Design of modified CuZnAl catalysts for higher alcohols synthesis

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Introduction

The demand for clean energy manufactured from alterative and renewable sources has been steadily growing around the world. The renewable energy sources (including biomass) account for about 19% of total energy usage and have the potential to supply 50% of world energy demand in the next century. Gasification of biomass yields syngas (mixture of hydrogen and carbon monoxide). The catalytic conversion of syngas can lead to higher alcohols which can be used as fuels, fuel additives for octane or cetane enhancement, and intermediates for value-added chemicals. Several catalytic systems have been tested so far for higher alcohol synthesis: methanol synthesis catalysts modified with alkali promoters; modified Fischer-Tropsch and Group VIII metal-based catalysts [1]. All these attempts, however, have not resulted in any major industrial manufacturing. The major difficulties include catalyst deactivation, low alcohol productivity, insufficient selectivity and very complex mixture of reaction products

For a number of decades CuZnAl has been used for methanol synthesis. It is known that addition of different promoters could significantly modify the catalyst selectivity and in particular selectivity to higher alcohols. In this work, the influence of different promoters on the productivity of heavy alcohols synthesis and structure of modified CuZnAl catalysts was investigated using a combination of physico-chemical methods. The catalytic results were obtained in a fixed bed reactor.

Experimental

The catalysts were synthesized by co-precipitation using two aqueous solutions [2,3]: solution of copper, zinc and aluminum nitrates and carbonate solution. The promoting agent (nitrate salt of Fe, Co, Ru, Zr, Mo, Mg) was added to the solutions of Cu/Zn/Al nitrates. The two solutions are added simultaneously with peristaltic pump into precipitation vessel with water under vigorous stirring. The pH and the temperature are fixed and controlled at 7 and 70 °C, respectively. The catalyst solution was kept under stirring during 4h at constant temperature of 70 °C. The Cu/Zn/Al molar ratio in the catalysts was 6/3/1 ratio; the promoter content was 1% by mol. Then suspension was filtered and the catalyst was washed, dried and grinded. The catalyst powder was calcined under air flow at 350 °C for 3h (3 °Cmin^{-1}).

The surface areas and particles sizes of the samples were determined by BET and laser granulometry. Thermal stability of the solids evaluated under flowing air using thermo gravimetric analysis (TGA). Temperature-programmed reduction (TPR) was performed, using a gas mixture of 5 vol% H_2 in argon at a flow of 50 ml/min. The reactor was heated up to 450 ∘C at a ramp rate of 6 ∘C/min. Before TPR measurements, the sample was heated in argon atmosphere to 120 °C (10 °C/min) for 1 hour. X-ray diffraction (XRD) patterns of the calcined samples was recorded from $2\theta = 10°$ to $2\theta = 70°$ (step: 0.02°; integration time: 1.5 s) on a D8 Advance apparatus (Brüker AXS). The catalyst was also placed in a high temperature chamber to record XRD patterns as a function of increasing temperature until 800 °C (6 °C/min, with 2θ~15 s) under 3 vol% H_2 in nitrogen.

The catalytic performance was tested in a high pressure continuous tubular flow fixed-bed reactor. The catalyst (50-150 μm), 1,1 ml) was packed into a stainless-steel reactor (i.d., 8.0 mm) and reduced in flowing premixed H_2 flow of 40 mL. min^1 (NTP). The temperature was increased to 250 °C with a heating rate of 3 °C min^{-1} and then kept at this temperature for 5 h. After reduction, the gas flow was switched to premix $CO/H_2(1/2)$. The reaction was carried out under a pressure of 2.0 MPa, at 280 and 320 °C, and at an hourly space velocity (SV) of 3600 h^{-1}. All experimental data were obtained under steady-state conditions that were usually maintained for several hours before changing the reaction conditions to obtain another set of data.

Results and Discussion

The BET surface areas for all the catalysts are in the similar range (57-79 m^2/g). Granulometric analyses have shown that more than 50 % of the total catalysts were below 50 μm particle size. The TGA showed two weight loss peaks during the decomposition. The first peak corresponds to desorption of water (~ 100 °C) while the second to decomposition of nitrate (220 °C). The catalysts were calcined at 350 °C. This temperature seems to be sufficient for compete decomposition of metal nitrates. TPR profiles are shown in Figure 1. For all catalysts, two reduction peaks were observed. These peaks could be assigned to two steps reduction of copper, $Cu^{2+} \rightarrow Cu^+$ and $Cu^+ \rightarrow Cu^0$ [4]. It has been shown that catalyst reducibility depends on the promoter. With the catalyst promoted with Mo, the reduction proceeds at lower temperature, while for catalysts promoted by Co and Zr, the reduction peaks are shifted to higher temperatures.

