matrix.^{11,27} Vasiliadu *et al.*,¹⁸ have reported that the activity of the highly dispersed copper in a mesoporous silica-based catalyst for the hydrogenolysis of glycerol reduces due to the strong adsorption of carbonaceous material inside the pore structure.

3.1b *Field emission scanning electron microscope* (*FESEM*): FESEM micrographs of the copper chromite samples at 25 K magnification are shown in Figure 1. Catalysts are gold-coated for FESEM studies. The images show that the powders catalysts are irregular in shape and SiCuCr40 catalyst is different from others. This may be due to the higher loading of copper chromite where the proportion of silica reduces in the silica matrix, which results in a reduction of the probability of condensation between silica powders.

3.1c EDX (energy dispersive X-rav *spectroscopy*): Figure 2 is the elemental mapping of SiCuCr20, SiCuCr30 and SiCuCr40. This shows copper and chromium atoms are evenly distributed throughout the silica matrix. Table 3 is the EDX analysis of silicasupported copper chromite catalyst. The atomic per cent of copper and chromium is increasing order as the doping level increases in the silica support. EDX study is mainly the surface concentration of atoms, which are responsible for catalytic purposes. As expected 40 wt% samples show the highest content of copper and chromium. All the samples contain sodium ion which is common for precipitated silica samples. Kinage et al.,²⁸ has reported that 5 wt% of sodium loaded in metal oxide greatly enhances the acetol selectivity in glycerol conversion.

3.1d *Powder X-ray diffraction (XRD)*: Figure 3 shows the XRD diffraction of calcined silicasupported copper chromite catalyst. A broad and diffuse peak is observed at 20° in lower loading copper chromite as compared to higher ones. This peak is attributed to SiO₂. This is due to the diffraction of the amorphous nature of the silica. The strong crystalline peak of silica is observed at $2\theta = 31.9$ (ICDD# 89-1666) at a lower level of loading which reduces at higher catalyst loading.²⁹ The calcined samples

 Table 2.
 Surface area and pore volume of silica-supported copper chromite.

| Sample | BET surface area (m ² /g) | BJH Surface area (m ² /g) | Pore volume V_p (cm ³ /g) | Pore diameter D _p (nm) |
|----------|--------------------------------------|--------------------------------------|--|-----------------------------------|
| SiCuCr10 | 35.99 | 16.36 | 0.088 | 3.6 |
| SiCuCr20 | 76.54 | 43.14 | 0.36 | 3.6 |
| SiCuCr30 | 144.91 | 106.52 | 0.53 | 14.2 |
| SiCuCr40 | 96.32 | 65.71 | 0.45 | 14.3 |

(1)



Figure 1. FESEM images of (A) SiCuCr10, (B) SiCuCr20, (C) SiCuCr30 and (D) SiCuCr40 catalyst at 25 K magnification.

show peaks at 35.5 and 37.5 which are the mixture of the monoclinic structure of CuO (ICDD#89-5899) and tetragonal spinel structure of CuCr₂O₄ (ICDD#21-0874) in which spinel proportion is more.^{30,31} The tetragonal spinel structure of copper chromite contains copper and chromium atoms placed on the tetrahedral and octahedral spaces.³²

Figure 4 shows the XRD diffraction of the reduced form of silica-supported copper chromite catalyst. After reduction, the diffraction peak changes position indicating the change in compositions. In the reduced sample, the monoclinic structure of CuO and tetragonal spinal CuCr₂O₄ structure reduces and a new phase for metallic cubic Cu ($2\theta = 43.4$ and 50.1) (ICDD# 89-2838), cubic Cu₂O ($2\theta = 36.4$ and 65.25) (ICDD# 78-2076) and rhombohedral Cr₂O₃ ($2\theta = 24.4$ and 33.5) (ICDD# 84-1616) are observed. The possible reaction scheme is as follows

$$CuO.CuCr_2O_4 \xrightarrow{H_2} Cu + Cu_2O + Cr_2O_3 + H_2O$$

Plyasova *et al.*,³³ has reported that the copper chromite reduces into the Cu⁰ and Cu⁺¹ and Cr₂O₃ in a hydrogen atmosphere. The crystallite size of the CuCr₂O₄, CuO, Cu₂O, Cr₂O₃ and Cu are calculated by full-width at half maximum (FWHM) from the values of diffraction peaks, respectively by Scherrer equation, $L = \frac{K\lambda}{\beta Cos\theta}$ where L is the crystallite size, K is the Scherrer constant (0.89), λ is the wavelength of radiation in radiant, θ is the Braggs diffraction angle, β is the FWHM. The crystallite sizes of calcined and reduced catalysts are tabulated in Table 4 and Table 5.

