Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

TiO_2 polymorph dependent SMSI effect in Co-Ru/TiO_2 catalysts and its relevance to Fischer-Tropsch synthesis

Francine Bertella[a,b], Patricia Concepción[a], Agustín Martínez[a,*]

[a] Instituto de Tecnología Química, Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas, Avda. de los Naranjos s/n, 46022 Valencia, Spain
[b] CAPES Foundation, Ministry of Education of Brazil, 70040-020, Brasilia-DF, Brazil

ARTICLE INFO

Article history:
Received 15 May 2016
Received in revised form 18 July 2016
Accepted 2 August 2016
Available online xxx

Keywords:
Fischer-Tropsch synthesis
Cobalt catalyst
TiO_2 polymorph
Anatase
Rutile
SMSI effect

ABSTRACT

Pure anatase and rutile TiO_2 samples were synthesized by thermal treatment of reverse microemulsions and applied as supports for preparing Ru-promoted Co catalysts (0.5 wt% Ru, 10 wt% Co). The catalysts were characterized by ICP-OES, XRD, Raman spectroscopy, N_2 physisorption, H_2-TPR, electron microscopy (FESEM, HAADF-STEM), H_2 chemisorption, XPS, and *in situ* IR-CO after H_2 reduction and reaction with syngas, and their catalytic performance for Fischer-Tropsch synthesis (FTS) studied at industrial conditions (220 °C, 2.0 MPa, $H_2/CO = 2$). The two catalysts exhibited comparable mean Co particle sizes (5–6 nm) as well as high and alike degrees of cobalt reduction (ca. 90%). The SMSI decoration effect arising during H_2 reduction was much more pronounced for the anatase-supported catalyst resulting in lower cobalt-time-yield (CTY) compared to that supported on TiO_2-rutile. *In situ* IR-CO under syngas conversion conditions showed equivalent cobalt surface reconstruction and nature of the surface Co^0 sites for both catalysts in their *working* state, and revealed a partial reversibility of the SMSI effect during FTS by which a significant fraction of the decorated Co^0 centers in the anatase-based catalyst was uncovered and became available for reaction. The implication of this effect on TOFs is discussed. The C_{5+} selectivity was higher for the rutile-based catalyst, although a clear impact of the SMSI effect on selectivities was not inferred from our results.

1. Introduction

Fischer-Tropsch synthesis (FTS) is at the core of XTL processes allowing a variety of liquid fuels and chemicals to be produced from oil-alternative carbon resources such as natural gas (GTL), coal (CTL), and biomass (BTL) via syngas ($H_2 + CO$). Of particular interest is the Co-catalyzed low-temperature FTS in which syngas is selectively converted to long-chain *n*-paraffins (waxes) that are then hydrocracked to produce high-quality diesel [1,2].

Preparation of Co-based FTS catalysts commonly involves dispersion (via impregnation) of a cobalt salt precursor, most frequently cobalt nitrate, on a high surface area porous inorganic oxide carrier, among which SiO_2, Al_2O_3, and TiO_2 are the most widely employed, followed by drying, calcination, and H_2-reduction to generate the active metallic Co sites on the catalyst surface [1]. Commonly, some metals (*e.g.* Ru, Re, Pt) and/or metal oxides are included in the catalyst formulation in order to promote the reduction and dispersion of the supported Co particles [3,4]. The final catalytic performance of Co-based FTS catalysts becomes mainly dictated by the metal content, the dispersion (*i.e.* Co particle size), and the degree of Co reduction which ultimately determine the concentration of surface metal Co sites. These properties are affected by a number of factors such as the nature of the cobalt precursor and loading method [1], the chemical identity and porosity of the oxide carrier [1,5,6], and the so-called thermal history (*i.e.* the drying, calcination, and reduction conditions) [7].

