

Mössbauer and XPS spectroscopies studies of SMSI effect on Fe/Nb₂O₅ catalysts for the Fischer–Tropsch synthesis

M.V. Cagnoli^{a,1}, A.M. Alvarez^{a,1}, N.G. Gallegos^{a,1}, J.F. Bengoa^{a,1},
C.D. Duarte de Souza^b, M. Schmal^b, S.G. Marchetti^{a,*}

^a *Cindec, Fac. Cs. Exactas, Fac. Ingeniería, UNLP, CONICET, CICPBA, Calle 47 No 257, 1900 La Plata, Argentina*

^b *NUCAT, COPPE, UFRJ, Ilha do Fundão, CC.P. 68502, CEP 21941, Rio de Janeiro, Brazil*

Received 7 December 2006; received in revised form 3 April 2007; accepted 7 April 2007

Available online 19 April 2007

Abstract

In order to study if the SMSI effect produces beneficial results on the Fischer–Tropsch (FT) reaction using the Fe/Nb₂O₅ system we prepared two catalysts by reduction at two different temperatures. The solids were characterized by Mössbauer spectroscopy, XRD, XPS, N₂ adsorption, atomic absorption, CO chemisorption and volumetric oxidation. It was demonstrated that the support is partially reduced leading to a covering of the Fe^o crystals by NbO_x species. At the higher reduction temperature studied (773 K) this effect produced a very important activity decrease, an increase in methane production and a shift of the product distribution towards to higher molecular weight hydrocarbons.

© 2007 Elsevier B.V. All rights reserved.

Keywords: SMSI effect; Fischer–Tropsch synthesis; Fe/Nb₂O₅ catalysts; Mössbauer spectroscopy

1. Introduction

In the last years, CO hydrogenation has recovered interest as an attractive way to produce hydrocarbons in gasoline or diesel range, due to the reduction reserves and high crude oil prices.

One of the most important aims in Fischer–Tropsch (FT) research is the design of selective supported catalysts for an specific hydrocarbon range. The nature of the support has a strong influence on the metal catalytic properties for the CO hydrogenation. The supports traditionally used have been inert oxides such as SiO₂ and Al₂O₃. However, interesting results have been obtained when reducibles oxides like TiO₂ and Nb₂O₅ were used [1–8]. In these systems the product selectivity changed, depending on the reduction temperature. In this way, metal catalysts supported on niobia showed a higher selectivity towards long chain saturated hydrocarbons compared to the alumina supported ones. In Co/Nb₂O₅ system, these results were explained by the formation of new catalytic sites involving the metal and the partially reduced support during

high temperature reduction [1,2] through strong metal support interaction effect (SMSI) [9]. However, for CO hydrogenation it have been demonstrated that the SMSI effect is destroyed during the reaction itself, due to the presence of water [10]. But this effect is rather stable on Nb₂O₅ systems and the activity was not completely reversed and the selectivity was drastically changed after high temperature reduction. Therefore, in these systems the SMSI effect remains during the FT reaction [1,2,11].

Bearing in mind that, iron is the other metal used in the FT reaction and it is cheaper than Co but when it is supported it is not able to get long chain hydrocarbons, it is interesting to study if it is possible to use the SMSI effect in order to improve the selectivity towards C₅⁺. With this purpose, we have studied the structural and catalytic properties of Fe/Nb₂O₅ system reduced at different temperatures in the FT synthesis.

2. Experimental

Nb₂O₅ used as support was obtained by calcination of niobic acid from CBMM (Companhia Brasileira de Metalurgia e Mineração, AD 1264) in air at 773 K for 2 h. The catalyst precursor was prepared impregnating the Nb₂O₅ by incipient wetness using an aqueous solution of Fe(NO₃)₃·9H₂O at a high

* Corresponding author. Tel.: +54 221 4210711; fax: +54 221 4211353.

E-mail address: march@quimica.unlp.edu.ar (S.G. Marchetti).

¹ Tel.: +54 221 4210711; fax: +54 221 4211353.

enough concentration to yield a catalyst with 5% (w/w) of iron. Twenty grams of this precursor was calcined in dry N₂ stream (150 cm³/min) from room temperature (RT) to 603 K at 0.21 K/min and kept at this temperature for 1 h.

The precursor (p-Fe/Nb₂O₅) was reduced in H₂ stream (60 cm³/min) at two different final temperatures: 698 K (c698-Fe/Nb₂O₅) and 773 K (c773-Fe/Nb₂O₅). The heating rate was 2.5 K/min and the solids remained at the final temperature during 26 h.

Mössbauer spectroscopy (MS) in controlled hydrogen atmosphere at RT and low temperatures, X-ray diffraction (XRD), CO chemisorption, atomic absorption, N₂ adsorption (BET), volumetric oxidation and X-photoelectron spectroscopy (XPS) were used to characterize the solids.

The Mössbauer spectra were obtained in transmission geometry with a 512-channel constant acceleration spectrometer. A source of ⁵⁷Co in Rh matrix of nominally 50 mCi was used. Velocity calibration was performed against a 6 μm-thick α-Fe foil. All isomer shifts (δ) mentioned in this paper are referred to this standard. The temperature between 17 and 298 K was varied using a Displex DE-202 Closed Cycle Cryogenic System.

