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Fischer–Tropsch synthesis on sulphur poisoned Co/Al_2O_3 catalyst

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Abstract

The effect of sulphur poisoning (in the range 0–2000 ppm) on the characteristics and catalytic performances in the Fischer–Tropsch synthesis (FTS) of a bench-scale alumina supported cobalt catalyst is investigated in this study. It is found that sulphur did not lead to appreciable variations in the catalyst morphological characteristics; however, the catalyst reducibility/hydrogenating capability is significantly modified upon increasing the sulphur loading.

The comparison between the catalytic performances of the sulphured samples pointed out that the presence of sulphur remarkably affected the productivity and the selectivity of the reaction. In particular for low S amounts (<100 ppm) the CO conversion is decreased whereas the product distribution is not significantly affected; at higher S loadings a significant decrease in the formation of heavier products is observed along with a decrease in CO conversion. This leads to significant changes in the selectivity of the reaction.

These effects have been tentatively associated with different effects of sulphur on the catalyst active sites, i.e. on the sites (or site ensembles) responsible for CO hydrogenation and for the chain growth processes. Finally, the experimental data of CO conversion decay with S-loading were nicely described according to a simple deactivation model which implies a strong effect of sulphur on the catalyst active sites.

Keywords: Fischer–Tropsch synthesis; Catalyst deactivation; Sulphur poisoning; Cobalt

1. Introduction

The catalytic conversion of the 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 [1,2]. Syngas, typically produced from either natural gas (partial oxidation, steam reforming) or coal (gasification), is transformed by means of the FTS into a complex mixture of gaseous, liquid and solid hydrocarbons and alcohols, that can be further processed to maximize the liquid products yield. In general heavy paraffins (waxes) are the preferred products of FTS, since they can be easily hydrocracked to liquid fractions (gasoline and diesel fuels) which represent the highest added value FT products.

It is generally recognized that S-compounds contained in coal or natural gas are effective poisons for Fischer–Tropsch catalysts [3–8]. It has been suggested that in order to minimise the deactivation of both iron- and cobalt-based industrial Fischer–Tropsch catalysts, the sulphur content of syngas should be kept lower than 0.02 mg/m^3 [3].

The effects of sulphur poisoning of iron-based Fischer–Tropsch catalysts have been analyzed in various literature studies [4–8]. From these investigations it appears that sulphur has a rather complex and often controversial effect on the catalytic performances. In fact it has been shown that changes in activity and selectivity depends on the S-concentration in the feed stream [5–11]. As a matter of facts, while few authors have reported that S-poisoning leads to a decrease in the selectivity towards long-chain products [5,7,8], other studies reveal an opposite effect [4,6]. Also, in some cases [5,6,8,9] it has been reported that the presence of sulphur reduces the FT catalyst activity, whereas in other investigations [4,7,10,11] different effects have been observed, depending on the sulphur concentration in the syngas.

Notably, studies on Co-based FT catalysts are rather scarce [6,10,11], specifically on Al_2O_3 supported samples. However, also in this case, a few authors have reported that the effects of

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S-poisoning on both the catalyst activity and selectivity is rather complex and depends on the sulphur concentration on the catalyst [6].

With the aim of providing further insights on the effects of S-poisoning on the activity and selectivity of alumina supported FT Co-based catalysts, a dedicated investigation has been undertaken in ours labs. This has been carried out by controlled poisoning of a bench-scale Co/Al_2O_3 un-promoted catalyst according to an ex-situ procedure.

The possibility of studying S-poisoning adopting a catalyst prepoisoning procedure (ex-situ poisoning) has been considered in many literature reports [6–9,11], basically to overcome the experimental complexity associated to the use of S-carrier molecules, such as H_2S (the typical FT S-containing poison). In fact, the low S-concentration which is required in the feed stream, associated with the high adsorption capability of H_2S in the rig lines makes very difficult to precisely know the amounts of S reaching the catalyst samples. In addition it is reported that the high adsorption capability of H_2S leads to the presence of intra-particle sulphur gradients in the catalyst pellet and, in the case of fixed bed reactors, to the presence of axial concentration gradients in the catalyst bed as well. This makes very complex the analysis of reactivity data obtained in the presence of sulphur.

