

# CARBON MONOXIDE HYDROGENATION OVER SAPO-SUPPORTED Co-Mo CATALYSTS

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## Summary

Hydrocarbon production during CO hydrogenation over a set of factorially designed Co-Mo catalysts impregnated on to silicoaluminophosphate support has been studied at 473K and atmospheric pressure in a fixed bed reactor. Physicochemical attributes of the catalyst system were correlated to preparation factors via multi-linear regression polynomials. While hydrocarbon synthesis rate and ethylene selectivity improved with increase Co loading, the residual organic carbon was substantially reduced with catalysts containing high Mo content. However, neither have any effect on the chain growth probability. A fit of the rate data to the Anderson-Schulz-Flory model revealed two distinct chain growth factors for all catalysts.

## Keywords

Co-Mo catalyst, SAPO support, Fischer-Tropsch reaction, Anderson-Schulz-Flory model

## Introduction

The effect of conventional semiconductor oxides on Fischer-Tropsch (FT) catalysts have been examined in a variety of studies<sup>1</sup>. However, relatively fewer investigations have been conducted on the shape-selective characteristics of microporous supports such as silicoaluminophosphates (SAPO) in order to control product distribution during hydrocarbon synthesis. Due to their chemical composition,  $(Si_xAl_yP_z)O_2$ , SAPOs possess zeolitic properties and unique physicochemical features which have been responsible for their excellent catalytic performance in several reactions<sup>2</sup>. In a previous study<sup>3</sup>, we have shown that methane suppression during FTS can be obtained using a silica-supported Co-Mo catalyst. In the present study, we examine the effect of Co and Mo loading as well as calcination temperature on the FT performance when the catalyst is supported on a sol-gel synthesized SAPO.

## Experimental

The SAPO support was prepared using morpholine as the organic template. The SAPO catalyst is then calcined at 700°C to remove the morpholine before impregnation of

the metals. 2 different levels of cobalt (5 and 15%) and molybdenum (2 and 10%) were used for wet impregnation, followed by 2 different calcination temperatures (500 and 700°C) and drying. BET surface area, pore volume, acid site strength and concentration of the catalyst were measured. TGA and H<sub>2</sub>-TPR were used to identify oxide and metal phases present upon calcination and reduction respectively. Total organic carbon (TOC) content on used catalysts was also measured. The Fischer-Tropsch reaction was carried out with different compositions (H<sub>2</sub>:CO = 1:2-5:1) at 220°C with gas hourly space velocity at 50 L.g<sub>cat</sub><sup>-1</sup>.h<sup>-1</sup> under conditions with negligible transport resistances.

## Results and Discussion

Temperature-programmed calcination of the catalyst suggest that the SAPO support is thermally stable up to 1000K while the decomposition of the Co(NO<sub>3</sub>)<sub>2</sub> to its oxides occurred between 433-473K and the Mo existed as (MoO<sub>3</sub>)<sub>p</sub>-SAPO obtained during drying at 393K. H<sub>2</sub>-TPR also revealed the formation of Co<sup>2+</sup>/Co<sup>3+</sup> and Mo<sup>4+</sup> species at about 573K and 743K respectively. Yates' treatment (analysis of variance) of the measured physicochemical properties provided in Table 1 indicates that Co loading does not have statistically significant effect on BET area,

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pore structure while Mo addition has a distinct impact on these physical properties.

Table 1: Physicochemical properties of catalysts

Cat.	BET (m <sup>2</sup> ·g <sup>-1</sup> )	Pore Vol. (cc·g <sup>-1</sup> )	Pore Dia. (nm)	TOC (%)	Heat of desorption (kJ mol <sup>-1</sup> )		NH <sub>3</sub> uptake (mol·NH <sub>3</sub> ·g <sub>cat</sub> <sup>-1</sup> x 10 <sup>4</sup> )	
					Lewis Site	Bronsted Site	Lewis Site	Bronsted Site
S1	8.862	0.3688	166.5	1.776	68.2	32.0	10.9	5.80
S2	12.29	0.1426	46.44	1.776	43.0	96.6	6.43	3.55
S3	17.71	0.07251	16.38	1.577	54.2	79.2	9.48	6.42
S4	19.82	0.3103	62.61	1.776	48.9	139.1	7.25	3.65
S5	8.343	0.294	141.0	1.710	42.9	256.6	5.82	3.46
S6	8.144	0.4801	235.8	1.829	42.0	414.4	5.62	3.93
S7	5.335	0.1074	80.50	1.794	58.5	70.8	3.47	1.74
S8	14.00	0.07039	20.12	1.742	44.1	117.8	7.68	5.72

