

Fischer-Tropsch Synthesis over Mo/Zeolite Catalysts

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Introduction

Conventional Fischer-Tropsch synthesis (FTS) over Fe- or Co-based catalysts produces linear alkanes/alkenes as the dominant products, and the product molecular weight distribution follows the Anderson-Schulz-Flory (ASF) law [1, 2]. It is a challenge to maximize the product selectivity towards a given hydrocarbon fraction such as gasoline or diesel. Composite catalysts combining the conventional FTS catalysts with acidic zeolites were investigated to overcome the limitations in both product selectivity and quality through secondary reactions of the linear hydrocarbons on the zeolites to form aromatic compounds and branched alkanes, but encountering problems such as catalyst deactivation and loss in CO conversion [3]. Another possible way to modify the ASF product distribution is to change the mechanism and kinetics of the chain-growth process. Incorporation of a FTS active component into the zeolite cage/channel to limit the reaction inside the micro-space of the zeolite may effectively modify the FTS products distribution.

Mo/HZSM-5 is an active catalyst for the dehydroaromatization of methane [4]. Molybdenum carbide or oxycarbide formed during the reaction by methane reduction of molybdenum oxides anchored on the Brönsted acid sites of HZSM-5 is generally accepted as the active species. On the other hand, molybdenum carbides have been reported to be active for mixed alcohol synthesis [5], and they were also reported to be active catalysts for alkane isomerization [6]. Furthermore, Mo/HZSM-5 has been applied in the aromatization reactions of methanol and ethanol [7]. Dehydration of the alcohols on Mo/HZSM-5 was supposed to occur during the aromatization process. These literature results may be combined to pose the potential of applying Mo/HZSM-5 as an innovative catalyst for the FTS to produce high quality gasoline. This presentation will show the unique performance of Mo/HZSM-5 in FTS, most probably through a potential route that directly transforms mixed alcohols to branched alkanes and aromatics.

Experimental

Mo/Zeolite catalysts were prepared by incipient wetness impregnation of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ aqueous solution with the ammonium form of ZSM-5, Zeolite Y, and Zeolite β . For comparison, Mo/SiO₂ was also prepared using the same preparation method. The Mo metal loading amount was 5 wt.% in all of these samples.

The FTS reaction was performed using a continuous flow fixed-bed Micro BTRS-Jr. systems (Autoclave Engineers) at 523-653 K and 500-1000 psig. The catalyst loading was 1g (40-60 mesh). The H₂/CO molar ratio of the syngas was 1.0, typical of a synthesis gas derived from biomass gasification, and the gas hourly space velocity (GHSV) was 3,000 h⁻¹. Before each reaction, the catalyst was pretreated in flowing syngas at 673 K for one hour or in flowing methane gas at 923 K for two hours. Product gas analysis was performed using an on-line chromatograph equipped with both TCD and FID. Liquid products were analyzed using an Agilent GC/MS. CO conversion and product selectivity were calculated using the internal standard method.

Results and Discussion

Reaction of syngas on Mo/HZSM-5

The FTS reaction was first performed on Mo/HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) at 623 K and 100 psig after *ex-situ* activation in flowing methane at 923 K for two hours. A CO conversion about 15% was obtained. Methane, ethane and propane were the most abundant hydrocarbons in the gas phase product. Butane, *iso*-butane, 2-methyl-butane, pentane and 2-methyl-pentane as well as trace amounts of aromatics were also detected in the gaseous product using the on-line GC. The CO conversion was greatly increased with a sample pretreated in flowing syngas at 673 K. A liquid product, composed clearly of water and oil phases, was also collected from the condenser kept at 271 K.

GC-MS analysis of the oil phase product is shown in Fig.1a. Over 100 hydrocarbon compounds were identified from the analysis and they are grouped into three categories: (i) branched and cyclized C_4 - C_8 alkanes such as methyl-butane, methyl-pentane and methyl-cyclohexane, *etc.* (ii) aromatics including almost all the isomers of alkyl-substituted benzenes, naphthalenes and indenes, with xylene, trimethyl-benzene and tetramethyl-benzene as the most abundant components; (iii) C_4 - C_{20} aliphatic hydrocarbons, mostly in minor amounts. These results clearly indicated that Mo/HZSM-5 is active and selective for FTS directly to aromatic compounds, branched and cyclized alkanes of gasoline range, which is distinct from the product distribution from conventional Fe- or Co-based catalysts producing aliphatic hydrocarbons as the dominant products.

