Characterization of Fe-promoted sulfated zirconia catalysts used for the n-butane isomerization by XPS and Mössbauer spectroscopies

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Iron-promoted sulfated zirconia catalysts have been characterized by Mössbauer spectroscopy and XPS before and after catalytic test for the isomerization of n-butane. The data obtained by Mössbauer spectroscopy show that iron is present in the fresh catalysts at the surface of zirconia both as isolated cations and small ferric oxide particles. The diameters of these particles do not exceed 4 nm. The characterization of the catalysts by Mössbauer spectroscopy after 20 and 120 min of reaction shows no apparent reduction of the iron cations. However, the analysis of the peak of Fe $3d_{3/2}$ in the XPS spectra shows that iron has been partially reduced in the used catalysts. These apparently contradictory results could be explained by the study of a pre-reduced catalyst by both techniques. This study shows first that the Fe^{3+} cations in the particles can be reduced into Fe^{2+} and reoxidized at room temperature, and second that the reduction observed by XPS corresponds to the departure of the O_2 re-adsorbed at room temperature under air, occurring when the catalysts are placed under vacuum. All the data obtained seemed to confirm that the loss of the promoting effect of iron during the catalytic reaction may partially be due to the irreversible reduction of the iron species susceptible to undergo such reduction.

Keywords: sulfated zirconia, Fe–Mn-promoted catalysts, n-butane isomerization, Mössbauer spectroscopy, X-ray photoelectron spectroscopy

1. Introduction

The worldwide interest in solid acid catalysis that has developed over the last few years has focused on the exceptional properties of sulfated zirconia (SZ). To improve these properties, which remain largely unsatisfactory, the addition of various noble or transition metals has been investigated [1–7]. Among the promoters, Fe and Mn appear to give very efficient catalysts (FMSZ) especially in the n-butane isomerization reaction [3]. The nature of the promoting effect of these transition metals remains controversial. Some authors have proposed that Fe and Mn ions influence somewhat the surface energy of ZS [8], but others proposed that they intervene via an oxido-reduction process in the formation of an olefinic intermediate triggering the acid reaction [7–11].

Recently it has been proposed that when the Fe component of the FSZ or MFSZ catalysts becomes reduced, the catalytic promotion effect is lost [7]. The reduced iron species were revealed by ambient temperature adsorption of CO. In the present study we characterized MFSZ catalysts using Mössbauer and XPS spectroscopies in order to confirm these data. The spectra have been recorded before and after catalytic testing. The reduction by H_2 and the reoxidation of the fresh catalyst has also been studied.

2. Experimental

Hydrous zirconia was prepared by the sol–gel method starting from $Zr(OPr)_4$ in i-PrOH [1]. The wet gel was dried overnight at 383 K to yield a xerogel. The sulfatation was performed by incipient wetness, using an appropriate amount of a 1 M aqueous solution of $(NH_4)_2SO_4$ to produce a final theoretical 8% weight amount of $(SO_4)^{2-}$ in the sample. Promotion of sulfated zirconia with Fe was achieved by sequential incipient wetness impregnation by using appropriate amounts of aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ as to obtain 1.5 wt% of Fe and 0.5 wt% of Mn. Since the iron content of the solid was too low to allow the recording of Mössbauer spectra in suitable conditions, the compounds were synthesized using ^{57}Fe nitrate. After each impregnation, the samples were dried overnight at 383 K. Finally, the calcination step was carried out in dry air flow at 923 K. After calcination, the catalysts were cooled to ambient temperature and allowed to rehydrate by exposure to the ambient atmosphere.

The Mössbauer spectra of the samples pressed into pellets, were recorded at 298, 4.2 and 1.45 K using a 2 GBq ^{57}Co/Rh source and a conventional constant acceleration spectrometer, operated in triangular mode. The spectrum at 1.45 K was obtained by pumping on the helium bath in a standard helium cryostat. The isomer shifts (δ) are given with respect to α-Fe and are obtained, as the quadrupole splittings (Δ), with a precision of about 0.02 $mm\,s^{-1}$.

