

## Sulphur poisoning of a Co/Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch catalyst

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The catalytic conversion of synthesis gas into hydrocarbons (Fischer-Tropsch Synthesis, FTS) is recently receiving great attention as a powerful way of exploiting natural gas wells located in remote areas. It is generally recognized that S-compounds contained into natural gas, coal or biomasses act as effective poisons for FT catalysts. As a matter of fact, in order to minimise both iron- and cobalt-based industrial FT catalysts deactivation, it has been proposed that the S-content of syngas should be kept below 0.02 mg/m<sup>3</sup>. The issue of S-poisoning of FT catalysts has been addressed in various literature studies, many of which deal with iron catalysts. From these investigations, it appears that the effect of S-poisoning on catalytic performances is complex and often controversial. Accordingly, an investigation on the effect of S-poisoning on the activity and selectivity of an alumina-supported Co catalyst has been undertaken in our labs. For this purpose various catalyst samples have been loaded ex-situ with different S-amounts, in the range 0-2000ppm, characterized and tested in the FTS. Four simple deactivation kinetic models have also been developed in order to fit experimental data.

Characterization data indicate that from a morphologic point of view, sulphur addition does not lead to appreciable variations; on the contrary, S-presence induces a modest decrease of the catalyst reducibility. In addition, the comparison between the catalytic performances in the FTS of different sulphured samples evidences that the S-poisoning remarkably influences the system productivity and selectivity. In particular, it determines a progressive decrease of the catalytic activity, so that the most sulphured catalyst (2000 ppm S) is almost inactive. Notably, the S-presence decreases the catalyst reactivity (i.e. the CO conversion) for low S amounts (< 100 ppm), and affects the product distribution as well at high S loadings, favouring the formation of light products. Also the CO<sub>2</sub> and methane formation increases at high S-amounts. Four deactivation models, considering different dependences of the catalyst activity on the sulphur content, were used to describe the catalyst activity decay with the S loading. The obtained results are satisfactory, especially in the case of the models predicting a dependence of the CO consumption rate from the sulphur content (S) in the form  $r_{CO}=f(1+\alpha S)^{-\beta}$ , where  $\alpha$  and  $\beta$  are two positive adaptive parameters, indicating highly selective S-poisoning of the adopted catalyst.