

FISCHER-TROPSCH SYNTHESIS ON Mo CARBIDE CATALYST: EFFECT OF SUPPORT TYPE ON PHYSICOCHEMICAL PROPERTIES AND ACTIVITY

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Summary

Molybdenum carbide synthesized by temperature-programmed carburization of supported-Mo oxide (10wt% Mo) using H₂/C₃H₈ mixture has been characterized and evaluated for Fischer-Tropsch activity as a function of support type. Mo oxide carburization rate depended on the C₃H₈ composition and revealed an optimum at a H₂:C₃H₈ ratio = 5 for all four supports. However, BET area varied with support type from 23 (ZrO₂) to 194 (Al₂O₃) m²g⁻¹. Weak Lewis (peak at 525-570 K) and Bronsted (peak at 730-790K) acid sites were found on all catalysts. The TiO₂-supported Mo carbide, however, gave the highest FT activity and chain growth factor while olefin content in the product stream was greatest in the Al₂O₃ catalyst. Olefin-to-paraffin ratio decreased exponentially with carbon number on all supports.

Keywords

Mo₂C, Fischer-Tropsch Synthesis, Temperature programmed carburization.

Introduction

Since the discovery of noble-like behavior of Mo₂C, there has been a growing interest in the utilization of molybdenum carbide for Fischer-Tropsch (FT) reaction¹. The improved olefin selectivity of an alumina-supported Co-Mo oxide conditioned in CO-rich gas has been attributed to the presence of a surface Mo carbide phase². The catalyst high resistance to sulphur poisoning and carbon deposition was also reported². Temperature programmed-reaction of MoO₃ with H₂/CH₄ is a common method for synthesizing Mo₂C at T >1073 K. However, employing higher hydrocarbons can reduce carburization temperature and hence increase surface area³. In this study, H₂/C₃H₈ carburizing mixture was utilized to produce MoC_{1-x} from Mo oxide impregnated on various semiconductor oxides (0 < x < 1). The aims of this study were to investigate effect of different supports, namely; Al₂O₃, SiO₂, TiO₂, and ZrO₂ on the physicochemical properties and reaction metrics for CO hydrogenation in order to develop useful quantitative relation for a tailored Mo carbide catalyst.

Experimental

Quantitative amounts of aqueous (NH₄)₆Mo₇O₂₄·4H₂O solution were mixed with the measured support pre-treated at 973 K in air for 6 h to ensure phase stability. After drying in an oven at 403 K for 16 hours, the resulting Mo oxide/support solid was carburized with 5H₂:1C₃H₈ mixture at 973 K for 2 h in a 6 mm OD stainless steel fixed bed reactor. Fischer-Tropsch reactions were carried out in-situ by switching to feed syngas with different composition (H₂:CO = 1:5-5:1) at 473 K. Gas hourly space velocity was maintained at 10 L g_{cat}⁻¹h⁻¹ to ensure negligible mass transfer limitations. Quantachrome Autosorb-1 unit was used to determine surface area and pore volume of the catalysts at 77 K while total organic carbon content was measured on a Shimadzu TOC 5000 Solid Sample Module Analyzer conducted at 1173 K in ultra-pure oxygen flow. NH₃ temperature-programmed desorption was analyzed in a Micromeritics 2910 AutoChem unit using 4 heating rates (5-20 K min⁻¹). Temperature-programmed carburization (303-873 K for 4 heat ramps at 5-20 K min⁻¹) of the supported MoO₃ samples was performed in ThermoCahn TGA 2121 module with H₂/C₃H₈ gas mixture flow of 55 ml min⁻¹.

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Results and discussion

As seen in Table 1, the BET area and residual total organic carbon (%TOC) after carburization was each highest on the Al_2O_3 -supported catalyst and smallest on the ZrO_2 system. All catalysts possess two peaks in the NH_3 -TPD spectra (Peak 1 located at 525-570K and Peak 2 located at 730-790K) which may be attributed to the presence of weak Lewis and Brønsted acid sites respectively⁴. The strength of the acid site as indicated by the NH_3 heat of desorption, E_d , indicates that the co-ordinative adsorption bond strength of the Lewis acid sites (Peak 1) decreased in the order $\text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{ZrO}_2$.

