

# Partial oxidation of methanol for hydrogen production over carbon nanotubes supported Cu-Zn catalysts

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## Abstract

Carbon nanotubes (CNTs) were used as support to Cu-Zn catalysts and tested their feasibility for hydrogen production from partial oxidation of methanol. The CNTs were synthesized by CVD method using acetylene as carbon source over anodic aluminum oxide template. The structural characteristics of CNTs were analysed by SEM, TEM, XRD, Raman spectroscopy and TGA. Using these CNTs as support, Cu-Zn catalysts with varying metal loading were prepared by co-precipitation method. The reducibility of the catalysts was tested with H<sub>2</sub>-TPR. N<sub>2</sub> adsorption and CO chemisorption were used to monitor the surface area and total CO uptake of catalysts, respectively. The metal particle size of Cu-Zn/CNTs catalysts were measured from XRD and TEM. The nature of copper species and acidity were analysed by DRIFT study of CO adsorption and pyridine adsorption method, respectively. The deposition of Cu on CNTs surface resulted in creation of strong Lewis acid sites. The methanol conversion rate and H<sub>2</sub> selectivity are increased from 0.066 to 0.11 mol/h/g cat and 57 to 70.6%, respectively, when increasing Cu loading from 5 to 12 wt% at 260 °C and further increase shows a fall in activity. The enhanced activity of 12 wt% Cu-9 wt% Zn/CNTs is due to the improved metal dispersion, narrow particle size distribution and almost complete reduction of Cu particles. The XRD analysis of spent catalyst indicates that during the POM reaction, the active Cu<sup>0</sup> species is slowly converted into CuO, which is responsible for fall in activity.

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## 1. Introduction

The scarcity of petroleum related fuels and the associated pollution problems during their combustion have attracted the attention towards the search of alternative fuels [1–3]. Hydrogen is expected to become an important energy carrier for sustainable energy consumption due to its clean-burning nature. It can be used as fuel either directly in internal combustion engines (ICE) or, indirectly to supply electricity using polymer electrolyte membrane (PEM) fuel cells, in which electricity is produced by electrochemical oxidation of hydrogen across a proton conducting membrane, resulting a significantly low impact on the environment [4,5]. Currently H<sub>2</sub> in the form of compressed gas (200–300 bar), liquid (–253 °C) or in hydrogen-storage materials are being used for onboard storage of hydrogen in fuel cell vehicles (FCVs). But the

technical limitations associated with storage, safety, and refueling restrict the use of H<sub>2</sub> for mobile fuel cell applications. These problems can be overcome by the production of hydrogen onboard the vehicle from a suitable H<sub>2</sub> rich liquid fuel, such as methanol. Methanol can easily be converted into a hydrogen-rich gas in the temperature range of 200–300 °C using a catalytic reactor. Also, the hydrogen/carbon ratio is high and there is no carbon–carbon bond, minimizing the chance for coke formation.

Hydrogen is being obtained from methanol by steam reforming [6,7], decomposition [8,9], partial oxidation [10–13] or oxidative steam reforming [14,15] techniques. Among these methods, selective production of H<sub>2</sub> by partial oxidation (POM) is having some obvious advantages, since it is an exothermic reaction and higher reaction rate is expected which shortens the reaction time to reach the working temperature from the cold start-up conditions. The most widely used catalysts for hydrogen production from methanol by partial oxidation are Cu-Zn-based catalysts over conventional supports such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> [16–18]. The metallic copper is an active

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species for hydrogen generation from CH<sub>3</sub>OH in Cu-Zn-based catalysts and the activity of the catalyst is linearly dependent on the metallic copper surface area of the catalyst [19–22]. Also, it is reported that Cu<sup>+</sup> species helps to increase the activity of the Cu-based catalyst. Both Cu<sup>0</sup> and Cu<sup>+</sup> species are essential for hydrogen generation from CH<sub>3</sub>OH and the activity of catalyst is dependent on the ratio of Cu<sup>+</sup>/Cu<sup>0</sup> in the catalyst [23]. Still there are some controversies concerning the nature of active species of Cu and the role of Zn in Cu-Zn-based POM catalysts. It was reported that addition of Zn results an increase in dispersion of copper as well as the stability of Cu<sup>+</sup> species in the catalyst [24,25].

