

# Evidence for the Formation of $W^{5+}$ Centers and OH Groups upon Hydrogen Reduction of Platinum-Promoted Tungstated Zirconia Catalysts

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The redox behavior of Pt-promoted tungstated zirconia catalysts which are active in the isomerization of light alkanes was investigated. For this purpose, the catalysts were reduced in hydrogen and characterized by EPR, FTIR, and diffuse reflectance UV–Vis. EPR shows evidence of formation of  $W^{5+}$  at reduction temperatures above 473 K for the unpromoted catalyst and room temperature when platinum is present, indicating the increased reducibility of the catalyst by the latter. Diffuse reflectance UV–Vis spectroscopy confirms the formation of  $W^{5+}$  on the unpromoted catalyst. FTIR spectroscopy carried out with  $D_2$  shows that hydroxyl groups are formed upon reduction of  $W^{6+}$ . Low-temperature CO adsorption on these hydroxyl groups reveals that the acid strength is lower than that of the hydroxyl groups present prior to reduction. The higher reducibility of the tungstate phase due to platinum is potentially responsible for the strong enhancement of the catalytic activity and selectivity observed when hydrogen is present in the feed during the isomerization of small alkanes.

## Introduction

The isomerization of straight-chain alkanes is a technologically important reaction for the production of new formulations of high-octane-number gasolines, in the absence of aromatics. Sulfated zirconia (SZ) catalysts<sup>1,2</sup> were proposed as solid catalysts to replace the environmentally unfriendly liquid acids presently used for this reaction. Although the SZ catalysts have proved to be very active initially, they suffer from fast deactivation owing to reduction of sulfate groups, sulfur loss, and coke deposition. A solution to this problem has not yet been reported in the open literature. In recent years, another type of zirconia-based isomerization catalyst, namely tungstated zirconia (WZ), has attracted much interest.<sup>3–5</sup> Although this type of catalyst is less active and requires higher reaction temperatures, it has a higher stability under reductive conditions. Furthermore, platinum- and transition-metal-promoted tungstated zirconia has been shown<sup>6</sup> to develop very high selectivity, and deactivation can be completely suppressed.

Extensive work is reported in the literature on the synthesis and structural characterization of these materials.<sup>3,7</sup> Active catalysts are usually synthesized by impregnation of amorphous zirconium hydroxide with water-soluble tungsten precursors<sup>3,4</sup> or by coprecipitation of  $ZrOCl_2$  in aqueous solution containing the tungsten precursors,<sup>8</sup> followed by drying and calcination. Crystallization of the amorphous zirconia support occurs under these conditions. The tetragonal high-temperature modification of zirconia is typically stabilized in the presence of X-ray amorphous polyoxo-tungstates (most likely three-dimensional) located on the surface of the zirconia crystallites.<sup>3,7</sup> The tungsten atoms in these surface tungstates are located in a distorted

octahedral environment<sup>9,10</sup> and form W–O–W bridges,<sup>3,7</sup> the polyoxo species being grafted to the support through W–O–Zr bridges.<sup>3</sup>

The presence of hydrogen in the reaction feed generally improves both activity and selectivity. This improvement is observed for the unpromoted catalyst,<sup>11</sup> but is ever more pronounced with Pt-containing catalysts. The role played by hydrogen during the isomerization reaction is a key issue, which was addressed in numerous publications.<sup>4,9,10,12–15</sup> The improvement of catalytic properties was related to a slight reduction of the tungsten phase, with formation of  $W^{5+}$  and hydroxyl groups playing an important role in the isomerization mechanism.<sup>4,9,10,12–15</sup>

Recently, we succeeded in demonstrating for the first time the in-situ partial reduction of  $W^{6+}$  by the reactants (which was inferred in the literature) by spectroscopic methods.<sup>16</sup> The formation of  $W^{5+}$  in the presence of hydrogen and/or hydrocarbons at the reaction temperature was observed by EPR confirming the “slight reduction” of the tungsten phase. Furthermore, we could monitor the appearance of new OH/OD groups appearing during the reduction with deuterium. The acid strength of these OH groups was characterized by IR spectroscopy of CO adsorbed at low temperature.<sup>16</sup>

In the present work, we report on investigations of the platinum-promoted catalyst and compare the results obtained for the unpromoted and the platinum-promoted catalysts. FTIR and EPR techniques are applied for the investigation of the reduction properties of the platinum-promoted catalyst. As a technique complementary to EPR, we also report optical spectra of catalysts during the reduction process.

