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Fischer–Tropsch synthesis on Co and Co(Ru-doped) ETS-10 titanium silicate catalysts

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Titanium silicate ETS-10 was found to be a suitable support for metal catalysts, having high surface area, high ion-exchange capability and no acidic functions. In this paper, the M-ETS-10 commercial form (where M stands for Na and K) was first exchanged with Co and thus tested in CO hydrogenation (Fischer–Tropsch synthesis). Moreover, the sample was also doped with small amounts of ruthenium to improve the Co reducibility. The successive catalytic tests revealed a strong increase in the CO conversion and a modification in the selectivity of the hydrocarbon fractions.

Keywords: Fischer–Tropsch synthesis; titanium silicate molecular sieves; cobalt and cobalt ruthenium-doped catalysts

1. Introduction

Cobalt-based catalysts have been widely used for Fischer–Tropsch synthesis (FTS) because of cobalt's intrinsic ability to hydrogenate dissociated carbon species and promote chain growth [1,2]. The properties of Co catalysts for the production of hydrocarbons also depend on the support material used [2–6] and on the nature of Co surface species formed after the catalyst preparation [7,8]. Correlation between the Co oxidation state and CO hydrogenation activity were widely reported [7–11] especially concerning the difficulty to reduce Co species and the possibility to add noble metals (known for having considerable hydrogen storage capability) to Co catalysts to affect the reduction of Co oxides and the ratio of unreduced Co to metallic Co. For example many studies were performed on Co–Rh catalysts supported on different materials [12–14].

A particular kind of molecular sieve containing titanium in framework position (ETS-10 by Engelhard [15]) was already tested for FTS by the authors, after ruthenium imbibition, with interesting results [16].

In the present paper ETS-10 was used after Co ion-exchange in order to evaluate Co performance on this kind of support. Moreover two Co-based samples were subsequently doped by ruthenium imbibition to increase the Co reducibility and also to improve the catalyst activity.

Characterization measurements are also reported.

2. Experimental

ETS-10 titanium silicate (commercial mixed sodium-potassium form, $(Na+K)/Ti = 1.8$, $Si/Ti = 5.0$) was calcined at 773 K for 4 h. A suitable ion-exchange-form of ETS-10 was prepared by multiple ion-exchange with a $Co(NO_3)_2{\cdot}6(H_2O)$ (Merck) solution (1.0 N, 20 ml/$g_{ETS} \approx 5 \times 4$ meq/g_{ETS}) following the procedures proposed by Rabo et al. [17] (sample A). Ruthenium-doped samples (samples B and C with 0.2 and 0.4 wt% Ru, respectively) were prepared by a slurry impregnation of the ion-exchanged ETS-10 with a solution of $Ru(NO)(NO)_3$ (Engelhard) in pure ethanol and the excess ethanol was evaporated under vacuum. All the samples were reduced, as suggested by Praliaud et al. [18] in flowing H_2 ($F_{H_2} = 80$ ml/min) at 623 K for 4 h and then characterized by means of XPS (M-Probe Instrument, SSI), SEM-EDX (Cambridge Scan 150) and ICP-AES (Jobin Yvon JY24) analyses. Moreover, ruthenium dispersion was measured by the single-introduction–back-sorption coupled method on the basis of irreversibly adsorbed hydrogen, as described elsewhere [19,20].

Reaction tests were performed in a stainless steel tubular reactor, inside coated with copper, especially designed for FTS of hydrocarbons (C_n: $n < 15$), described elsewhere [21]. The reaction was carried out with a mixture of high purity CO and H_2 (SIAD); the H_2/CO ratio of the inlet mixture was 2. The catalysts (always 1 g of fresh sample for each run) were tested at 548 K, 500 kPa and space velocity (GHSV) of 2160 V/(V h) (space velocity, GHSV, is defined as the gas hourly reactant flow at STP per total bed volume) and the hydrocarbons products were analysed on-line by gas-chromatography (see ref. [21] for details).

3. Results and discussion

All the samples were firstly characterized by ICP-AES technique: the amount of cobalt introduced by ion-

Table 1
Data from ICP-AES analysis

Component (wt%)	Co-ETS-10 (sample A)	Co (Ru-doped)-ETS-10 (sample B and C)
Co theoretical value	13.4	–
Co ICP analysis	7.4	7.4 (sample B) 7.4 (sample C)
Ru ICP analysis	–	0.2 (sample B) 0.4 (sample C)

exchange and the amount of ruthenium are reported in table 1. It is possible to observe a rather good comparison to the theoretical ion-exchange capability.

