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# Quantitative measurement of the Brønsted acid sites in solid acids: Toward a single-site design of Mo-modified ZSM-5 zeolite

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containing zeolites to get more insight about the anchoring of these metals inside the microporosity.

Mo-modified ZSM-5 zeolites were used as a case study due to their importance in the methane aromatization reaction.<sup>15–18</sup> Furthermore, an accurate determination of the number of Brønsted acid sites consumed during Mo introduction can serve as a basis for a better understanding of the geometry of the active metal center. Finally, the knowledge gained from such studies can lead to the design of new kinds of uniform single-site catalysts.<sup>19</sup>

## 2. Experimental Section

**2.1. Preparation of Mo-ZSM-5 Samples.** Two starting NH<sub>4</sub>-ZSM-5 zeolites, provided by Zeolyst International, were used: CBV3024E and CBV8014 having Si/Al = 15 and 40, respectively. The Mo/HZSM-5 catalyst was obtained by mixing the ammonium form NH<sub>4</sub>-ZSM-5 with an aqueous solution containing the desired amount of molybdenum oxide (MoO<sub>3</sub>, Strem Chemicals, 99.5%). In fact, the MoO<sub>3</sub> powder was dispersed in a small amount of distilled water using sonication in order to avoid large MoO<sub>3</sub> aggregates, which could lead to some inhomogeneity in the final catalyst. The sample was then dried overnight at room temperature and for 2 h at 100 °C. Finally, it was calcined in air at 700 °C during 30 min. During the calcination process, MoO<sub>3</sub> molecules undergo vaporization and homogeneously penetrate in the microporosity of the zeolite. This procedure was used to prepare Mo/HZSM-5 samples with Mo loadings of 2 and 4 wt %, for both the ZSM-5 with a Si/Al ratio of 15 and the one with a ratio of 40. A sample with a loading of 6 wt % was also prepared in the case of the most acidic ZSM-5, i.e., Si/Al = 15. The samples were noted 2/15, 4/15, 6/15, 2/40, and 4/40. Zeolites calcined in the same conditions without MoO<sub>3</sub> were also prepared and were noted 0/15 and 0/40.

**2.2. Characterization Techniques.** The nature of the catalysts was characterized by means of powder X-ray diffraction technique using a Siemens D5000 diffractometer (Cu K $\alpha$  radiation) and operated at 40 kV and 20 mA with a  $\theta/2\theta$  mode.

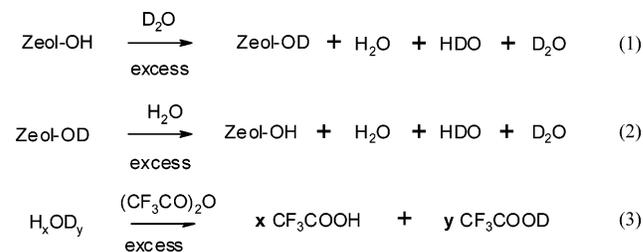
Specific surface area measurements were carried out on a Coulter-Beckman SA 3100 sorptometer using N<sub>2</sub> adsorption at –196 °C. Before measurement, the sample was outgassed at 325 °C for 14 h in order to desorb moisture from its surface.

<sup>27</sup>Al ( $I = 5/2$ ) magic angle spinning nuclear magnetic resonance (MAS NMR) was carried out with a Bruker DSX 400 spectrometer operating at  $B_0 = 9.4$  T (Larmor frequency  $\nu_0 = 104.2$  MHz). A single pulse of 0.7  $\mu$ s with a recycle delay of 1 s was used for all experiments. The spinning frequency was 8 kHz. Measurements were carried out at room temperature with [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> as external standard reference.