## Experimental Section

**(a) Catalyst Preparation.** The unpromoted samples were prepared by impregnation of amorphous  $Zr(OH)_4$  (MEL Chemi-

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cals, XZO880/01) 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), as reported earlier.<sup>3</sup> The resulting suspension was refluxed overnight at 393 K and dried in an oven at 353 K. The samples were then calcined at 923 K in static air for 3 h.

The concentration of tungsten in the precursor solution was chosen to give a coverage slightly below the theoretical monolayer capacity (ca. 19 wt %  $\text{WO}_3$  based on the molecular area of a  $\text{WO}_3$  unit).<sup>3</sup> For the EPR and diffuse reflectance UV–Vis experiments, a sample with a loading of 17.7 wt %  $\text{WO}_3$  was used, whereas FTIR experiments were performed with a sample containing 19 wt %  $\text{WO}_3$ . The unpromoted tungstated zirconia samples are denoted 17WZ and 19WZ, respectively.

For the promotion with platinum, the WZ samples were impregnated in a second step with a 0.6 M aqueous solution of  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  using the incipient wetness method. The concentration of Pt and the amount of the solution were chosen such that the amount of platinum in the finished catalysts was 1 wt % Pt. The freshly impregnated catalysts were dried at 383 K for 12 h and calcined in air at 873 K for 3 h. The catalysts are denoted Pt17WZ and Pt19WZ, respectively.

**(b) EPR Spectroscopy.** Measurements were carried out with a Bruker ESP 300E spectrometer. The spectra were recorded in X-band at room temperature (298 K) and at low temperature (80 K) with a microwave power of 10 mW. The  $g$ -value determination was done with the WINEPR Simfonia Program from Bruker. Prior to each experiment, the sample was pretreated in situ in a flow of  $\text{O}_2$  at 673 K for 1 h. The reduction was carried out in situ in a flow of  $\text{H}_2$  at 473, 573, or 673 K for 1 h. A fresh sample was used for each reduction experiment.

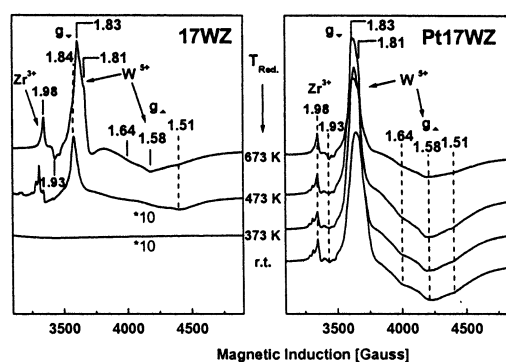
**(c) FTIR Spectroscopy.** IR spectra were recorded with a Bruker IFS-66 FTIR spectrometer equipped with a liquid- $\text{N}_2$ -cooled MCT detector. Self-supporting wafers (ca. 15–20 mg/ $\text{cm}^2$ ) were pretreated in situ in a flow of  $\text{O}_2$  (30 mL/min) at 673 K for 12 h in a purpose-made IR transmission cell. Spectra were recorded by averaging 256 scans at a spectral resolution of 1  $\text{cm}^{-1}$ . Low-temperature measurements were carried out in situ after reduction of the sample in 4 kPa  $\text{D}_2$  for 20 min at 673 K followed by evacuation at 673 K for 5 min. This reduction step was repeated several times. CO was adsorbed on the reduced samples at low temperature (85 K) and at increasing equilibrium pressures in the range  $0 \leq p \leq 25$  kPa.

**(d) Diffuse Reflectance UV Spectroscopy.** For diffuse reflectance UV–Vis measurements, a Lambda 15 UV–Vis spectrometer (Perkin-Elmer) was used in the diffuse reflectance mode. The spectral range measured was between 200 and 800 nm with a scan speed of 60 nm/min and a spectral resolution of 2 nm.