The Mössbauer spectra were evaluated using a fitting commercial program named Recoil [12]. Lorentzian lines were considered with equal widths for each spectrum component. The spectra were folded to minimize geometric effects.

Support and precursor were characterized by XRD using Cu Kα radiation.

CO chemisorption experiments were carried out in conventional volumetric static equipment [13].

XPS was performed on a Perkin-Elmer 1257 Surface Science Instruments (SSI) X-Probe spectrometer. To calculate “surface atomic ratio” from the XPS spectra it was followed the methodology described in Ref. [14].

Catalytic evaluation of the samples with the CO hydrogenation reaction was performed on a small scale stainless steel unit. Gases used were H₂ (commercial grade, for sample reduction), N₂ (commercial grade, for reactor purge) and 31.7% CO/64.3% H₂/4% He (feed gas for reaction). Helium was used as an internal standard to calculate the total CO conversions. A set of valves was used to select the required gases. These gases were passed through the following filtering elements (at RT): a Pd-based catalyst to remove residual O₂ and a molecular sieve to remove water traces. In addition, the mixture CO/H₂/He passed through an activated carbon filter (heated at 353 K) to remove any Fe carbonyl compounds formed in the gas bottle. The fixed bed reactor was a vertical stainless steel tube approximately 1.5 cm i.d. with a wall thickness of 2 mm and a length of 15 cm. A stainless steel screen was placed 5 cm from the bottom of the reactor to hold the catalyst sample. The gas flow went from the bottom to the top. A J-type thermocouple, used to monitor reaction temperature, was inserted into a 3.18 mm diameter tube welded to the wall of the reactor at 2 cm above the screen. The thermocouple tip reached the center of the reactor. The reactor was enclosed by a ceramic oven equipped with another J-type thermocouple connected to a temperature programmer and controller. A mass of powder

catalyst of 4.0 and 2.0 g were used in the experiments carried out at 4 and 20 bar, respectively. Nitrogen passed through the sample for 5–10 min to purge the air from the reactor. Hydrogen flow for catalyst reduction was 60 cm³/min. The oven temperature programmer was set to heat from RT to 698 K at a rate of 2.5 K/min. The final temperature was maintained for 26 h and then cooled down under H₂ flow to the reaction temperature (543 K). The reaction was started after the temperature had stabilized by flowing the CO/H₂/He (H₂/CO = 2:1) mixture into the reactor at a rate of 30 cm³/min for 50 h. Reaction products were analyzed online with two gas chromatographs placed in parallel: a VARIAN-3700 equipped with a flame ionization detector and a CG-25 equipped with a thermal conductivity detector. A megabore HP-1 column was installed on the VARIAN-3700 (methyl silicone; 0.53 mm in diameter; 30 m in length). The CG-25 had a porapak Q packed column, 3.18 mm i.d. and 2 m long. The carrier gas on both chromatographs was H₂ at a flow of 20 cm³/min. After the reactor, the tubing lines were kept at ≈503 K to avoid product condensation. This hot stream passed through a six-way injection valve that collected ≈0.1 cm³ of gas sample to be injected in the megabore column for hydrocarbons. After the six-way valve, gas product passed through a trap heated at 353 K to collect residue of condensable products. After this trap, the remaining products were mainly unreacted CO, He, CO₂, light hydrocarbons from C₁ to C₄ and water, which were injected in the porapak Q column.

3. Results and discussion

The complete decomposition of niobic acid to obtain Nb₂O₅ (specific surface area: 67 m²/g) was verified by XRD. The total iron loading, determined by atomic absorption was of 4.5% (w/w).

The p-Fe/Nb₂O₅ XRD pattern (not shown) is identical to that displayed by the support. The combination of low iron loading and the small oxide crystal size would be responsible of this result. Therefore, XRD is inappropriate to characterize the present system.

The p-Fe/Nb₂O₅ Mössbauer spectra at 298 and 17 K (Fig. 1) displayed a central doublet and a sextet. From the hyperfine parameters of the sextet obtained in fitting (Table 1), it can be determined that 64% of iron is present as α-Fe₂O₃. A crystal size of about 6.5 nm of this species was calculated using the “core” and “shell” model [15]. This value is consistent with the fact that these α-Fe₂O₃ crystals did not present the Morin transition (that is, when the temperature decreases the quadrupole shift (2ε) did not change from ≈−0.22 to ≈+0.38 mm/s), which occurs for crystals lower than 20 nm [16]. The remainder doublet could be assigned to superparamagnetic (sp) α-Fe₂O₃ or Fe³⁺ diffused into the support, perhaps as FeNbO₄. The former possibility can be discarded since the quadrupole splitting (Δ) is too large (Table 1) for an iron oxide and at 17 K there is not any evidence of magnetic blocking. This temperature is low enough to produce, at least, a background curvature if a sp iron oxide would be present. Therefore, we can conclude that this signal may be assigned to