The relative areas of the observed doublets have been used to quantitatively evaluate the relative amounts of the iron species present in the catalysts. This has been done by assuming equal free recoil fraction for all of them. Samples have been examined *in situ* at 298 K following treatment in hydrogen for 2 h at 653 K in a reactor equipped with Be windows and built up in the laboratory.

XPS measurements were performed with a VG ESCALAB 200 R. Charging of catalysts samples was corrected by setting the binding energy of adventitious carbon (C 1s) at 284.5 eV. Qualitative analysis of the peaks, in terms of elemental ratios, was carried out as previously described [12]. Deconvolution of the Fe $2p_{3/2}$ peak was accomplished using a Voigt function. Only the shake-up satellite occurring in Fe^{3+} has been considered for the calculation of the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratios. Due to low signal/noise ratio the experimental precision on XPS quantitative measurements is considered to be around 10%.

The catalytic activity of the samples has been investigated in a microflow reactor operating at atmospheric pressure and using a feed containing n-butane and helium in a 1 : 4 ratio at 323 K [7]. Before reaction, the catalyst underwent an activation step, in dry air at 723 K for 90 min. Catalytic tests of the same MFSZ catalyst have been conducted in the same conditions but stopped after, respectively, 20 and 120 min to characterize the solid at different stages of reaction.

3. Results and discussion

The fresh catalyst has been characterized by Mössbauer spectroscopy at 298, 4.2 and 1.45 K. The spectrum obtained at 298 K was fitted with two doublets (figure 1, table 1). The values of the isomer shifts and the quadrupolar splittings are characteristic of ferric cations in octahedral environment. The relative areas of the two doublets are equal to 60 : 40. The spectrum at 4.2 K consists of a very broad magnetic hyperfine six-line pattern (40% relative intensity) and of a quadrupolar doublet with a splitting of about 0.94 $mm\,s^{-1}$. At 1.45 K, the spectrum is analogous to that at 4.2 K, but the magnetic sextet is better resolved; a good fit of the 1.45 K spectrum is obtained with the superposition of a quadrupolar doublet with a splitting of 0.87 $mm\,s^{-1}$ (43%) and a distribution of magnetic hyperfine splittings, with hyperfine fields ranging from about 100 to 520 kOe (figure 2, table 1). The sample contains thus two Fe^{3+} species: one of them (40% relative intensity) corresponds to isolated ions which show no magnetic ordering down to 1.45 K, their spectrum being a quadrupolar doublet over the whole temperature range. These species could correspond to Fe^{3+} at the surface or in the bulk near the surface of ZrO_2. The other species (60% relative intensity) presents a magnetic hyperfine splitting at 1.45 and 4.2 K; its spectrum is probably a superposition of a magnetic and of a quadrupolar sub-spectrum, but the latter cannot be resolved from the doublet arising from the other Fe^{3+} species (table 1). This behavior can be attributed to superparamagnetic ferric oxide particles; their blocking temperature with respect to ^{57}Fe Mössbauer spectroscopy can be roughly estimated to be 10–15 K. Using a magnetocrystalline anisotropy density typical for ferric oxides

Table 1

Calculated Mössbauer parameters from the spectra of the MFSZ catalyst before catalytic test, recorded at 298 and 1.45 K.

Temperature (K)	Site	δ^a ($mm\,s^{-1}$)	Δ^b ($mm\,s^{-1}$)	H^c (kOe)	Relative intensity (%)
298	Fe^{3+}	0.33	0.83		43
	Fe^{3+}	0.34	1.48		57
1.45	Fe^{3+}	0.38	0.87		45
	Fe^{3+}	0.28	0.00	100–520	55

[a] δ: isomeric shift (referred to α-Fe).

[b] Δ: quadrupolar splitting.

[c] H: internal field.

