

# Characterization of Iron Promoter in Tungstated Zirconia Catalysts by Mössbauer Spectroscopy at Very Low Temperatures

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*Received: February 7, 2006; In Final Form: June 21, 2006*

A tungstated zirconia (WZ) catalyst with iron promoter used for the conversion of *n*-pentane into isopentane has been characterized by Mössbauer spectroscopy. The Mössbauer spectra have been recorded in zero magnetic field in the temperature range 0.05–295 K and with a magnetic field up to 7 T between 4.2 and 50 K. Both the recording of Mössbauer spectra with an applied magnetic field and at extremely low temperature allowed for the demonstration that iron is present in the catalysts as (i) hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) particles a few 10 nm in size, (ii) very small oligomeric Fe<sup>III</sup> species, probably in solid solution in zirconia, and (iii) Fe<sup>III</sup> oxide clusters showing magnetic ordering, probably embedded in the first surface layer and thus forming “rafts”. These latter clusters form two ensembles with quite different sizes: one with diameters of about 3 nm, the other with diameters larger than 30 nm. These results are in agreement with those recently obtained by X-ray absorption spectroscopy and electron paramagnetic resonance.

## 1. Introduction

While tungstated zirconia as solid acid catalyst has been discovered almost two decades ago, it has not been given much attention because of its lower activity and higher temperature of utilization compared to sulfated zirconia. Recently tungstated zirconia catalysts found renewed interest because of their high thermal stability and regenerability.<sup>1–4</sup> Furthermore, doping tungstated zirconia with noble metals such as Pt or Pd was shown to promote the activity of the catalysts in the presence of a hydrogen containing feed, rendering them possible candidates for practical alkane isomerization catalysts. These noble metals form at the surface of zirconia large clusters of 100 nm diameter whose role is to provide atomic hydrogen to contribute to the reduction of the dispersed tungsten cations involved in the catalytic conversion of the hydrocarbon.<sup>5–7</sup>

Addition of iron to the platinum-containing catalysts was shown to be beneficial for the catalytic performance.<sup>8,9</sup> The exact nature and function of the iron promoters remain controversial, but it is generally accepted that their action is related to their redox properties affecting the dehydrogenation activity of the catalysts, like in the case of iron promoted sulfated zirconia catalysts.<sup>10,11</sup>

All the studies dealing with the characterization of the iron species present at the surface of tungstated or sulfated zirconia showed that iron was present as Fe<sup>III</sup>. Several studies proposed that iron ions were present in dispersed small clusters or rafts at the surface of zirconia.<sup>12,13</sup> A broad distribution of coordination environments in such a case was reported by Scheithauer et al.<sup>13</sup> In contrast, other studies proposed that iron formed a

solid solution with zirconia exhibiting a distorted octahedral environment.<sup>14</sup> Finally, it was also proposed that the iron 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.<sup>10,11</sup> In the surface solid solution, iron cations were shown on the basis of XAS, EPR, and Mössbauer data to be present in a distorted octahedral environment.<sup>10</sup> The amount of the iron present in the form of small iron oxide particles seems to vary depending upon the preparation conditions and the heat treatment of the catalyst.

Among the techniques used to characterize the solids, Mössbauer spectroscopy appears to be very powerful in determining the Fe oxidation state and the nature of the Fe containing phases or species, both in a qualitative and quantitative manner. Mössbauer spectroscopy on <sup>57</sup>Fe has been extensively used in the study of Fe in catalysts and surfaces and in zero magnetic field as well as in the presence of a field.<sup>15</sup> We therefore undertook the study by this technique of an iron promoted tungstated zirconia sample with and without Pt to obtain a more detailed knowledge of the oxidation state, coordination number, and location of iron cations on both catalysts. To thoroughly characterize the Fe species present in the catalyst, we have recorded spectra in zero field down to very low temperature (below 1 K) and with an applied magnetic field (above 4.2 K). Very low-temperature spectra in the 0.05 K range had never been recorded before in catalyst studies, and they have proved very useful for a better understanding of the problem and by showing that, surprisingly, the spectra can still change below 4.2 K in these systems.

