

Thermochemical conversion of syngas to higher alcohols over CuZnAl catalysts

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Introduction

Gasification of biomass to synthesis gas, followed by catalytic conversion of syngas, produces ethanol, plus C₃-C₄ alcohols. The resulting alcohols could be used directly as fuels, as fuel additives for octane or cetane enhancement, as oxygenate fuel additives for environmental reasons, and as intermediates to form other fuel additives such as methyltertiarybutylether (MTBE), as discussed by G. A. Mills [1]. The catalytic conversion of syngas to alcohols has been limited up-to-date by low yields and poor catalyst selectivity [2]. The reaction has been studied over a wide range of catalytic materials [2-3], which can be categorized to modified low and high temperature methanol synthesis catalysts based on ZnO/Cr₂O₃ and Cu-ZnO/Al₂O₃ respectively, modified Co and Fe Fischer-Tropsch catalysts and Mo-based materials in oxidic and sulfided form. Alkali promotion (Li, Na, K and Cs) was found to improve selectivity to oxygenates [3].

In this study, the production of higher alcohols from syngas is investigated over K-promoted and unpromoted Cu-ZnO/Al₂O₃ catalysts. We report results on the effect of Cu, Zn and Al molar composition in the as-synthesized catalytic materials, as well as the effect of K-promotion, on both the physicochemical characteristics and the catalytic behavior in higher alcohols formation.

Experimental

Catalyst preparation

CuZnAl catalysts with Cu/Zn/Al molar content of 60/30/10, 45/45/10 and 33/33/33 were prepared via co-precipitation.

An aqueous solution of Na₂CO₃ (0.1M) was added dropwise to an aqueous solution of Cu, Zn and Al nitrates at 70°C and pH of 6-7. The resulting precipitate was dried for 24h at 100°C and calcined under air flow for 4h at 350°C. For K promotion, 0.5wt%K was added by dry impregnation with K₂CO₃ on the calcined catalysts with the higher Cu content (60Cu/30Zn/10Al and 45Cu/45Zn/10Al), followed by drying and calcination under air for 4h at 350°C.

Catalyst characterization

The catalysts were characterized by ICP to measure the elemental composition. Surface areas of the samples were determined by BET analysis. XRD patterns were obtained on a Siemens D500 diffractometer. Temperature programmed reduction with H₂ was employed to study the reducibility of the catalysts. The TPR-H₂ measurements were conducted in a gas-flow unit equipped with online MS, at temperatures up to 700°C at a rate of 10°C/min in a 5%H₂/He flow.

Activity measurements

The higher alcohol synthesis reaction was investigated in the temperature range 280–320°C at 40 bar, W/F ratio of 0.64 g.s/cm³ and inlet feed composition CO/H₂/N₂=21%-43%-36%. Prior to testing, the catalyst was reduced in-situ with H₂ at 350°C for 3h. The steady-state activity measurements were taken after at least 24 h on-stream. Product analysis was performed on-line with a GC Agilent 7890A equipped with two detectors (FID & TCD) and three columns (MS, Porapak Q and DB-FFAP) in a series-bypass configuration.

Results and Discussion

Catalyst characterization

The surface area of the samples varied from 39 to 79 m²/g. Potassium impregnated materials exhibited the lowest surface areas. This could be attributed to the presence of potassium on one hand and to the extra calcination step involved during the synthesis process, that could possibly cause sintering. Cu content can not be associated with the surface area variation.

ICP analysis of the materials indicated compositions near the nominal, while XRD identified the presence of CuO and ZnO crystal phases, along with amorphous structures, in all samples. The amorphous nature was found to increase with decreasing Cu molar content. Promotion with K did not affect the crystal structure of the catalysts.

TPR-H₂ measurements, presented in Figure 1, showed that the reduction of CuO is facilitated in all CuZnAl catalysts compared to reference CuO sample, with complete reduction of Cu²⁺ to Cu⁰. Promotion of K was found to increase the reduction temperature. It is possible that the presence of electropositive K increases the Cu-O bond strength, increasing as a consequence the temperature necessary for its rupture.