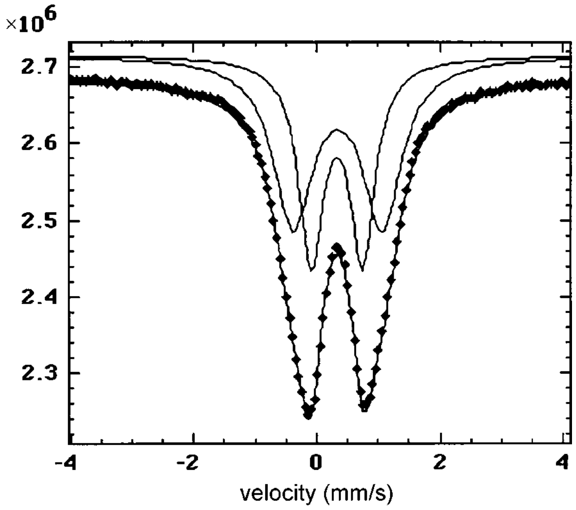

Figure 1. Experimental ^{57}Fe Mössbauer spectrum of the activated MFSZ catalyst recorded at 298 K. Solid lines are derived from least-square fits.

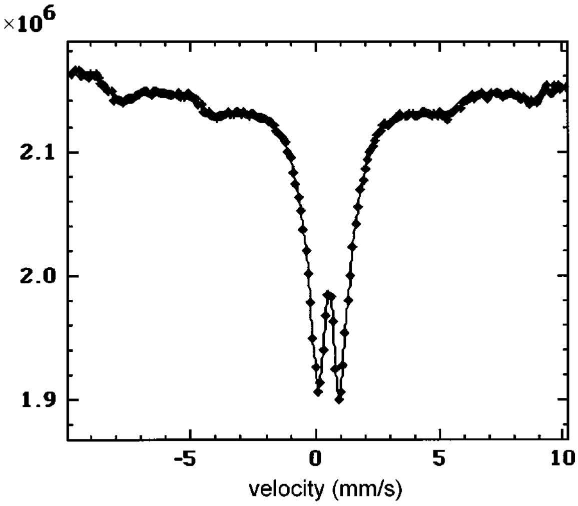

Figure 2. Experimental ^{57}Fe Mössbauer spectrum of the activated MFSZ catalyst recorded at 1.45 K.

(3×10^5 erg cm^{-3}), the diameter of these particles can be estimated to be around 4 nm [13].

The catalytic tests of the catalyst have been conducted in the conditions given in section 2. Figure 3 shows the evolution of the n-butane isomerization conversion vs. time-on-stream plot with the SZ and MFSZ catalysts at 323 K. We could observe, for the MFSZ catalyst, an initial activation step during the first 25 min followed by a deactivation step over 150 min. Comparable profiles have already been reported for the promoting effect of iron-doped sulfated zirconia [3,7]. Samples have been tested for 20 and 120 min and recovered for characterization by XPS and Mössbauer spectroscopies. After 20 min the catalyst is not far from its maximum of activity, whereas after 120 min it is almost completely deactivated. The XPS spectra of the tested catalysts have been recorded and compared to that of the fresh catalyst. The results obtained are gathered in table 2. For all the spectra, the Zr, O and Fe peak positions are consistent with those previously reported [14–16]. It can be observed that the surface Fe/Zr and O/Zr ratios do not change significantly during the catalytic test. The O 1s peak could systematically be deconvoluated into two peaks. The peak located at higher binding energy is attributed to oxygen present in sulfate species [14,16]. It represents 26% of the total area which corresponds approximately to 7% $(SO_4)^{2-}$. Such a determination is in agreement with the amount actually deposited (8%). This ratio did not change under reaction conditions. The Fe $2p_{3/2}$ peak, whose position is consistent with Fe_2O_3 [17], displays a shoulder and it has been possible to distinguish, in each spectrum after deconvolution, two peaks separated by approximately 1.5 eV, which are attributed to ferrous and ferric cations (table 2). The variation of the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio calculated from the fitting with the time-on-stream, is presented in figure 4. It was observed that the fresh catalysts contain Fe^{2+} in small amounts and that this amount increases strongly with the time-on-stream.