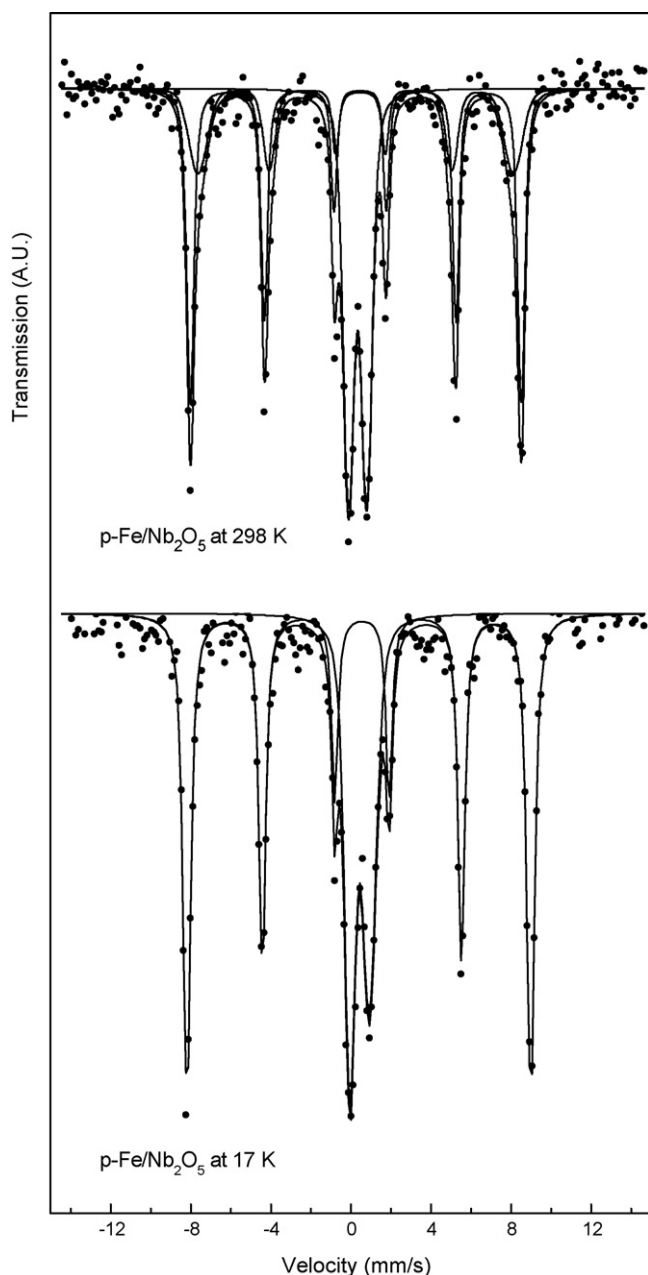


Fig. 1. Mössbauer spectra at 298 and 17 K of the precursor p-Fe/Nb₂O₅.

FeNbO₄. However, Fe₂O₃–Nb₂O₅ system is very complex since FeNbO₄ is the end member of the mixed solid series Fe³⁺Nb⁵⁺O₄ to Fe²⁺Nb⁵⁺O₆ (Fe_{1–X/3}Nb_{1+X/3}O₄, 0 ≤ X ≤ 1) [17,18]. Taking into account that this sample was prepared in oxidant atmosphere, “X” value must be zero. Besides FeNbO₄ presents at least three polymorphs [19,20]:

- Polymorph I is stable between 1653 and 1723 K, and crystallizes in the rutile-type structure with tetragonal symmetry.
- Polymorph II stable between 1373 and 1653 K, forms an α-PbO₂ type structure with orthorhombic symmetry.
- Polymorph III stable below 1373 K forms a wolframite type structure with monoclinic symmetry.

Table 1
Mössbauer parameters of p-Fe/Nb₂O₅ at 298 and 17 K

Species	Parameters	p-Fe/Nb ₂ O ₅ at 298 K	p-Fe/Nb ₂ O ₅ at 15 K
α-Fe ₂ O ₃ “core”	<i>H</i> (T)	51.3 ± 0.1	–
	<i>δ</i> (mm/s)	0.37 ± 0.01	–
	2 <i>ε</i> (mm/s)	–0.22 ± 0.01	–
	%	41 ± 7	–
α-Fe ₂ O ₃ “shell”	<i>H</i> (T)	49 ± 1	–
	<i>δ</i> (mm/s)	0.37 ± 0.04	–
	2 <i>ε</i> (mm/s)	–0.24 ± 0.08	–
	%	23 ± 8	–
α-Fe ₂ O ₃	<i>H</i> (T)	–	53.3 ± 0.1
	<i>δ</i> (mm/s)	–	0.48 ± 0.01
	2 <i>ε</i> (mm/s)	–	0.15 ± 0.02
	%	–	62 ± 2
FeNbO ₄	Δ (mm/s)	0.90 ± 0.02	0.97 ± 0.03
	<i>δ</i> (mm/s)	0.35 ± 0.01	0.45 ± 0.02
	%	36 ± 5	38 ± 2

H: hyperfine magnetic field in Tesla; *δ*: isomer shift (all the isomer shifts are referred to α-Fe at 298 K); 2*ε*: quadrupole shift; Δ: quadrupole splitting.

Since the maximum temperature used during the preparation steps of p-Fe/Nb₂O₅ was of 603 K, FeNbO₄ might have wolframite type structure (polymorph III). However, taking into account that the quadrupole splitting value is very large in comparison with that obtained from the literature for a bulk compound [18], the FeNbO₄, present in our precursor, must be a surface compound.