The diffraction peaks for reduced SiCuCr10 sample is very weak due to the low amount of copper chromite present in the silica matrix and is not shown in the reduced catalyst.

3.1e *Thermo gravimetric analysis (TGA)*: Figure 5 is the TGA curve of silica-supported copper chromite catalyst. 10 wt% and 20 wt% copper chromite loaded samples shows nearly 10 wt% of weight loss below



Figure 2. Elemental mapping of A) SiCuCr20, B) SiCuCr30, C) SiCuCr40 and D) EDX of SiCuCr40 catalyst in FESEM.

Table 3. EDX analysis of copper chromite containing silica.

| | | Atomic Weight % | | | | | |
|--|------------------------------|------------------------------|----------------------------------|----------------------------------|------------------------------|--|--|
| Sample | Cu | Cr | Si | 0 | Na | | |
| SiCuCr10 SiCuCr20 SiCuCr30 SiCuCr40 | 0.37 1.62 3.38 5.51 | 0.34 2.70 5.77 9.60 | 23.83 23.02 18.27 15.55 | 60.37 60.11 58.23 54.94 | 9.42 8.55 6.79 8.60 | | |

100 °C. This is due to adsorbed moisture by the silica samples. SiCuCr40 sample does not show any moisture adsorption as the silica proportion is less in the sample and the sample shows a low amount of weight loss (nearly 4 wt%) up to 700 °C.³⁴ The residue at 700 °C is highest for 40 wt% loading and it reduces as the loading decreases. This is expected as the copper chromite is stable at high temperature and the weight loss takes place from the condensation of the silica matrix.



Figure 3. XRD patterns of calcined catalysts at different loading. (X) Monoclinic CuO,(O) Tetragonal spinal CuCr₂₋O₄, (\bullet) Silica.

3.1f Hydrogen temperature programmed reduction $(H_2$ -TPR): Dehydration of glycerol takes place in the presence of an acidic catalyst. Literature reported



Figure 4. XRD patterns of reduced catalysts at different loading. (c) Cubic Cu, (y) Rhembohedral Cr_2O_3 , (z) Cubic Cu_2O , (\bullet) Silica.

that copper chromite is an effective catalyst for glycerol dehydration. Pre-reduced copper-based catalyst is an indispensable part of the glycerol hydrogenolysis. To have high activity, reduction conditions would have a great influence on catalytic performance. The TPR patterns of the calcined catalysts are shown in Figure 6. No peak is observed for 10 wt% loading catalyst (SiCuCr10) but for 20 wt% loaded sample (SiCuCr20) shows hump above 250 °C and is continued to 550 °C temperature. That means some amount of hydrogen has been consumed above 250 °C. Similarly, for SiCuCu30 catalyst, the hydrogen consumption started above 250 °C and a broad peak near 450 °C is



Figure 5. TGA curve for silica-supported copper chromite catalyst.

Temperature(°C)

observed. In the case of SiCuCr40, the hydrogen consumption started above 250 °C with a peak value of 320 °C for 1st peak and 500 °C for the second peak. The different peak position may be due to the size of the CuO species in the matrix. The surface CuO is more easily reducible than the bulk. XRD analysis of 30 wt% and 40 wt% sample (Table 5) supports the formation of Cu⁰, Cu¹⁺ and Cr₂O₃. The change of catalytic phase Cu²⁺ to Cu⁺¹ has a great influence on glycerol dehydration.

