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In-situ study of the promotional effect of chlorine on the Fischer–Tropsch synthesis with Ru/Al_2O_3

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ABSTRACT

The effect of the addition of Cl to $Ru/\gamma\text{-}Al_2O_3$ catalysts for the Fischer–Tropsch synthesis has been investigated. A series of four catalysts containing 3 wt.% of Ru supported on $\gamma\text{-}Al_2O_3$ and promoted with different amounts of chlorine (Cl/Ru atomic ratios of 0, 1, 5 and 10) has been prepared. The catalysts were tested in the Fischer Tropsch synthesis in a fixed bed reactor. The initial rates for the CO hydrogenation increase with the increasing amount of Cl in the catalyst. However, at the steady-state all catalysts exhibit similar Fischer Tropsch yields, irrespectively of their initial amount of Cl. The nature of the CO adsorption sites in the Cl-promoted Ru/Al_2O_3 catalysts has been studied by means of DRIFT concluding that Cl addition leads to a higher fraction of CO_{ad} species adsorbed on Ru atoms with low coordination numbers. In addition, the stability of such CO_{ad} species, characterized by high frequency bands in the IR, increases with the increasing content of Cl in the catalysts. The reactivity of the CO_{ad} species in hydrogen atmospheres and under FTS environments has been studied by *in situ* MS-DRIFT. We have observed that low-coordinated Ru atoms are more reactive for CO dissociation than those in a higher coordination environment. However, the former sites are prone to deactivation during FTS catalysis, at the steady-state, and only CO adsorbed on highly coordinated Ru atoms is observed in the IR spectra. Consequently, all catalysts exhibit the same reaction rates at the steady-state.

1. Introduction

The Fischer–Tropsch synthesis (FTS) is a suitable technology to transform syngas (a mixture of H_2 and CO) obtained from various sources, such as coal, natural gas, biomass and/or shale gas, into liquid fuels (jet fuel and diesel) and chemicals (olefins and waxes). The renewed scientific interest in the FTS accounts to several factors including the recent crude oil crisis, the discovery of abundant sources of natural gas [1] and to the possibility of obtaining second generation biofuel from biomass via thermochemical routes [2]. Although Fe- or Co-based catalysts are the only ones used at the industrial level for the FTS, the interest in Ru-based catalysts has triggered, at least in academia [3–13]. It is well known Ru-based catalysts exhibit higher CO conversions rates and higher α values, *i.e.*, a higher fraction of high molecular weight hydrocarbons, than Fe- or Co-based catalysts when measured under similar reaction conditions [2,14,15]. Furthermore, Ru-based catalysts can also operate in the presence of high partial pressure of water (the main co-product of the FTS reaction) and other oxygenate-containing atmospheres without deactivation [16,17] making it possible to operate under mild reaction conditions in aqueous phase slurry reactors [18,19]. However, the high cost of Ru requires increasing the normalized activity per mass of Ru.

Recent experimental and theoretical investigations have shown that FTS is a highly structure-sensitive reaction [11,18,20–22]. Our previous publications have clearly demonstrated that FTS is structure sensitive when Ru particles smaller than 10 nm are used; *i.e.*, the turnover frequency for CO consumption (TOF_{CO}) increases with Ru particle size, reaching a constant value for Ru particles larger than 10 nm. The normalized activity per mole of Ru is optimized for Ru particle of 10 nm [11,20]. Some theoretical studies claim that the very high initial activity of Ru particles for the dissociation of CO is due to the presence of step-edge ensembles, usually referred to as B5 sites, which are not stable in Ru particles smaller than ca. 9 nm [21]. It should be noted that Ru atoms in such step/edge sites present coordination numbers lower than Ru atoms in terraces.