Activity testing results

The performance of the K-promoted and unpromoted CuZnAl materials in the higher alcohol synthesis reaction, in

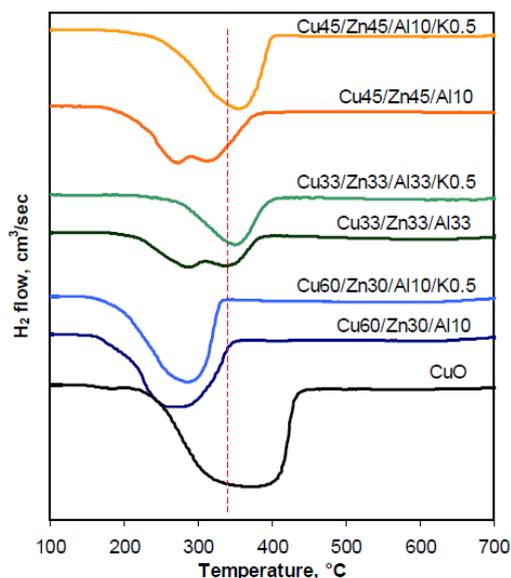


Figure 1: TPR-H₂ profiles of K-promoted and unpromoted Cu/Zn/Al catalysts with different molar ratio

terms of CO conversion and carbon-based selectivity to the different products, is shown in Table 1 for three temperatures.

The results indicate that the main reaction products are methanol and CO₂, with a low selectivity to higher alcohols. In all samples, activity increases with temperature. Concerning the product distribution as a function of temperature, a general trend observed is that increased temperature favors the formation of CO₂ and hydrocarbons at the expense of the production of methanol and higher alcohols.

Among the unpromoted CuZnAl samples, variation of the molar composition induces only small changes to the catalytic performance. At low temperature, both activity and higher alcohols selectivity is higher for the Cu₄₅/Zn₄₅/Al₁₀, with an intermediate amount of copper and high amount of zinc. However, at the highest temperature investigated in this study, Cu₆₀/Zn₃₀/Al₁₀, the catalyst with the higher Cu content, exhibits the highest CO conversion and selectivity to higher alcohols.

The effect of K-promotion was found to be beneficial to the formation of higher alcohols in accordance to previous literature data^[1-2]. As shown from the data in Table 1, the addition of K decreased CO conversion and increased C₂-C₅ alcohols selectivity in expense to hydrocarbons and methanol formation. Still, the main products of the reaction even with alkali promotion remained methanol and carbon dioxide.

Table 1: Performance of K-promoted and unpromoted Cu/Zn/Al catalysts

Catalyst	Temperature, °C	CO conversion, %	Carbon based-selectivity, %				
			C ₂ -C ₅ OH	CH ₃ OH	C ₂ -C ₇ HC	CH ₄	CO ₂
Cu ₆₀ /Zn ₃₀ /Al ₁₀	280	6.70	4.09	50.68	7.36	2.03	35.68
	300	8.53	5.03	35.69	11.21	2.65	45.41
	320	11.40	3.06	27.53	19.25	3.75	46.41
Cu ₄₅ /Zn ₄₅ /Al ₁₀	280	8.63	6.32	47.86	6.27	2.30	28.79
	300	9.12	6.51	31.78	14.43	4.11	43.17
	320	9.35	2.81	16.96	19.32	6.53	49.49
Cu ₃₃ /Zn ₃₃ /Al ₃₃	280	5.80	4.46	51.06	12.05	3.03	29.29
	300	6.86	5.63	36.69	14.84	6.94	35.91
	320	9.96	2.32	15.22	27.48	9.63	45.35
Cu ₆₀ /Zn ₃₀ /Al ₁₀ /K _{0.5}	280	6.74	6.43	46.51	6.33	1.88	38.85
	300	6.55	3.23	34.11	11.62	3.05	47.99
	320	8.21	4.47	36.55	12.97	3.56	42.45
Cu ₄₅ /Zn ₄₅ /Al ₁₀ /K _{0.5}	280	5.51	5.45	57.02	2.25	1.66	33.62
	300	6.19	8.41	43.73	5.94	2.39	39.52
	320	6.02	8.60	32.61	8.60	3.33	45.71

Conclusions

Physicochemical characterization and activity testing of CuZnAl catalysts showed that variation of composition induces small changes, with the optimum catalytic performance exhibited by the material with molar content Cu₄₅/Zn₄₅/Al₁₀. K-promotion decreased reducibility of the materials and reduced activity to the reaction. However, the addition of potassium increased selectivity to C₂-C₅ alcohols. Nevertheless, independent of chemical composition and K-promotion the main products of the reaction are methanol, carbon dioxide and hydrocarbons at high temperature.

Acknowledgments

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