For the diffuse reflectance UV–Vis experiments, a U-shaped reactor connected to a quartz cell was used. Prior to each experiment, the catalyst was treated at 673 K in a flow of oxygen (30 mL/min) and then cooled to room temperature. This oxidized sample was transferred in the closed cell to the spectrometer and measured. After the oxidation step, the cell was purged with argon (30 mL/min) for 30 min and then heated sequentially in a flow of hydrogen (30 mL/min) to the reduction temperature and kept at this temperature for 30 min. After each reduction step the cell was closed, transferred to the spectrometer, and spectra were recorded.

## Results

**(a) Formation of  $\text{W}^{5+}$ .** The calcined 17WZ and Pt17WZ samples exhibit an EPR signal at  $g = 4.24$  (not shown), assigned



**Figure 1.** EPR spectra (X-band) of the 17WZ and Pt17WZ samples after reduction at different temperatures (normalized gain, spectra recorded at 80 K).

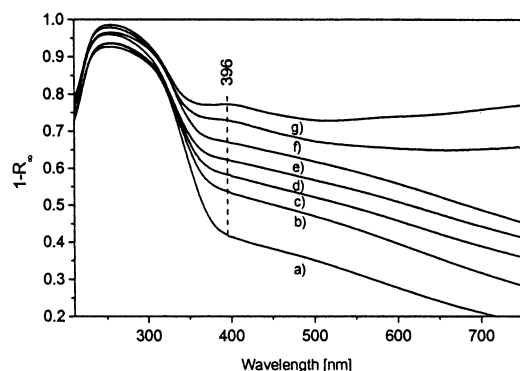
to isolated  $\text{Fe}^{3+}$  impurities in octahedral or tetrahedral symmetry with strong rhombic distortion.<sup>17,18</sup>

Figure 1 shows the EPR spectra of the 17WZ and Pt17WZ samples reduced at various temperatures. The spectra of the unpromoted sample were discussed earlier.<sup>16</sup> The conclusions are briefly summarized below for comparison with the spectra of the Pt-promoted catalyst.

On 17WZ as well as on Pt17WZ, a complex signal is observed at  $g \sim g_e$ . This feature is temperature-dependent, being barely observed at 298 K but clearly visible at 80 K. On both samples the signal disappears at reduction temperatures higher than 473 K. This signal, assigned to nitrogen-containing paramagnetic impurities originates from ammonium ions introduced during the synthesis of the samples or being present as impurities due to the technical synthesis of zirconium hydroxide.<sup>16</sup>

The signal observed at  $g_{\perp} = 1.98$  and  $g_{\parallel} = 1.93$  on both samples is assigned to  $\text{Zr}^{3+}$  ions in accordance with the literature.<sup>19,20</sup> Because these ions are formed upon thermal reduction of the sample, we infer that the  $\text{Zr}^{3+}$  ions are likely located at the catalyst surface. On 17WZ, the  $\text{Zr}^{3+}$  signal can only be seen at reduction temperatures above 473 K. The signal gains intensity with increasing reduction temperature. In the case of Pt17WZ, the signal is already clearly visible after reduction at room temperature and does not increase in intensity with increasing reduction temperature. This indicates that the reduction of  $\text{Zr}^{4+}$  to  $\text{Zr}^{3+}$  by hydrogen is effectively catalyzed by platinum.

