

# The Support as a Chemical Reagent in the Preparation of $\text{WO}_x/\gamma\text{-Al}_2\text{O}_3$ Catalysts: Formation and Deposition of Aluminotungstic Heteropolyanions

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**Abstract:** We show in this study that suspending alumina in a tungstate solution leads to the formation of Keggin-type aluminotungstic species in solution. This process occurs even at “nonaggressive” (near-neutral) pH. This can be rationalized as a ligand-promoted oxide dissolution effect which is well-known in geochemistry: the ability of tungstates to complex dissolved aluminum causes a shift of the alumina dissolution equilibrium toward the formation of dissolved aluminic species. Mixed Al–W–O species can easily be identified in solution by means of <sup>27</sup>Al liquid-state NMR. We also demonstrate the deposition of aluminotungstic species onto the support during the preparation of  $\text{WO}_x/\text{Al}_2\text{O}_3$  catalysts by equilibrium adsorption. This means that the tungstic species deposited on the support are not always isopolyanions, contrary to what is suggested in most of the previous studies on this type of system. This study as well as previous studies on  $\text{M}(\text{II})/\text{Al}_2\text{O}_3$  (d'Espinose de la Caillerie et al. *J. Am. Chem. Soc.* **1995**, *117*, 11471) and  $\text{MoO}_x/\text{Al}_2\text{O}_3$  catalysts (Carrier et al. *J. Am. Chem. Soc.* **1997**, *119*, 10137) imply that the alumina support can act as a real chemical reagent in the first steps of catalyst preparation.

## Introduction

In a recent study,<sup>1</sup> we challenged the idea that the alumina support used in  $\text{MoO}_x/\text{Al}_2\text{O}_3$  catalysts preparation is chemically inert; we demonstrated that this support can act as a true chemical reagent (by releasing aluminum ions into the solution) from the very first steps of the synthesis that occur at the oxide/water interface. This behavior can be understood by considering concepts coming from the field of geochemistry where it is generally accepted that oxide solubility can be promoted by the presence of ligands in solution.

The term of “promotion” covers two different phenomena. One can encounter a *kinetic* promotion if the grafting of ligands (typically the organic species present in natural media) enhances the rate of oxide dissolution<sup>2–4</sup> without modifying the equilibrium solubility. In other cases, ligands *in solution* are able to complex dissolved metal ions ( $\text{Al}^{3+}$  in  $\text{Al}_2\text{O}_3$ ), and the complexation reaction will shift the solubility reaction toward the dissolution of the oxide.<sup>5,6</sup> One can then speak of a *thermody-*

*namic* promotion of oxide dissolution. In fact, this simply means that the total amount of Al in solution is now  $[\text{Al}^{3+}] + [\text{AlL}^{x+}]$  (supposing for the sake of simplicity that  $\text{Al}^{3+}$  forms a 1:1 complex with ligand L) which may be orders of magnitude higher than  $[\text{Al}^{3+}]$ .

These geochemical concepts can be transferred easily to the field of catalyst preparation if we consider that the anionic precursors used for preparation of catalysts can play the same roles as the organic ligands considered by geochemists. A thermodynamic effect was actually demonstrated in  $\text{MoO}_x/\text{Al}_2\text{O}_3$  synthesis where we evidenced the formation of an aluminomolybdate complex in solution [the Anderson-type heteropolyanion  $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}^{3-}$ ]. This was a clear demonstration that molybdate species can play a role analogous to the organic ligands present in natural media. The formation of this mixed species drastically increases the solubility of  $\gamma\text{-Al}_2\text{O}_3$ , especially in the pH range between 4 and 6.5.<sup>7</sup>

It was considered worthwhile to extend these results to the synthesis of  $\text{WO}_x/\text{Al}_2\text{O}_3$  catalysts, which are used for instance in olefin metathesis<sup>8</sup> or as an intermediate in the synthesis of bimetallic systems such as  $\text{Pt}-\text{WO}_x/\text{Al}_2\text{O}_3$ .<sup>9,10</sup>

