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Highly Active Zn-Cu-Ce-Al Catalysts For Hydrogen Production Via Steam Reforming Of Methanol

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Abstract:

The rapid exhaustion of fossil fuel reserves and the unfavourable effects of climate change have attracted global attention and have posed serious threats to the population. The emergence of new energy technologies based on the development of new materials is crucial if the world is to arrest the negative effects of climate change and ensure the global energy security based on sustainable and renewable energy sources. Hydrogen is thought to be a solution as a clean and renewable future energy vector. Before it can be turned into an energy carrier, it has to be produced. The H_2 production via steam reforming of methanol (SRM) **(1)** issued from biomass seems to be an attractive alternative energy vector used in the fuel cell technology.

$$CH_3OH + H_2O \longrightarrow 3\,H_2 + CO_2 \quad \mathbf{(1)}$$

Knowing that the presence of the minor amount of CO can poison the platinum anode of the PEM fuel cells, a highly performed reforming catalyst must be developed. The Cu-containing catalysts showed particularly high activity and high selectivity for the steam reforming of methanol. Zinc oxide is known not only to promote the dispersion of Cu and the reducibility of CuO, but also to improve its adsorptive properties, including the adsorption of methanol [1]. On the other hand, the CeO_2 has a cubic fluorite structure that facilitates the introduction of the Cu^{2+} cations into their lattice and can improve their physical properties [2]. The high oxygen mobility, strong interaction with the supported metal and the modifiable ability [3] make the CeO_2-based materials very interesting for catalysis and as a support. The use of the CeO_2-based catalysts exhibits high activities for the total oxidation of carbon monoxide and methane [4].

The performances of different *x*Cu10Ce, *x*Cu10Ce10Al (*x* = 1, 3 and 5) catalysts prepared by impregnation method then calcined (600°C) and pelletized, were investigated in the steam reforming of methanol. A given amount of $Zn(NO_3)_2$ was impregnated on the calcined 5Cu10Ce and 5Cu10Ce10Al catalysts in order to obtain 5 wt.% of Zn on each catalyst. Solids were stabilized by calcinations under air at 600°C for 4h. All the tests were performed at 350 °C, a Gas Hourly Space Velocity of 15500 h^{-1} and a steamed mixture of water and methanol ($H_2O/CH_3OH = 2$). Catalysts were characterized by TPR, XRD, EPR spectroscopy in order to study their behaviour during the SRM reaction.

The catalytic activity was found to be strongly dependent on the nature of the copper species and on the surface area of the support. The 5Cu10Ce catalysts with high copper content (18.77 wt.%) were evidenced as highly active solids due to a synergistic effect between Cu and Ce species. The addition of copper to ceria and alumina support contributes to better hydrogen selectivity in the reaction of steam reforming of methanol even at a low copper content 1Cu10Ce10Al (3.6 wt.%). The SRM was also studied by adding 5 wt.% of ZnO over 5Cu10Ce and 5Cu10Ce10Al catalysts. Test results have shown that, the H_2 selectivity was about 100% for both catalysts with a conversion rate of 99.9% for the 5%Zn5Cu10Ce and 96% for the 5%Zn5Cu10Ce10Al. In addition, an aging test have shown that the 5%Zn5Cu10Ce catalyst was kept performing for one month. These performances are attributed to the formation of an optimum Cu^0-Cu_2O active phase stabilized by chemical interaction on ceria support.

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