The Mössbauer spectra of the tested catalysts recorded at 298 K are presented in figure 5 and the calculated parameters gathered in table 3. The spectra could be fitted with only the two doublets identified in the fresh sample with approximately the same relative ratios. The iron species appear thus not to have undergone a reduction during the testing. These results are apparently in contradiction with those obtained by XPS spectroscopy, which show an important reduction of the iron. It was proposed that iron is

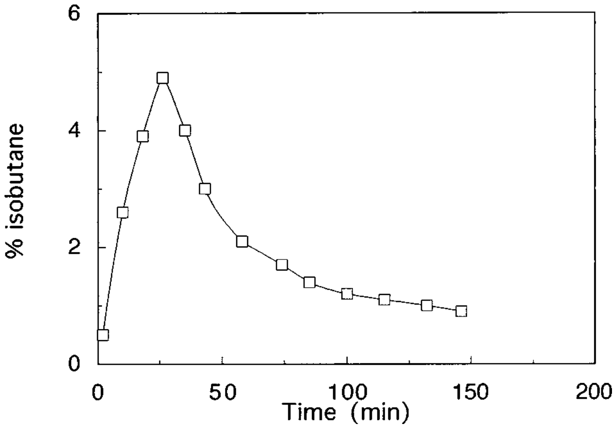

Figure 3. n-butane isomerization conversion vs. time-on-stream measured at 323 K over the MFSZ catalyst calcined at 923 K and activated in dry air at 723 K.

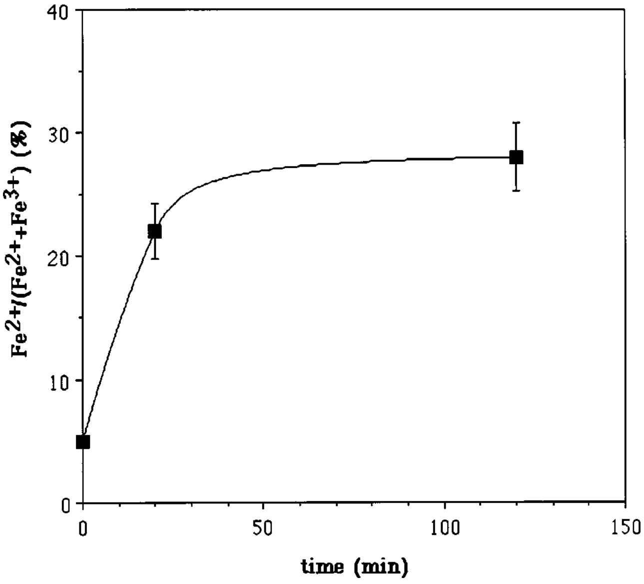

Figure 4. Variation of the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio, calculated from XPS data, as a function of the time-on-stream.

Table 2

XPS spectroscopic data obtained on the fresh and used catalysts and on the catalyst after reduction by H_2 at 653 K and reoxidation in air at 298 K.

Sample	Fe $2p_{3/2}$ (eV)	Fe^{2+} (%)	O 1s (eV)	$(SO_4)^{2-}$ (%)	Zr $3d_{5/2}$ (eV)	Fe/Zr	O/Zr
Fresh	710.50		532.40	26	182.25	0.025	2.2
	709.10	5	530.45				
After 20 min of reaction	710.60		532.30	23	182.30	0.028	2.2
	709.10	22	530.40				
After 120 min of reaction	710.60		532.40	27	182.20	0.029	2.4
	709.10	28	530.45				
After reduction and reoxidation	710.60		531.20	26	181.60	0.025	2.2
	709.10	36	530.50				