Luo *et al.*,³⁵ proposed that the metallic copper is primarily responsible for the activation of hydrogenation while Cu^+ is for dehydration due to its presence of Lewis acid sites.^{36–38} Ten dam and

Table 4. Crystallite size calculated from XRD data for calcined catalyst.

| | CuO (nm) | | | CuCr ₂ O ₄ (nm) | | |
|----------|------------------|-------------------|-------------------|---------------------------------------|------------------|-------------------|
| Sample | $2\theta = 35.6$ | $2\theta = 53.64$ | $2\theta = 56.44$ | $2\theta = 37.5$ | $2\theta = 42.2$ | $2\theta = 64.72$ |
| SiCuCr10 | 12.78 | - | 12.03 | _ | 16.83 | _ |
| SiCuCr20 | 16.44 | 25.61 | 8.83 | 10.8 | 19.55 | 7.74 |
| SiCuCr30 | 22.41 | 16.61 | 9.09 | 20.45 | 14.48 | 7.35 |
| SiCuCr40 | 23.44 | 14.24 | 10.03 | 24.54 | 15.96 | 8.07 |

 Table 5.
 Crystallize size calculated from XRD data for reduced catalyst.

| | Cu (nm) | | Cu ₂ O (nm) | | Cr ₂ O ₃ (nm) | |
|----------|------------------|------------------|------------------------|-------------------|-------------------------------------|------------------|
| Sample | $2\theta = 43.4$ | $2\theta = 50.1$ | $2\theta = 36.4$ | $2\theta = 65.25$ | $2\theta = 24.4$ | $2\theta = 33.5$ |
| SiCuCr20 | 17.24 | _ | 14.99 | 1.01 | 5.35 | 37.06 |
| SiCuCr30 | 13.58 | 23 | 17.03 | 5.38 | 3.3 | 33.36 |
| SiCuCr40 | 12.8 | 23.54 | 16.94 | 3.7 | 8.96 | 20.12 |



Figure 6. Temperature Programmed Reduction (TPR) profile for silica-supported copper chromite catalyst.

Hanefeld³⁹ have discussed the dehydration mechanism of vicinal alcohol (Scheme 1). A Bronsted acid will help in the elimination of secondary alcohol which is subsequently dehydrated to acrolein (Scheme 2). Lewis acid more easily coordinates with primary alcohol which is easily accessible by the catalyst sites. This will lead to the formation of hydroxyacetone (HA) or acetol. Vasiliadou et al.,¹⁸ have mentioned about the strong adsorption of glycerol on copper via its terminal C-O bond, and the fact that it is not affected by the presence or absence of solvent. Based on the above discussion we are proposing that Cu₂O is the active form of the catalyst, which acts as Lewis acid, and will produce acetol in glycerol dehydration reaction. Hence, we have decided to reduce the catalyst at 350 °C for the 4 h in hydrogen atmosphere.

3.1g Ammonia temperature programmed desorption (NH_3-TPD) : Dehydration of glycerol is greatly influenced by acidic catalyst/support. To determine the acidic properties of catalyst towards the formation of a dehydration product, NH₃-TPD (Ammonia

Temperature programmed desorption) is carried out (Figure 7). It investigates the amount of acid sites and the strength of acid distribution. In the NH₃-TPD experiment, ammonia is adsorbed on acid sites of catalyst due to its basic nature. The maximum temperature in temperature versus TCD signal plot gives information of acidity of the catalyst and area under the desorption peak indicates acidic strength of the catalyst.⁴⁰ There are three ranges of ammonia desorption peak: weak, intermediate and strong.²² It is said that if the area under the desorption curve is large then acid sites of the catalyst is higher in that region. Strength of the solid acid sites within TPD profile can be classified by NH₃ desorption temperature ranges from 100-200 °C as weak' 250-400 °C as moderate and 400-650 °C as strong.

The SiCuCr20 showed a peak at 120 °C indicating the presence of weak acid sites (164 μ mol.g⁻¹). This range of peak corresponds to weak acid sites for a surface hydroxyl group.⁴⁰ The concentration of these sites is not important catalytically. While SiCuCr30 does not show any distinct peak but a hump at 150 °C in the low region with acidity 127 μ mol.g⁻¹ and 2nd peak at 320 °C in the moderate region with surface acidity 234 μ mol.g⁻¹. This peak is closely related to surface acid properties. SiCuCr40 shows a broad peak at 583 °C but it starts above 150 °C. The cumulative surface acidity for SiCuCr40 is $1250 \,\mu mol.g^{-1}$. Higher surface acidity for the catalyst is very much influential for catalyzing the glycerol dehydration to acetol. The nature of the surface acidity Bronsted/or Lewis acid sites is not distinct from the NH₃-TPD studies. This may be due to the dry state adsorption of NH₃ gas on catalyst surface at a higher temperature. To get more information about acidic sites, pyridine adsorption study by FTIR is carried out.