## 2. Experimental Section

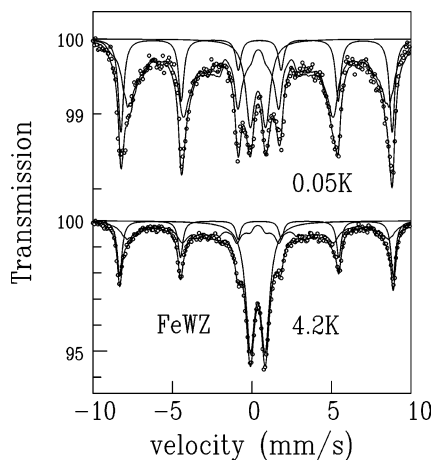
**2.1. Synthesis of the Catalysts.** The preparation of the catalyst has been described elsewhere.<sup>16,17</sup> The tungstated zirconia was prepared by impregnation of amorphous Zr(OH)<sub>4</sub>

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**Figure 1.**  $^{57}\text{Fe}$  Mössbauer absorption spectra at 0.05 and 4.2 K in FeWZ in zero magnetic field, showing the three spectral components. The broad magnetic sextet is fitted using a histogram of hyperfine fields.

(MEL chemicals, XZO 880/01) with an aqueous solution of ammonium metatungstate  $[(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}]$ , Aldrich] and iron nitrate  $[\text{Fe}(\text{NO}_3)_3]$ . The suspension rapidly formed was refluxed overnight at 393 K under vigorous stirring. The obtained solid was separated by filtration and dried at 373 K for 12 h prior to calcination at 923 K for 3 h in static air. The amount of tungsten and iron precursors was chosen to obtain a catalyst with a nominal content of 17.7 wt %  $\text{WO}_3$  and 1.0 wt %  $\text{Fe}_2\text{O}_3$ . The tungsten loading was close to, but below, the theoretical monolayer capacity of approximately 19 wt %  $\text{WO}_3$  based on the molecular area of a  $\text{WO}_3$  unit.<sup>17</sup> It was shown earlier<sup>16,17</sup> by XRD and Raman spectroscopy that the  $\text{ZrO}_2$  phase was exclusively tetragonal for this catalyst. Natural iron contains only 2.2% of the  $^{57}\text{Fe}$  isotope active for nuclear resonant (Mössbauer) absorption; the 1 wt % iron loading of the catalyst was therefore considered too low to record Mössbauer spectra in the best conditions. Therefore, a  $^{57}\text{Fe}$  enriched precursor (98 %  $^{57}\text{Fe}$ ) was used for the preparation of the tungstated catalyst (FeWZ). A platinum promoted catalyst (Pt-FeWZ) was prepared by incipient wetness impregnation of the calcined FeWZ catalyst. An aqueous solution of  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  was used to yield a nominal Pt loading of 1 wt %. The drying and calcination protocol used for the FeWZ catalyst and described above was applied to the resulting solid.

**2.2.  $^{57}\text{Fe}$  Mössbauer Spectroscopy.** The Mössbauer spectra of the powder samples were recorded using a 2 GBq  $^{57}\text{Co}/\text{Rh}$  source and a conventional constant acceleration spectrometer, operated in triangular mode. The spectra below 4.2 K were obtained with a  $^3\text{He}$ – $^4\text{He}$  dilution refrigerator. The in-field spectra were obtained in a superconducting coil with the magnetic field ( $H$ ) parallel to the  $\gamma$ -ray direction of propagation. The isomer shifts ( $\delta$ ) are given with respect to  $\alpha$ -Fe. The relative areas ( $A$ ) of the observed spectral components have been used to quantitatively evaluate the relative amounts of the iron species present in the catalysts. This has been done by assuming equal recoil-free fractions for Fe in all the phases or species.