$\text{WO}_x/\text{Al}_2\text{O}_3$  are closely related to the  $\text{MoO}_x/\text{Al}_2\text{O}_3$  system. Indeed, tungstates, as well as molybdates, can act as complexing

(7) A different effect was reported by Clause et al. for alumina solubility in the presence of cationic metal precursors. In this case, the precursors do react with dissolved aluminic species, but only to form insoluble mixed phases (hydrotalcites). The Al concentration in solution at equilibrium is not much increased; but the amount of Al that undergoes dissolution followed by reprecipitation is very high. See d'Espinose de la Caillerie, J.-B.; Kermarec, M.; Clause, O. *J. Am. Chem. Soc.* **1995**, *117*, 11471; d'Espinose de la Caillerie, J.-B.; Kermarec, M.; Clause, O. *J. Phys. Chem.* **1995**, *99*, 17273.

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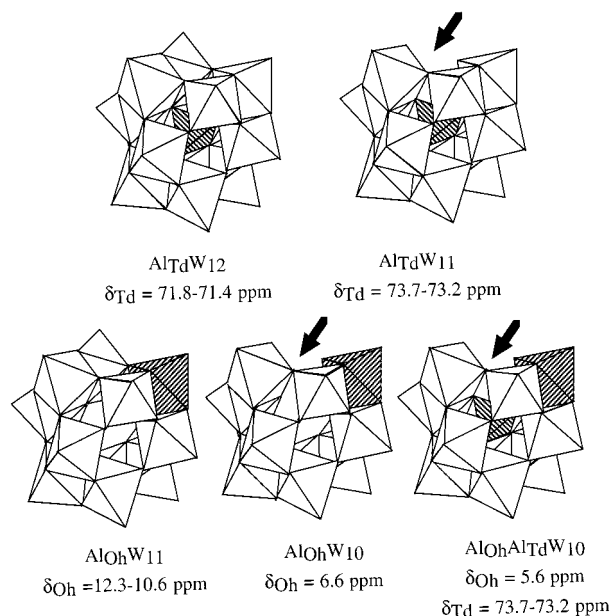
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**Figure 1.** Structure of the different aluminotungstic heteropolyanions reported in Carrier et al.<sup>11</sup> The octahedra containing Al atoms are represented by the dark shade. The proposed <sup>27</sup>Al NMR chemical shift is indicated, below each species. The subscripts Td and Oh refer to an aluminum in the central tetrahedron (Td), or substituting one tungsten atom in an octahedral environment (Oh), respectively. Each formula (AlTdW<sub>11</sub>, for example) is a simplified one and only intends to locate the aluminum atoms and to specify whether the Keggin unit is complete (12 octahedra) or lacunary. The distinction between the chemical shifts of Al<sub>Oh</sub> in AlOhW<sub>10</sub> and AlOhAlTdW<sub>10</sub> was not made in the previous study;<sup>11</sup> it is explained in the text.

agents for dissolved aluminic species because several aluminotungstic heteropolyanions have been reported (vide infra). All these species adopt a Keggin-type structure (built by four groups of three edge-sharing tungsten octahedra surrounding one central tetrahedron). The aluminum atom can either be located in the central tetrahedron or substitute one octahedral tungsten. We recently reported the synthesis and the proposed <sup>27</sup>Al liquid-state NMR fingerprints of these different species.<sup>11</sup> (Although <sup>183</sup>W has been used successfully for the characterization of polytungstates,<sup>12</sup> it would not be suitable for our investigations because tungsten concentrations are too low in realistic situations.) The currently known Al–W–O mixed species are schematically depicted in Figure 1. For ease of reference, we have also indicated the diagnostic <sup>27</sup>Al NMR peaks (at  $\nu_{\text{L}} = 104.26 \text{ MHz}$ ) which are proposed in the text for each species.