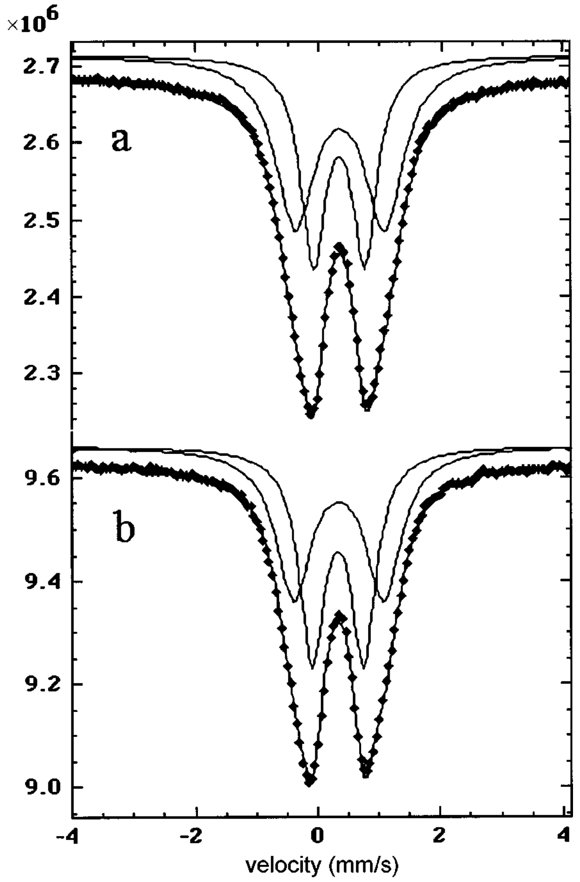

Figure 5. Experimental ^{57}Fe Mössbauer spectra of the activated catalyst recorded at 298 K after catalytic reaction for 20 (a) and 120 min (b). Solid lines are derived from least-square fits.

Table 3

Calculated Mössbauer parameters from the spectra recorded at 298 K of the MFSZ catalyst after 20 and 120 min of catalytic reaction.[a]

Time (min)	Site	δ^a (mm s^{-1})	Δ^b (mm s^{-1})	Relative intensity (%)
20	Fe^{3+}	0.33	0.83	44
	Fe^{3+}	0.34	1.45	56
120	Fe^{3+}	0.33	0.84	48
	Fe^{3+}	0.35	1.47	52

[a] δ: isomeric shift (referred to α-Fe).
[b] Δ: quadrupolar splitting.

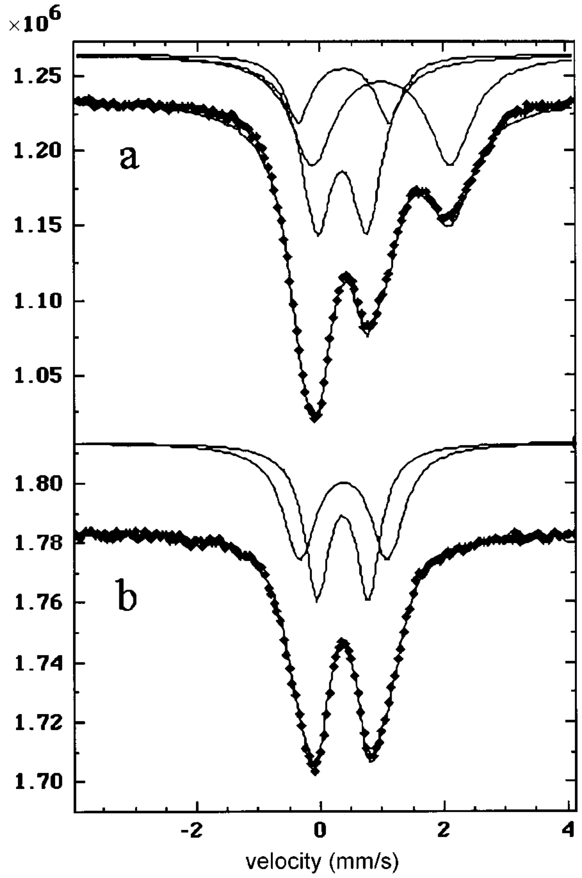

Figure 6. Experimental ^{57}Fe Mössbauer spectra of the activated MFSZ catalyst recorded at 298 K (a) after reduction at 653 K under hydrogen and return back at 298 K under pure nitrogen, (b) after reduction and exposure to air at 298 K. Solid lines are derived from least-square fits.

Table 4

Calculated Mössbauer parameters from the spectra of the MFSZ catalyst recorded at 298 K after reduction by H_2 at 653 K and after reoxidation in air at 298 K. For the recording the catalyst was, respectively, under pure nitrogen and air.