The third and most intense signal at relatively high field was identified earlier as  $\text{W}^{5+}$ .<sup>16</sup> It is a composite signal and the several components have previously been identified on 17WZ.<sup>16</sup> The weak anisotropic signal at  $g_{\perp} = 1.84$  and  $g_{\parallel} = 1.51$  visible on 17WZ reduced at 473 K (Figure 1) was attributed to coordinatively unsaturated  $\text{W}^{5+}$  ions on the catalyst surface.<sup>16</sup> The signal is observed for higher reduction temperatures together with several other components at  $g_{\perp} = 1.83$ ,  $g_{\parallel} = 1.58$  (most intense) and  $g_{\perp} = 1.81$ ,  $g_{\parallel} = 1.64$  which successively appear and grow with increasing reduction temperature. It is suggested that these components represent  $\text{W}^{5+}$  centers located deeper in the tungstate layer consisting of three-dimensional polyoxoclusters. However, recent EPR experiments showed that the signal at  $g_{\perp} = 1.84$  and  $g_{\parallel} = 1.51$  remains nearly unaffected by  $\text{O}_2$  in contrast to the more intense components at  $g_{\perp} = 1.83$ ,  $g_{\parallel} = 1.58$  and  $g_{\perp} = 1.81$ ,  $g_{\parallel} = 1.64$  which do react on exposure to  $\text{O}_2$ . The earlier conclusion that the first signal was related to cus centers in the surface must therefore be modified. Undoubtedly, the three EPR signals are characteristic for  $\text{W}^{5+}$  centers in different environments. In the case of Pt17WZ, the same-components representative of  $\text{W}^{5+}$  located deeper in the bulk can be identified ( $g_{\perp} = 1.83$ ,  $g_{\parallel} = 1.58$  and  $g_{\perp} = 1.81$ ,  $g_{\parallel} =$



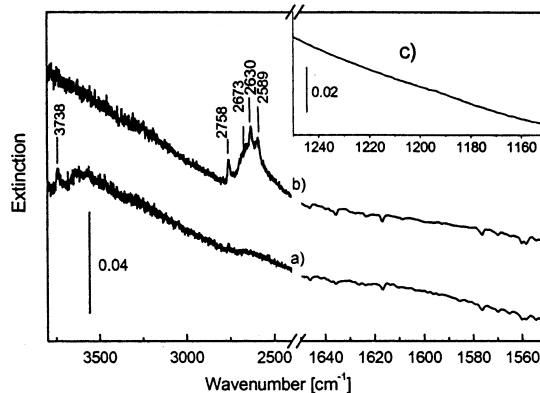
**Figure 2.** Diffuse reflectance UV-Vis spectra of the 17WZ sample in the oxidized state (a) and after reduction with hydrogen at 373 (b), 473 (c), 523 (d), 573 (e), 623 (f), and 673 K (g).

1.64). Whereas the  $g_{\perp} = 1.84$  component is hidden by more intense  $g_{\perp}$  components of bulk W<sup>5+</sup> centers appearing at higher reduction temperatures, its associated  $g_{\parallel} = 1.51$  component can still be observed after reduction at 673 K in hydrogen. All components appear even when the reduction of Pt17WZ is carried out at room temperature. The overall W<sup>5+</sup> signal intensity observed in this case is comparable to that characterizing 17WZ after reduction at 673 K. With increasing reduction temperature, only a slight change in the relative intensities of the components occurs.

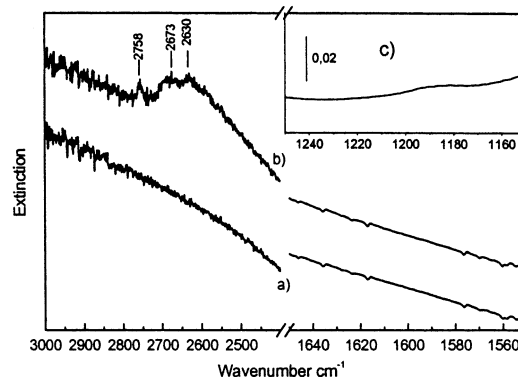
The formation of W<sup>5+</sup> centers can also be followed by diffuse reflectance UV-Vis spectroscopy, as done earlier by Barton et al.<sup>10</sup> Figure 2 shows the spectra of 17WZ in its oxidized state and after reduction at different temperatures. Reduction generally leads to an increased absorption at wavelengths longer than that corresponding to the band gap of zirconia which is located at ca. 350 nm. Even at the lowest reduction temperature of 373 K, an enhanced absorption can be observed. At reduction temperatures >573 K, the absorption increase becomes even more pronounced at wavelengths above 500 nm. Furthermore, a weak absorption maximum at 396 nm develops which is attributed to d-d transitions of W<sup>5+</sup> centers in accordance with Barton et al.<sup>10</sup> Analogous to tungsten bronzes of the H<sub>x</sub>WO<sub>3</sub> type, the reduction was suggested to lead to the insertion of electrons into the LUMO band of overlapping d-orbitals, thus allowing d-d transitions to be observed in the visible region of the spectrum.<sup>10</sup>