To our knowledge, such species have never been characterized or even taken into account in previous studies on the preparation of WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. Indeed, in most of these studies, the complexity of tungsten chemistry goes unrecognized and the catalysts are usually prepared from only one tungstic precursor {often ammonium metatungstate, (NH<sub>4</sub>)<sub>6</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]}.<sup>13–15</sup> Some authors<sup>16</sup> have attempted to prepare WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts with different tungstic precursors (metatungstate and monotungstate WO<sub>4</sub><sup>2-</sup>) or to take into account the complex-

ity of the aqueous tungsten chemistry,<sup>17,18</sup> but even so the two thermodynamically stable polymeric species (metatungstate, H<sub>2</sub>W<sub>12</sub>O<sub>40</sub><sup>6-</sup>, a Keggin-type isopolyanion, and paratungstate, H<sub>2</sub>W<sub>12</sub>O<sub>42</sub><sup>10-</sup>, discussed below) are rarely compared. In view of this fact, it is hardly surprising that aluminotungstic species have not been considered yet in studies on WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> preparation.

A recent study<sup>19</sup> showed the formation of a Keggin-type mixed species similar to SiW<sub>12</sub>O<sub>40</sub><sup>4-</sup> during WO<sub>x</sub>/SiO<sub>2</sub> catalysts preparation. The authors propose that this species is formed during the thermal treatment (from 100 to 400 °C) leading to the final catalysts. However, a close examination of published evidence leaves open the possibility that SiW<sub>12</sub>O<sub>40</sub><sup>4-</sup> species could in fact be formed during the initial impregnation step. From a catalytic point of view, it is interesting to note that the authors attribute the high Brønsted acidity in these catalysts to the presence of the silicomolybdc heteropolyanion.

In our previous studies,<sup>1,11</sup> we emphasized the benefits of characterizing the liquid phase involved during catalyst preparation. This characterization allowed us to demonstrate the formation of at least four aluminotungstic species in solution during the preparation of WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts depending on the tungstic precursors and the pH.<sup>11</sup> The present study will show for the first time that aluminotungstic species are also deposited on the support. Thus, in the same way as for molybdates, the tungstic species deposited on the alumina support might be some kind of mixed species instead of an isopolytungstate as generally assumed in the literature.

## Experimental Section

**Sample Preparation.** The support was a  $\gamma$ -alumina from Rhône-Poulenc, with a surface area of 189 m<sup>2</sup>·g<sup>-1</sup> and a pore volume of 0.64 cm<sup>3</sup>·g<sup>-1</sup>. Before use, the alumina pellets were ground in a mortar and the fraction 150 <  $\phi$  < 400  $\mu\text{m}$  was collected by sieving. The catalysts were prepared by the equilibrium adsorption method. Two different tungstate salts (Fluka) were used as precursors: sodium monotungstate, Na<sub>2</sub>WO<sub>4</sub>, and ammonium paratungstate, (NH<sub>4</sub>)<sub>10</sub>H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>. The solution of monotungstate (pH = 9.5) was prepared at a concentration of 0.15 M. The less soluble paratungstate precursor was dissolved with a concentration of 0.1 M in hot water (~80 °C), then cooled to room temperature and left to stand for 24 h (final pH = 6.2) before contact with the alumina suspension. Ground alumina was then suspended in the tungstate solutions with an oxide/solution ratio of 1 g/100 mL. The resulting alumina/tungstate suspensions were then stirred at room temperature for 24 or 168 h. The pH was kept constant at either 6.8 (monotungstate) or 4.5 (paratungstate) throughout equilibration by addition of either concentrated HNO<sub>3</sub> or NH<sub>3</sub>. After filtration (on a filter paper with a pore size of 8  $\mu\text{m}$ ), the solid phases were washed three times with distilled water and left to dry in air at room temperature. The filtrates were kept for <sup>27</sup>Al NMR measurements. They were initially transparent clear solutions, although in some instances a solid precipitate formed after very long aging times. The elemental analyses were performed by the Laboratoire d'Analyses Élémentaires (CNRS, Vernaison, France) using Atomic Emission Spectroscopy (ICP/AES). The weight loading for the catalyst *ex*-monotungstate is 9.5 W wt % (after 168 h of contact); for the catalyst *ex*-paratungstate, it is 16.9% after 24 h of contact and 17.5 W wt % after 168 h of contact.