GC-MS analysis of the aqueous phase (Fig.1b) indicated the presence of oxygenates primarily composed of C_1 - C_6 alcohols (methanol, ethanol, propanol, butanol and 2-methyl-butanol) and carboxylic acids (C_1 - C_5). Acetone and acetaldehyde were also detected in the products. The total concentration of these oxygenates in the aqueous phase was about 3 wt.%. The presence of the various oxygenates of appreciable amounts in the products and the high formation of multi-alkyl-aromatics are indications that the FTS over Mo/HZSM-5 proceeds possibly *via* syngas to mixed alcohols to hydrocarbons transformation route.

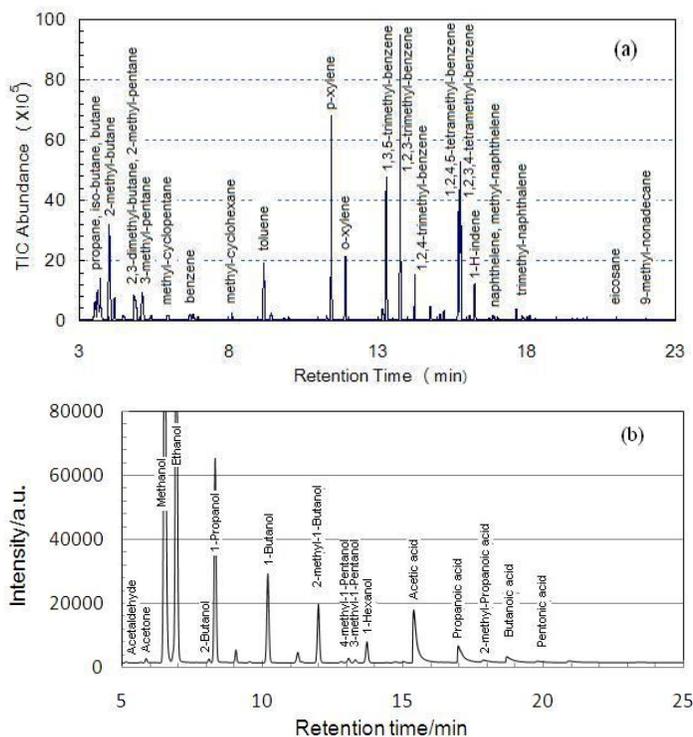


Figure 1 GC/MS identification of oil (a) and aqueous (b) phase products from FTS on 5% Mo/HZSM-5

Temperature dependence of Mo/HZSM-5 for FTS

The temperature dependence of FTS on Mo/HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=50$) was examined at 1000 psig. The conversion of CO at 523 K was negligible, and it reached 3-5% at 543 K. The CO conversion reached a maximum at 68% when the reaction temperature was 653 K, and it decreased slowly with reaction time on stream, which is most probably due to catalyst deactivation at higher temperatures. The calculated selectivity of liquid products (hydrocarbons + oxygenates) was around 20% and 15% at

573 K and 623 K, respectively. Production of lower alkanes increased with increasing reaction temperature. CO₂ formation remained at around 50% at different temperatures. The decrease in the formation of liquid hydrocarbons at higher temperatures was accompanied by an increase in lower alkanes production at similar levels.

Table 1 Composition of liquid hydrocarbons from FTS on Mo/HZSM-5 at 1000 psig and different reaction temperatures

T/(°C)	CO Conv. (%)	Effluent H ₂ /CO	S _{Liq.} (%)	Selectivity of Products (% , carbon basis)		
				Aromatics	iso-Alkanes	Linear Alkanes
250	~1.0	1.00	~	91.8	9.7	0
275	3.8	1.01	~	90.2	9.7	0.1
300	14.0	1.05	18.4	87.5	12.1	0.4
350	54.0	1.29	14.6	88.7	9.6	1.7
380	64.4	1.32	9.9	97.6	2.1	0.4

The composition of liquid products obtained at different reaction temperatures on the Mo/HZSM-5 is summarized in Table 1. The formation of aromatics was dominant in the products at all temperatures examined. Aromatics and *iso*-alkanes (branched + cyclized alkanes) consist of more than 98% in the oil phase products. The formation of linear alkanes was only in minor amounts even at low temperatures (<300 °C). This is interesting because it is different from the conventional Fe- or Co-based catalysts for which linear alkanes/olefins are always the major products. It is an indication that FTS proceeds on Mo/HZSM-5 most probably through a mechanism involving mixed alcohols as the intermediates for hydrocarbons formation. Zeolite acidity and isomerization activity of Mo-species greatly contribute to the isomerization and cyclization reactions. On the other hand, it is also an indication that the active sites are located inside zeolite channels. To confirm this, the FTS was performed on Mo/SiO₂ and the results were compared with that obtained on Mo/HZSM-5. A CO conversion of 17% was reached at 573 K, 1000 psig, but the collected liquid consisted of only an aqueous phase. Oxygenates including alcohols and carboxylic acids were detected. The total content of these oxygenates in water was 6.7 %, much higher than that formed on Mo/HZSM-5 (3%), which indicates that HZSM-5 promotes the conversion of oxygenates to hydrocarbons.

