Copper supported on $Zn_xAl_yO_z$ catalysts for methanol synthesis

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Introduction

Methanol plays an important role as basic chemical compound, a kind of transportation fuel and source of hydrogen for fuel cells. Industrially, methanol is produced from synthesis gas $CO/CO_2/H_2$ under high temperature and high pressure conditions. The most known catalysts for methanol synthesis are copper/zinc based oxide catalyst [1]. For these catalysts the linear relationship between the catalytic activity and the metallic copper area was observed. Additionally, the methanol synthesis occurred exclusively on the surface of metallic copper. The catalytic activity of methanol synthesis from CO_2/H_2 on the $Cu/ZnO/Al_2O_3$ catalyst showed the maximum yield of methanol formation correlated with growth of the metallic copper surface area and Cu/ZnO molar ratio being about 8 [2]. Additionally Cu/ZnO - based catalysts are used for other catalytic reactions such as water gas shift reaction WGS [3], the methanol steam reforming and synthesis of higher alcohols.

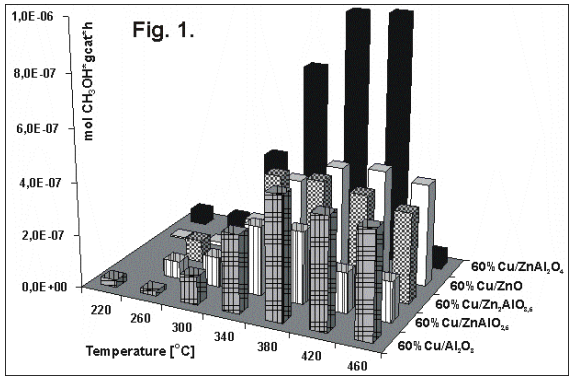
Materials and Methods

In the present work copper supported catalysts ($Cu/ZnAl_2O_4$, $Cu/ZnAlO_{2,5}$, $Zn_2AlO_{3,5}$, Cu/Al_2O_3, Cu/ZnO) were prepared by conventional impregnation methods and there were examined their physicochemical properties (surface area and porosity, reduction behavior, phase composition) and the catalytic performance in carbon dioxide hydrogenation to methanol.

Results and Discussion

The investigation of the influence of composition of binary oxide $ZnAl_2O_4$, $ZnAlO_{2,5}$, $Zn_2AlO_{3,5}$ on their activity and physicochemical properties of copper catalysts in methanol synthesis was the main goal of this work. We confirmed that reduction and activity of copper supported catalysts depends strongly on copper loading and support composition. For copper (60% wt.) catalysts supported on various supports calcined at 400°C two reduction steps were observed and attributed to copper oxide reduction $CuO \rightarrow Cu_2O \rightarrow Cu$. The same shape of TPR curves have copper catalysts calcined at 700°C supported on various oxides: ZnO, $ZnAlO_{2,5}$ and $Zn_2AlO_{3,5}$. Three reduction effects observed in the case of $60\%Cu/ZnAl_2O_4$ and $60\%Cu/Al_2O_3$ catalysts calcined at 700°C are assigned to copper oxide and spinel $CuAl_2O_4$ reduction. XRD results confirmed for $60\%Cu/ZnAl_2O_4$ supported catalyst the presence of following oxidic phases: ZnO, CuO and $ZnAl_2O_4$. On the contrary XRD analysis of $60\%Cu/Al_2O_3$ shows the presence of γ-Al_2O_3, CuO and $CuAl_2O_4$ phases and ZnO, CuO oxidio phases in the case of 60%Cu/ZnO catalyst. The temperature characteristics of catalytic activity of copper supported catalysts in hydrogenation of CO_2 expressed in mol CH_3OH $g^{-1}_{cat.}$ h^{-1} are presented in Fig. 1. Activity tests in methanol synthesis show that the most suitable support for methanol formation was spinel type $ZnAl_2O_4$ system, what can be explained by fact that this bioxide have the most stabilizing effect on the copper ions present on the catalyst surface. TPD-CO_2 measurements showed that $ZnAl_2O_4$ system adsorbed the largest amount of CO_2 on the catalysts surface, what can explained high activity of $60\%Cu/ZnAl_2O_4$ catalyst in methanol formation (see Fig. 1).

Figure 1. Catalytic activity in methanol synthesis for copper catalysts supported on different supports.



Significance

1. The calcination temperature and composition of catalyst strongly influence on reduction behavior of copper supported catalysts. Only for catalysts with high aluminum content and after its calcination at 700°C high temperature reduction effects were observed originating from $CuAl_2O_4$ spinel phase reduction.
2. XRD results confirmed the presence of $CuAl_2O_4$ spinel phase in the case of Cu/Al_2O_3 catalyst and presence of this phase can not be ruled out for catalysts supported on binary oxides.
3. The catalytic activity depends strongly on support composition.
4. The most active was $60\%Cu/ZnAl_2O_4$ catalyst exhibiting largest uptake of CO_2 in low temperature range.

References

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