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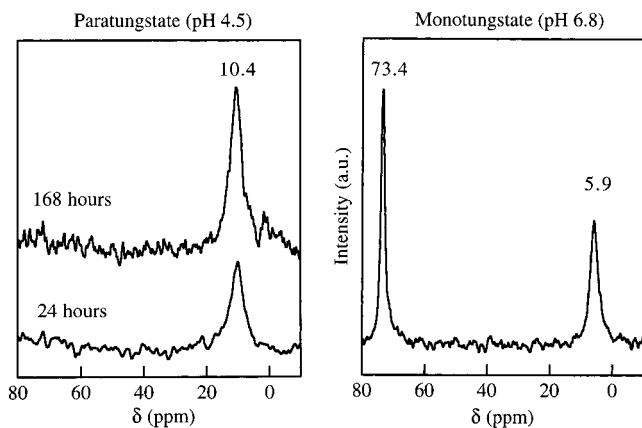
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**Figure 2.**  $^{27}\text{Al}$  liquid-state NMR spectra of filtrates obtained after equilibrium adsorption with different tungstic precursors at room temperature: monotungstate at pH 6.8 during 168 h and paratungstate at pH 4.5 during 24 h and 168 h.

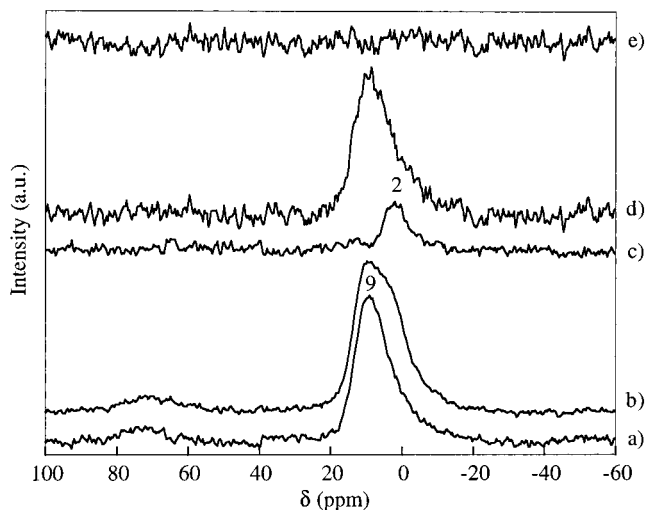
**NMR Spectroscopy.** Liquid-state  $^{27}\text{Al}$  NMR spectra were obtained with a Bruker MSL 400 spectrometer. Simple one-pulse sequences with phase cycling were used. The Larmor frequency was 104.26 MHz; the pulse length was 1  $\mu\text{s}$ , and the recycle delay was 500 ms. A 0.1 M solution of aluminum nitrate was used as the 0 ppm external reference. The solid-state  $^{27}\text{Al}$  NMR spectra were obtained with a Bruker ASX 500 spectrometer in 4-mm zirconia rotors. The Larmor frequency was 130.32 MHz. We used a proton cross-polarization (CP) sequence with a recycle delay of 5 s, a contact time of 500  $\mu\text{s}$ , and a magic angle-spinning (MAS) rate ( $\omega_{\text{rot}}$ ) of 8 kHz. For more details on  $^{27}\text{Al}$  CP-MAS NMR experiments, see Mertens et al.<sup>20</sup>

## Results

Characterization of the liquid phase. The  $^{27}\text{Al}$  liquid-state NMR spectra recorded for the filtrates obtained after 168 h of equilibration from monotungstate at near-neutral pH (6.8) and after 24 and 168 h of equilibration from paratungstate at acidic pH (4.5) are presented in Figure 2.

When  $\text{WO}_4^{2-}$  (monotungstate) is used as a precursor at near-neutral pH, we can identify two peaks at 73.4 and 5.9 ppm which both can be attributed to aluminotungstic species (Figure 1). The peak at 73.4 ppm is attributed to Al in the central tetrahedron of a lacunary Keggin-type species:  $\text{Al}_{\text{Td}}\text{W}_{11}$ .