The temperature-programmed desorption (TPD) of ammonia was used to titrate the different acid sites but essentially to compare the behavior of Brønsted acid sites with our H/D exchange technique. The measurements were performed in a U-shaped glass plug flow reactor. The catalysts (500 mg) were pretreated under He flow at 500 °C for 2 h. The adsorption of NH<sub>3</sub> (20% in He flow) was performed at 100 °C during 1 h. After a flush of 1 h in He flow, the sample was heated (20 °C.min<sup>-1</sup>) up to 800 °C in a He flow. A Saturn 3 Varian mass spectrometer was used to analyze the outlet gas-phase composition and was calibrated for  $m/e = 17$ .

**2.3. Description of the H/D Exchange Method.** All the reactions were performed in an all-glass, grease-free, flow system with a U-shaped reactor as reported elsewhere.<sup>14</sup> The temperature was controlled with a thermocouple placed in the

### SCHEME 1: Set of H/D Exchange Steps between H<sub>2</sub>O/D<sub>2</sub>O and the OH Groups of the Zeolite



catalytic bed, while the gas flow was regulated with a Brooks 5850E mass flow controller. The catalyst (300 mg) was first activated under dry N<sub>2</sub> flow (40 cm<sup>3</sup>.min<sup>-1</sup>) at 450 °C for 1 h to desorb the water present in the void volume but prevent dehydroxylation of the zeolite framework. The temperature of the catalyst was then lowered to 200 °C for deuteration. Scheme 1 describes the different H/D steps involved during this method.

First, the catalyst deuteration was performed by passing for 1 h through the sample bed with 40 cm<sup>3</sup>.min<sup>-1</sup> of dry N<sub>2</sub> previously bubbled, at room temperature, through a U-shaped tube containing D<sub>2</sub>O (about 0.05 g). The excess of D<sub>2</sub>O was removed by flushing dry N<sub>2</sub> at 200 °C during 90 min.

Then, the deuterated catalyst (Zeo-OD) was back-exchanged (Scheme 1, eq 2) at 200 °C for 1 h with 40 cm<sup>3</sup>.min<sup>-1</sup> of dry N<sub>2</sub> previously bubbled through a U-tube containing H<sub>2</sub>O (3% of H<sub>2</sub>O in N<sub>2</sub> stream). This step was necessary since the trifluoroacetic anhydride contains 0.11 mmol of trifluoroacetic acid per gram of anhydride as controlled in blank experiment. For this reason it is desirable to titrate the Brønsted sites by using the anhydride with the partially exchanged water obtained after the last step (Scheme 1, eq 2).

The partially exchanged water H<sub>x</sub>OD<sub>y</sub> (Scheme 1, eq 3), composed of H<sub>2</sub>O, HDO, and D<sub>2</sub>O, was collected in a U-tube cooled at –117 °C (ethanol melting point). The recovered H<sub>x</sub>OD<sub>y</sub> was weighted and chemically trapped by trifluoroacetic anhydride (used in a 2-fold excess). The acid solution thus obtained was transferred under argon to a NMR tube for analysis. The spectra were recorded on a Bruker AM400 spectrometer (400 MHz) after an addition of a CDCl<sub>3</sub> (10 wt %)/CHCl<sub>3</sub> mixture as reference. The integration of CF<sub>3</sub>COOH-(D) and CH(D)Cl<sub>3</sub> on both <sup>1</sup>H and <sup>2</sup>H spectra allows an accurate quantification of the H/D content of the sample. The acid site density was then calculated based on the H/D ratio measured and the mass of H<sub>x</sub>OD<sub>y</sub> collected. The precision of this titration method for the total number of acid sites is between 0.05 and 0.07 mmol/g.