SEM analysis underlined a high morphological homogeneity (see fig. 1) with the presence of 0.4–0.6 nm sized particles aggregates. Moreover, EDX analysis (coupled at the SEM instrumentation) showed a good agreement with the cobalt quantitative data so to assert the local atomic density of Ti and Co also represents the density extended to the whole sample ($Co_{EDX}/Ti = 0.77$ in comparison to a theoretical Co/Ti ratio = 1.0).

XPS analyses were performed both on the as-prepared catalysts and on the reduced ones. The reduction treatment was performed inside the reaction chamber joined to the XPS apparatus in order to avoid any air contamination which can oxidize the sample surface again. The C 1s (used as internal reference), Ti 2p, Co 2p, O 1s and Ru 3d (in samples B and C) regions were deeply investigated and the Co^{2+}/Ti, Co^{α}/Ti (where $0 < \alpha < 2+$) and Co^0/Ti atomic ratio are reported in table 2. It is necessary to observe that, for Co^{2+} species the Co^{2+}/Ti ratio strongly decreases after the reduction treatment and this datum can be explained with the migration of the cation inside the support cages as it is really difficult to think of a reduction of the Co^{2+} species to metallic Co under the reduction conditions used [22]. By contrast, a particular trend can be observed for the Co^{α} species, probably due to partial oxidation of the Co precursor during the ion-exchange step: a large decrease in the Co^{α}/Ti atomic ratio is coupled with the presence of Co^0 on the surface of the sample after the reduction and thus it seems that this kind of Co species is more easily reducible than the Co^{2+} one. The Ru-doped samples showed the same Co^{2+}/Ti and Co^{α}/Ti atomic ratios of the sample A meaning that the ruthenium impregnation did not modify the surface composition. After the hydrogenation treatment, only Co^0 species was found: small amounts of ruthenium were able to activate hydrogen and make it more available for Co reduction.

The chemisorption measurements showed a very good dispersion value of the ruthenium atoms (D_M is 66% for sample B, 63% for sample C).

FTS activities and selectivity data for all samples are summarized in table 3 (including data of Ru/Na-ETS-10 [16]) and product distribution curves as a function of carbon number are shown in fig. 2. It is important to underline that for all samples the production of hydrocarbons is limited to C_1–C_7 fractions, present in a small amount, as a result of reaction parameters and a significant "cage effect" of ETS-10, which acts as a molecular sieve preventing the classical Flory distribution of FTS products [23].

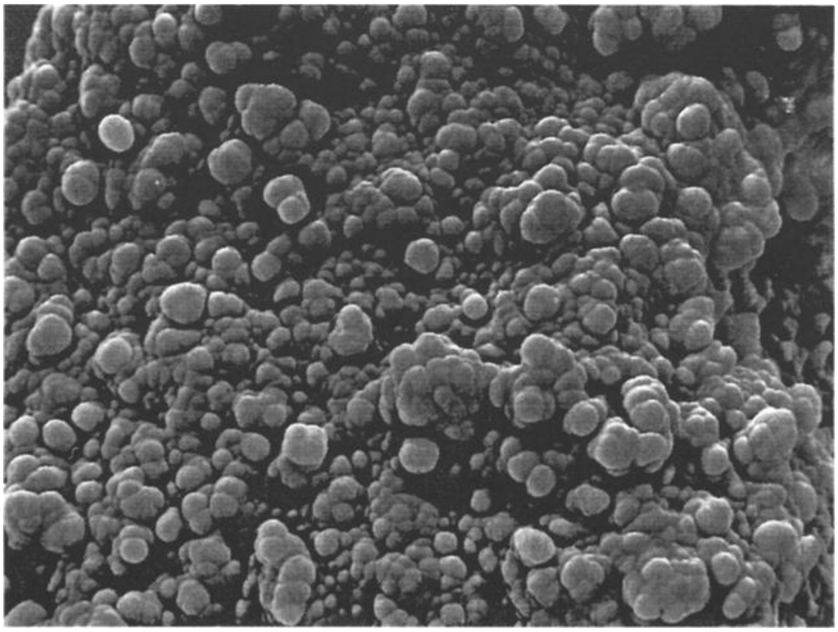

Fig. 1. Electron micrograph of Co-ETS-10 (sample A).

Table 2
Atomic ratios as measured by XPS

Sample	Co^{2+}/Ti	Co^{α}/Ti	Co^{0}/Ti
$A_{(fresh)}$	2.0	0.8	0.0
$A_{(after\ reduction)}$	0.4	0.3	0.3
$B_{(fresh)}$	2.0	0.8	0.0
$B_{(after\ reduction)}$	0.0	0.0	0.4
$C_{(fresh)}$	2.0	0.8	0.0
$C_{(after\ reduction)}$	0.0	0.0	0.4

Experimental results of the catalytic tests showed that Co-ETS-10 (sample A) is a very active FTS catalyst, showing a CO conversion of 53%, but a large amount of C_1 fraction, in comparison to Ru (1%)/Na-ETS-10 [16]: in that case the reaction, performed with the same parameters (T, P, GHSV, H_2/CO), showed a CO conversion of only 8%, but a lower production of CH_4 (see table 3).