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The catalytic performance of Ru-based catalysts for the FTS is also influenced by the nature of the support [10]. Indeed, we have previously found that when supported in the rutile phase of TiO_2, Ru particles show an epitaxial growth with the rutile structure of TiO_2 leading to the formation of large 2D like Ru islands exposing a large fraction of step/edge/step ensembles. As a consequence, when deposited on the rutile phase of TiO_2, Ru particles have a large fraction of very active centres for the hydrogenation of CO, thus achieving very high initial FTS rates [10]. However, recent experimental evidences sustain that such sites become deactivated during FTS catalysis due to the formation of adsorbed species ($C_{x,ad}$) that remain strongly adsorbed on such step/edge sites [20,23]. As a result, CO dissociation and subsequent formation of hydrocarbons at the steady-state take place exclusively on the Ru atoms located at the terrace surfaces of the particles, via the so-called H-assisted CO dissociation mechanism [24,25].

The performance of Fe-, Co- or Ru-based catalysts in FTS can be tuned by adding some promoters, such as halogens, alkali, transition metals (Ce, Mn, Cu…) or even noble metals (Pt, Pd, Re...) [26–31]. However, the actual role of these promoters is not well understood. For instance, conflicting results regarding the promotional effect of chlorine have been disclosed. Thus, CO and H_2 chemisorption experiments conducted at room temperature [32,33] and at 373 K [34] clearly indicate that the presence of Cl suppresses CO and H_2 adsorption on Ru particles. On the other hand, it has also been reported that the presence of Cl improves the performance of Ru/Al_2O_3 catalysts [6,7,35]. Thus, Mieth and Schwarz [35] have observed that for Ru/Al_2O_3 catalysts with similar Ru particle size (2.8 and 4 nm), the TOF for the CO hydrogenation reaction ($H_2/CO = 3$, 523 K) increases from 0.005 to 0.145 s^{-1} upon addition of 321 $\mu mol_{Cl}\, g_{cat}^{-1}$. In contrast, other authors claim that the presence of Cl does not modify the catalytic performance of Ru/Al_2O_3 in FTS [34], and yet other studies report a detrimental effect of Cl for the FTS with Ru/SiO_2 catalysts [36]. In this latter case, Iyagba et al. [36] reported that the CO conversion rate decreases from 3.1 to 1.9, 1.7 and 1.2 $mmol_{CO}\, s^{-1}\, g_{cat}^{-1}$ when the Cl/Ru atomic ratio was increased from 0 to 0.01, 0.3 and 1.0, respectively. A recent study with $Co/NiAl_2O_4$ catalysts has shown that Cl addition increases their FT catalytic performance measured at $H_2/CO = 2.1$, 483 K, and 2.02 MPa. The influence of Cl on Co-based catalysts has also been a matter of debate and in fact, promotion-like [37] and poisoning-like [38] effects have been reported in the literature. Recently, the effect of the introduction of Cl (as trichloroethylene) during the CO hydrogenation with Co/Al_2O_3 has been reported concluding that under the studied reaction conditions, *i.e.*, atmospheric pressure and 220 °C, chlorine induces a strong poisoning effect [39]. Finally, a recent patent shows that Cl addition to Co based catalysts results in a promotional effect for the production of high molecular weight hydrocarbons [40].

In view of these conflicting results, we have devised a series of experiments to understand the role of Cl addition to Ru/Al_2O_3 catalysts for the FTS. The main objective of these investigations is to understand the influence of Cl on the size of the Ru particles, on the nature of CO adsorption sites and as a consequence, on the reactivity of the Ru nanoparticles for the Fischer–Tropsch synthesis.