## 3. Results

**3.1. Methodology for Determining the Chemical Composition of Solid Acids.** Table 1 presents the comparison between the theoretical number of Brønsted acid sites of different solid acids and the measured number of OH groups by the H<sub>2</sub>O/D<sub>2</sub>O isotope exchange technique. The number of Brønsted acid sites appears to be in good agreement with the theoretical one (given by the Si/Al ratio) for five zeolite samples: MOR, EMT, HUSY, MFI, BEA. So, this isotopic exchange can be used as an efficient tool to determine the whole quantity of Brønsted acid sites on zeolites. Furthermore, an accurate amount of OH groups has been titrated on H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> heteropolyacid, as well as on SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>. Thus, by knowing the crystalline structure of a given zeolite or any solid acid, one is able to determine the number  $n$  of H atoms as described in Figure 1a. It is important to note

**TABLE 1: Theoretical and Measured Amount of Brønsted Acid Sites of Different Solid Acids**

solid acid	theoretical no. of Brønsted acid sites (mmol/g)	no. of Brønsted acid sites determined by H <sub>2</sub> O/D <sub>2</sub> O exchange (mmol/g)
MOR	2.78	2.66
EMT	2.26	2.38
HUSY	3.00	3.16
MFI	1.21	1.18
BEA	1.15	1.07
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>a</sup>	0.89	0.91
SO <sub>4</sub> -ZrO <sub>2</sub>	0.31 <sup>b</sup>	0.33

<sup>a</sup> Activation 1 h at 300°C. <sup>b</sup> Measured via isotope-exchange between propane and deuterated SZ.<sup>20</sup>

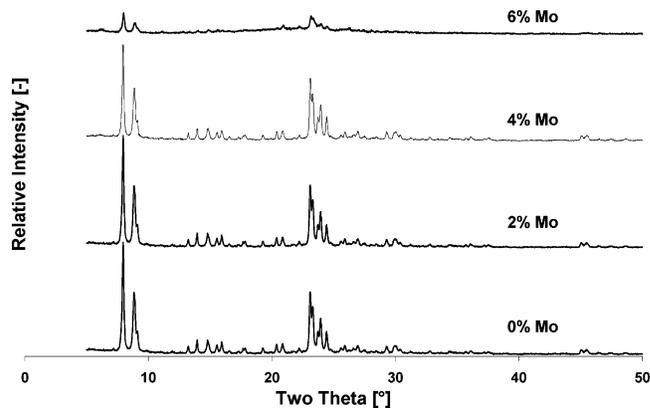
that the Si/Al ratio, which is a key parameter for the study of the catalysis by zeolites, can be directly deduced from this measurement. Moreover, this method is easy, fast, and nondestructive and could therefore replace the costly <sup>29</sup>Si solid-state MAS NMR for the estimation of the Si/Al ratio.

The next step of the present study consists of getting further information about both the localization and the geometry of transition metal cations introduced in zeolitic channels due to their importance in light alkanes activation. Mo-modified ZSM-5 materials were chosen as a case study since these materials are promising candidates for the transformation of cheap methane into aromatics.<sup>15–18,21–24</sup>

Since the leading work of the group of Iglesia,<sup>18</sup> it is commonly accepted that the molybdenum is anchored inside the micropores of the ZSM-5, on the Brønsted acid sites via substitution of the acidic H. However, the anchoring mode of the molybdenum species and the geometry of the metal center are still a matter of debate: Borry et al. suggested a (Mo<sub>2</sub>O<sub>5</sub>)<sup>2+</sup> dimer anchored on two neighboring acid sites,<sup>18</sup> whereas other groups rather proposed a monomer, either (MoO<sub>2</sub>)<sup>+</sup> or (MoO<sub>2</sub>)<sup>2+</sup> anchored respectively on one or two Brønsted acid sites.<sup>49,54,55</sup> As the anchoring of the molybdenum leads to a loss of acid sites, we believed that the H/D isotopic exchange developed in our group should give more insight about the anchoring mode of Mo, i.e., monomer or dimer.

**3.2. Characterization of the Mo-ZSM-5 Zeolites.** Elemental analysis was performed by using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique to quantify the molybdenum in the different samples. For the ZSM-5 zeolite having Si/Al = 15, 2.03, 3.98, and 6.22 wt % of Mo have been introduced. The MFI sample having a Si/Al = 40 presented 1.96 and 3.97 wt % of Mo introduced. It is important to note that this method of preparation is efficient to introduce any desired amount of Mo.