Surface concentration values for Nb, Fe and O, obtained by XPS, are shown in Table 2.

The Mössbauer spectra of the reduced samples at 698 and 773 K, measured in controlled hydrogen atmosphere, at 298 and 22 K are displayed in Figs. 2 and 3, respectively. All spectra are very similar showing an intense central doublet and a magnetic signal. At room temperature the spectra of both catalysts were fitted with one sextet and two doublets (Table 3). The sextet was assigned to Fe⁰. The doublet with larger area corresponds to Fe²⁺ in FeNb₂O₆ according to Eibschütz et al. [21]. The small doublet could be assigned to Fe²⁺ in the same compound but located in other crystallographic site of the Nb₂O₅ lattice. The FeNb₂O₆ presence could be attributed to the reduction of Fe³⁺ diffused into the Nb₂O₅ lattice in the precursor. Since the FeNb₂O₆ percentage is about twice of the diffused Fe³⁺, we can conclude that during the reduction treatment an important percentage of Fe²⁺ also diffused into the Nb₂O₅. For both catalysts when the temperature decreases the signal between the doublet peaks nearly disappears

Table 2
Surface concentration of Nb, Fe and O (at.%) in p-Fe/Nb₂O₅, c698-Fe/Nb₂O₅ and c773-Fe/Nb₂O₅, determined by XPS

Element	p-Fe/Nb ₂ O ₅	c698-Fe/Nb ₂ O ₅	c773-Fe/Nb ₂ O ₅
Nb	21.2	20.2	28.2
Fe	3.1	2.1	1.8
O	75.7	77.7	70.0

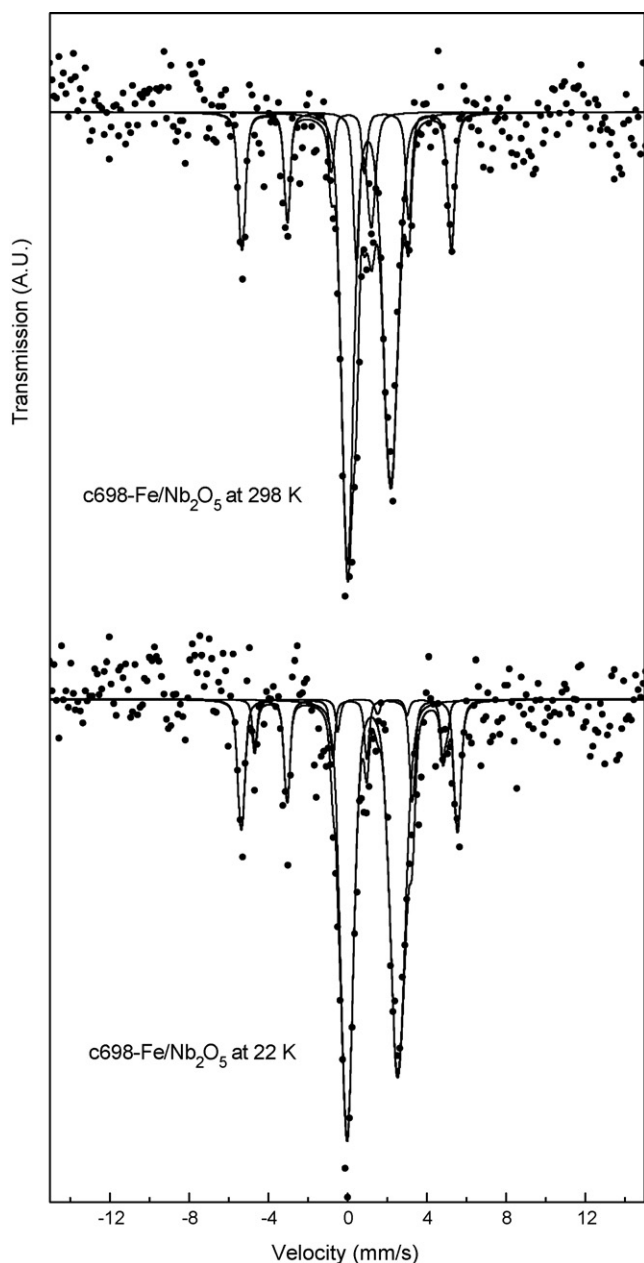


Fig. 2. Mössbauer spectra at 298 and 22 K of the catalyst c698-Fe/Nb₂O₅.

transforming it into a small sextet. The hyperfine parameters of this new sextet correspond to FeNb₂O₆ according to Yaeger et al. [22] (Table 3). The remaining signals were assigned in the same way that at room temperature. It is important to remark that this is a very complex system. Therefore, the previous discussion must be considered as a first attempt to explain it.

From Table 3 it can be seen that neither iron species nor their percentages changed with the reduction temperature (the comparison was carried out using the percentages obtained at 22 K since the free recoil fractions are nearly equals in this condition).