For these reasons, in line with other literature reports, we have prepared sulphur-poisoned samples having different S loadings by impregnation (ex-situ poisoning). In this way the poison concentration is a priori known, and S-concentration gradients in the catalyst bed can be safely neglected. An obvious disadvantage of this method is that the S-catalyst interaction may be different with that established under actual reaction conditions. Accordingly, to better simulate the Co-S interaction under real conditions, where Co is in a reduced state, the S-poisoning was carried out on catalyst samples which have been preliminary pre-reduced with H_2. It is expected that this procedure will lead to a representative effect of S-poisoning on catalytic activity.

The prepared samples have been characterized and tested in the FTS under actual synthesis conditions. A simple deactivation kinetic model has also been developed in order to describe the effect of sulphur on the catalyst activity.

2. Experimental

2.1. Preparation of S-poisoned Co/Al_2O_3 catalysts

The Co/Al_2O_3 un-promoted catalyst used in this study was a bench-scale prepared sample obtained by impregnation of a γ-Al_2O_3 with a Co nitrate solution. The Co loading was 15% w/w. S-poisoning of the Co/Al_2O_3 catalyst samples has been carried out by the incipient wetness impregnation technique with an ethanol–water solution of ammonium sulphide. In order to limit the water concentration during impregnation, the starting ammonium sulphide aqueous solution (Carlo Erba, 20% w/w) has been diluted with ethanol. To simulate the Co–S interaction under representative conditions the S-poisoning was carried out (as explained in the Introduction section) on reduced catalyst samples. For this purpose, the catalyst samples (sieved at 100–150 μm) were reduced with H_2 in a tubular reactor and then impregnated with the ammonium sulphide solution under inert atmosphere. Catalysts reduction was carried out at atmospheric pressure heating the samples at 673 K (heating rate 2 K/min) for 16 h in pure hydrogen. After reduction, the catalysts were cooled to room temperature (RT) under a N_2 flow and then impregnated with proper amounts of ammonium sulphide solutions. The samples were finally dried slightly above RT in dry N_2 and finally passivated at the same temperature in an O_2 (2% v/v in N_2) flow.

With this method catalyst samples loaded with 10, 100, 250 and 2000 ppm of sulphur were prepared. This quantities correspond to 250, 2500, 6250 and 50,000 h on stream, respectively, of a FT reactor working at 2000 cm^3(STP)/h/g_{cat} with a sulphur content of syngas equals to 0.02 mg/m^3 [3] under the hypothesis that all the fed sulphur adsorbs on the catalyst. A reference sample impregnated with an ethanol–water solution without sulphur was also prepared.

In the following, catalyst samples will be named referring to their nominal S content, i.e. S2000 will be the sample loaded with 2000 ppm of sulphur. The reference catalyst sample (i.e. the catalyst reduced and impregnated with a S-free ethanol–water solution) will be referred as S0. Table 1 reports the list of samples used in this study with the corresponding nominal sulphur loading, the nominal S/Co and S/Co_{sup} molar ratios and the relevant morphological characteristics. Data of the undoped calcined sample (precursor) are also reported.

2.2. Catalyst characterization

Prior the catalysts characterization (except TPR measurements), the passivated samples were reduced again at 673 K in H_2 and passivated at RT in a O_2 (2% v/v in N_2) flow.

Surface area and pore size distribution have been obtained upon nitrogen adsorption and desorption at 77 K with a Micromeritics Tristar 3000 instrument.

Table 1
Characteristics of S-poisoned Co/Al_2O_3 samples

Sample name	Nominal S loading [$\mu g_S/g_{cat}$]	S/Co [mol/mol]	S/Co_{sup}* [mol/mol]	Surface area [m^2/g]	Pore volume [cm^3/g]	Average pore diameter [Å]
Precursor	–	–	–	118	0.31	85
S0	0	0	0	116	0.31	84
S10	10	$1{,}2 \times 10^{-4}$	$1{,}2 \times 10^{-2}$			
S100	100	$1{,}2 \times 10^{-3}$	$1{,}2 \times 10^{-1}$	122	0.33	87
S250	250	$3{,}1 \times 10^{-3}$	$3{,}1 \times 10^{-1}$	121	0.32	83
S2000	2000	$2{,}5 \times 10^{-2}$	2,5	122	0.33	87

* Co_{sup} is the number of exposed Co atoms, estimated by H_2 pulse chemisorption (Co dispersion, defined as the ratio Co_{sup}/Co, ~1% in all the samples).