The peak at 5.9 ppm is clearly in the region of octahedrally coordinated aluminums. In our previous study,<sup>11</sup> we emphasized that this chemical shift could be caused either by  $\text{Al}_{\text{Oh}}$  in  $\text{Al}_{\text{Oh}}\text{W}_{10}$  or by  $\text{Al}_{\text{Oh}}$  in the  $\text{Al}_{\text{Oh}}\text{Al}_{\text{Td}}\text{W}_{10}$  species represented in Figure 1. (In the latter case, the  $\text{Al}_{\text{Td}}$  in the same species could contribute to the peak at 73.4 ppm.) Now, because for reference compounds a peak at 6.6 ppm was observed without any peak in the tetrahedral region ( $\delta \approx 70$  ppm) and a peak at 5.6 ppm was observed in addition to one peak at 73 ppm, we propose to attribute the chemical shift of 6.6 ppm to the  $\text{Al}_{\text{Oh}}$  in  $\text{Al}_{\text{Oh}}\text{W}_{10}$ , and the chemical shift of 5.6 ppm to the  $\text{Al}_{\text{Oh}}$  in  $\text{Al}_{\text{Oh}}\text{Al}_{\text{Td}}\text{W}_{10}$ . Fedotov and Kazanskii<sup>21</sup> have attributed a peak at 7 ppm to an octahedral aluminum atom in a complete Keggin-type structure containing two aluminums in different coordinations (the simplified formula would be  $\text{Al}_{\text{Oh}}\text{Al}_{\text{Td}}\text{W}_{11}$ ). Unfortunately, such species ( $\text{Al}_{\text{Oh}}\text{Al}_{\text{Td}}\text{W}_{10}$  or  $\text{Al}_{\text{Oh}}\text{Al}_{\text{Td}}\text{W}_{11}$ ) have not been isolated in pure form so far; thus, our assignment (5.6 ppm for  $\text{Al}_{\text{Oh}}\text{Al}_{\text{Td}}\text{W}_{10}$ ) would need to be confirmed.



**Figure 3.**  $^1\text{H}/^{27}\text{Al}$  CP-MAS NMR of (a)  $\text{Al}_2\text{O}_3$ , (b)  $\text{WO}_x/\text{Al}_2\text{O}_3$  from paratungstate (pH 4.5), (c) difference of spectra b–a, (d)  $\text{WO}_x/\text{Al}_2\text{O}_3$  from monotungstate (pH 6.8), and (e) difference of spectra d–a.

For the synthesis performed at acidic pH (4.5) from paratungstate, we can identify one peak at 10.4 ppm which is attributed to an aluminum atom in octahedral coordination in a “complete” Keggin-type species:  $\text{Al}_{\text{Oh}}\text{W}_{11}$ . The amount of dissolved aluminum still markedly increased between 24 and 168 h of contact (in opposition to what was found for molybdates where dissolved Al remained constant after 24 h<sup>1</sup>); the aluminum content after 168 h of equilibrium was found to be  $120 \text{ mg}\cdot\text{L}^{-1}$ , whereas it was only  $63 \text{ mg}\cdot\text{L}^{-1}$  after 24 h.

**Characterization of the Solid Phase.** The  $\text{WO}_x/\text{Al}_2\text{O}_3$  catalysts were characterized by  $^1\text{H}/^{27}\text{Al}$  CP-MAS NMR. This technique had been used successfully in the identification of an aluminomolybdc species on alumina in our previous study.<sup>1</sup> In alumina-supported catalysts, CP-MAS NMR is surface-sensitive because we only observe aluminum in dipolar contact with protons (mainly surface aluminums from the support,  $\text{Al}-\text{OH}$ , or deposited surface species containing protons). This will exclude most of the aluminums from the bulk of the support. The efficiency of cross-polarization was recently demonstrated by Mertens de Wilmars et al.<sup>20</sup> in the characterization of  $\text{MoO}_x/\text{Al}_2\text{O}_3$  catalysts. It was shown that CP is able not only to suppress the signal arising from bulk aluminums but also to enhance the contribution of aluminums involved in surface mixed compounds over the signal of surface OH-bearing aluminums, providing the experimental conditions are properly set.