We have verified the partial support reduction under the present reduction conditions, by volumetric oxidation technique. When the support was reduced at 698 K, the oxygen uptake for re-oxidation was of 8 μmol/g support, instead at

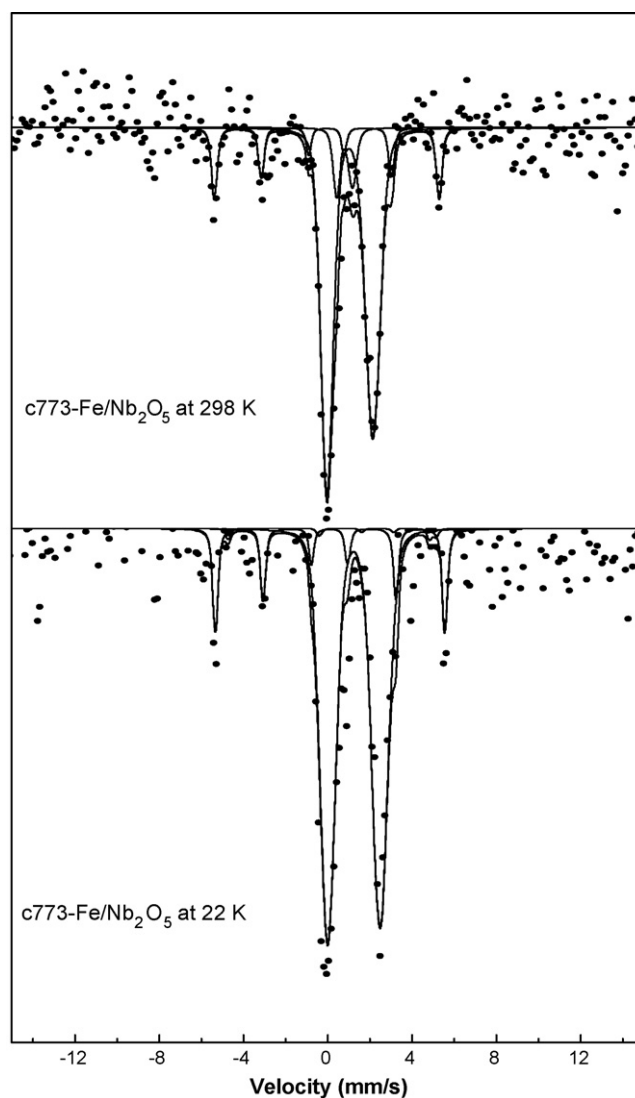


Fig. 3. Mössbauer spectra at 298 and 22 K of the catalyst c773-Fe/Nb₂O₅.

773 K this value was of 27 μmol/g support. The experimental oxygen uptakes of the catalysts, after subtracting the support consumptions, were higher than that calculated from the iron species percentages evaluated by MS (Table 4). Bearing in mind that the last technique is reliable to quantify the different iron species percentages [23], we can conclude that the support is more reducible in metallic iron presence. These results could indicate that the conditions for the SMSI effect appearance would be fulfilled.

In fact, as it was determined by XPS (Table 2), a diminution of the surface iron concentration of 22% and an increase of 39% in surface Nb concentration when the reduction temperature increased from 698 to 773 K, confirm the existence of SMSI.

Another probe to verify this effect was obtained through CO chemisorption technique (Table 4). The CO uptake for c698-Fe/Nb₂O₅ is about twice the c773-Fe/Nb₂O₅ one. Therefore, the support partially reduced (NbO_x) have covered in a substantially degree the surface Fe⁰ of the particles when the reduction temperature was increased.