3.1h *Pyridine adsorption by FTIR*: The nature of acidic Brønsted/Lewis sites of Silica supported copper chromite is characterized by Pyridine adsorbed FTIR



Scheme 1. Reaction mechanism on catalyst surface.



Scheme 2. Reaction scheme for dehydration of glycerol.



Figure 7. NH₃-Temperature Programmed desorption profile for reduced silica-supported copper chromite catalyst.

spectra and are shown in Figure 8. In the case of SiCuCr20 and SiCuCr30 catalyst, no distinguished peaks are observed whereas SiCuCr40 has shown many strong peaks. That means that the catalyst surface is acidic in nature due to which it adsorbed pyridine vapour. The Pyridine adsorbed IR bands near 1605 cm^{-1} and 1454 cm^{-1} are assigned to Lewis acid site and the band at 1480 cm⁻¹ indicates both Lewis and Brønsted acid site.^{41,42} The existence of high Lewis acid site on SiCuCr40 compared to SiCuCr30 and SiCuCr20 seems to influence the conversion of glycerol and also the product distribution. A Brønsted acid will help in eliminating secondary alcohol whereas a Lewis acid more easily coordinates to a primary alcohol thereby weakening the C-O.⁴³ In fact, primary alcohol is more reactive than secondary alcohol if a non-acidic condition is applied.



Figure 8. Pyridine IR spectra of reduced silica-supported copper chromite catalyst with different loading.

Acid-catalyzed dehydration of glycerol takes place in two ways. Secondary alcohol dehydration proceeds *via* a relatively stable intermediate secondary carbocation, which is kinetically controlled. The primary alcohol dehydration *via* Lewis acid mechanism leads to the formation of acetol, which is the thermodynamically a more stable product. The free energy change in the dehydration reaction of glycerol to 3-hydroxypropyl *via* secondary alcohol is -70.2 kJ/mol whereas primary alcohol dehydration to acetol is -87.4 kJ/mole.⁴⁴

3.2 Catalyst activity test

Many reactions are happening simultaneously such as dehydration, degradation, polymerization, dehydrogenation, etc. (Scheme 3). The type of reaction depends on many factors such as type of catalyst, reaction temperature, concentration of catalyst, concentration of glycerol, stirring speed, etc. To minimize the effects, we have studied reactions with the same instrument with constant stirring speed.



Scheme 3. Reactions of glycerol into different product.

In the glycerol dehydration reaction, four categories of reactions are formed simultaneously. One is oligomerization, which leads to non-volatile products. Second is dehydration, and the others are three carbon atom containing products.⁴⁵ The third is the degradation product which is less than 3C atoms carbon compounds like acetaldehyde, acetic acid, etc.⁴⁶ The fourth category products are the hydrogen and water which do not contain carbon atom in their molecular structure.^{47,48} Among all the products, one of the dehydration product is acetol (distilled product) which is our prime concern and is used as a reference in analysis.

Dehydration is an endothermic process and proceeds more rapidly at a higher temperature. Glycerol dehydration with silica-supported copper chromite catalyst is studied over three different catalyst sample at 220 °C. The reaction is carried out with 20 vol% aqueous solution of glycerol with 1 gram of reduced catalyst sample for the duration of 3 h. Figure 9 is the percentage of glycerol conversion and percentage selectivity of distilled product for different silicasupported copper chromite catalyst. Here HPLC technique is used to determine the product compositions. Acetol production is the main product target of our objective. Hence product characterization is compared with reference to acetol yield. The results are shown for three catalyst system as no distilled product is obtained for SiCuCr10. This may be due to the absence of active sites of the catalyst. Glycerol conversion is highest reached 100% for SiCuCr40 catalyst and is lowest for SiCuCr30 catalyst. In the case of 30 wt% catalyst more viscous residue is left after reactions which may be oligomeric products due to which glycerol conversion into distilled product reduces.



Figure 9. Screening of different silica-supported copper chromite catalyst. Reaction conditions: Glycerol:Water 20:80 (vol%/vol%), Reaction temperature 220 °C, Catalyst amount 1 g and Reaction duration 3 h.