**(b) Formation of OH Groups.** It has been suggested<sup>4,9,12-15</sup> that the reduction of tungstated zirconia with H<sub>2</sub> at elevated temperatures leads to the formation of new OH groups associated with W<sup>5+</sup> centers, which together or separately may play a crucial role in the isomerization of light alkanes. Previously we observed the appearance of new OH groups on the 19WZ catalyst by low-temperature FTIR spectroscopy.<sup>16</sup>

Since the hydrated samples showed broad OH bands typical of adsorbed molecular water, the samples were dehydrated to allow observation of new OH groups possibly formed upon reduction. The spectra of the dehydrated 19WZ and Pt19WZ samples are shown in Figure 3 (spectrum a) and Figure 4 (spectrum a), respectively, after exposure to flowing O<sub>2</sub> (10 mL/min at 673 K for 12 h) followed by evacuation at a pressure of 10<sup>-3</sup> mbar at 673 K. The deformation mode of molecular water bound to the surface near 1610 cm<sup>-1</sup> was totally absent after this thermal treatment, confirming that the samples were fully dehydrated. In the dehydrated state the W=O stretching



**Figure 3.** IR spectra measured at 298 K of the 19WZ sample: (a) dehydrated; (b) and (c) reduced several times at 673 K with D<sub>2</sub> and evacuated at the same temperature.



**Figure 4.** IR spectra measured at 298 K of Pt19WZ sample: (a) dehydrated; (b) and (c) reduced several times at 673 K with D<sub>2</sub> and evacuated at the same temperature.

vibration shifted from lower wavenumbers in the hydrated state to 1022 cm<sup>-1</sup> on both samples (not shown).

Although the samples were completely dehydrated, the 19WZ sample still shows two weak bands in the OH stretching region (Figure 3, spectrum a), namely a sharp band at 3738 cm<sup>-1</sup>, characteristic of ZrOH groups, and a broad band around 3620 cm<sup>-1</sup> previously attributed to WOH groups.<sup>16</sup>

For the Pt19WZ sample, the transparency is very low in the OH stretching region and consequently, the signal-to-noise ratio is low. Therefore, bands of unperturbed OH groups remain undetected. However, for reduction carried out in D<sub>2</sub>, OD stretching bands are in fact observed below 2800 cm<sup>-1</sup> (Figures 3b and 4b), a region where the background transparency is more favorable than in the OH stretching region, leading to a better signal-to-noise ratio. Since water is formed during reduction, the OH/OD groups are perturbed by hydrogen-bonding interactions. Therefore, the bands of unperturbed OH/OD groups can be detected only if additional dehydration is performed after the reduction step.

Reduction in D<sub>2</sub> was carried out under static conditions and repeated several times at a pressure of 4 kPa. After each reduction step in D<sub>2</sub> at 673 K for 20 min, the sample was evacuated for 5 min at the same temperature. This procedure was repeated until molecular D<sub>2</sub>O was no longer formed during the D<sub>2</sub> treatment, as confirmed by the complete or near-complete absence of the D<sub>2</sub>O deformation band at 1194 cm<sup>-1</sup> (Figures 3c and 4c). The spectra of the two samples in the OD stretching region are shown in Figures 3b and 4b, respectively. Previously, we attributed the isotopically shifted OD bands of the unperturbed sample at 2758, 2673, 2630, and 2589 cm<sup>-1</sup> to the



