

Development of methanol synthesis at low-temperature from CO₂-rich syngas over metal oxide catalyst

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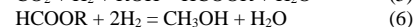
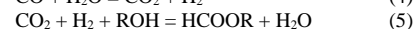
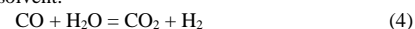
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Introduction

Methanol, an alternative fuel, is commercially produced from syngas [1-2]. The conventional source of syngas is natural gas or coal but nowadays it has been focused on an alternative source such as biomass. The syngas derived from biomass can also be used to synthesize methanol which can reduce the amount of CO₂ [3-5]. Methanol is alternatively produced from syngas via the esterification at relative low temperature using alcohol as a co-catalytic solvent:



In this present work, the CO₂-rich syngas has been used to synthesize the methanol in the present of a copper-based catalyst and a catalytic solvent. Moreover, this work has been studied not only the effect of catalytic solvent but also finding the way to develop the catalyst for methanol synthesis.

Materials and Methods

Copper-based catalysts were prepared by the conventional co-precipitation method. A mixed solution of copper and zinc nitrates was precipitated with a solution of sodium carbonate at 338 K and aged overnight. The precipitate was washed, dried, and followed by calcined at 493 K for 1 h. The solid oxide was reduced with 5% H₂ in N₂ and then passivated with 2% O₂ in Ar. The methanol synthesis was carried out in a flow-type semi-batch. The 3.0 g of catalyst and 20 ml of alcohol were added to the reactor and then purged by reactant gas (CO/CO₂/H₂/Ar = 32/5/60/3). The reaction was conducted at 50 bar, 443 K, 20 ml/min flow rate for 20 h. Products were analyzed by an online GC with TCD and an offline GC with FID.

Results and Discussion

Table 1 show the conversion and selectivity of various catalysts performed in methanol synthesis. Considering the catalysts with different supports, Cu/ZnO exhibited higher the conversion than un-supported Cu, and Cu/Cr₂O₃. For catalyst prepared from different precursors, Cu/ZnO^c (acetate precursor) exhibited the highest conversion, while Cu/ZnO^a (sulfate precursor) gave the lowest conversion. This could be attributed to the small metal size of Cu/ZnO^c, and might relate to the decomposition of organic groups existed in the precursor [4]. In case of catalysts with different promoters, 0.5%Zr-Cu/ZnO showed the highest conversion which could be attributed to the high dispersion of copper and high surface area.

Table 1. Conversion and selectivity of various catalysts performed in methanol synthesis.

Catalyst	Conversion (%)				Selectivity (%)		MeOH Yield (%)
	CO	CO ₂	total carbon	methanol	HCOOCH ₃	HCOOR	
pure Cu	12.8	-48.7	4.1	100.0	-	-	8.3
Cu/Cr ₂ O ₃	12.4	-32.6	6.0	100.0	-	-	4.1
Cu/ZnO	39.4	-3.0	33.2	100.0	-	-	4.7
Cu/ZnO ^a	19.3	-4.6	15.9	100.0	-	-	25.6
Cu/ZnO ^b	39.0	-1.0	33.3	100.0	-	-	31.4
Cu/ZnO ^c	45.8	1.3	39.5	100.0	-	-	15.9
0.50%wt Zr-Cu/ZnO	40.0	-2.4	34.0	100.0	-	-	33.3
1.00%wt Zr-Cu/ZnO	34.7	-5.9	29.0	100.0	-	-	50.3
0.10%wt Pd-Cu/ZnO	31.7	-11.7	25.6	100.0	-	-	39.5
0.50%wt Pd-Cu/ZnO	39.9	10.1	35.7	100.0	-	-	42.8
1.00%wt Pd-Cu/ZnO	36.3	1.4	31.3	100.0	-	-	25.7

Temperature = 443 K, Pressure = 50 bar, catalyst(prepared with nitrate soln.) = 3.0 g, reaction time = 20 h, isoPrOH = 20 ml, CO/CO₂/H₂/Ar = 32/5/60/3 = 20 ml/min.

Note: a = Cu/ZnO prepared with sulfate soln., b = Cu/ZnO prepared with chloride soln., c = Cu/ZnO prepared with acetate soln.

M-Cu/ZnO catalyst (M=Zr, Pd) were prepared by the impregnation method.

The effect of different alcohols on the activity of methanol synthesis is showed in Fig. 1. The results indicated that iso-propanol had the highest total conversion, and hexanol exhibited the highest in CO₂ conversion.

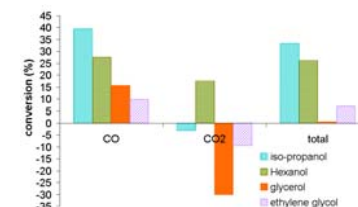


Figure 1. The effect of solvent on the conversion of methanol synthesis: CO/CO₂/H₂/Ar = 32/5/60/3, 20 ml/min, 50 bar, 443 K, 3 g of Cu/ZnO(nitrate), 20 ml of solvent.

Significance

0.5 wt% Zr or 0.5 wt% Pd promoted the activity of catalyst for methanol synthesis at low temperature.

Acknowledgements

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References

- 1.Reubroycharoen, P.; Vitidsant, T.; Yoneyama, Y.; Tsubaki, N. Catal. Today. 2004, 89, 447-454.
- 2.Yang, C.; Ma, Z.; Zhao, N.; Wei, W.; Hu, T.; Sun, Y. Catal. Today. 2006, 11, 5222-227.
- 3.Yang, R.; Yu, X.; Zhang, Y.; Li, W.; Tsubaki, N. Fuel 2008, 87, 443-450.
4. Bao, J.; Liu, Z.; Zhang, Y.; Tsubaki, N. Catal. Comm. 2008, 9, 913-918.
5. Hu, B.; Fujimoto, K. Appl Catal A: General. 2008, 346, 174-178.