The acetol selectivity increases and is highest for SiCuCr40 which is near 70%. This is expected as the loading of active compounds (copper chromite) into silica matrix increases more acidic sites generated on the catalyst surface which are responsible for catalytic dehydration.⁴⁹ The selectivity of acetaldehyde is almost similar for the three catalyst system and is below 5%. But another compound selectivity (byproducts) is highest for SiCuCr20 which is nearly 70% and lowest for SiCuCr40 which is nearly 25%. The lower content of acetol selectivity and formation of by-products with SiCuCr20 and SiCuCr30 samples are due to its low content of acidic sites (164 and 234 μ mol.g⁻¹ respectively) in NH₃-TPD and absence of Bronsted and/or Lewis acid sites in the pyridine adsorbed FTIR analysis. At lower loading, by-products



Figure 10. Effect of reaction temperature on SiCuCr40 catalyst.

are formed in higher amounts because silica support is not fully covered by the copper chromite. When copper chromite loading increases, by-products decrease, and as a result, main product acetol selectivity increases. In lower loading, the reducibility of the catalyst also plays a key role in product selectivity and glycerol conversion. In glycerol dehydration, higher acidic sites of our synthesized catalysts are found to be a crucial part of product selectivity. So SiCuCr40 is found to be the best catalyst for glycerol dehydration.

3.2a Effect of reaction temperature on catalyst activity: Figure 10 shows the effect of reaction temperature on catalyst activity with SiCuCr40 in 20 vol% glycerol solution with 1 gram reduced catalyst for 3 h in the range of temperature $180-240 \text{ °C.}^4$

At 180 °C glycerol conversion is 47% and it reaches its maximum (100%) above 220 °C. At 220 °C glycerol conversion and acetol selectivity reaches a maximum of 70% with an increase in temperature. But at 240 °C, acetol selectivity drops drastically from 70% to 24.2% due to an increase formation of by-products.⁵⁰ This test indicates that at a higher temperature catalyst favours C-C bond cleavage and oxidation is carried out instead of dehydration. This could be promoted by the active phases of the catalyst.^{9,51} The major by-products formed are acetaldehyde due to C-C bond cleavage of glycerol and oxidation of acetaldehyde leads to form acetic acid formation. Thus, the high temperature is only favourable for acetol oxidation by SiCuCr40 catalyst.

3.2b Effect of catalyst amount on catalyst activity: The effect of catalyst loading on the dehydration reaction is studied in the range of 0.5-1.5 g catalyst at 220 °C and the results are presented in Figure 11. 20 vol% glycerol solutions



Figure 11. Effect of catalyst amount on SiCuCr40 catalyst.

are used and the reaction is continued up to 3 h in all cases. It is observed that the conversion of glycerol increased from 76 to 100% with an increase in catalyst weight from 0.5 to 1.5 g. The selectivity of acetol initially increased from 56 to 70% for an increase in catalyst weight from 0.5 to 1 g, but after that, it reduces to 63% for 1.5 gm of catalyst loading. The decrease in acetol product may be due to the formation of side products at higher catalyst loading. The increase in glycerol conversion with increasing catalyst loading could be due to the more available active sites on the catalyst surface for the glycerol dehydration, which leads to excess dehydration to form acetol and lower degraded products.

3.2c Effect of substrate ratio on catalyst activity: The effect of glycerol concentrations on the conversion of glycerol and selectivity pattern is studied in the range of 10–40 vol% glycerol with 1 g SiCuCr40 catalyst at 220 °C for 3 h and the results are shown in Figure 12.

The conversion of glycerol remains constant at 100% while the selectivity of acetol increased from 62 to 69% with the increase in glycerol concentration from 10–20 vol%. Interestingly, acetol selectivity decreased from 70 to 35.46% at 40 vol % glycerol solution. Acetol selectivity decreases as undesired reaction product may form at high concentration of glycerol aqueous solution. According to Figure 12, the highest selectivity of acetol is obtained at 20 vol% of glycerol concentration which is found to be the optimum glycerol concentration.

3.2d *Effect of reaction time on catalyst activity*: The effect of the reaction time on catalyst activity is studied with optimized temperature



Figure 12. Effect of substrate ratio on SiCuCr40 catalyst.