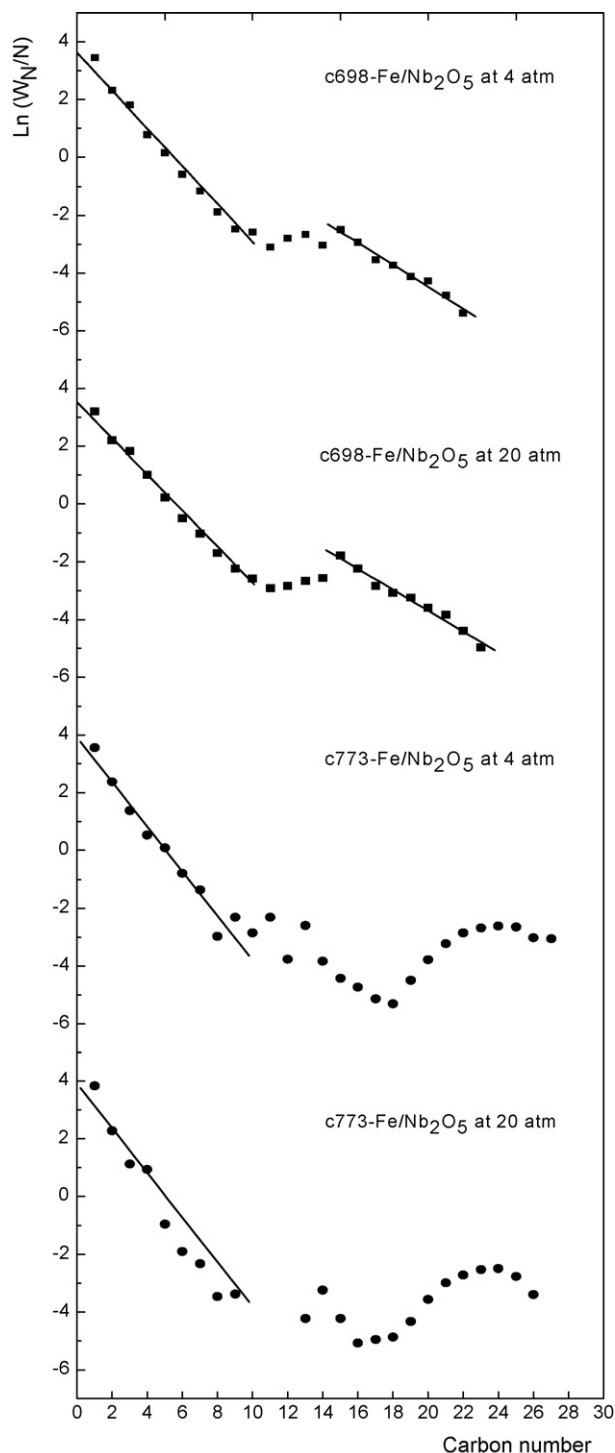


Fig. 4. Anderson-Schultz-Flory distribution for c698-Fe/Nb₂O₅ and c773-Fe/Nb₂O₅ at 4 and 20 atm. m_i is the weight percentage of hydrocarbon with n_i carbon number and n_i is the carbon number. The straight lines were obtained by linear fitting.

The average metallic crystal diameters estimated through CO chemisorption measurements were extremely small to be considered as real values (≈ 2 nm for c698-Fe/Nb₂O₅ and ≈ 1.5 nm for c773-Fe/Nb₂O₅) taking into account the low support specific surface area. Since the CO support uptakes were subtracted, we believe that the surface FeNb₂O₆

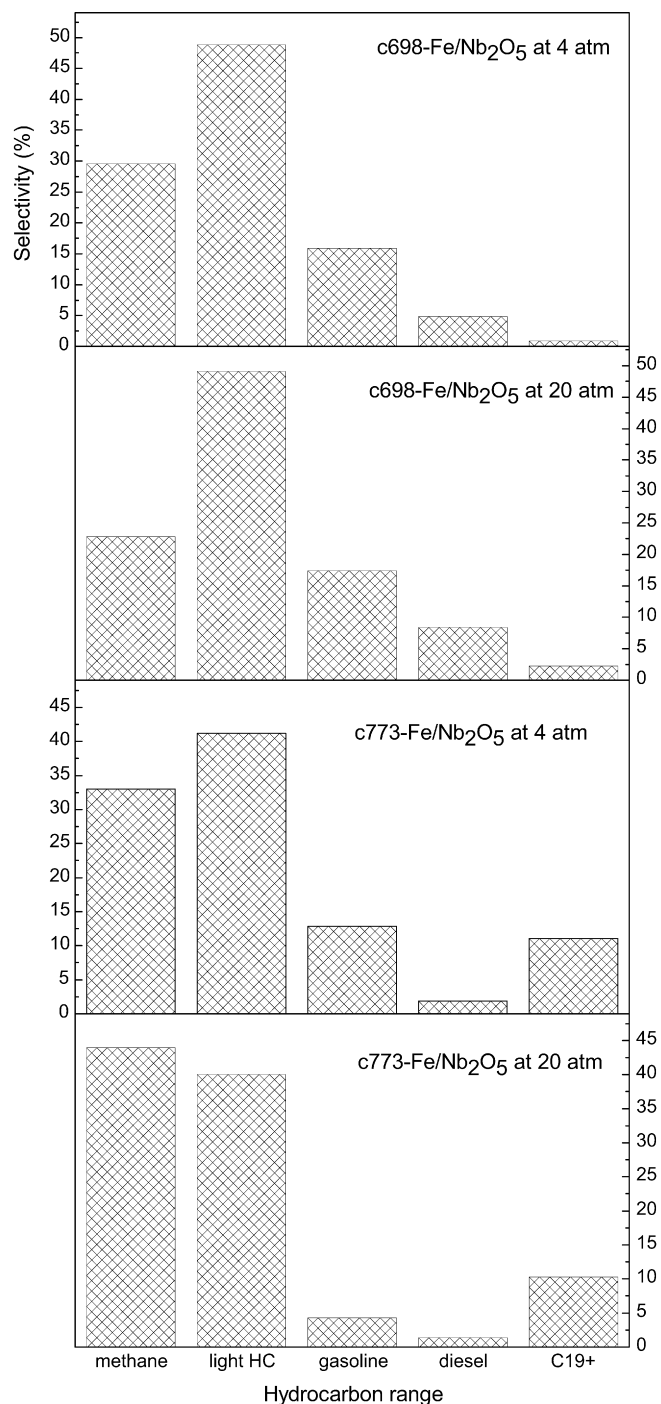


Fig. 5. Selectivity diagrams for c698-Fe/Nb₂O₅ and c773-Fe/Nb₂O₅ at 4 and 20 atm reaction pressure.

chemisorbs CO. In consequence this technique is not adequate to determine the surface metallic Fe sites. Therefore, it is not appropriate to estimate the reaction TOF values.