2. Experimental

2.1. Preparation of Cl promoted Ru/Al_2O_3 samples

A series of four Cl–Ru/Al_2O_3 catalysts containing different Cl/Ru atomic ratios were prepared by the incipient wetness impregnation technique using $Ru(NO)(NO_3)_3$ (31.30% Alfa Aesar) as Ru precursor, γ-Al_2O_3 (240 $m^2\, g^{-1}$) as support, and NH_4Cl (Fluka > 99.5%) as the chlorine source. The catalysts (3 wt.% Ru and Cl/Ru atomic ratios of 0, 1, 5 and 10) were prepared as follows: 2.3 mL of a solution containing the adequate amounts of $Ru(NO)(NO_3)_3$ and NH_4Cl was added dropwise to 970 mg of γ-Al_2O_3. The solids were dried at room temperature overnight and labelled as Ru-0Cl, Ru-1Cl, Ru-5Cl and Ru-10Cl, where the suffix indicates the Cl/Ru ratio in the catalyst.

2.2. Catalytic activity test

The catalytic performance in FTS was tested in a down-flow fixed-bed microreactor. The reactor system and the analysis of reactant gases and products have been described previously [10]. Briefly, 0.2 g catalyst was diluted with 2.0 g quartz (0.25–0.30 mm particle size) and loaded into the reactor. The samples were pretreated *in situ* with H_2 at 523 K (10 K min^{-1}) for 1 h. After this pretreatment, the H_2 flow was switched to a N_2 flow and the pressure was raised to 4.04 MPa. Next the N_2 flow is switched to the reactants flow ($H_2/CO/N_2 = 62/31/7$, GHSV = 3000 mL $g_{cat}^{-1}\, h^{-1}$), and this point is considered as the starting point (t_0) for the FTS. The catalytic activity was measured for 24 h. Turn over frequencies (TOF) have been calculated from Ru particle sizes derived from TEM analyses. First, dispersion (*D*) was calculated from Eq. (1):

$$D = \frac{6M}{\rho\, \sigma\, Na\, d_m} \tag{1}$$

where *M* is the atomic mass of Ru (101.07 g mol^{-1}), ρ is the density of Ru (12.3 g cm^{-3}), σ is the surface of one Ru atom (0.0187 nm^2 $atom^{-1}$), *Na* is the Avogadro's number and d_m is the Ru particle size. Next, the CO conversion rate (mol_{CO}/at gr_{Ru}/h) is divided by the fraction surface exposed Ru atoms as calculated from *D*.

2.3. DRIFT and MS-DRIFT studies

Infrared spectra (DRIFT) were recorded with a Jasco FTIR-6300A spectrometer provided with a MCT detector. The spectra were recorded with a resolution of 4 cm^{-1} and an accumulation of 256 scans. CO was adsorbed using a flow of 5 vol.% CO in Ar. In order to identify the nature of the species evolved during the reactions, a mass spectrometer was coupled on line to the outlet of the DRIFT chamber.

Three sets of experiments were carried out and described next.

2.3.1. CO adsorption at room temperature and at 473 K

Previous to CO adsorption, all catalysts were reduced *in situ* in the DRIFT cell by using the same reducing protocol used in the fixed-bed microreactor tests. First, 20 mL min^{-1} of pure H_2 was flown at 523 K (10 K min^{-1}) and atmospheric pressure for 1 h. Then, the H_2 flow was switched to He (20 mL min^{-1}) and maintained for 30 min at 523 K. Then, the temperature was decreased to room temperature and the He flow was switched to a CO/Ar flow (20 mL min^{-1}) and kept for 30 min. Then, the CO/Ar flow was switched to a He flow (20 mL min^{-1}) and kept during 30 min in order to remove non-adsorbed CO from the DRIFT cell. After this treatment, an IR spectrum was recorded. This experiment has been named as *CO adsorption at room temperature.*

Next, and in order to study the stability of the CO_{ad} species, the temperature was increased to 473 K (10 K min^{-1}) under He flow (20 mL min^{-1}) and maintained at this temperature for 30 min. A further IR spectrum was recorded. This experiment is referred to as *CO adsorption at 473 K.*

2.3.2. Reactivity of the CO adsorbed at 473 K

After the treatment with He at 473 K for 30 min (see previous section), the reactivity of the CO_{ad} species was monitored by