Site	δ^a (mm s^{-1})	Δ^b (mm s^{-1})	Relative intensity (%)
After reduction by H_2 at 653 K			
Fe^{3+}	0.34	0.82	44
Fe^{3+}	0.38	1.48	15
Fe^{2+}	1.00	2.23	41
After reoxidation by air at 298 K			
Fe^{3+}	0.35	0.84	48
Fe^{3+}	0.38	1.42	52

[a] δ: isomeric shift (referred to α-Fe).
[b] Δ: quadrupolar splitting.

reduced during the XPS measurements when the catalysts are placed under vacuum (1.333×10^{-8} Pa). However, such an interpretation would not explain the differences observed between the fresh and used catalysts. In order to understand why the reduction rate of the catalysts observed by XPS varies with the time-on-stream, we have reduced the fresh catalyst *in situ* by H_2 at 653 K and recorded its Mössbauer spectrum after cooling at room temperature under pure nitrogen (figure 6(a)). The spectrum obtained was fitted with two ferric and one ferrous doublets (table 4). The two ferric doublets correspond exactly to those observed before reduction. The comparison of the parameters and the relative ratios of the doublets show that the iron cations which have been reduced are only those in the small oxide particles and that the isolated species remains unchanged. Approximately 75% of the cations in the ferric oxide particles are reduced. After the spectrum has been recorded, the nitrogen flow has been stopped and the sample has been put back under static air. A new Mössbauer spectrum has then been recorded (figure 6(b)). The sample appears totally reoxidized at room temperature and the two doublets with