The formation of liquid hydrocarbons was very low on Mo/SiO₂. However, the comparison of gas phase hydrocarbons formed on Mo/HZSM-5 and Mo/SiO₂ as illustrated in Fig.2 allows one to draw some valuable conclusions. The formation of methane and ethane on Mo/SiO₂ was much higher than on Mo/HZSM-5. It also produced more butane and pentane on Mo/SiO₂. More significantly, Mo/SiO₂ produced only trace amounts of *iso*-butane and *iso*-pentane, while Mo/HZSM-5 produced much more *iso*-alkanes. These results clearly indicated that the HZSM-5 as the support for Mo is superior to SiO₂ if one desires the production of *iso*-alkanes and aromatics.

Effect of zeolite acidity on FTS

The effect of zeolite acidity of Mo/HZSM-5 on FTS was investigated with samples having the same Mo loading (5 wt.%) and different SiO₂/Al₂O₃ ratios at 623 K, 500 psig and 573 K, 1000 psig. As shown in Table 2, the sample with SiO₂/Al₂O₃ of 50 showed the highest formation of liquid products. The other samples having lower (23) or higher (80, 280) SiO₂/Al₂O₃ ratios produced less liquid products. This result indicates that a balance between the acid sites (SiO₂/Al₂O₃ ratio) and active molybdenum species on the zeolite support is necessary for the optimum production of liquid products.

As the molybdenum oxides loaded on the HZSM-5 prefer to interact with *Brønsted* acid sites resulting in a decrease in the zeolite acid amount [8], an optimum Mo loading amount must exist for the optimum performance of the catalyst. It is thus proposed that the FTS on Mo/HZSM-5 catalyst is a synergistic bifunctional - molybdenum metal function with zeolite acid function catalytic process.

Table 2 Catalytic performances of Mo/zeolite catalysts for FTS

Catalyst	SiO ₂ /Al ₂ O ₃	T (K)	P (psig)	CO Conversion (%)	Products Distribution*	
					C ₁₋₃	Liq. Products
5% Mo/HZSM-5	23	573	1000	10.5	0.26	0.05
	50	573	1000	15.2	0.49	0.52
		623	500	31.8	0.68	0.25
	80	573	1000	32.4	0.43	0.18
623		500	51.2	0.73	0.01	
280	573	1000	20.6	0.38	0.16	
	623	500	44.6	0.59	0.03	
5% Mo/H-Y	80	573	1000	13.9	0.79	0.80
5% Mo/H-β	25	573	1000	13.5	0.64	---

*Product distribution was based on carbon basis and 1 mole CO₂ formation.

Effects of zeolite structure on FTS

Table 2 also summarizes the reaction results using different zeolite as the support. The best result was obtained with zeolite Y having a SiO₂/Al₂O₃ = 80, on which 0.8 mole liquid products was obtained for each mole CO₂ formation at a CO conversion of 14%. Zeolite β (SiO₂/Al₂O₃ = 25) as the support for Mo produced minor amount of liquid hydrocarbons.

Variation of the composition of liquid hydrocarbons obtained on different zeolite supported Mo catalysts is shown in Fig.2. Branched & cyclized alkanes and aromatic compounds are dominant species in the oil produced on Mo/HZSM-5 or Mo/H-β. Aromatic compounds showed product concentrations of 30% to 78% on these catalysts depending on the reaction conditions. In contrast, the products obtained from Mo/H-Y were dominated by linear and isomerized alkanes. Aromatic compounds were about 11% and 7% at 623K, 500 psig and 573K, 1000 psig, respectively, which is much less than that obtained from either Mo/HZSM-5 or Mo/H-β. The zeolite structure appears to affect greatly the formation of aromatic compounds. Fig.2 also shows the data at different reaction conditions. Lower temperature and higher pressure decreased the formation of aromatic compounds and increased the formation of linear, isomerized and cyclized alkanes. A product with less than 8% of aromatic

compounds and more than 50% isomerized and cyclized alkanes was obtained at 573K, 1000 psig over 5% Mo/H-Y

