CO hydrogenation over alumina-supported Mo carbide catalysts

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Introduction
Fischer-Tropsch synthesis (FTS) has been regarded as a promising technology for producing an alternative and clean energy to replace fossil fuels due to the depletion of petroleum resources and environmental concerns. Conventionally, Co- and Fe-based catalysts were employed for FTS. Molybdenum carbide is also an attractive and promising catalyst due to its carbon resistance and sulphur resilience [1]. The objective of this study was to investigate the effect of Mo loading on both physicochemical properties and FT performance of Al2O3-supported MoC1-x catalysts produced via propane carburization.

Materials and Methods
Impregnation method employed for the preparation of Xwt%MoO3/Al2O3 (0.5≤X≤20) precursors was reported in previous studies [2]. A calculated amount of aqueous (NH4)6Mo7O24.4H2O solution was mixed and stirred for 3 h with pretreated γ-Al2O3 support. The impregnated slurry was subsequently dried in an oven for 16 h at 393 K and calcined in air at 773 K for 5 h to produce Xwt%MoO3/Al2O3. The Mo carbide catalysts were obtained from the temperature-programmed carburization of the corresponding Xwt%MoO3/Al2O3 with a mixture of 5H2/1C2H4 (50 ml min−1) at 973 K for 2 h in a computer-controlled fixed-bed reactor. FTS evaluation was conducted in-situ in the same reactor with different H2:CO ratios of 1.5-5:1 at 453-493 K and atmospheric pressure. BET surface area, average pore volume and pore diameter were measured in a Quantachrome Autosorb-1 unit using N2 physisorption at 77 K. X-ray diffraction measurements for both fresh and spent Mo carbide catalysts were performed on a Philips X’pert Pro MPD system with Ni-filtered Cu Kα (λ= 1.542 Å) at 45 kV and 40 mA. Temperature-programmed desorption (TPD), namely; NH3-, CO2-, CO- and H2- TPD was carried out on a Micromeritics 2910 AutoChem unit. Temperature-programmed calcination and carburization runs were also conducted in a Thermocahn TGA 2121 unit.

Results and Discussion
As seen in Figure 1, both hexagonal closed packed (hcp) β-MoC1-x (with 20 = 34.0° and 39.5°) and face-centered cubic (fcc) α-MoC1-x (20 = 36.6° and 61.3°) phases were detected on catalyst support. Spent Mo carbide catalyst exhibited a similar X-ray diffractogram to that of fresh catalyst and did not possess deposited carbon (typically located at 2θ=26°) and peak for MoO3 phase suggesting that MoC1-x phase may be stable during FTS run and tolerant of carbon deposition. Regardless of the Mo loading, (rco) exhibited a maximum at H2 mole fraction of 0.67-0.75 suggesting that the reaction mechanism was unchanged with variation in Mo content. CO consumption rate increased with Mo loading and the optimal FT activity was located at 15wt%Mo loading for different feed compositions. Figure 2 shows that (rco) increased monotonically with increasing specific CO active site strength approaching an asymptotic value beyond about 10 kJ m−2. This suggests that CO chemisorption site was the active center for CO hydrogenation over the Mo carbide catalyst system.

Significance
Total hydrocarbon synthesis rate trend with Mo loading paralleled the pattern observed for the CO specific site strength whilst optimal olefin-to-paraffin ratio was located at 10wt%Mo loading. Optimal FTS rate was found at yund=0.67-0.75 with optimum chain growth probability at yund=0.33.

References