



Influence of niobium on carbon nanofibres based Cu/ZrO₂ catalysts for liquid phase hydrogenation of CO₂ to methanol



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ABSTRACT

A series of carbon nanofibres supported Cu/ZrO₂/Nb₂O₅ catalyst synthesized by deposition precipitation method were extensively investigated in relation to their performance in hydrogenation of CO₂ to methanol. In order to study the promotion effect of niobium, catalysts were loaded with 0.4, 0.8 and 1.2 wt.% of Nb₂O₅. Incorporation of Nb₂O₅ facilitated copper reduction by exhibiting a shift of highly reduced copper peak to lower temperature. Likewise, surface enrichment of copper was also enhanced by introduction of Nb₂O₅ to the catalysts. Activity studies of Nb₂O₅ doped Cu/ZrO₂ catalysts were evaluated in a slurry reactor with a CO₂/H₂ gas mixture of 1:3 volume ratio, 180°C temperature and 3.0 MPa total pressure. The highest activity was achieved with the incorporation of 0.8 wt.% of Nb₂O₅, illustrating the high degree of CuO crystallization on the surface of catalyst are beneficial for the generation of copper catalyst with enhanced activities.

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1. Introduction

Chemical transformation of carbon dioxide into petrochemical products has been extensively investigated over the last few decades [1]. At present, catalytic reduction of CO₂ to methanol is considered as a promising economical route which could contribute to CO₂ mitigation. In fact, current industrial scale methanol synthesis is carried out over Cu–ZnO/Al₂O₃ catalysts with a mixture of syngas (CO/H₂) and CO₂ at high operating temperature 300 °C [2]. Furthermore, alumina based catalysts displayed poor activity for CO₂ hydrogenation to methanol due to its high water-affinity [3,4]. These research outcomes have stimulated the development of new catalytic system for hydrogenation of pure CO₂ to methanol. Nevertheless, the lack of probative evidence on the mechanism of CO₂ hydrogenation is the major obstacle for the development of new catalyst formulation [5].

Carbon nanofibres (CNFs) with a high surface area and hydrophobic nature could be a good alternative as a catalyst support for hydrogenation of pure CO₂ to methanol. ZrO₂ doped Cu catalysts have shown promising results for CO₂ hydrogenation [4,6].

Incorporation of promoters like ZnO, Cr₂O₃ and Nb₂O₅ into the Cu/ZrO₂ catalysts have resulted in higher activity and selectivity to methanol in the CO₂ hydrogenation reaction [2,7]. The improved performance of the niobia-supported catalysts was attributed to the formation of new active sites due to the greater interaction of support with the metal atoms [8]. In addition, niobia-supported catalysts were reported to have low acidity property and therefore exhibited better activity and selectivity in hydrogenation reaction of CO and CO₂ [9–11].

In the above context, the specific objectives of this work are to investigate the effect of Nb₂O₅ on the physical, structural and activity of CNFs based Cu/ZrO₂ catalysts in the CO₂ hydrogenation to methanol. The CNFs based Cu/ZrO₂ catalyst was used as reference in the catalytic tests.

2. Experimental

2.1. Functionalization of carbon nanofibres (CNFs)

Surface of CNFs was modified by treating with 35 vol. % nitric acid solution. The refluxing was continued for 16 h at elevated temperature of 90 °C. After refluxing, CNFs were cooled to room temperature and filtered by vacuum filtration. After washing

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several times with distilled water, oxidized CNFs (CNFs-O) were dried overnight in oven at 100 °C.

2.2. Synthesis of Nb₂O₅ doped Cu/ZrO₂/CNF (CZC-Nb) catalysts

Deposition precipitation method was utilized for the synthesis of Nb₂O₅ promoted Cu/ZrO₂/CNF catalysts [12,13]. A series of catalyst containing a constant loading of 15 wt.% Cu and 15 wt.% ZrO₂ with varying Nb₂O₅ content ranged from 0.4, 0.8 and 1.2 wt.% were synthesized. A known quantity of zirconyl nitrate hydrate (SIGMA-ALDRICH, USA) was added gradually to the solution of Cu (NO₃)₂·3H₂O (R&M Chemicals, UK). When both nitrate salts were completely dissolved, required quantity of CNFs-O was added to the solution. The suspension was vigorously stirred and heated to 90 °C, then the slurry solution was precipitated with 0.1 g/mL of urea solution. The precipitates were aged at 90 °C for 20 h, cooled and filtered by vacuum filtration. The precipitates were dried in oven at 110 °C for overnight. The catalysts were calcined in N₂ flow at 450 °C for 3 h and labelled as CZC-Nb0.4, CZC-Nb0.8, and CZC-Nb1.2 catalysts. A reference CNF based Cu/ZrO₂ catalyst with a nominal composition of Cu:Zr=50:50 (wt.%) was prepared using similar technique described above.

2.3. Characterization

PANalytical model Empyrean X-ray diffractometer was employed for phase studies of catalyst components. PANalytical High Score Plus software was used for phase identification. The XRD data were measured at room temperature from 20° to 80° 2θ Bragg angle.

Nitrogen adsorption-desorption isotherms technique was carried out for investigations of catalysts surface area and pore volume using Micrometrics ASAP 2020 [3].

