



Insights into the deactivation and reactivation of Ru/TiO₂ during Fischer–Tropsch synthesis

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ABSTRACT

The catalytic performance of Ru/TiO₂ for the production of hydrocarbons via Fischer–Tropsch synthesis (FTS) has been evaluated in this work. Ru/TiO₂ exhibits high CO conversion rates (523 K, 2.5 MPa H₂, 1.25 MPa CO) that decrease significantly with time-on-stream. To recover the initial catalytic performance, different treatments using H₂ or air have been tested. The evolution of the catalyst structure during FTS and after the re-activation protocols have been explored by a combination of *ex situ* and *in situ* techniques. Ru agglomeration, oxidation, and formation of Ru–volatile species are not responsible for the observed deactivation. However, Raman and infrared (FTIR) spectroscopy have confirmed the presence of coke and alkyl chains on the spent catalysts. These species hinder the adsorption of the reactants on the active sites and are the primary reason for the observed decrease in the catalytic activity. These carbonaceous species can be removed by severe thermal treatments in air. However, this latter treatment drastically alters the morphology of the Ru/TiO₂, which leads to a substantial loss of catalytic activity.

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1. Introduction

There is a renewed interest in the hydrogenation of CO using Ru catalysts [1–11] because of its potential for producing clean bio-fuels from biomass-derived syngas (CO/H₂ mixtures) in modern biorefineries [12]. It is well established that Ru is the most active metal for CO hydrogenation with higher CO/H₂ conversion rates and higher average molecular weight hydrocarbon yields compared to Fe- or Co-based catalysts [12–14]. Furthermore, Ru-based catalysts can operate at high H₂O pressures (the main co-product of the reaction) and in oxygenate-containing atmospheres without significant deactivation [15,16].

A higher catalytic activity for the Fischer–Tropsch synthesis (FTS) with the TiO₂-supported Ru catalysts compared to other supported Ru catalysts has been reported by several groups [8,17,18]. Kikuchi et al. [17] measured a higher reaction rate for Ru/TiO₂ with respect to Ru/γ-Al₂O₃ (2 wt.% Ru, 523 K). Similarly, Vannice and Garten [18] also reported higher FTS activities (548 K) with Ru/TiO₂ compared to Ru/Al₂O₃ and Ru/SiO₂. Recently, we have reported [8] higher CO conversion rates normalized per metal atom with Ru/TiO₂ compared to Ru/SiO₂·Al₂O₃ (3 wt.%, 523 K). Our previous work also reveals the importance of the crystalline phase of the

TiO₂ support, which indicated that the rutile phase was responsible for the most active catalyst for FTS. Nevertheless, the high initial performance displayed by the Ru/TiO₂ catalysts during FTS decreases over time on stream (*i.e.*, both CO conversion and C₅₊ selectivity decreases on stream).

Several causes, such as the oxidation of the metallic particles, the formation of volatile metallic oxides and/or other metallic compounds, agglomeration of the metallic particles, poisoning, surface reconstruction, modification of the support and metal-support interactions, leaching of the active phase, vapor–solid and/or solid–solid reaction and formation and deposition of inactive species on the active sites, have been proposed as the primary deactivation mechanisms of catalysts during the synthesis of hydrocarbons [19–24]. Saib et al. [25] studied the performance of Co/Pt/Al₂O₃ in the FTS during 55 days. The CO conversion declined to a value of *ca.* 40% of the original value after 55 days on stream concluding that deactivation accounted to three mechanisms: sintering of Co active phase (at the first stages of FTS), carbon deposition and surface reconstruction. Catalyst deactivation caused by metal oxidation has been widely reported for Fe- and Co-based catalysts. For example, the oxidation of Co⁰ during FTS has been postulated as the primary deactivation mechanism of Co-based catalysts, because H₂O, an oxidizing agent and the main co-product in the FTS, can oxidize the metallic Co particles [19]. However, Claeys et al. [15] rejected the oxidation of Ru-based catalysts by H₂O as the primary deactivation mechanism because

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H₂O (0–0.5 MPa) increased the CO conversion rate and improved the C₅₊ selectivity over the Ru/SiO₂ catalyst (473 K, 1.5–2.0 MPa, H₂/CO = 2). Another proposed deactivation mechanism is the formation of volatile metallic oxides and/or other metallic compounds during the FTS reaction [20]. Goodwin et al. [21] reported the formation of Ru–carbonyl complexes on Ru/Al₂O₃ catalysts under CO flow (185 kPa, 488 K), but the catalyst lost up to 40% of the initial metallic content. The formation of volatile species as a possible deactivation mechanism of Ru/ZrO₂ and Ru/Al₂O₃ catalysts during the production of oxygenated compounds from syngas at 473–573 K has also been proposed by other groups [22]. The formation of volatile Ru–carbonyl species appears to be strongly affected by the Ru particle size. Abrevaya et al. [23] showed that Ru–volatile species were only formed during FTS when small Ru clusters (<4 nm) were present.

Another deactivation mechanism described in the literature is the agglomeration or sintering of the smaller metallic particles, which leads to a lower active surface area [19]. For Co-based catalysts, this process is strongly affected by the support and the presence of H₂O. Thus, alumina stabilizes Co particles preventing their agglomeration during FTS, whereas H₂O accelerates Co sintering. Abrevaya et al. [23] established that the formation of the volatile species resulted in the formation of large aggregates of Ru particles; however, when using catalysts with relatively large Ru particles (>4 nm), Ru particle size remained invariable.