catalyst. As shown in Table 2, this catalyst

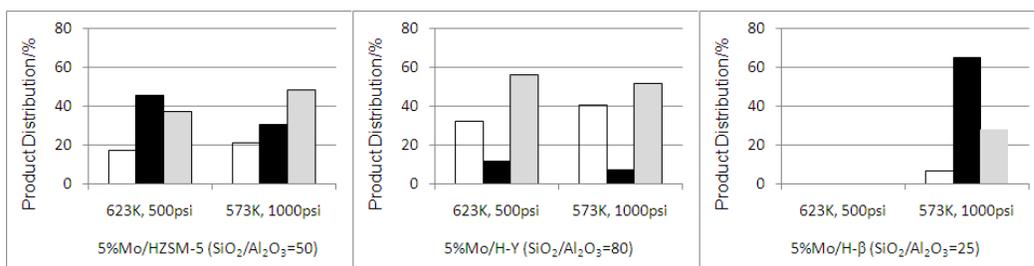


Figure 2 Product distribution in oil phase from FTS over different catalysts.

□: Linear Alkanes+Alkenes; ■: Aromatics; ■: Branched & Cyclized Alkanes

is one of the most active and selective catalysts we have produced. The organic phase produced with this catalyst is very promising for high quality gasoline products that satisfy the restrictions of low aromatics content in gasoline.

Conclusion

The experimental results revealed that Mo/HZSM-5 is an active catalyst for FTS with a low H₂/CO (molar ratio ~1.0) syngas, typical of a synthesis gas derived from biomass gasification. Branched alkanes and aromatics were the dominant products over the Mo/HZSM-5. Higher alcohols and carboxylic acids (C₁-C₆) can be produced with Mo/zeolite catalysts. The FTS reaction proceeds mainly inside the zeolite channel *via* mixed alcohol formation as the first step for hydrocarbons formation.

The results indicated that the zeolite structure and acidity greatly affect the formation of liquid hydrocarbons. It also greatly modifies the product distribution. Zeolite Y was found to be a good support for Mo for the FTS reaction in that the high quality gasoline product mainly consisted of branched and cyclized alkanes when the reaction conditions were 573K and 1000psig.

A drawback of the Mo/Zeolite catalyst is its high formation rate of CO₂ and light hydrocarbons. This result may relate to its high activity for the water gas shift (WGS) reaction and hydrogenation reactions of the formed hydrocarbon fragments on Mo sites. Possible strategies to inhibit the formation of CO₂ and lower alkanes involve 1) regulating zeolite acidity, 2) varying the micro-space environment of zeolite cage and 3) modifying the metallic property of Mo species by introducing a third component.

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References

1. E. Iglesia, S. C. Reyes, R. J. Madon, S. L. Soled, "Selectivity control and catalyst design in the Fischer-Tropsch synthesis: site, pellets, and reactors", *Adv. Catal.*, 39 (1993) 221-302.
2. R. B. Anderson, "Kinetics and reaction mechanism of the Fischer-Tropsch synthesis", in "Catalysis" (P.H. Emmett, *ed.*), Vol. 4, P. 257. Reinhold, New York, 1956.
3. A. Mertinez, C. Lopez, "The influence of ZSM-5 zeolite composition and crystal size on the in situ conversion of Fischer-Tropsch products over hybrid catalysts", *Appl. Catal. A: Gen.*, 294 (2005) 251-259

4. S. Liu, L. Wang, R. Ohnishi, M. Ichikawa “Bifunctional catalysis of Mo/HZSM-5 in the dehydroaromatization of methane to benzene and naphthalene: XAFS/TG/DTA/MASS/FTIR characterization and supporting effects”, *Journal of Catalysis*, 181(2) (1999) 175-88.
5. M. Xiang, D. Li, H. Qi, W. Li, B. Zhong, Y. Sun, “Mixed alcohols synthesis from carbon monoxide hydrogenation over potassium promoted beta-Mo₂C catalysts”, *Fuel*, 86(9), (2007) 1298-1303.
6. G. Boskovic, P. Putanov, K. Foettinger, H. Vinek, “Activation of Mo-based catalyst for paraffins isomerization”, *Applied Catalysis, A: General*, 317(2) (2007) 175-182.
7. R. Barthos, T. Bánsági, T. S. Zakar, F. Solymosi, “Aromatization of methanol and methylation of benzene over Mo₂C/ZSM-5 catalysts”, *Journal of Catalysis*, 247 (2007) 368-378.
8. Y. Xu, Y. Shu, S. Liu, J. Huang, X. Guo, “Interaction between ammonium heptamolybdate and NH₄ZSM-5 zeolite: the location of Mo species and the acidity of Mo/HZSM-5”, *Catalysis Letters*, 35 (1995) 233-43.