XRD analyses indicate the presence of small nanoparticles of copper and zinc oxides. The crystallite size of copper oxide phase calculated from the (111) reflection is about 10 nm. The in-situ XRD has provided further information about catalyst activation in hydrogen. The H_2-XRD analysis (Figure 2) showed that the catalyst reduction of mixed

oxide catalysts proceeded in three distinct stages (Figure. 2). Initially, between 25 and 250 °C, the phase of copper oxide is reduced (blue circle). In a second step, between 250 and 350 °C, a phase of metallic copper appears. Finally, between 350 and 800 °C, the zinc oxide phase starts to be reduced (circle red) and shows a phase CuZn alloy [5].
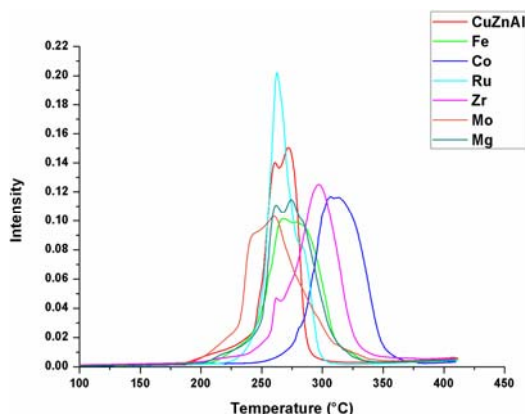
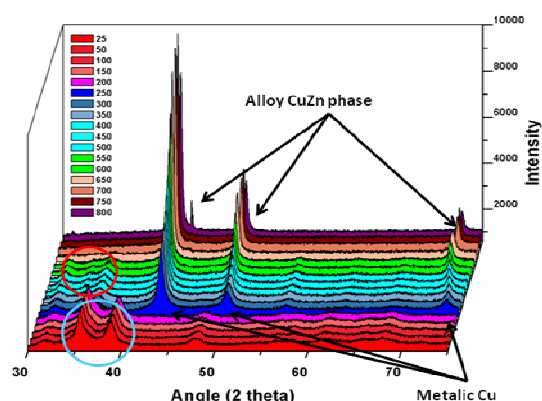

Figure 1: TPR profiles of all catalysts

Figure 2: H_2-XRD profiles of $CuOZnOAl_2O_3$

The catalytic results obtained for $CuOZnOAl_2O_3$ catalysts promoted by molybdenum, zirconia and magnesium are summarized in Table 1. The reaction rate slightly depends on the promoting metal. It was higher for Mo-containing catalyst and lower for Zr-promoted counterpart. Methanol, higher alcohols, hydrocarbons and carbon dioxide were among the reaction products. Higher temperature seems to favor the production of methane and heavier alcohols. The catalytic activity gradually declines with time on stream which could be attributed to catalyst deactivation. The catalyst promoted with the magnesium exhibits so far the best productivity in heavy alcohol with 8 mg/gcat.h. Further characterization and catalytic tests are currently underway to provide additional information about the structure and catalytic performance of the modified CuZnAl catalysts.

Table 1: Conversion and selectivities over doped catalysts

Catalyst	React temp (°C)	Pressure (bar)	CO conversion χ_{CO} (%)	React. Velocity R_{CO} (mol.h^{-1}.gcat^{-1}) $*10^{-3}$	Alcohols selectivities (%)				Hydrocarbons selectivities (%)			CO_2 Select. (%)	STY alcohols (mg/gcat.h)	STY alcohols C2+OH (mg/gcat.h)
					C1OH	C2OH	C3OH	C4+OH	CH$_4$	C2-C4	C5-C7			
1% Mo	280	20	9.8	4.82	43.8	1.7	0.4	1.5	3.7	4.2	2.6	23.5	72	3.7
	320		16.3	8.29	13.8	0.5	1.1	0.7	22	17.8	9.6	44.2	40	3.8
1 % Zr	280	20	6.8	3.47	39.1	2.1	0.4	1.3	0.7	2.1	0.6	3.8	45.2	2.7
	320		5.4	2.62	40.8	1.4	2.9	3.8	3.4	10.1	2.6	19.4	39.7	4.3
1% Mg	280	20	11.2	5.61	41.7	2.4	0.6	1.3	1.1	3.9	0.9	15.6	79.7	5.1
	320		7.4	3.75	41.2	1.7	6.1	3.2	5.9	14.6	4.5	42.5	56.8	8.1

Conclusion

Promotion of CuZnAl catalysts with a number of transition metals results in significant modifications in catalyst reducibility and affects the catalytic performance in carbon monoxide conversion. Higher productivity to higher alcohols was observed on Mg-promoted catalysts. Further optimization of the catalyst formulation is currently in progress.

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