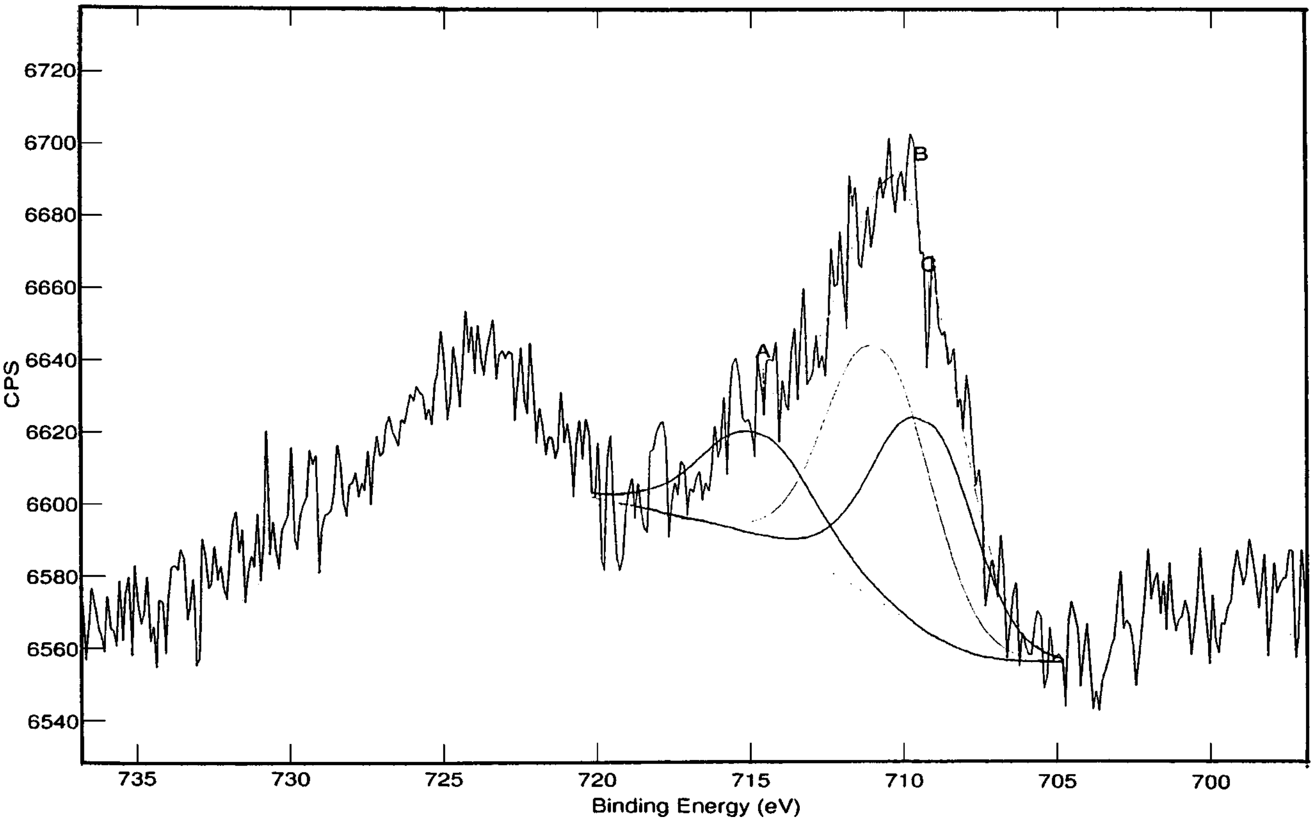

Figure 7. Fitting of the X-ray photoelectron spectrum of Fe $2p_{3/2}$ in the MFSZ catalyst after reduction at 653 K under hydrogen and reoxidation at 298 K in air. (A) Shake-up satellite peak, (B) Fe^{3+} $2p_{3/2}$ peak and (C) Fe^{2+} $2p_{3/2}$ peak.

their starting relative ratios are again observed (table 4). Such O_2 uptake at room temperature after reduction under vacuum at high temperature had already been evidenced by CO adsorption experiments, the adsorption of CO occurring only on the reduced iron cations [7]. It was reported that the reoxidation of the sample at room temperature did not transform the sample back to its original state since it did not restore its promoting activity. Furthermore, the oxygen species adsorbed were reported to be rather labile since a vacuum treatment (1.333×10^{-3} Pa) at mild temperature was sufficient to reduce the solid back to the original state [7]. These results could explain why although both, fresh and used, samples appear to be fully oxidized, they do not exhibit the same behavior upon submission to vacuum during the XPS experiments. The reduced and reoxidized catalyst has further been analyzed by XPS. The results obtained are presented in table 3. The deconvolution of the Fe $2p_{3/2}$ peak shows that iron appears partially reduced with a reduction level around 36%, which is lower but not far from that determined from Mössbauer spectroscopic data (41%) (figure 7). This result tends to confirm that the reduction observed by XPS corresponds to O_2 adsorbed at room temperature after the recovering of the catalyst from the catalytic reactor. We can thus conclude that iron was partially reduced during the catalytic reaction. Taking into account the fact that only iron cations in the iron oxide particles are reducible, the amount of reducible iron effectively reduced represents already 42% after 20 min to reach 54% after 120 min.

The results obtained show that a part of the iron cations are reduced during the catalytic reaction. This observation supports the proposition that iron intervenes in the reaction mechanism by promoting the oxidative dehydrogenation of butane into butene. With this hypothesis, the deactivation of the catalyst could not only be due to carboneous poisoning of the active sites but also to the irreversible reduction of iron. However, at this point, only *in situ* characterization of such catalysts would ascertain the role of iron. The results obtained did not allow to discuss at all the role of Mn that remained to be determined, but it should at least be mentioned that the formation of a mixed iron and manganese oxide was excluded.

4. Conclusion

The major conclusions drawn from the present work are:

(i) Characterization of fresh iron-doped sulfated zirconia shows that two types of iron species are present at the surface of the zirconia approximately in equal relative amount. These species correspond to isolated iron cations at the surface or in the bulk near the surface of zirconia, and to iron cations in small ferric oxide particles. Among these two species, only the Fe^{3+} cations in the oxide particles can be reduced to Fe^{2+} to an extent close to 75%. After reduction they can be reoxidized rapidly in air at room temperature.

(ii) The oxygen re-adsorbed at room temperature can as easily be desorbed when the sample is placed under high vacuum for XPS measurements, confirming previous results obtained by following the selective adsorption of CO by Fe^{2+} cations [7].

(iii) The characterization of the sample after catalytic reaction suggests that the reducible iron species have been reduced in the catalytic conditions most probably in the course of the oxidative dehydrogenation of n-butane to butene proposed to be at the basis of the promoting effect of iron. The deactivation could partially be to the irreversible reduction of iron leading to the loss of the promoting effect.

(iv) The reoxidation of the used catalysts upon exposure to air does not restore the catalysts in its original state since the re-adsorbed oxygen can be easily removed under vacuum, which agrees with previous results showing that the promoting effect is lost and that its regeneration needs an oxidation treatment at high temperature [7].

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