As for the chemical nature of the support, TiO_2 has proven to be particularly beneficial from the standpoint of both catalyst activity and selectivity to the targeted liquid (C_{5+}) hydrocarbon fraction [6,8,9]. As a support, TiO_2 is known to exhibit the SMSI (strong-metal-support-interaction) decoration effect by virtue of which TiO_{2-x} sub-oxides form during H_2 reduction and migrate on top of the supported metal nanoparticles inhibiting their H_2 and CO chemisorption capability [10–14]. For Co/TiO_2, partial encapsulation of Co nanoparticles by a few atomic layers of thick TiO_{2-x} phase during reduction was directly imaged by HRTEM [15]. In nature, TiO_2 exists in three distinct crystallographic forms, namely anatase, rutile, and brookite. Previous studies have shown that the

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* Corresponding author.
E-mail address: amart@itq.upv.es (A. Martínez).

http://dx.doi.org/10.1016/j.cattod.2016.08.008
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TiO_2 crystal phase composition is highly influential to the ultimate FTS performance of Co/TiO_2 catalysts, albeit with controversial results. For instance, by supporting 20 wt% Co on TiO_2 with different anatase:rutile ratios, Jongsomjit et al. observed a maximum CO conversion rate under methanation conditions ($H_2/CO = 10$) for the catalyst comprising 19% rutile and 81% anatase which also exhibited the highest H_2 chemisorption capacity [16]. This behavior was ascribed to a weaker interaction of Co with rutile in comparison to anatase that prevented the formation of barely reducible mixed Co-O-Ti compounds assisted by water generated during the H_2 reduction treatment thus increasing the amount of available surface Co^0 atoms [17]. Other authors also reported higher CO conversion rates for Co/TiO_2 catalysts prepared from TiO_2 with more than 15% rutile in comparison to those based on pure anatase [18,19]. However, in contrast with the previous study, the effect was related to a stronger Co-support interaction in presence of rutile that inhibited the aggregation of Co particles during reduction improving the final Co^0 dispersion, although the possibility of a suppressed SMSI effect over rutile was not excluded [18].

It is apparent from the previous discussion that further work is required to clarify the role of the TiO_2 crystalline phase, with a special focus on the little studied phase-dependent SMSI effect, in determining the FTS performance of Co/TiO_2 catalysts. To this aim, we synthesized 100% pure anatase and rutile TiO_2 phases and used them as supports for preparing Ru-promoted Co/TiO_2 catalysts (nominal loadings of 10 wt% Co and 0.5 wt% Ru). The prepared catalysts display alike mean Co^0 particle sizes (5–6 nm) and particle size distributions as well as high and similar extents of cobalt reduction (ca. 90%), enabling a fair study of the TiO_2 crystalline phase dependent SMSI effect and its consequences on the catalytic behavior for FTS under industrially relevant conditions (220 °C, 2.0 MPa, $H_2/CO = 2$).

2. Experimental

2.1. Materials

Triton X-100 [(*tert*-octylphenoxy)polyethoxyethanol] (Aldrich), titanium(IV) butoxide (99+%, Alfa Aesar), 1-hexanol (>98% GC, Fluka Chemika), cyclohexane (99%, Aldrich), hydrochloric acid (37%, Aldrich), and acetic acid (99,5%, Aldrich) were used as received.

2.2. Synthesis of pure anatase and rutile TiO_2 phases

Pure anatase and rutile TiO_2 phases were synthesized by thermal treatment of reverse microemulsions following a procedure similar to that reported in [20]. In short, an aqueous solution containing the acid (acetic acid for anatase and hydrochloric acid for rutile) and the Ti source (titanium(IV) butoxide) was added to an organic mixture containing the surfactant (Triton X-100), cosurfactant (1-hexanol), and solvent (cyclohexane) under stirring at room temperature (r.t.). The formed microemulsion was then either heated at 40 °C for 24 h under reflux (for rutile) or introduced into a Teflon-lined stainless steel autoclave and hydrothermally treated at 120 °C for 5 h (for anatase). After the thermal treatments the solids were recovered by centrifugation, washed 5 times in ethanol in a process involving redispersion and centrifugation, dried at 60 °C overnight, and finally calcined in flowing air at 400 °C for 8 h. The obtained TiO_2 anatase and rutile supports are labeled as Ti-A and Ti-R, respectively. The conditions and composition of the microemulsions employed for the syntheses of pure anatase and rutile phases are gathered in Table 1.