The CP-MAS NMR spectra of the catalysts obtained after 168 h of equilibration at pH 6.8 from monotungstate and at pH 4.5 from paratungstate are shown in Figure 3.

The spectrum obtained for the bare alumina (spectrum a) shows only one peak at 9 ppm which is attributed, as previously,<sup>1</sup> to octahedral surface aluminums from the support. The spectrum obtained for the catalyst *ex*-paratungstate (spectrum b) shows one shoulder at about 2 ppm which is not observed for the spectrum of the bare alumina. This shoulder can be resolved in one symmetric peak at 2.0 ppm by subtracting the contribution from the support (spectrum c). This clearly indicates the presence of a new aluminic species on the support after equilibration with the tungstate solution. However, the position of this peak does not correspond to any of the chemical shifts observed for reference compounds (Figure 1). Concerning the catalyst *ex*-monotungstate, the spectrum shows no peak besides the one arising from the alumina support. This is further

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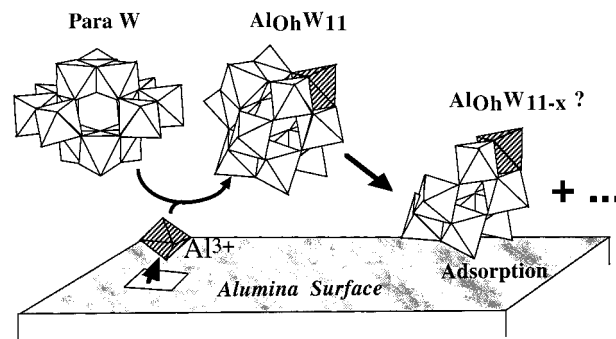
confirmed by subtracting the contribution from the alumina support (spectrum e); no peak is apparent on the subtracted spectrum. Incidentally, this demonstrates that the symmetric peak at 2 ppm revealed by the previous subtraction (spectrum c) is not an artifact of the subtraction procedure.

## Discussion

**Alumina Dissolution.** The presence of  $\text{Al}_{\text{Td}}\text{W}_{11}$  and  $\text{Al}_{\text{Oh}}\text{W}_{10}$  in the filtrate obtained at pH 6.8 (monotungstate) demonstrates that alumina dissolution and subsequent reaction with tungstic precursors occurred during preparation of  $\text{WO}_x/\text{Al}_2\text{O}_3$  catalysts at near-neutral pH. At first sight, this could be surprising because alumina solubility is reported to be very low at these pH values.<sup>21</sup> However this can be rationalized as an effect of ligand-promoted dissolution. For supported molybdates, it was shown<sup>1</sup> that the complexation reaction between molybdates and dissolved aluminum shifts the solubility reaction toward the dissolution of alumina. The same phenomenon can certainly explain the dissolution of alumina at near-neutral pH in tungstates. In our previous study,<sup>11</sup> we evidenced the formation of the  $\text{Al}_{\text{Td}}\text{W}_{11}$  species (chemical shift at about 73 ppm) in slightly basic solutions (pH between 8 and 8.5). We have now seen that this species is stable at near-neutral pH. Thus, ligand-promoted alumina dissolution by formation of aluminotungstic species can occur even in “nonaggressive” media.

However, the kinetics of this phenomenon seems slower than in molybdates.<sup>1</sup> We emphasized that in the latter case the amount of dissolved aluminum was nearly constant after 24 h of equilibrium. In tungstates, the amount of aluminum in solution after 168 h of equilibrium is twice the amount after 24 h of equilibrium. It is well-known<sup>22,23</sup> that the interconversion reactions of isopolytungstates are much slower than analogous reactions of isopolymolybdates; thus, the formation of meta-tungstate (Keggin-type isopolytungstate) from monotungstate is only complete after 15 days. This kinetic inertness can certainly explain that the phenomena occurring at the oxide/water interface during  $\text{WO}_x/\text{Al}_2\text{O}_3$  preparation are much slower than in  $\text{MoO}_x/\text{Al}_2\text{O}_3$  synthesis. It follows that this kinetic restriction can constitute a valuable tool for controlling the type of species (iso- or heteropolytungstates) actually deposited on the support. This line of research has not been explored so far.