The CO conversion values at steady state were about one magnitude order higher for c698-Fe/Nb₂O₅ than c773-Fe/Nb₂O₅: 20% versus 2% at 4 bar and 20% versus 4% at 20 bar, respectively. This difference can be attributed to a nearly total covering of Fe⁰ particles by NbO_x species when the reduction temperature was of 773 K. These results follow the same trend

Table 3
Mössbauer parameters of c698-Fe/Nb₂O₅ and c773-Fe/Nb₂O₅ at 298 and 22 K

Species	Parameters	298 K		22 K	
		c698-Fe/Nb ₂ O ₅	c773-Fe/Nb ₂ O ₅	c698-Fe/Nb ₂ O ₅	c773-Fe/Nb ₂ O ₅
Fe ^o	<i>H</i> (T)	32.8 ± 0.3	33.1 ± 0.4	33.9 ± 0.3	33.8 ± 0.4
	δ (mm/s)	0.00 ± 0.03	−0.05 ± 0.05	0.11 ± 0.04	0.11 ± 0.05
	2 ε (mm/s)	−0.07 ± 0.07	0.1 ± 0.1	0.01 ± 0.08	0.1 ± 0.1
	%	25 ± 4	16 ± 5	25 ± 6	17 ± 9
FeNb ₂ O ₆ Site I	Δ (mm/s)	2.18 ± 0.06	2.18 ± 0.06	2.56 ± 0.06	2.48 ± 0.08
	δ (mm/s)	1.10 ± 0.03	1.06 ± 0.03	1.26 ± 0.03	1.25 ± 0.04
	%	63 ± 5	76 ± 6	69 ± 6	81 ± 10
FeNb ₂ O ₆ Site II	Δ (mm/s)	0.75 ^a	0.75 ^a	–	–
	δ (mm/s)	0.84 ± 0.06	0.8 ± 0.1	–	–
	%	12 ± 3	8 ± 4	–	–
FeNb ₂ O ₆ Site III	<i>H</i> (T)	–	–	29.4 ± 0.9	30 ± 3
	δ (mm/s)	–	–	1.2 ± 0.1	1.2 ± 0.5
	2 ε (mm/s)	–	–	−2.2 ± 0.2	−2.3 ± 0.9
	%	–	–	6 ± 5	2 ± 6

H: hyperfine magnetic field in Tesla; δ : isomer shift (all the isomer shifts are referred to α -Fe at 298 K); 2 ε : quadrupole shift; Δ : quadrupole splitting.

^a Parameters held fixed in fitting.

than that found by Phadke and Ko [24] for Fe/Nb₂O₅ system and by Silva et al. [1] for Co/Nb₂O₅ catalysts. The results suggest that the SMSI state was not completely destroyed by the reaction, in concordance with [1,2,11].

According to Anderson–Schultz–Flory (ASF) distribution [25], in Fig. 4 it can be seen that c698-Fe/Nb₂O₅ shows a preferential chain growth for C₁₂–C₁₄ for both reaction pressures, while for C₁–C₁₁ and C₁₅–C₂₂ the ASF distribution is verified obtaining very similar α (chain growth probability) of about 0.7. Instead, for c773-Fe/Nb₂O₅ the model validity is observed only up to C₉ for both pressures with an α value of 0.46. However, from C₁₈ a very important deviation of this linear behaviour is noticeable. Therefore, we can conclude that when a higher reduction temperature is used, the quantity of the new catalytic sites (involving the metal in contact with NbO_x species [1,2]) must be increased, in coincidence with Co/Nb₂O₅ system.

Fig. 5 displays the selectivity diagrams for both catalysts at 4 and 20 atm. The selectivity (*S_i*) is defined as:

$$S_i = \frac{m_i \times n_i}{M_i \times \sum_{i=1}^n (m_i \times n_i / M_i)}$$

where *m_i* is the weight percentage of component *I*, *n_i* the carbon number for the component *I* and *M_i* is the molecular weight of the component *i*.

Table 4
CO chemisorption uptakes and volumetric oxidation results for Nb₂O₅, c698-Fe/Nb₂O₅ and c773-Fe/Nb₂O₅

Solid	CO uptake (μmol/g _{cat})	Oxygen uptake (μmol/g _{cat})	
		Experimental	Theoretical
Nb ₂ O ₅ ⁽⁶⁹⁸⁾	3	8	
Nb ₂ O ₅ ⁽⁷⁷³⁾	5	27	
c698-Fe/Nb ₂ O ₅	46	406	299 ± 40
c773-Fe/Nb ₂ O ₅	24	359	268 ± 61

⁽⁶⁹⁸⁾ and ⁽⁷⁷³⁾ means supports treated in the same way that the catalysts.

It is not possible to compare the selectivity diagrams of c698-Fe/Nb₂O₅ and c773-Fe/Nb₂O₅ due to the high difference between the conversion levels. Notwithstanding, considering that when CO conversion diminishes, CH₄ production diminishes too [25], the results obtained with c773-Fe/Nb₂O₅, where methane increases, could be attributed to another effect different from the conversion. We believe that the migration of reduced moieties from the support onto metallic particles are diluting the active surface Fe^o ensembles, inhibiting the chain growth. Therefore on the iron particles there are two kinds of sites: one of them constituted from the NbO_x–Fe^o interaction, on which a long chain growth occurs, and the other one by nearly isolated surface iron, where only CH₄ is formed.