Table 1
Nomenclature and conditions employed for the synthesis of pure TiO_2 anatase and rutile phases.

Support	Acid	Temperature (°C)	Time (h)	$w = [H_2O]/[Triton]$ (mol/mol)	$h = [H_2O]/[Ti]$ (mol/mol)
Ti-A	CH_3COOH	120	5	19.4	33.8
Ti-R	HCl	40	24	15.0	18.8

2.3. Synthesis of Co-Ru/TiO_2 catalysts

Co-Ru/TiO_2 catalysts with nominal loadings of 10 wt% Co and 0.5 wt% Ru (added as reduction promoter) were prepared by incipient wetness co-impregnation of the calcined TiO_2 carriers with an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (Aldrich) and ruthenium(III) nitrosyl nitrate (Aldrich) as metal precursors, followed by drying at 100 °C overnight and calcination in flowing air at 300 °C for 3 h. The catalysts based on anatase and rutile are denoted as Co-Ru/Ti-A and Co-Ru/Ti-R, respectively.

2.4. Characterization techniques

X-ray powder diffraction (XRD) patterns were recorded on a Philips X'Pert diffractometer using monochromatic Cu Kα radiation ($\lambda = 0.15406$ nm). The average TiO_2 crystallite size was estimated by the Scherrer's equation applied to the most intense reflections (1 1 0) for rutile ($2\theta = 27.44°$) and (1 0 1) for anatase ($2\theta = 25.28°$), assuming a shape factor $k = 0.9$.

Textural properties were derived from the N_2 adsorption isotherms measured at −196 °C in an ASAP-2420 equipment (Micromeritics). Specific surface areas were calculated following the Brunauer–Emmett–Teller (BET) method, total pore volumes (TPV) were determined at a relative pressure of 0.98, and the pore size distributions were obtained by applying the Barrett–Joyner–Halenda (BJH) approach. Prior to the adsorption measurements, the samples were degassed at 300 °C and vacuum overnight.

The morphology of the samples were studied by field emission scanning electron microscopy (FESEM) using a ZEISS Ultra-55 microscope.

The Co and Ru contents were determined by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) in a Varian 715-ES spectrometer after dissolution of the solids in an acid mixture of 20%HNO_3:20%HF:60%HCl (% volume).

The reduction behavior of the oxidized Co-Ru/TiO_2 catalysts was studied by hydrogen temperature-programmed reduction (H_2-TPR) in a Micromeritics Autochem 2910 equipment. The samples were initially flushed with an Ar flow at r.t. for 30 min, and then the gas was switched to 10 vol% H_2 in Ar and the temperature linearly increased up to 900 °C at a heating rate of 10 °C/min. A downstream 2-propanol/$N_{2(liq)}$ trap was used to retain the water generated during the reduction. The H_2 consumption rate was monitored in a thermal conductivity detector (TCD) previously calibrated using the reduction of a standard CuO sample. This setup was also used to measure the degree of cobalt reduction (DR) after submitting the catalysts to the same reduction protocol applied *in-reactor* prior to the FTS experiments (400 °C in H_2 flow for 10 h).

Cobalt dispersions were determined by H_2 chemisorption at 100 °C in an ASAP 2010C Micromeritics equipment by extrapolating the total H_2 uptake to zero pressure [21]. Metal particle sizes ($d(Co^0)_{H2}$) were estimated from the total amount of chemisorbed H_2, the Co content (from ICP-OES) and the degree of cobalt reduction by assuming a chemisorption stoichiometry $H/Co = 1$ and a surface atomic density for Co^0 of 14.6 atoms/nm^2.

Cobalt particle sizes were studied by electron microscopy in a JEOL-JEM-2100F microscope operating at 200 kV in scanning-

Please cite this article in press as: F. Bertella, et al., TiO_2 polymorph dependent SMSI effect in Co-Ru/TiO_2 catalysts and its relevance to Fischer-Tropsch synthesis, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.08.008