corresponding OH bands at 3738, 3620, 3560, and 3505  $\text{cm}^{-1}$ .<sup>16</sup> The ratio of OH and OD stretching frequencies is 1.35, which is close to the theoretical isotope shift calculated according to the diatomic harmonic oscillator approximation (1.41). The latter two bands not observed in the spectrum of the sample prior to reduction have not been reported previously, and must be a consequence of the reduction. On the Pt19WZ sample, the signal-to-noise ratio is much lower and the OD stretching bands consist of a broad band between 2700 and 2550  $\text{cm}^{-1}$  together with a band at 2758  $\text{cm}^{-1}$ . However, the bands at 2673 and 2630  $\text{cm}^{-1}$  can also be identified in addition to the band at 2758  $\text{cm}^{-1}$  characteristic of ZrOH groups. The band at 2589  $\text{cm}^{-1}$  detected on the unpromoted sample might be present but is not resolved, presumably because of the low signal-to-noise ratio. The bands observed on the two samples are not related to adsorbed heavy water because the deformation band of molecular  $\text{D}_2\text{O}$  at 1194  $\text{cm}^{-1}$  remains undetectable. Hence, the observed OD stretching bands must be a result of the reduction of the  $\text{W}^{6+}$  tungsten oxide layer.

The acid strength of the newly formed OH/OD groups of the unpromoted sample was investigated by FTIR of adsorbed CO at low temperature.<sup>16</sup> CO interacts with the OD groups via OD...CO hydrogen bonds at 85 K and CO pressures between 0 and 0.25 KPa. The resulting OD stretching frequency shift, which is a measure of the hydrogen bond strength, could not be determined accurately. It was found to be  $\leq 100 \text{ cm}^{-1}$  for the unpromoted as well as for the promoted sample corresponding to a frequency shift in OH...CO hydrogen bonds of 140  $\text{cm}^{-1}$ . This shows that the acid strength of the OH/OD groups is less than that of the samples prior to reduction (frequency shift 160  $\text{cm}^{-1}$  for OH...CO hydrogen bonds)<sup>21</sup> and that on neither of the two samples strongly acidic Brønsted sites were detected. The results also show that the platinum function has no effect on the proton acidity.

## Discussion

**(a) Formation of  $\text{W}^{5+}$ .** As shown by EPR, the promotion by platinum has a significant effect on the reducibility of the surface tungstate phase of the catalyst by  $\text{H}_2$ . Whereas the  $\text{W}^{5+}$  signal of the tungsten phase appears only at reduction temperatures  $\geq 473 \text{ K}$  on the unpromoted 17WZ catalyst, it appears on the promoted Pt17WZ catalyst already at room temperature. In the latter case, the  $\text{W}^{5+}$  signal intensity is comparable to that obtained after reduction at 673 K of the 17WZ sample, and does not increase on reduction of Pt17WZ at 673 K. This indicates that the maximum possible reduction is already obtained at room temperature. These results show that the reduction of the tungsten phase of the platinum-free 17WZ catalyst is kinetically hindered although it would be thermodynamically possible.

The  $\text{W}^{5+}$  centers formed on the promoted catalyst are comparable to those observed on the unpromoted catalyst. The  $g$ -tensor components at  $g_{\perp} = 1.84$  and  $g_{\parallel} = 1.51$  characterizing surface  $\text{W}^{5+}$  centers that are most probably of direct importance to catalysis<sup>16</sup> could also be identified on Pt17WZ by the component at  $g_{\parallel} = 1.51$ . The intensity ratios of the various components differ only slightly, showing that the tungstate phase appears to be structurally similar in both catalysts.

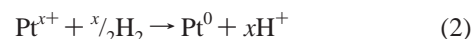
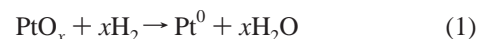
The  $\text{W}^{5+}$  species can also be detected by UV-vis spectroscopy, although it has a much lower sensitivity than EPR. The surface tungstate phase of 17WZ is already slightly reduced at 473 K with  $\text{W}^{5+}$  centers detected by EPR. In contrast, the band at 396 nm attributed to  $\text{W}^{5+}$  becomes visible only for reduction temperatures above 573 K. This can be explained by the distorted octahedral environment of the tungsten ions<sup>4,9</sup> that leads

to low d-d transition intensities due to the broadening of the bands as a result of the unresolved splittings of the original bands. The overall increase of the sample absorption at reduction temperatures as low as 373 K is probably due to physical effects such as changes in the refractive index influencing the reflectivity of the sample.

