The Effect of Catalyst Porosity on Methane Selectivity in the Fischer–Tropsch Reaction

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An examination of the relationship between the catalyst porosity and selectivity for methane formation in the Fischer–Tropsch reaction has shown that variation in product spectrum may be the result of changing adsorption patterns of hydrogen and carbon monoxide rather than mass transfer phenomena as previously thought.

The effect of catalyst porosity on product distribution in the Fischer–Tropsch reaction remains a subject of controversy. The observed increase in methane selectivity as a consequence of a decrease in the average pore diameter of the catalyst was attributed by Anderson et al.[1] to mass transport phenomena. He suggested that the greater rate of diffusion of hydrogen inside the liquid filled pores compared to that of carbon monoxide causes an increase of H_2/CO ratio in the vicinity of active sites located inside the catalyst particles. Such conditions would be expected to shift the product spectrum towards the light molecular mass hydrocarbons and thus favour CH_4 formation.[2]

This postulate was further supported by other workers.[3–6] Concerns about mass transfer effects on the Fischer–Tropsch product distribution led to the development by the Shell Oil Co. of 'rim catalysts', where the active metallic component is deposited on the outside of the catalyst particles to minimise the diffusion path of the reactants.[7,8] Another approach to reduce the intraparticle mass transfer was adopted by Yokota and Fujimoto,[9,10] who carried out the Fischer–Tropsch reaction in the supercritical phase. On the other hand, evidence that intraparticle diffusion effects on the Fischer–Tropsch reaction are negligible has been presented by Zaidi et al.[11] and Deckwer et al.[12]

In this communication we report the results of an investigation into the effect of pore size distribution on carbon monoxide conversion and methane selectivity in the Fischer–Tropsch reaction. They show that the changes in the product distribution may be caused by variation in the amount of

hydrogen and carbon monoxide chemisorbed on the catalyst surface. As the chemisorption measurements were carried out at equilibrium, the observed differences could not be affected by mass transfer limitations.

Four undoped cobalt catalysts with metal loadings ranging from 10.2 to 12.6 wt% were investigated. A series of silicas of different pore diameters and narrow pore distributions (Merck Kieselgel 40, 60, 100, 200) were used as supports. The pore size distributions of the catalysts as calculated from nitrogen desorption isotherms are shown in Fig. 1.

The catalytic performance was measured in a slurry autoclave (CSTR). Experimental conditions used were as follows: pressure 2 MPa, temperature 202 °C, feed H_2/CO = 2.5, total inlet gas flow 180 ml min⁻¹, 5 g of catalyst suspended in 80 g of octacosane, catalyst particle size <75 μm. Prior to each experiment the catalyst was reduced in pure hydrogen at 400 °C for 24 h to achieve complete reduction of cobalt oxide. Hydrogen chemisorption was measured by the method of Jones et al,[13] while CO adsorption was measured using the standard pulse flow method.[14] The catalysts' characteristics and performance are summarised in Table 1.

As expected, an inverse dependence exists between the average pore diameter and the surface area of the catalyst. This in turn leads to variation in cobalt dispersion, as calculated using hydrogen chemisorption which is well understood.[13,15] However, these differences in cobalt dispersion were found to have little effect on carbon monoxide adsorption, which was identical for all four catalysts.

The most likely explanation of this phenomenon is variation in the stoichiometry of carbon monoxide adsorption on different size cobalt crystallites.[15] As a consequence, the ability of the catalysts to adsorb both reactants, expressed as the ratio of the number of hydrogen atoms and the number of carbon monoxide molecules adsorbed on the surface (H/CO ratio), varies with their pore size distribution.

The differences in the adsorption properties of the catalysts show a clear correlation with their performance (Fig. 2). The rates of carbon monoxide conversion and methane formation are expressed as turnover numbers (TONs) to link them directly to the number of exposed cobalt atoms. The TON for carbon monoxide conversion is almost identical for all catalysts, while the TON for methane formation rises sharply with increasing H/CO ratio on the catalyst surface.