Figure 13. Percentage product selectivity of products after 60 min interval up to 3 h reaction time.

(220 °C) for 20 vol% glycerol concentration with optimized (1 gm) catalyst and the results are shown in Figure 13. Samples are collected after 60 min interval and are analysed by HPLC. The fractions are collected after reaching the desired reaction temperature. The first fraction (60 min) shows the highest acetol selectivity (65%) which reduces to 35% in the second fraction and 17% in the last fraction. Acetic acid selectivity is less than 5% and is absent in the last fraction. In the second fraction acetaldehyde shows 28% selectivity.⁵²

3.3 Recycle of the catalyst

Finally, the catalyst (SiCuCr40) stability is evaluated under optimum conditions. The experiment shows that



Figure 14. XRD of reduced and spent catalyst of SiCuCr40 catalyst. (c) Cu, (y) Cr_2O_3 , (z) Cubic Cu₂O, (\bullet) silica.



Figure 15. Raman spectroscopy of reduced and spent SiCuCr40 catalyst.

glycerol conversion decreases from 100% to 93.3% whereas the main product acetol selectivity also decreases from 70% to 19.4%, respectively. The support SiO₂ in catalyst SiCuCr40 is thermally stable but active Cu has a tendency to lose or agglomerate after each catalytic test. This maybe the reason behind the decrease in the acetol selectivity of the glycerol dehydration. These findings indicate that all catalysts are hydrothermally stable and no coke formation occurs in the reused catalyst based on XRD and Raman spectroscopy.

At the end of the reaction, all the catalysts are recovered, filtered and washed with methanol and dried in a vacuum oven until constant weight. XRD analyses of the spent and reduced SiCuCr40 catalyst are shown in Figure 14. XRD pattern shows that Cu₂O ($2\theta = 36.4$) the active compound is absent in spent catalyst through metallic Cu ($2\theta = 43.4$ and 50.1) is still present. As the active compound Cu₂O is absent, this will lose its catalytic behaviour. The catalyst should be regenerated after each reaction. In Figure 15 Raman spectroscopy shows that there is no coke formation on the catalyst surface after dehydration reaction.

The oxidised catalyst (SiCuCr40) is used for glycerol dehydration and it gives 23.3% acetol production with glycerol conversion of 62%. All the above discussion supports the functions of Cu^{1+} in acetol production.⁵³

4. Conclusions

Silica-supported copper chromite catalyst were synthesised by acid hydrolysis of sodium silicate. The BET surface area for the synthesized catalyst is maximum for SiCuCr30 followed by SiCuCr40. The elemental mapping shows even distribution of copper and chromium throughout the catalyst. EDX result showed the increasing atomic percentage of copper and chromium with an increasing amount of loading. XRD spectra of calcined catalyst showed the tetragonal spinal structure of CuCr₂O₄ and monoclinic CuO. XRD spectra of reduced catalyst showed the presence of Cu^0 , Cu^{+1} and Cr_2O_3 . The reducing temperature was 350 °C determined by H2-TPR analysis where Cu^{+2} ion converted to Cu^{+1} ion. The highest amount of acidic sites (1250 μ mol.g⁻¹) was obtained for (SiCuCr40) 40 wt% catalyst in NH₃-TPD studies. Pyridine adsorption FTIR showed strong Lewis acid sites for reduced catalysts. Cuprous oxide which acts as Lewis acid sites on catalyst surface was responsible for high acetol selectivity in glycerol dehydration. Glycerol dehydration was carried out with four different catalysts at different temperatures. The optimized reaction temperature was 220 °C for 3 h with 1 gm catalyst and 20 vol% aqueous glycerol solution for 3 h. SiCuCr40 showed the highest acetol selectivity (70%) and nearly 100% glycerol conversion. The XRD analysis of the spent catalyst showed the presence of copper metal but the absence of Cu^{+1} ion indicates the loss of activity after the reaction. The calcined SiCuCr40 catalyst (oxidised form) showed 23.3% acetol selectivity and low glycerol conversion 62%. Spent SiCuCr40 catalyst also showed low acetol selectivity (19.4%) with 93.3% glycerol conversion. Hence, cuprous ion is the reason for high acetol selectivity for glycerol conversion.

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