Copper metallic surface area (S_{Cu}), dispersion of Cu (D_{Cu}), average particle size (d_{Cu}) and distribution of Cu content (R_{Cu}) were determined by N₂O chemisorption technique [14–17]. Catalysts were first reduced with H₂ at 500 °C. Reduced samples were cooled in He flow to 60 °C and purged for 30 min. Then N₂O gas was introduced for 1 h. Residual N₂O was flushed out by He flow for 1 h. Finally, the samples were reduced for the second time at 500 °C. Surface area and dispersion of Cu were measured by assuming 1.46×10^{19} Cu_{at}/m² surface atomic density and Cu:N₂O=2 stoichiometry, respectively. Average particle size (d_{Cu}) was obtained by a relationship displayed as follows [3,18,19].

$$d_{Cu}(nm) = \frac{104}{D_{Cu}(\%)}$$

The distribution of Cu content was estimated by the following equation [20].

$$R_{Cu} = \frac{Cu^0 \text{ surface area}}{Cu \text{ content} \times \text{BET surface area}}$$

Transmission Electron Microscopy (TEM) was used to study morphology and particle size measurement of the catalysts. Zeiss LIBRA 200TEM with accelerating voltage of 200 kV was utilized for this purpose [21].

Temperature Programmed Reduction (TPR) technique was used to study the reduction behaviour of catalyst and metal support interactions. TPDRO1100 MS equipped with thermal conductivity detector (TCD) was used in temperature range of 30–800 °C with heating rate of 10 °C min⁻¹. The analyses were performed in 5 vol.% H₂/N₂ flow with a flow rate of 20 cm³ min⁻¹.

X-ray photoelectron spectroscopy was utilized to investigate chemical nature and surface composition of Cu. X-ray

photoelectron spectroscopy (XPS, Thermo-Fisher K-Alpha) equipped with monochromitized AlK source having ultimate energy resolution of ≤0.5 eV was used in XPS studies. Avantage software was used for peak fitting and chemical state identification.

Surface basicity was examined by using CO₂ temperature programmed desorption (CO₂-TPD). Prior to TPD analysis, samples were subjected to temperature of 500 °C for 60 min under inert atmosphere to desorb the surface moisture and other adsorbed molecules. Pre-reduced catalysts were cooled to room temperature and were saturated with pure CO₂. The adsorption of gases was continued for 1 h at 90 °C and physisorbed molecules were desorbed with He flow. The adsorbed gas was desorbed in temperature range of 40–800 °C. Desorption of CO₂ at relative degree of temperature were quantified by calibrated TCD.

2.4. Catalytic Tests

Activity of catalysts in CO₂ hydrogenation to methanol was evaluated in autoclave slurry reactor (Parr 4593). Prior to the activity studies, the catalysts were reduced for 6 h in H₂ with flow rate of 2000 cm³/h at 380 °C. A 0.5 grams of reduced sample was suspended in 25 ml of ethanol placed in reaction vessel. The reactor was purged at room temperature and then pressurized with mixture of H₂/CO₂ gases with 3:1 molar ratio to the desirable pressure of 3.0 MPa. The reaction studies were performed at 180 °C. Reaction mixture was agitated by stirrer and a speed of 1300 rpm was selected to avoid mass diffusion constrains. Analysis of reactants and products were carried out on Agilent GC-6890 system chromatograph equipped with a flame ionization and thermal conductivity detectors. Experiments were repeated three time to check for reproducibility. Measurements are in general reproducible within a maximum of 10%. Turnover frequency of methanol was calculated by following formula [22,23]:

$$TOF_{MeOH} (s^{-1}) = \frac{A \times N_a}{3600 \cdot S_{Cu} \cdot n_a}$$

where A represents methanol activity in mol/g h, N_a is Avogadro's number (6.023×10^{23}), S_{Cu} denotes metallic copper surface area in m²/g and n_a designates number of Cu atoms in a monolayer ($n_a = 1.469 \times 10^{19}$ atoms/m²)

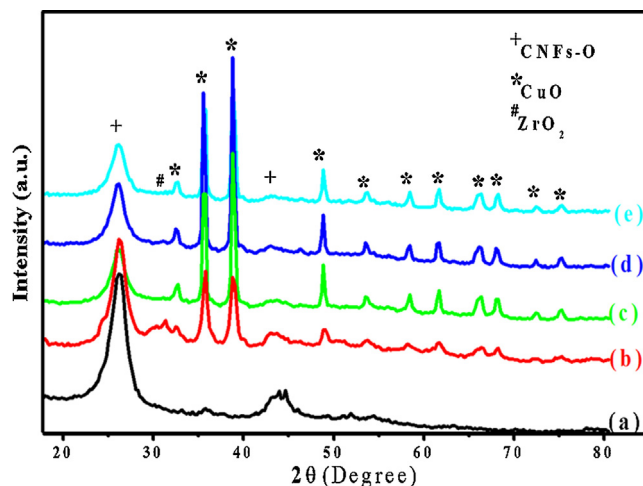


Fig. 1. XRD profile of (a) CNFs-O, (b) CZC, (c) CZC-Nb0.4, (d) CZC-Nb0.8 and (e) CZC-Nb1.2 catalysts.

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