Table 1. Physicochemical properties of supported MoC_{1-x}

Catalyst	Average BET surface area (m^2g^{-1})	Total organic carbon (TOC) %	Adsorbed NH_3 , A (mol $\text{NH}_3/\text{g}_{\text{cat}} \times 10^5$)	Heat of desorption (kJ mol^{-1})	
				Peak 1	Peak 2
$\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$	194.00	11.72	35.1	37.91	320.12
$\text{Mo}_2\text{C}/\text{TiO}_2$	69.09	8.76	14.7	49.25	101.10
$\text{Mo}_2\text{C}/\text{ZrO}_2$	22.86	3.94	4.29	33.55	53.98
$\text{Mo}_2\text{C}/\text{SiO}_2$	112.20	5.72	5.74	37.06	57.28

However, the variation in strength of the Brønsted acid site (Peak 2) with support type seems to correlate with the trend in TOC content suggesting that carbon deposition arising from C_3H_8 decomposition was more facile on H^+ sites and highest on the Al_2O_3 catalyst because E_d was maximum for its Brønsted acid centre. Interestingly, the concentration of acid sites, A, on the support also paralleled this behaviour. Temperature-programmed carburization of MoO_3 with $\text{H}_2/\text{C}_3\text{H}_8$ is shown in Figure 1. The first peak may be ascribed to the reduction of MoO_3 to MoO_2 , which was a precursor for the oxycarbide (second peak) and carbide phase (third peak at $T > 800 \text{ K}$)³.

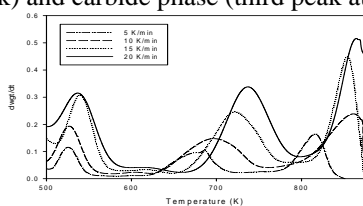


Figure 1. Temperature-programmed carburization of representative Mo oxide with different heating rates

Figure 2 shows that the optimum carburizing gas composition, $y_{\text{C}_3\text{H}_8}$, is about 0.17. Carburization rate declined at $y_{\text{C}_3\text{H}_8}$ beyond 0.2 because of insufficient H_2 to remove deposited carbon which inhibited the reaction. Although not shown, the TOC content on solid catalysts from these runs is a sigmoid with a plateau at $y_{\text{C}_3\text{H}_8} > 0.5$.

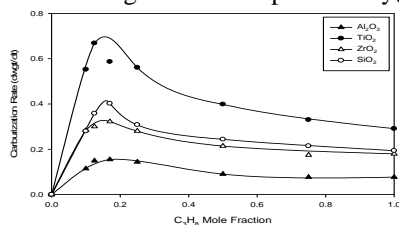


Figure 2. Carburization rate vs. C_3H_8 mole fraction

The influence of feed composition ($\text{H}_2:\text{CO}$ ratio) on FT reaction rate is seen in Figure 3. Maximum activity was at y_{H_2} of about 0.7 for all catalysts unlike with traditional Fischer-Tropsch catalysts -Co and Fe - which gave highest reaction rate at $0.80 < y_{\text{H}_2} < 0.9$ well above the stoichiometric requirement⁵. The carbide catalysts were more tolerant of higher CO partial pressure and appeared to require less H_2 chemisorption for hydrocarbon synthesis because the active site for the carbide catalyst is an oxycarbide surface species formed from initial molecular CO adsorption³ whereas in conventional FT catalysts, the active site is the H_2 -reduced metal oxide phase. Thus, the rate-composition curve is skewed towards higher y_{H_2} values in the latter catalyst system. Among the carbide catalysts, however, Fischer-Tropsch activity and chain growth factor decreased in the order $\text{MoC}_{1-x}/\text{TiO}_2 > \text{MoC}_{1-x}/\text{Al}_2\text{O}_3 > \text{MoC}_{1-x}/\text{SiO}_2 > \text{MoC}_{1-x}/\text{ZrO}_2$ identical to the trend seen for the weak Lewis acid sites. Thus, the latter may be the active site on which CO molecularly adsorbed for FT synthesis. Our data are also consistent with results on supported-Co catalyst⁶.

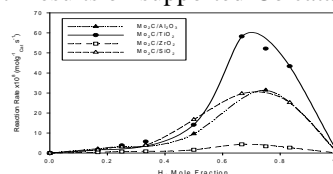


Figure 3. Overall reaction rate vs. H_2 mole fraction

Conclusions

Supported Mo carbide catalysts exhibited maximum rate and chain growth rate at $y_{\text{H}_2} = 0.7$ although the titania-supported system was the most superior among the 4 catalysts and the trend was well correlated with the strength of the Lewis acid sites.

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