### 3. Results and Discussion

Spectra of the as-prepared FeWZ and Pt-FeWZ catalysts were first recorded at various temperatures. No significant differences were observed between the two types of catalysts, indicating that Pt promotion has no effect on the nature of the Fe species. The zero field spectra at 0.05 and 4.2 K in the FeWZ catalyst are shown in Figure 1. Three components can be distinguished: a magnetic hyperfine sextet with narrow lines and a

hyperfine field of 53.5 T (relative intensity 20% at both temperatures), a quadrupolar hyperfine doublet with quadrupole separation  $\Delta = 0.93(1)$  mm/s (relative intensity 15 and 40%, respectively, at 0.05 and 4.2 K), and a magnetic hyperfine sextet with broad lines, accounted for by a distribution of hyperfine fields (relative intensity 65 and 40%, respectively, at 0.05 and 4.2 K). The isomer shifts of these three components are similar:  $\delta = 0.26(1)$  mm/s, which allows assigning these spectra to  $\text{Fe}^{\text{III}}$ .

The first component with a hyperfine field of 53.5 T at 4.2 K can be assigned without ambiguity to antiferromagnetic hematite  $\alpha$ - $\text{Fe}_2\text{O}_3$ . This was confirmed by a spectrum with a magnetic field of 7 T at 4.2 K (not shown), where this component shows the typical response of hematite above the spin-flop field (6.8 T), with the hyperfine field oriented close to perpendicular to the applied field. The hematite spectrum is unchanged at room temperature (except for the small thermal decrease of the hyperfine field). An interesting feature emerges from the hematite spectra: the effective quadrupole splitting is  $\Delta \cong -0.2$  mm/s in the whole temperature range, i.e., there is no Morin transition where the  $\text{Fe}^{\text{III}}$  magnetic moments reorient from parallel to perpendicular to the  $\langle 111 \rangle$  axes as temperature increases. This is characteristic for  $\alpha$ - $\text{Fe}_2\text{O}_3$  particles with a diameter smaller than a few tens of nanometers.<sup>18</sup>

Furthermore, small magnetic particles with volume  $V$  show superparamagnetic fluctuations, where the magnetization or Néel vector (for antiferromagnets) fluctuates across the anisotropy barrier  $U = KV$  with a frequency<sup>19</sup>

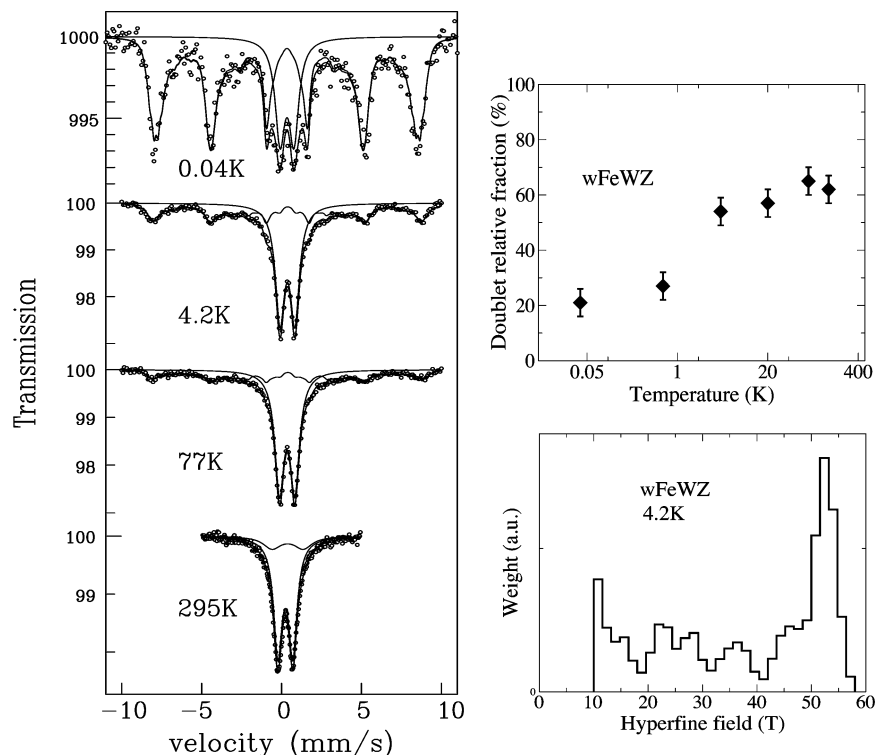
$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp\left(-\frac{U}{k_B T}\right) \quad (1)$$