**(b) Formation of OH Groups.** The similarity of the tungsten phase of the unpromoted and promoted samples is confirmed by FTIR of the reduced Pt19WZ catalyst. Although the appearance of the OD band formed by reduction of Pt19WZ in  $\text{D}_2$  is slightly different from the one observed after the reduction of 19WZ, the band positions of the O-D stretching mode at 2673, 2630, and 2589  $\text{cm}^{-1}$  are exactly the same as those seen on the unpromoted catalyst. Low-temperature CO adsorption suggests that the acid strength of the newly formed OD/OH groups on both catalysts is lower than that of the OH groups present prior to reduction. This is in contradiction to the conclusion of Shimizu et al.<sup>14</sup> who reported an increase of the density of hydroxyl groups and of their acid strength by thermal reduction of tungstated zirconia with hydrogen. Our FTIR spectra suggest that the density of OD groups formed on the two catalysts is quite similar. This observation is in apparent contradiction to the more important reduction of the platinum-containing catalyst as also reported by others.<sup>4,9</sup> However, the high reduction temperature of 673 K used for the FTIR must be noted. As shown by EPR, the Pt17WZ and 17WZ catalysts are both reduced to approximately the same extent at a reduction temperature of 673 K. However, in the case of the unpromoted sample the extent of reduction as measured by the  $\text{W}^{5+}$  signal intensity decreased with decreasing reduction temperature, whereas the platinum-promoted sample is reduced to the same extent at reduction temperatures between room temperature and 673 K. Since we infer that the amount of  $\text{W}^{5+}$  formed corresponds to the amount of newly formed OH groups, we may conclude that the Pt19WZ exhibits a higher density of Brønsted acid sites formed at reduction temperatures below 673 K.

**(c) Effect of the Promotion with Platinum.** We infer that the reduction process on the unpromoted samples is fundamentally different from that on the platinum-promoted samples where the metallic function leads to a reduction through atomic hydrogen.

Low-temperature CO adsorption on the Pt19WZ catalyst shows that on the as synthesized catalyst the platinum is present in an oxidized form characterized by a CO stretching band at 2094  $\text{cm}^{-1}$ . This is confirmed by Arribas et al.<sup>22</sup> who found platinum in the oxidation state II+ and IV+ after the synthesis of a comparable  $\text{Pt}/\text{WO}_3/\text{ZrO}_2$  catalyst by XPS. Transmission electron micrographs (not presented) show that the platinum dispersion in our catalyst is high, perhaps even atomic, with only few, barely detectable platinum clusters being present.<sup>23</sup> In the presence of hydrogen, the platinum is reduced to small  $\text{Pt}^0$  clusters or perhaps even atomic  $\text{Pt}^0$  which is confirmed by CO pulse chemisorption<sup>23</sup> and XPS.<sup>22</sup> This can only lead to water or protons bound to oxygen:

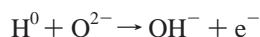


Since after the reduction with deuterium the spectrum in the OD region of Pt19WZ is very similar to that of 19WZ (Figures 3b and 4b) no OD/OH groups can be attributed to reaction 2. We therefore infer that only reaction 1 takes place.

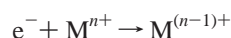
After reduction to  $\text{Pt}^0$ ,  $\text{H}_2$  is known to dissociatively chemisorb and H-atoms "spill over" to the tungstate phase. This "spill-

over" step has been extensively investigated during the reduction of Pt/WO<sub>3</sub> mixtures by H<sub>2</sub> which leads to tungsten bronzes such as H<sub>x</sub>WO<sub>3</sub> ( $x = 0.35$ ).<sup>24–26</sup> It was found that the reduction by "spill-over" hydrogen proceeds only at room temperature if water is present as cocatalyst on the metal surface.<sup>24</sup> Whereas the electron of the adsorbed atomic hydrogen is thought to be injected into the conduction band of the platinum, the proton should form H<sub>3</sub>O<sup>+</sup>.<sup>25</sup> This "ion–electron pair moves across to the surface of WO<sub>3</sub>".<sup>26</sup> We infer that this "spill-over" mechanism might also be operative on Pt17WZ leading to the observed room-temperature reduction. The necessary water might be formed via reaction 1.