This is an important finding, as it clearly demonstrates that changes in the catalyst porosity affect the product distribution by varying the chemisorption ratio of both reactants on the catalyst surface. Most importantly, this effect is independent of the mass transfer phenomena as it was measured at equilibrium.
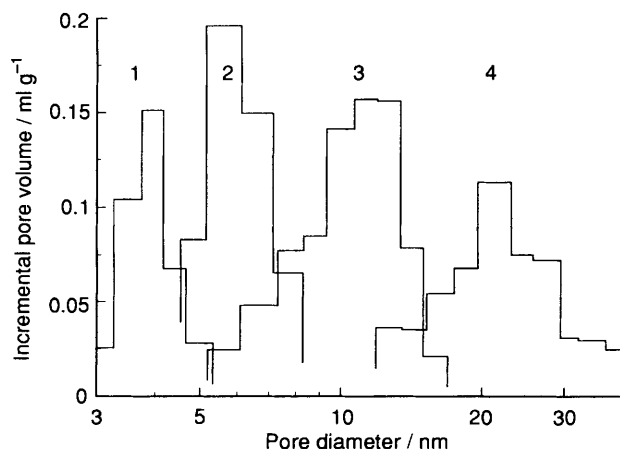

Fig. 1 Pore size distributions of the catalysts. Numbers indicate catalyst numbers as in Table 1

Table 1 Characteristics and performance of catalysts

Cat. No.	Cobalt loading (wt%)	CO conversion (%)	CH₄ selectivity (%)	Average pore diameter /nm	BET surface area[a] /m²g⁻¹	H₂ uptake /μm g⁻¹	CO uptake /μm g⁻¹	H/CO[b] ratio	Cobalt dispersion (%)
1	10.9	19.2	19.5	4	530.6	88.68	41.09	4.35	9.6
2	10.4	14.5	11.9	6	375.9	67.07	43.32	3.12	7.6
3	10.2	9.4	5.8	10	260.1	52.85	42.17	2.50	6.1
4	12.6	8.6	2.9	20	121.9	33.63	42.66	1.59	3.1

[a] BET = Brunauer–Emmett–Teller. [b] Calculated from H_2 and CO uptakes as (no. of H atoms)/(no of CO molecules).
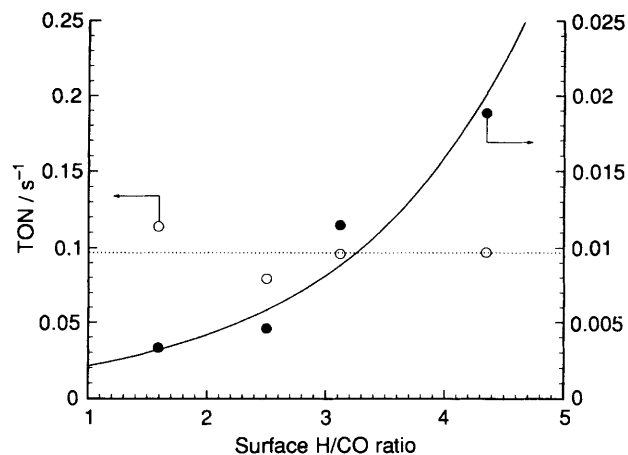
Fig. 2 Turnover numbers for CO conversion (○) and CH_4 formation (●) as a function of the ratio of hydrogen and carbon monoxide adsorbed on the catalyst surface

in some catalytic systems cannot be discounted, the inherent chemistry of the active sites has also to be examined as a potential cause for the variations of the products spectrum.

The results depicted in Fig. 1 can be interpreted on the basis of the most simplistic concept of the Fischer–Tropsch reaction, whereby the product spectrum is determined by the rates of two competing steps: chain termination and chain propagation.[2] Chain termination (hydrogenation) would be favoured by higher H/CO ratios on the catalyst surface, as shown by the experimental results. The fact that the TON for carbon monoxide consumption is independent of the surface H/CO ratio suggests that it may be limited by the ability of the catalyst to adsorb and/or dissociate the CO molecule.

The most important conclusion from this work is the discovery of the link between the catalyst porosity and the intrinsic properties of the active site which in turn have an effect on the product distribution in the Fischer–Tropsch reaction. While the existence of the mass transport limitations

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