where  $K$  is the anisotropy energy density characteristic of the material, and  $\tau_0 \cong 10^{-9}$ – $10^{-11}$  s is a microscopic time. The hyperfine Larmor period associated with  $^{57}\text{Fe}$  Mössbauer spectroscopy is  $\tau_L \cong 10^{-8}$  s, and, therefore, at a given temperature  $T$ , the magnetization of small magnetic particles with volume  $V < V_b$ , such that

$$V_b = \frac{k_B T}{K} \ln\left(\frac{\tau_L}{\tau_0}\right) \quad (2)$$

undergoes “fast” fluctuations ( $\tau < \tau_L$ ) and their Mössbauer spectrum is a quadrupolar doublet; conversely, big particles with  $V > V_b$  show a magnetic sextet. According to Kündig et al.,<sup>18</sup> the anisotropy density in hematite at elevated temperature is  $K = 4 \times 10^4$  ergs/cm<sup>3</sup>. Hence, the hematite particles in the FeWZ catalyst, which present a magnetic hyperfine sextet at 295 K, are bigger than about 30 nm. So it can be inferred that they have an approximate mean size around 50 nm.

To obtain less complex spectra, the FeWZ catalyst was washed with an HCl solution (0.1 M), and the Mössbauer spectra of the washed catalyst (wFeWZ) were then recorded. In the following, we will only discuss the spectra in the washed sample. The zero field spectra at selected temperatures are shown in Figure 2 left. By comparing the 4.2 K spectra in FeWZ and wFeWZ, it is clear that hematite has disappeared upon washing with HCl. This can be ascribed to dissolution of  $\alpha$ - $\text{Fe}_2\text{O}_3$  and subsequent rinsing, provided the hematite particles were located at the surface of the zirconia. The two spectral components in wFeWZ, a quadrupolar doublet and a magnetic sextet, are identical with those in the as-prepared catalyst. They are resolved up to at least 150 K; at room temperature, the quadrupolar doublet alone is visible, although a good fit to the spectrum needs an extra broad doublet to be introduced (see Figure 2



**Figure 2.**  $^{57}\text{Fe}$  Mössbauer absorption spectra of the wFeWZ catalyst: Left:  $^{57}\text{Fe}$  Mössbauer absorption spectra in zero magnetic field at selected temperatures; the spectra are fitted with two components: a quadrupolar doublet and a hyperfine field distribution (histogram), except for the 295 K spectrum which is fitted with two doublets. Right top: thermal variation of the relative fraction of the quadrupolar doublet, in a semilogarithmic plot. Right bottom: hyperfine field histogram accounting for the magnetic sextet at 4.2 K.

left), which could represent the central part of a low intensity residual magnetic subspectrum. These spectra are reminiscent of those observed in assemblies of superparamagnetic iron oxide nanoparticles with a large size distribution.<sup>20</sup> However, a peculiar feature of these spectra is the persistence of a quadrupolar doublet down to the lowest temperature (0.05 K). In ensembles of nanoparticles, to our knowledge, this is not observed, as the fluctuations of the magnetization are “frozen” below 4.2 K with respect to the Mössbauer Larmor period  $\tau_L$ .

The doublet relative weight at 0.05 K is about 20%; it increases then rapidly to about 60% at 4.2 K and shows no significant variation on further heating to 150 K (Figure 2 right top). Its quadrupole splitting (0.9 mm/s) is close to that of the quadrupolar doublet observed in iron promoted sulfated zirconia catalysts,<sup>11</sup> which also persists down to 1.45 K with a relative weight of about 35%, and of the doublet present in a sample of  $^{57}\text{Fe}$  (0.5% at.) in  $\text{ZrO}_2$  with the same relative weight (35%) at low temperature.<sup>21</sup>