**Tungsten Speciation and Deposition of Aluminotungstic Species.** The position of the  $^{27}\text{Al}$  NMR peak in the catalyst *ex-paratungstate* (+2.0 ppm in Figure 3, spectrum c) clearly corresponds to a species containing an aluminum atom in octahedral coordination, and we may safely conclude that an Al-containing species has been deposited on the surface. However, the filtrate corresponding to this synthesis (Figure 2) shows only one peak at the very different position of 10.4 ppm (attributed to  $\text{Al}_{\text{Oh}}\text{W}_{11}$ ). It follows that the deposited species is not similar to the one in solution. It must be noted that Fedotov and Kazanskii<sup>21</sup> have reported one peak at 2.3 ppm for the same type of compound ( $\text{PA}_{\text{Oh}}\text{W}_{11}\text{O}_{39}^{4-}$ ), which is very different from the 10.6–12.3 ppm range reported by others. Unfortunately, Fedotov and Kazanskii did not specify their preparation procedure; therefore, it is difficult to judge if they indeed synthesized the target compound. As we will see, there is reason to believe that  $\text{Al}_{\text{Oh}}\text{W}_{11}$  can easily be transformed into different species with a noticeably lower value of  $\delta$ . Thus, we maintain



**Figure 4.** Ligand-promoted alumina dissolution during the preparation of  $\text{WO}_x/\text{Al}_2\text{O}_3$  catalysts and deposition of a lacunary Keggin-type species.

our previous assumption: that is, the aluminum in  $\text{Al}_{\text{Oh}}\text{W}_{11}$  species has a chemical shift close to 10 ppm.

Another point of interest is that the attribution of the peak at 10.4 ppm was initially made by comparison with two reference Keggin-type compounds containing one aluminum in octahedral coordination:  $\text{HAlW}_{11}\text{O}_{36}\text{F}_3(\text{H}_2\text{O})^{5-}$  ( $\delta = 10.6$  ppm, Chauveau<sup>24</sup>) and  $\text{PAIW}_{11}\text{O}_{39}(\text{H}_2\text{O})^{4-}$  (prepared from Zonnevijlle et al.,<sup>25</sup>  $\delta = 12.3$  ppm). Both formulas include one water molecule. Indeed, Baker and Figgis<sup>26</sup> have demonstrated that the terminal oxygen linked to the heteroatom in this type of structure is doubly protonated. The presence of this water molecule close to the aluminum would involve that such species are detectable by  $^1\text{H}/^{27}\text{Al}$  CP-MAS NMR.

We may now propose a tentative explanation for the low  $\delta$  value of the deposited species. In Figure 1, we can see that the chemical shift of the octahedral aluminum decreases with the departure of one tungsten octahedron (compare  $\text{Al}_{\text{Oh}}\text{W}_{11}$  and  $\text{Al}_{\text{Oh}}\text{W}_{10}$ ). Thus we propose to attribute the peak observed at 2 ppm for  $\text{WO}_x/\text{Al}_2\text{O}_3$  catalyst *ex-paratungstate* to a lacunary Keggin-type species related to  $\text{Al}_{\text{Oh}}\text{W}_{11}$  but with more than one W vacancy, in other words  $\text{Al}_{\text{Oh}}\text{W}_{11-x}$  with  $x > 1$ .

Lambert and Che<sup>27</sup> recently reported that the pH in the vicinity of a charged oxide surface can be significantly different from the one in the bulk of the solution. For example, for a pH < PZC, the surface is positively charged and will “concentrate” the  $\text{OH}^-$  ions in its vicinity. Thus, the pH close to the surface will be higher than in the bulk. This explanation could well account for the observation of a “complete” Keggin unit in solution ( $\text{Al}_{\text{Oh}}\text{W}_{11}$ ,  $\delta = 10.4$  ppm) coexisting with a lacunary one on the surface of the catalyst ( $\text{Al}_{\text{Oh}}\text{W}_{11-x}$  with  $x > 1$ ) because the formation of lacunary species is favored over that of “complete” ones when the pH is increased.<sup>28</sup>

The processes (dissolution, complexation, and deposition) occurring at the oxide/water interface during the preparation of  $\text{WO}_x/\text{Al}_2\text{O}_3$  catalyst at pH 4.5 from paratungstate are schematized in Figure 4.