The formation and deposition of inactive species on the surface of the active sites during CO hydrogenation have also been proposed as an important deactivation mechanism [19,26–28]. The direct consequence of these deposits is the physical blocking of the active sites impeding the adsorption of the reactants and suppressing the catalytic activity [24]. Earlier studies concluded that the deactivation of Ru/Al₂O₃ during FTS was due to carbon deposition, which was strongly affected by the reaction conditions (*i.e.*, CO and H₂ partial pressures and temperature) [29,30]. Similar studies with Ru/TiO₂ catalysts [28] suggest that the formation and accumulation of carbidic carbon and alkyl chains during the FTS reaction results in the loss of the CO chemisorption properties of the catalyst [28,31].

Most studies dealing with the reactivation of Ru-based catalysts are based on the observation that catalytic performance is depressed by formation of carbonaceous deposits. Thus, Ragaini et al. [32] explored the effect of chlorine in the performance of Ru/Al₂O₃ for the FTS and concluded that catalyst deactivation is due predominantly to the presence of inactive carbon species on the surface of the catalyst. A regeneration protocol based on thermal treatment in H₂ at 553 K during 16–18 h was used. The catalytic performance was recovered to some extent but they reported that the presence of chlorine results in a lower degree of catalytic recovery. Krishna and Bell [28] reported that the main cause of deactivation of Ru/TiO₂ catalysts during the FTS is the formation of various types of carbon species. The activity of the catalysts could be restored by means of H₂ treatments at 503 K overnight.

Herein, we report a thorough analysis of the deactivation processes for the Ru/TiO₂ catalyst during FTS and focus on the study of the morphologic evolution of the Ru particles during the FTS and reactivation processes. The identification of the primary deactivation mechanism and the consequences of different regeneration processes by means of thermal treatments with H₂ or air are also explored. The evolution of the Ru particles during the FTS reaction and after the reactivation treatments has been monitored by *in situ* infrared spectroscopy (FTIR) via the adsorption of H₂/CO at different temperatures and times. In addition, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) allowed us to identify the morphologic changes of the Ru particles during FTS and regeneration treatments.

2. Experimental methods

2.1. Preparation of Ru/TiO₂

The Ru/TiO₂ catalyst was prepared via the incipient wetness impregnation technique. The nominal metal loading is 3 wt.%. RuCl₃·nH₂O (40.49%, Johnson Matthey) was used as the ruthenium precursor, and TiO₂ Degussa P25 (80% anatase phase and 20% rutile phase) with a BET surface area of 45 m² g⁻¹ and pore volume of 0.27 cm³ g⁻¹ was used as the support. The Ru precursor was dissolved in distilled H₂O, and the solution was then added dropwise to the support. The solid was dried at room temperature overnight, treated in air at 723 K (10 K min⁻¹) for 3 h [8] and labeled as Ru/TiO₂.

2.2. Characterization techniques

Powder X-ray diffraction (XRD) patterns were recorded in the 4–90° 2θ range in the scan mode (0.04°, 20 s) using an X'Pert Pro PANalytical diffractometer.

A JEM-2100F 200 kV transmission electron microscope (JEOL Ltd.) equipped with an Oxford INCA-Sight EDS detector (Oxford Instruments Ltd.) was used. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images were obtained by operating the microscope in the scanning mode with an electron probe size of 1 nm. The signal was recorded with an annular dark field detector with an inner collection angle of 59 mrad (Z-contrast) and a maximum point resolution of 0.1 nm.

Raman spectra were recorded with a Renishaw inVia Raman Microscope spectrometer equipped with a laser beam emitting at 532 nm and a 100 mW output power. The photons scattered by the sample were dispersed by an 1800 lines/mm grating monochromator and simultaneously collected on a CCD camera. The collection optic was set at 50× objective.

The samples selected to be studied by Raman spectroscopy or HAADF-STEM analyses were recovered from the FTS reactor and directly mounted into the analyses chambers without further treatment.

The temperature programmed reduction (TPR) analysis was carried out in a Micromeritics TPR/TPD 2900 apparatus. 30 mg of the catalyst (0.25–0.30 mm pellet size) were loaded into a U-shaped quartz reactor and thermally treated under flowing H₂ at 393 K for 30 min. The hydrogen consumption profile was recorded by subjecting the sample to a temperature program from 298 to 1173 K at 10 K min⁻¹ under a 10 vol.% H₂/Ar flow. H₂ consumption was monitored with a thermal conductivity detector (TCD).

2.3. Infrared studies

FT-IR spectra were recorded with a Nicolet Nexus Fourier Transform instrument, using conventional IR cells connected to a gas manipulation apparatus under static conditions. Pressed disks of the pure catalyst (~20 mg) were thermally pretreated within the IR cell by means of a thermal treatment in H₂ (80 kPa) at 673 K for 30 min. After evacuation for 30 min at 673 K, an additional reduction cycle was performed under the same experimental conditions, and the sample was evacuated. For the room temperature CO adsorption experiments, CO (1.3 kPa) was introduced to the IR cell. Then the sample was evacuated for 30 min at room temperature. For the FTS experiments, a mixture of H₂/CO ~ 6 was introduced to the IR cell after the reduction treatment, and the spectra of the catalysts surface and the gas phase were recorded at room temperature, 473, 523 and 573 K at increasing exposure times.

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