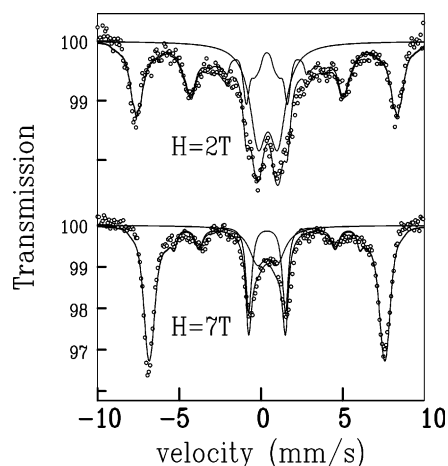
As this value of the quadrupole splitting is characteristic for  $\text{Fe}^{\text{III}}$  ions in octahedral coordination, we think this doublet represents “isolated” Fe ions in solid solution in  $\text{ZrO}_2$  and located in the first surface layer of the catalyst, following the analysis of ref 10. The question then arises why this “isolated”  $\text{Fe}^{\text{III}}$  magnetic species shows a quadrupolar spectrum, implying fast magnetic relaxation even at 0.62 K. An explanation could be that these Fe ions are actually arranged in small oligomers (dimers, trimers ...), with fast exchange (or dipole–dipole) driven spin fluctuations. These oligomers must have a sufficiently small size, or present a loose connectivity, so that exchange via Fe–O–Fe paths does not lead to magnetic ordering.

The other spectral component in wFeWZ is a magnetic hyperfine sextet, with a distribution of hyperfine fields, accounted for in the fits by a histogram (Figure 2, right bottom).

As temperature increases from 0.05 K up, one observes, together with a decrease of its relative weight, a broadening of the distribution of hyperfine fields, the maximum remaining however near 51.5 T, a value currently observed in ferric oxides at low temperature.<sup>22</sup> As the sextet is still present at 150 K, and probably at 295 K, this  $\text{Fe}^{\text{III}}$  species corresponds to exchange coupled  $\text{Fe}^{\text{III}}$  ions with an ordering temperature higher than 200–300 K. One possibility is that it pertains to small ferric oxide particles, either ferrimagnetic like maghemite  $\gamma\text{-Fe}_2\text{O}_3$  or antiferromagnetic like ferric oxyhydroxides. The other possibility is that it corresponds to rather large clusters of  $\text{Fe}^{\text{III}}$  ions more or less incorporated into the surface layer of  $\text{ZrO}_2$ . In this latter case, the hyperfine field value should be typical of Fe–O–Fe exchange, like in oxides, as indeed observed. Superparamagnetic-like effects could also be present in this case, as the magnetization of the very small clusters could progressively “freeze” below 4.2 K, leading to the observed increase of the relative fraction of the magnetic sextet below this temperature. In principle, application of a magnetic field  $H$  could help distinguishing between these two assumptions, as the response of ferrimagnetic  $\gamma\text{-Fe}_2\text{O}_3$  to a field is well-known: the two magnetic sublattices reorient parallel and antiparallel to the field, yielding two magnetic sextets with hyperfine fields differing by  $2H$ .<sup>23</sup>

The spectra at 4.2 K with 2 and 7 T are represented in Figure 3. They consist of two components: a magnetic sextet (62% relative weight with 2 T, 80% with 7 T) and a broad doubletlike subspectrum. A salient feature of the 7 T spectrum is that the intermediate lines of the sextet have almost zero intensity. For in-field spectra, the ratio  $r$  of the intensities of the intermediate to external lines of the sextet depends on the relative orientation of the hyperfine field(s) and the  $\gamma$ -ray direction of propagation, i.e., the applied magnetic field direction in our geometry,





**Figure 3.**  $^{57}\text{Fe}$  Mössbauer absorption spectra of the wFeWZ catalyst at 4.2 K, with a magnetic field of 2 and 7 T applied parallel to the  $\gamma$ -ray direction of propagation. The solid lines are phenomenological fits as explained in the text.

according to the relation

$$r = 4\sin 2\beta/3(1+\cos 2\beta) \quad (3)$$

where  $\beta$  is a mean angle between the hyperfine field and the external field. For random orientation,  $r = 2/3$ , and when all the hyperfine fields in the sample are parallel to the applied field ( $\beta=0$ ),  $r = 0$ . Furthermore, for  $\text{Fe}^{\text{III}}$ , the magnetic moment is antiparallel to the hyperfine field. In the wFeWZ sample, the fits of the magnetic sextet with a distribution of hyperfine fields yield  $r = 0.33$  with 2 T and  $r = 0.11$  with 7 T. Therefore, as the applied magnetic field increases, the hyperfine fields of the  $\text{Fe}^{\text{III}}$  species reorient progressively toward the field, and the amount of oriented  $\text{Fe}^{\text{III}}$  moments increases. With 7 T, the hyperfine field distribution is very narrow and peaks at 45 T. This means that 80% of the  $\text{Fe}^{\text{III}}$  species has its hyperfine field ( $\approx 52$  T) practically aligned, but antiparallel, to the applied field.