Lewis and Bronsted acid sites were present on all catalysts with Co addition having a statistically negative effect on Lewis acidity (strength and concentration). However it seems that the Bronsted sites had been formed during the initial SAPO synthesis. Residual TOC of used FT catalysts showed that increased Co loading caused higher carbon deposits while Mo-rich catalysts experienced reduced carbon deposition. Fig. 1a shows representative rate-consumption profile for the FTS (total hydrocarbon) reaction. The composition corresponding to the maximum rate depends on the catalyst type and ANOVA revealed that increased Co loading improved synthesis rate as well as the olefin production (Fig. 1b). However, unlike the Co-Mo/SiO<sub>2</sub> system, methane selectivity was unaffected by the preparation factors considered in this study. However, an Anderson-Schulz-Flory plot of the product distribution, illustrated in Figure 2 revealed the possibility of two different chain growth probabilities. The C<sub>1</sub> to C<sub>5</sub> products generally give lower chain growth factor,  $\alpha_1$  ( $\alpha_1 < 0.5$ ) than that of  $\alpha_2$  ( $\alpha_2 > 0.5$ ) obtained for C<sub>5</sub>-C<sub>10</sub> species. Even so, both are dependent on the feed composition as well as catalyst type. Increasing Co loading reduced  $\alpha_1$  values but improved  $\alpha_2$  values.

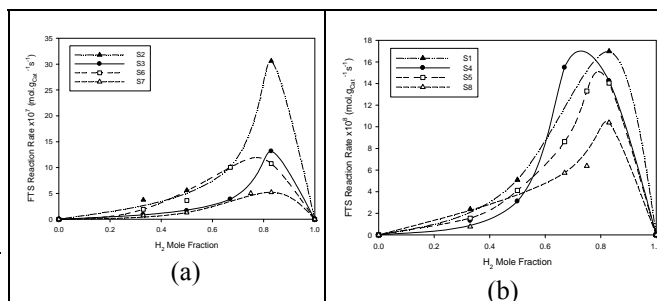


Figure 1: FTS reaction (a) and olefin production rate (b)

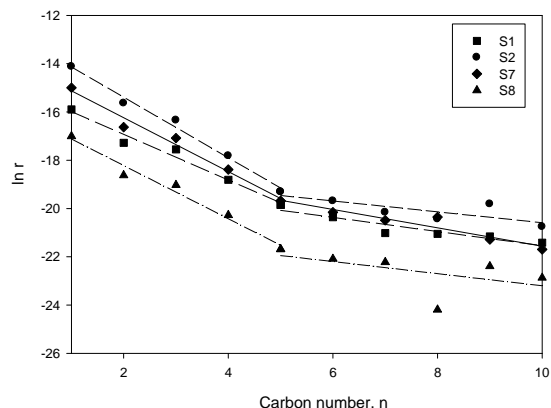


Figure 2: ASF Plot for run with feed H<sub>2</sub>:CO ratio= 2:1

Since two types of growth sites are implicated, it would seem that C<sub>6+</sub> hydrocarbons require a Co-contained site while C<sub>1</sub>-C<sub>5</sub> hydrocarbons were produced on site in competition with Co. Change in Mo loading did not affect  $\alpha_1$  values although  $\alpha_2$  was negatively impacted by the presence of Mo.

## Conclusions

SAPO catalysts are suitable for olefin production and the addition of Co-Mo decreases methane formation. High cobalt loading gives good olefin reaction rate and higher hydrocarbons whereas addition of molybdenum makes the catalyst more carbon-resilient.

## References

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