The reduction of supported transition-metal catalysts (MoO<sub>3</sub>/SiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>) at low temperature (77 K) by atomic hydrogen (from a microwave discharge) has been investigated in the literature.<sup>27</sup> It was shown that the H-atoms react with O<sup>2–</sup> surface ions in a first step:



The electrons are then trapped by transition metal ions according to the process



In a similar way, the room-temperature reduction of Pt17WZ may lead to the formation of W<sup>5+</sup> ions characterized by the EPR signals at  $g_{\perp} = 1.84$ ,  $g_{\parallel} = 1.51$  and at  $g_{\perp} = 1.83$ ,  $g_{\parallel} = 1.58$  and  $g_{\perp} = 1.81$ ,  $g_{\parallel} = 1.64$ .

The thermal reduction of the 17WZ sample shows a similar trend but in a stepwise manner: the most stable W<sup>5+</sup> centers ( $g_{\perp} = 1.84$ ,  $g_{\parallel} = 1.51$ ) are produced at the lowest temperatures whereas less easily reducible W<sup>6+</sup> centers require higher temperatures for their reduction to W<sup>5+</sup>. We conclude that hydrogen for the thermal reduction is activated on the tungsten phase of 17WZ. This can principally occur through: (a) heterolytic dissociation leading to an initial formation of a hydride and a proton followed by the formation of two surface W<sup>5+</sup> ions and two OH groups; and (b) homolytic dissociation to atomic hydrogen leading to the direct formation of W<sup>5+</sup> ions and OH groups.

Reduction temperatures higher than 473 K may lead to the migration of electrons from surface W<sup>5+</sup> ions to W<sup>6+</sup> ions being located in the bulk of the polyoxo tungstate clusters.

## Conclusions

The tungsten phase of unpromoted and platinum-promoted catalysts can be reduced by hydrogen at temperatures below 673 K leading to W<sup>5+</sup> ions and OH groups. EPR shows that the unpromoted catalyst starts to be reduced at a temperature of 473 K leading to W<sup>5+</sup> ions ( $g_{\perp} = 1.84$ ,  $g_{\parallel} = 1.51$ ). With increasing reduction temperature, additional W<sup>5+</sup> ions ( $g_{\perp} = 1.83$ ,  $g_{\parallel} = 1.58$  and  $g_{\perp} = 1.81$ ,  $g_{\parallel} = 1.64$ ) are formed. The W<sup>5+</sup> ions can also be detected by a band at 396 nm in diffuse reflectance UV–vis spectra. On the platinum-promoted catalyst, reduction occurs even at room temperature leading to the formation of surface and bulk W<sup>5+</sup> ions. The degree of reduction in this case is comparable to that reached at a reduction temperature of 673 K on the unpromoted sample. Increasing the reduction temperature to 673 K does not enhance the degree of reduction. The results suggest that the reduction is thermodynamically feasible at room temperature and that it is catalyzed by the platinum promotion. This is inferred to occur via the dissociative adsorption of the dihydrogen on the platinum particles and a subsequent "spill over" of the hydrogen atoms to the tungsten phase.

OD stretching bands at 2673, 2630, and 2589 cm<sup>–1</sup> were identified for both the unpromoted and the promoted catalyst after reduction in D<sub>2</sub>. These bands correspond to those at 3620, 3560, and 3505 cm<sup>–1</sup> in the OH stretching region. Low-temperature CO adsorption leads to a frequency shift of these newly formed OD groups corresponding to  $\leq 100$  cm<sup>–1</sup> for the unpromoted as well as for the promoted sample. This corresponds to an OH stretching frequency shift of less than 140 cm<sup>–1</sup> which is less than the frequency shift observed prior to reduction (160 cm<sup>–1</sup>).<sup>21</sup> We therefore conclude that the OH groups formed during the interaction with hydrogen on the unpromoted as well as on the promoted sample are less acidic than those present prior to the reduction.

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