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CO₂ hydrogenation to hydrocarbons over Co and Fe-based Fischer-Tropsch catalysts

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ABSTRACT

The performances of representative Co-based and Fe-based Fischer-Tropsch catalysts have been comparatively investigated in the hydrogenation of CO and CO₂. Over an un-promoted Co/ γ -Al₂O₃ catalyst, CO₂ is easily hydrogenated and its conversion rate is even faster than that of CO; however, the selectivities of the two processes are extremely different, with methane largely dominating the product distribution in the case of CO₂ hydrogenation and long-chain hydrocarbons dominating the products pool during CO hydrogenation. As opposite to cobalt, CO₂ hydrogenation rate over K-promoted 100Fe/10Zn/1Cu (at/at) catalysts is slower than that of CO, but the products are dominated by middle distillates when CO₂ replaces CO in the feed. Such behaviors depend on the different adsorption strengths of CO and CO₂, which affect the H/C atomic ratio on the catalyst surface. In the case of Fe-based catalyst, we have also found that the catalytic sites active in the chain growth process (iron carbides) are transformed into sites active in the hydrogenation reactions (iron oxides/reduced iron centers) at low CO partial pressures. Potassium has a key role in promoting the stability of chain growth sites, thus decreasing the secondary reactions of olefins.

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1. Introduction

The reduction of CO₂ emissions into the atmosphere has become an important research topic in recent years because carbon dioxide is one of the major contributors to the green-house effect, and its worldwide production is growing [1,2].

A first strategy to reduce CO₂ emissions, which has been deeply investigated in the last years and which has been recently applied for the first time to a large-scale power station in Canada [3], is Carbon Capture and Storage (CCS) [4], which consists in the permanent CO₂ storage deep underground in very specific geological sites. A very attractive alternative to this technology is represented by Carbon Capture and Utilization (CCU) processes, which consist in the chemical conversion of CO₂ to added-value carbon-containing products. Among them, the large-scale conversion of CO₂ into liquid fuels is of great interest, because the broad market of these products would guarantee an appreciable decrease of the global CO₂ emissions, limiting at the same time the consumption of fossil fuels.

In principle, carbon dioxide may be hydrogenated to liquid fuels either by direct or indirect routes. In the indirect route, CO₂ is converted to methanol, which can be then transformed into hydrocarbons through the commercially available methanol-to-gasoline (MTG) process based on zeolite catalysts [5]. On the contrary, in the direct route, CO₂ is converted to fuels through a modified Fischer-Tropsch (FT) process, eventually followed by a product upgrading (hydrotreating) step [2,6–29]. In this work we have focused on this latter alternative.

Literature data show that both CO and CO₂ can be hydrogenated over both cobalt [5–9,25–29] and iron [2,6,9,12–25] FT catalysts; however, most of the authors found that the product distribution during CO and CO₂ hydrogenation are very different. Indeed, CO₂ hydrogenation leads mainly to light saturated hydrocarbons with lower chain growth probability (α) values if compared to CO hydrogenation.

On cobalt-based catalysts, which are known to be substantially inactive in the water-gas-shift (WGS) and in the reverse-water-gas-shift (RWGS) processes, the reason of the different reactivity of CO and CO₂ is still debated. Moreover, the catalyst stability in the presence of CO₂ is still unclear and scarce experimental data are available to date. Zhang et al. [10] propose two different reaction pathways, with CO hydrogenation going through HC* and *OH ad-

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Table 1
Metal loading and textural properties of Fe and Co catalysts.

	Metalloading[wt.%]	Surface area[m ² /g]	Pore volume[cm ³ /g]	Average porediameter[Å]
Fe2K	61.9	76	0.21	90
Fe4K	61.0	114	0.25	66
Fe10K	58.4	102	0.21	63
Co/ γ -Al ₂ O ₃	15.0	120	0.31	85

species and CO₂ hydrogenation involving the HC*O intermediate, eventually leading to methane. As opposite, Visconti et al. [8] propose the same mechanism for CO and CO₂ hydrogenation processes, but ascribe the change in the product distribution to the different hydrogen to carbon ratio on the catalyst surface during the two processes. In the case of CO₂ hydrogenation, a higher H/C surface ratio would be obtained as a consequence of the weak CO₂ adsorption strength, which would favour the hydrogenation of the adsorbed C-containing surface intermediates, thus bringing to a decrease of the chain growth probability. Similarly to Visconti et al. [8], Riedel et al. [7] attribute the change in the product composition when switching from CO to CO₂ to the loss of “selective inhibition” which dominates the FT regime. Indeed, according to these authors, during CO hydrogenation, high CO partial pressure and strong CO adsorption result in a low concentration of H-adspecies. This slows down CH₃* hydrogenation to methane and secondary olefins hydrogenation to the corresponding paraffins, thus resulting in the high values of the chain growth probability typical of FT regime. The same does not happen during CO₂ hydrogenation, when both the low adsorption strength of CO₂ and the low CO partial pressure are insufficient to inhibit H₂ adsorption, thus bringing to low molecular weight saturated hydrocarbons.

