Catalyst Properties Determining the C5+ selectivity for Co based Fischer-Tropsch catalysts.

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Introduction

Supported cobalt catalysts are preferred in the Fischer-Tropsch synthesis of higher hydrocarbons from natural gas derived synthesis gas due to their high activity and selectivity, low water-gas shift activity and moderate deactivation. Co site-time yields have usually been considered independent of both particle size and support material provided that the Co particles are larger than about 8 nm, for smaller particles the Co site-time yield decreases with decreasing particle size [1]. The same relationship was also lately observed for supported Ru catalysts [2]. The selectivity, however, depends on the support material as well as on the Co particle size. Re addition increases the C5+ and Pt decreases the C5+ selectivity. The relationship between catalyst properties and selectivity is still far from being established.

The present contribution deals with a systematic study of the behaviour of catalysts with different particle sizes and different structural parameters of the support. Al2O3 phases (δ, θ, α) have been produced from a small and medium pore γ-Al2O3 (Puralox SSCa). The results are compared with studies of Co supported on SiC, on CNF and on Al2O3 supports modified with the addition of Zn, Ni, Mg. The experiments were all carried out at exactly the same conditions and in the same equipment.

Materials and Methods

Co catalysts (12-20 wt%) were prepared by incipient wetness impregnation. Ethylene glycol was added to the impregnation solution in cases where a small and predetermined Co particle size should be obtained. The catalysts were dried at 383 K for 4 h, and calcined at 573 K for 16 h in flowing air. The catalysts were then sieved to obtain a particle size in the range of 53-90 μm to avoid diffusion limitations. The catalysts were characterized by standard methods. The Fischer-Tropsch synthesis was performed in a fixed-bed reactor at 483 K, 20 bar, and H2/CO=2.1. The experimental details are given elsewhere [3].

Results and Discussion

It is important that the experiments are carried out at the same conversion, since the C5+ selectivity increases with increasing conversion. The high pressure experiments have also been carried out in such a way that information about the initial catalyst deactivation is obtained.

The results clearly show that the medium pore Al2O3 supports gave higher C5+ selectivity than the corresponding small pore Al2O3. The high C5+ selectivity for Co supported on δ-Al2O3 (or the low selectivity for θ-Al2O3) is surprising and does not follow the usual behaviour of pore sizes. The Lewis acid sites on the support as determined by pyridine adsorption and FTIR spectroscopy, show that the trend of the peak area of Lewis acid sites is that of a mirror image of the C5+ selectivity. These results were obtained using a constant Co particle size of about 9 nm.

Figure 1 shows that the C5+ selectivity for Co supported on θ-Al2O3 increases with increasing particle size up to about 8-9 nm. A maximum in C5+ selectivity is observed before the selectivity decreases somewhat and levels out with increasing particle size. The same behaviour was observed with δ-Al2O3 and α-Al2O3 although we were not able to obtain Co particles of 9 nm on α-Al2O3. Previous results with γ-Al2O3 showed the same behaviour. SiC contained alkali which influenced the performance and the addition of Ni, Zn, Mg showed interesting behavior on the Co site-time yields. Alkali reduces the site-time yields, and increases the C5+ selectivity. The Fischer-Tropsch synthesis involves a chain growing process and the relation between the O/P ratio and the C5+ selectivity is due to changes in hydrogenation activity.

The results show that the C5+ selectivity depends on the nature and pore characteristics of the catalyst support.

Significance

The results are important for the design of catalysts for maximizing the C5+ selectivity.

![Figure 1. Olefin/Parafin ratio and C5+ selectivity for Co/0-Al2O3 (medium pore). 20 bar, 483K, H2/CO=2.1, 12 wt% Co and 45% conversion of CO.](image)