Sample A also showed a low amount of olefins, but rather high production of branched isomers (the iso-C_4 species was deeply investigated by GC-MSD (HP-5890) and the data reported in table 3). Iglesia et al. ([24] and reference therein) showed that olefin readsorption on active metal centers is a fundamental step in FTS with supports without acidic functions like ETS-10. Slow removal of olefins from catalyst pores by diffusive processes increases the extent of readsorption leading to: (i) an improvement of the effectiveness of the chain-growth process; (ii) an increase of secondary products formation (branched isomers or internal olefins). This phenomenon was already observed for Ru /Na-ETS-10 [16], but in that case a large amount of internal olefins and a few branched isomers were present (table 3).

In the Co-exchanged sample the presence of well dispersed ruthenium atoms makes easier the Co reducibility, as shown by XPS measurements (table 2, samples B and C), leading to a significant increase of the metal sites density. It is well known how the difficulty to reduce Co species plays an important role in altering the activity and selectivity for FTS [2], but it is also true that higher CO hydrogenation activity was reported for Co catalyst after incomplete reduction relative to more fully reduced Co catalysts [7–10]. On ETS-10, an important factor seems to be the reduction of the largest part of Co: in fact on sample B a higher CO conversion was observed (table 3) and the C_{2+} selectivity shows larger and larger amounts of branched isomers (the amount of produced C_4 iso-hydrocarbons was 70% more than sample A).

Table 3
Activity and selectivity of the samples ($T = 548$ K, $P = 500$ kPa, GHSV = 2160 V/(V h), $H_2/CO = 2$, 1 g of fresh sample)

Sample	CO conv. (%)	CH_4	CO_2	C_{2+} [a]	$C_{3=}/C_3$	iso-C_4/C_4
Ru/Na-ETS-10 [22]	8.0	53.7	7.0	39.3	1.10	0.05
A	53.0	70.5	6.4	23.1	0.18	0.15
B	72.6	73.1	4.4	22.5	0.18	0.49
C	84.0	61.7	3.6	34.7	0.03	0.57

[a] C_{2+} stands for hydrocarbons C_2–C_7.

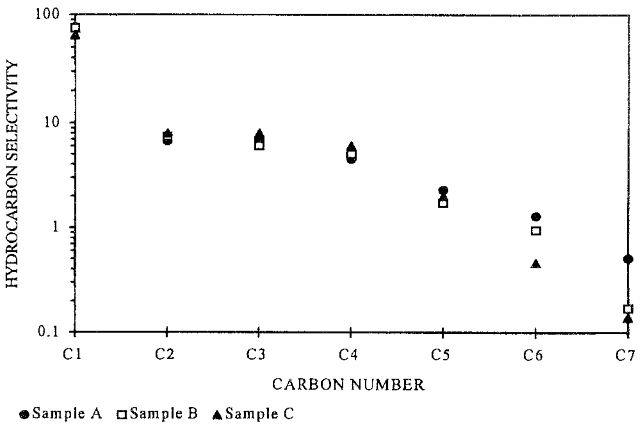

Fig. 2. Carbon number distribution of catalyst samples ($T = 548$ K, $P = 500$ kPa, GHSV = 2160 V/(V h), $H_2/CO = 2$, 1 g of fresh sample).

Lastly it is also necessary to point out that sample C, prepared with an even larger amount of ruthenium (0.4 wt%), showed the same C_{2+} selectivity joined to a good decrease of the CH_4 production and a further increase of the CO conversion (table 3).

All the activity and selectivity modifications could be explained as a bimetallic effect by supposing the occurrence of some intimate contact between Co and Ru components due to thermal reduction at high temperature (> 600 K), nevertheless no evidence of such phenomenon was obtained by characterization measurements.

4. Conclusions

It was already mentioned that the properties of Co-based catalysts strongly depend on the support used [2–6]; experimental results presented in this work showed, once more, that Co is an active metal for FTS. In particular, on ETS-10 Co performed a high CO conversion together with a non-Flory hydrocarbon production, but limited to the C_7 fraction.

The presence of small amounts of ruthenium (0.2 wt%, sample B), introduced by wet-impregnation, leads a complete reduction of the surface Co species and an increase of CO conversion and of the selectivity to iso-products. Increasing the amount of ruthenium (0.4 wt%, sample C), a further increase of the CO conversion and an interesting decrease of the C_1 fraction, was found.

Further work is needed to understand the real role of ruthenium atoms in the Co-ETS-10 catalyst.

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