4. Conclusions

The reduction temperature, between 698 and 773 K, affects neither the reduced iron species nor their percentages in Fe/Nb₂O₅ system. However, the surface composition has changed, showing an important surface Fe^o diminution, due to the covering by NbO_x species (SMSI effect), when the reduction temperature is increased.

The existence of this SMSI effect leads to a blocking and diluting of the active surface, modifying the activity and selectivity behaviour of Fe/Nb₂O₅ system in FT reaction. When the reduction temperature reaches 773 K the CO conversion drops drastically (one order of magnitude). This decrease is more noticeable than in Co/Nb₂O₅ system.

The beneficial effect of the SMSI on selectivity can be already observed for c698-Fe/Nb₂O₅ since the C₁₂–C₁₄ production is increased over the values predicted by the ASF model. This effect is more pronounced in c773-Fe/Nb₂O₅ since not only the ASF model deviation is higher but also the “breakpoint” of this distribution is shifted towards to higher molecular weight hydrocarbons. Reduction temperatures lower

than 698 K are not adequate since the iron reduction does not occur.

Acknowledgements

The authors acknowledge financial support of this work by Consejo Nacional de Investigaciones Científicas y Técnicas, Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Universidad Nacional de La Plata, and Agencia Nacional de Promoción Científica y Tecnológica (PICT No 14-11267).

References

- [1] R.R.C.M. Silva, M. Schmal, R. Frety, J.A. Dalmon, *J. Chem. Soc., Faraday Trans.* 89 (21) (1993) 3975.
- [2] A. Frydman, R.R. Soares, M. Schmal, *Stud. Surf. Sci. Catal.* 75 (1993) 2797.
- [3] R.R. Soares, A. Frydman, M. Schmal, *Catal. Today* 16 (1993) 361.
- [4] F.B. Noronha, A. Frydman, D.A.G. Aranda, C.A. Perez, R.R. Soares, B. Moraweck, D. Castner, C.T. Campbell, R. Frety, M. Schmal, *Catal. Today* 28 (1996) 147.
- [5] F.T. Mendes, F.B. Noronha, R.R. Soares, C.A. Perez, G. Marchetti, M. Schmal, *Stud. Surf. Sci. Catal.* 136 (2001) 177.
- [6] F.T. Mendes, F.B. Noronha, M. Schmal, *Stud. Surf. Sci. Catal.* 130 (2001) 3717.
- [7] R.C. Reuel, C.H. Bartholomew, *J. Catal.* 85 (1984) 78.
- [8] E.I. Ko, M. Hupp, K. Foger, *J. Catal.* 86 (1984) 315.
- [9] S.J. Tauster, S.C. Fung, R.L. Garten, *J. Catal.* 55 (1978) 29.
- [10] G.L. Haler, D.E. Resasco, *Adv. Catal.* 36 (1989) 173.
- [11] T. Uchijima, *Catal. Today* 28 (1996) 105.
- [12] K. Lagarec, D.G. Rancourt, Mossbauer Spectral Analysis Software, Version 1.0, Department of Physics, University of Ottawa, 1998.
- [13] M.V. Cagnoli, S.G. Marchetti, N.G. Gallegos, A.M. Alvarez, R.C. Mercader, A.A. Yeramian, *J. Catal.* 123 (1990) 21.
- [14] A. Frydman, D.G. Castner, M. Schmal, C.T. Campbell, *J. Catal.* 152 (1995) 164.
- [15] M. Vasquez-Mansilla, R.D. Zysler, C. Arciprete, M.I. Dimitrijewits, C. Saragovi, J.M. Greneche, *J. Magn. Magn. Mater.* 204 (1999) 29.
- [16] R.E. Vandenberghe, *Mössbauer Spectroscopy and Applications in Geology*, International Training Centre for Post-Graduate Soil Scientist, Belgium, 1991.
- [17] A. Burdese, M. Lucco Borlera, *Metall. Ital.* 57 (4) (1965) 150.
- [18] E. Schmidbauer, J. Schneider, *J. Solid State Chem.* 134 (1997) 253.
- [19] R. Theissmann, H. Ehremberg, H. Weitzel, H. Fuess, *J. Mater. Sci.* 37 (2002) 4431.
- [20] R. Theissmann, H. Ehremberg, H. Weitzel, H. Fuess, *Solid State Sci.* 7 (2005) 791.
- [21] M. Eibschütz, U. Ganiel, S. Shtrikman, *Phys. Rev.* 156 (1967) 259.
- [22] I. Yaeger, A.H. Morrish, C. Bounford, C.P. Wong, B.H. Wanklyn, B.J. Garrard, *Solid State Commun.* 28 (8) (1978) 651.
- [23] S.G. Marchetti, M.V. Cagnoli, A.M. Alvarez, J.F. Bengoa, R.C. Mercader, A.A. Yeramian, *Appl. Surf. Sci.* 165 (2000) 91.
- [24] M.D. Phadke, E.I. Ko, *J. Catal.* 100 (1986) 503.
- [25] M. Röper, in: W. Keim (Ed.), *Catalysis in C₁ Chemistry*, D. Reidel Publishing Co., Dordrecht, 1983, pp. 41–88.