On iron based catalysts, which are usually preferred to convert CO₂ to heavy hydrocarbons because of their intrinsic activity in the RWGS reaction [2,30], researchers agree that CO₂ hydrogenation pathway involves CO as intermediate [18] and the different H₂/CO ratio in the reactor during CO and CO₂ hydrogenation is considered the major reason for the different selectivity of the two processes [13,14,19]. Indeed, the H₂/CO ratio is reported to affect both the process kinetics [13,14,19] and the nature of the active sites [21]. However, as in the case of Co-based catalysts, only few information are available on the catalyst stability when CO₂ replaced CO in the feed.

The reactivity of CO₂ on Co- and Fe-based catalysts in the presence of CO is also a matter of discussion in the literature. Indeed, even if almost all the literature papers available so far report that CO₂ can be effectively hydrogenated only at low partial pressure of CO (e.g., [8,14]), different evidences have been reported on the effect of the presence of CO₂ on the CO conversion rate as well as on the product distribution. Chun et al. [31], for example, observe an inhibiting effect of CO₂ in terms of hydrocarbon yield, but also report that the product distribution is not affected by the presence of CO₂, as well as the olefin to paraffin (O/P) ratio in the hydrocarbon products. They attribute such effects to a competitive adsorption of CO and CO₂. As opposite to these results, other authors [20] have found that both CO conversion rate and product distribution are not affected by the presence of CO₂.

Given these premises, it is clear that further efforts to clarify the reactivity of Co and Fe Fischer-Tropsch catalysts in the presence of CO₂ and CO/CO₂ mixtures are needed. Accordingly, the first aim of this work is the cross-comparison between CO and CO₂ hydrogenation processes carried out for more than 400 h on representative iron and cobalt based FT catalysts. To the scope, both the CO_x conversion and the product distribution have been measured on two state-of-the-art catalysts under transient and steady-state conditions. A particular attention has been devoted to the quantification of paraffins and olefins in the products, because their relative

content can give informative indications on the nature of active sites.

In the second part of the work, the effect of alkali loading (K/Fe atomic ratio between 0.02 and 0.1) on a state-of-the-art Fe/Zn/Cu/K catalyst has been investigated. Indeed, it is expected that potassium, by donating electrons to iron, could affect the catalyst selectivity by changing the adsorption strength of reactants and products on the active sites. Such effect, which has been largely investigated during CO hydrogenation [32–35], has been only scarcely studied during CO₂ or CO/CO₂ mixtures hydrogenation [13,17,19,22,24].

2. Experimental

2.1. Catalysts preparation

2.1.1. Fe-based catalysts

Following the procedure reported in [32], a 100Fe/10Zn precursor (atomic ratios) was prepared via semi-batch co-precipitation of iron(III) and zinc nitrates at constant pH to form porous Fe-Zn oxy/hydroxycarbonates powder. Briefly, an aqueous solution containing Fe(NO₃)₃·9H₂O (3.0 M) was mixed with an aqueous solution of Zn(NO₃)₂·6H₂O (1.4 M). The resulting solution was slowly introduced in a jacketed quartz reaction cell kept at 80 °C, containing a buffer aqueous solution ((NH₄)₂CO₃ 1.0 M) acidified at pH of 7. A solution of (NH₄)₂CO₃ 1.0 M was also added to the cell by keeping the pH of the slurry at a value of 7 ± 0.2. The obtained slurry was filtered and the solid was washed with deionized water (further details can be found in Ref. [20]). The sample was eventually dried in static air at 120 °C overnight and the resulting powders were calcined in stagnant ambient air at 350 °C for 1 h (heating rate 1 °C/min). Obtained powder was promoted by incipient wetness impregnation with potassium carbonate and copper nitrate aqueous solutions, dried at 120 °C overnight and calcined at 400 °C for 4 h [20]. Samples with a Cu/Fe atomic ratio of 0.01 and K/Fe atomic ratios of 0.02, 0.04 and 0.1 were prepared, indicated in the following as “Fe2K” (100Fe/10Zn/1Cu/2K), “Fe4K” (100Fe/10Zn/1Cu/4K) and “Fe10K” (100Fe/10Zn/1Cu/10K), respectively.

2.1.2. Co-based catalysts

The 15 wt.% Co/ γ -Al₂O₃ catalyst used in this study (sample tag “Co/ γ -Al₂O₃”) was a bench-scale prepared sample obtained by incipient wetness impregnation of γ -Al₂O₃ with a cobalt nitrate hexahydrate aqueous solution. Details of the preparation procedure can be found in Ref. [8].

2.2. Catalyst characterization and testing

The morphological properties (BET area, BJH pore volume and average pore size) of the different catalysts, determined by nitrogen adsorption-desorption at 77 K using Micromeritics TriStar 3000 instrument, are reported in Table 1.

Activity tests of Fe-based and Co/ γ -Al₂O₃ catalysts were carried out in two separate lab-scale rigs and at different process conditions (Tables 2 and 3), similar to those adopted at the industrial scale for the Fischer-Tropsch synthesis. Those rigs are described in the

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