Alejo et al. [24] studied POM reaction with oxygen over a series of Cu-Zn catalysts and found that the catalytic activity is directly related to the copper metal surface area. Further they reported that presence of aluminum showed an inhibiting effect in methanol conversion, while the selectivities for H<sub>2</sub> and CO<sub>2</sub> and catalyst stability are enhanced. They concluded that the copper metal is active for POM to H<sub>2</sub> and CO<sub>2</sub>, whereas Cu<sup>+</sup> favors the formation of H<sub>2</sub>O and CO and Cu<sup>2+</sup> as CuO shows very low activity for methanol conversion producing only CO<sub>2</sub> and H<sub>2</sub>O. Navarro et al. [26] used Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> in oxidized, reduced and reduced + air-exposed samples for POM in order to study the importance of the initial state of the catalyst and found that the temperature at which the reaction starts was shifted to higher values, when the degree of surface oxidation increased. Mechanistic aspects of POM to H<sub>2</sub> and CO<sub>2</sub> over Cu/ZnO with different Cu<sup>0</sup> surface area were studied and found that the reaction depends on the presence of both ZnO and Cu<sup>0</sup> phases [27]. Wang et al. [18] investigated the POM activities of Cu/SiO<sub>2</sub> and Cu/Zn/SiO<sub>2</sub> prepared by deposition-precipitation method. The catalyst with 10% Cu loading (Cu:Zn, 7:3) exhibits the highest CH<sub>3</sub>OH conversion and H<sub>2</sub> selectivity. Further, Cu<sup>0</sup> is active species for higher activity, but Cu<sup>+</sup> inhibits the POM to H<sub>2</sub>. The appropriate introduction of Zn enhanced the Cu<sup>0</sup> dispersion, which resulted in higher activity for H<sub>2</sub> production. However, over loading of Zn resulted in the formation of bigger crystallites of Cu<sub>2</sub>O which decreases the activity of the catalyst.

Hydrogen production by POM over a series of binary Cu/Cr and ternary Cu/Cr/M (M = Fe, Zn, Ce, etc.) catalysts prepared by co-precipitation method was studied [28]. The results showed that Cu<sub>60</sub>Cr<sub>40</sub> catalyst exhibits high CH<sub>3</sub>OH conversion and H<sub>2</sub> selectivity as compared with other binary catalysts and the introduction of Zn as promoter not only helps to increase the activity of Cu<sub>60</sub>Cr<sub>40</sub> catalyst but also improves the stability of the catalyst. Recently, Navarro et al. [29] compared the POM activity of Cu-Zn catalysts deposited by impregnation on activated carbon, carbon black and carbon fibers and found that different degrees of dispersion and uniformity in the distribution of metal precursors depending on the nature of the support and metal loading. Further, in addition to copper dispersion, other factors such as distribution, accessibility and the nature of the active sites govern hydrogen generation from POM. Further they reported that 10.7% Cu-6.9% Zn on activated carbon exhibited good activity as a result of better accessibility of the active phase partially deposited on the

exterior of the carbon grains. Despite their higher activity and selectivity for the H<sub>2</sub> production from CH<sub>3</sub>OH, the conventional Cu/ZnO-based catalysts have problems associated with long-term stability, low resistance to contaminants and the formation of poisonous CO as a byproduct. Therefore, the development of new efficient catalyst systems that exhibit an improved long-term stability and selectivity towards hydrogen production is highly desired.

The new carbon forms like carbon nanotubes (CNTs) and nanofibers (CNFs) have generated an intense effervescence in the scientific community due to their well known fascinating properties. Exploring their ability as support for the production of efficient heterogeneous catalysts is one of the current objectives of research [30,31]. The CNTs are found to offer some advantages such as the electronic property, high mechanical strength and thermal stability and the possibility to create anchoring sites, over conventional supports such as carbon, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. Also, the catalytically active metal nanoparticles can be implemented in the cavities or in the external walls of the CNTs. The Ru/CNTs catalysts were used in the hydrogenation of cinnamaldehyde and higher (92%) conversion of cinnamaldehyde to cinnamyl alcohol was observed [32]. The CNTs induced a metal-support interaction of a different kind to that existing for Ru supported on alumina or activated carbon. Recently, CNTs and CNFs supported Ni catalyst was studied for H<sub>2</sub> production from ethylene decomposition and found that catalyst 0.5 wt% Ni/CNTs showed 50 times higher H<sub>2</sub> yield compared to 0.3 wt% Ni/SiO<sub>2</sub> catalyst under similar experimental conditions [33]. Further they found that 0.5 wt% Ni is approximately an optimum metal loading in the 0.15–10 wt% range studied. No report is available on the usage of CNTs as support for Cu-Zn catalysts for POM to hydrogen. Hence, in the present study, it is aimed to use CNTs as support for Cu-Zn catalysts and study their catalytic activity in POM reaction under different experimental conditions.

## 2. Experimental

### 2.1. Preparation of anodic aluminum oxide (AAO) template

Two-step anodization procedure reported by Masuda and Fukuda [34] was followed with slight modification to get AAO template. Pure (99.5%) aluminum metal piece was cleaned with mixture of H<sub>3</sub>PO<sub>4</sub>/HNO<sub>3</sub>/H<sub>2</sub>O/CuSO<sub>4</sub> (89 ml/7 ml/40 ml/0.5 g) at 80 °C. Using the chemically polished Al metal as anode, anodization was carried out at 1 °C in 0.3 M oxalic acid for 1 h at 40 V. Then the Al metal was deoxidized with a phosphoric acid/chromic acid mixture solution (3 g CrO<sub>3</sub> + 15.2 ml 85 wt% H<sub>3</sub>PO<sub>4</sub> in 250 ml of water) at 70–80 °C for 1 h. Further, the second anodization was carried out under the same experimental conditions for 60 h. Finally, the electrode terminals are exchanged in order to remove the formed AAO layer from Al surface. The optimization of pore diameter was made by etching the AAO template in 5% H<sub>3</sub>PO<sub>4</sub> solution for 30 min.

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