This type of response to the field is not ferrimagnetic nor antiferromagnetic, but rather ferromagnetic, which is rather surprising. This allows us to discard the assumption of ferromagnetic or antiferromagnetic nanoparticles as the origin of the hyperfine magnetic sextet in wFeWZ. Therefore, the picture of  $\text{Fe}^{\text{III}}$  clusters or “rafts”, in solid solution in the first surface layer of  $\text{ZrO}_2$ , seems the most likely. At 4.2 K with 7 T, 80% of the  $\text{Fe}^{\text{III}}$  ions belonging to the largest “rafts” align their magnetization with the field, while the remaining 20% belonging to the smaller oligomers keep fluctuating. The ferromagnetic nature of magnetic ordering in these “rafts” remains to be explained, perhaps by considering the possible exchange paths at play in such surface bidimensional assemblies. Let us notice that the sign of the exchange coupling in oxides of transition elements has been empirically investigated,<sup>24</sup> and it was shown that direct exchange of ferromagnetic nature can play a role, especially in  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$  oxides. Although it was concluded that direct ferromagnetic exchange is slightly, if at all, effective in  $\text{Fe}^{3+}$  oxides, it cannot be excluded that it can dominate over AF superexchange in special geometries such as those encountered in solid solution Fe “rafts” in zirconia catalysts.

We find therefore that, as concerns Fe, the composition of the washed tungstated zirconia catalyst can be separated into three parts: (i) about 30% of the  $\text{Fe}^{\text{III}}$  ions pertain to small oligomers and yield a paramagnetic doublet down to the lowest temperature (0.05 K); (ii) about 30% pertain to oligomers undergoing magnetic ordering, with a size somewhat larger, but small enough so that the fluctuation frequency of the magnetiza-

tion is faster than  $10^8 \text{ s}^{-1}$  at 4.2 K; an estimation using expression 2 yields an approximate diameter of 3 nm for these clusters, i.e., about 50–100  $\text{Fe}^{\text{III}}$  ions if the Fe–Fe distance is 0.35 nm; (iii) the remaining part (40%) consists of much larger “rafts”, with a diameter larger than 30 nm, as the corresponding spectrum is a magnetic sextet at 150 K, and probably at room temperature.

#### 4. Conclusion

We have characterized the iron species formed at or near the surface of a tungstated zirconia catalyst, unpromoted and promoted by Pt, by  $^{57}\text{Fe}$  Mössbauer spectroscopy. It has been observed that the Pt promotion has no effect on neither the nature nor the relative amount of the iron species formed.

We have been able to determine the presence of various types of iron species, which correspond, on one hand, to hematite particles with sizes in the 50 nm range and, on the other hand, to Fe at substitutional sites at the surface of zirconia; this latter species consists of small  $\text{Fe}^{\text{III}}$  oligomers, remaining paramagnetic down to very low temperature, and of larger clusters, undergoing a ferromagnetic type of ordering. The use of a nonstandardized  $^{57}\text{Fe}$  nitrate iron precursor in the present work may account for the less effective iron dispersion obtained here.

The different  $\text{Fe}^{\text{III}}$  species could be distinguished and characterized by recording spectra down to very low temperature (0.05 K) and with an external magnetic field at 4.2 K. This study emphasizes the importance of recording Mössbauer spectra below liquid helium temperature in Fe promoted catalysts, allowing a more precise identification of the different oligomeric and particulate  $\text{Fe}^{\text{III}}$  species: in particular, the presence of very small oligomeric or particulate species leads to spectral changes between 0.05 and 4.2 K. We believe that these techniques will be more systematically applied to the study of catalysts in the future.

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