In monotungstate, the  $^{27}\text{Al}$  NMR data indicate that a large quantity of heteropolytungstate has formed after 168 h of contact with the alumina surface at a *bulk* pH of 6.8. Polymerization is not surprising in itself because, according to published formation constants,<sup>29</sup> a homogeneous solution under these conditions

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would consist of 26% monotungstate and 74% paratungstate (with only trace species of other compounds). However, because the structure of the heteropolytungstate formed in our heterogeneous medium is Keggin-like, i.e., closer to the metatungstate than to the paratungstate, it appears that the aluminic species dissolved from  $Al_2O_3$  (and perhaps the special conditions in solution in the vicinity of the surface) have had considerable influence in directing the speciation of tungstates.

However, in the  $WO_x/Al_2O_3$  catalyst *ex*-monotungstate, there is no evidence of deposition onto the support of the heteropolytungstates that are formed in the solution. The difference  $^{27}Al$  NMR spectrum obtained for this catalyst (Figure 3, spectrum e) did not show any peak caused by an aluminic species, whereas the corresponding filtrate showed two peaks at 73.4 and 5.9 ppm (Figure 2). Actually, the technique used in this study (CP-MAS) does not allow a definite conclusion on the absence of any aluminotungstic species in this case; the absence of a new CP-MAS NMR signal does not necessarily mean that there are no aluminotungstic species present on the surface, because species that do not contain any protons in the vicinity of the aluminum atoms would not be detected by this technique. Furthermore, Mertens et al.<sup>20</sup> emphasized that CP-MAS can drastically enhance or suppress the  $^{27}Al$  NMR signal depending on the experimental conditions that are chosen. By changing the contact time in the CP-MAS experiment, these authors succeeded in selectively enhancing one signal at 14 ppm over the signal from the support at 8 ppm. In our study, the experimental conditions were not optimized for observing one signal in the tetrahedral region, in part because of lack of good reference compounds. Thus, we presently will refrain from concluding on the absence or on the presence of aluminotungstic species in this catalyst.

## Conclusion

In previous work, we had discussed the various possible roles that an oxide support can play in the synthesis of supported

metal catalysts.<sup>27,30</sup> It has long been known that the support can act as a stoichiometric reagent in syntheses realized with cationic metal precursors, as e.g.,  $[Ni(H_2O)_6]^{2+}/SiO_2$  which yields phyllosilicates.<sup>31</sup> More recently, we have evidenced the first clear case of stoichiometric reaction between a support and an anionic precursor ( $[Mo_7O_{24}]^{6-}/Al_2O_3$ , yielding  $[Mo_6AlO_{18}(OH)_6]^{3-}$ .<sup>1</sup> This article extends the domain of validity of support/precursor reaction: during the preparation of  $WO_x/Al_2O_3$  catalysts, the support cannot be considered as chemically inert either, because we have clearly observed the formation of several aluminotungstic species in solution. The formation of these Keggin-type species occurs at acidic and near-neutral pH values where alumina solubility is supposed to be negligible. This process can be rationalized as a *ligand-promoted oxide dissolution* effect; alumina dissolution is enhanced by subsequent reaction of the dissolved species with the tungstic precursors. This phenomenon is slower than in molybdates, which is probably related to the kinetic inertness of tungstates.

CP-MAS NMR allows us to conclude that aluminotungstic species are deposited on the support. Such heteropolytungstic species have never been considered in previous studies in which it was always implicitly considered that only isopolytungstic species are present in  $WO_x/Al_2O_3$  catalysts. The deposited species is not the same as the one identified in the liquid phase. The different nature of both species probably results from a local increase of pH in the vicinity of the surface with respect to the solution bulk. This study confirms the need to characterize not only the solid phase but also the liquid phase during catalyst preparation. The simultaneous characterization of both phases allows us to have more insight into the phenomena occurring at the oxide/water interface, such as dissolution, complexation, local increase of pH, etc.

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