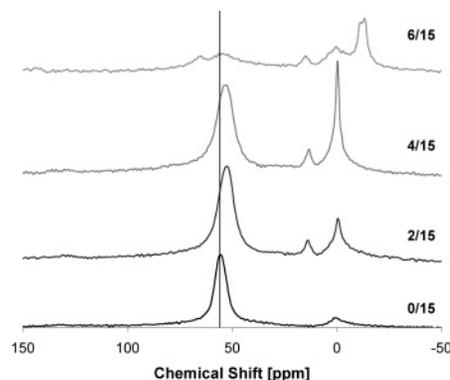
Figure 2 shows the XRD patterns of zeolite ZSM-5 (Si/Al = 15) with different Mo loadings (2, 4, and 6 wt %). The MFI structure appears to be preserved up to a 4 wt % loading of Mo, as no substantial loss of crystallinity was observed. Furthermore, this also confirms that the whole quantity of MoO<sub>3</sub> vaporized has been deposited on the surface without affecting the zeolite structure, thus reducing the formation of extraframework alumino-molybdeno species. However with a further increase of the Mo content (6 wt %), a drastic loss of crystallinity was observed, and new reflections corresponding to the Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> phase appeared at 2θ = 9, 23, and 28°. Thus, only the Mo-modified ZSM-5 samples having loadings of 2 and 4 wt % are suitable for the H/D exchange study. Table 2 shows the BET specific surface area (SSA) of the different samples for the two zeolites (Si/Al = 15 and 40). The introduction of Mo led to a decrease in the SSA value for both zeolites.

**Figure 2.** XRD pattern of Mo-containing ZSM-5 zeolite (Si/Al = 15).**TABLE 2: BET Specific Surface Areas of Mo-Substituted ZSM-5 Zeolites**

Mo content (wt %)	specific surface area (m <sup>2</sup> /g)	
	Si/Al = 15	Si/Al = 40
0	368	394
2	344	370
4	326	273

However the zeolite which possesses fewer acid sites (Si/Al = 40) was more affected after an introduction of 4 wt % Mo, with more than 30% loss in the SSA value, than the other zeolite, which had only a SSA decrease of 12%. It seems therefore that some MoO<sub>x</sub> species could not find enough grafting sites and are thus present as extraframework species which partially block the channels, resulting in a loss of the SSA. The presence of these polymolybdate or alumino-molybdate species on the external surface of the zeolite has been clearly evidenced by scanning electron microscopy (SEM).<sup>26</sup>

Mo-ZSM-5 (Si/Al = 15) has been further characterized by the <sup>27</sup>Al MAS NMR technique to get insights about the surface acidity of the zeolite via investigation of the nature and the environment of Al species.<sup>27–30</sup> Figure 3 shows the <sup>27</sup>Al MAS NMR spectra obtained for the different Mo loadings (0, 2, 4, and 6). Nonpromoted ZSM-5 presents two signals: an intense peak centered at 55 ppm corresponding to framework tetrahedral aluminum (Al<sub>F</sub>) and a weak signal centered at 0 ppm which corresponds to extraframework Al (EFAl).<sup>27–30</sup> While increasing the Mo content, the latter signal tends to increase, thus increasing the amount of extraframework Al species. Interestingly, a new contribution appears at 14 ppm (2% Mo) and has been attributed by Howe et al. to hydrated alumino-molybdate.<sup>31</sup> In fact, Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> species usually present a signal at -14 ppm, which shifts to +14 ppm after hydration.<sup>32</sup> This group has unambiguously proven the existence of a strong interaction between Mo

**Figure 3.** <sup>27</sup>Al MAS NMR spectra of Mo-ZSM-5 (Si/Al = 15).

**TABLE 3: Brönsted Acid Sites Measurement via H<sub>2</sub>O/D<sub>2</sub>O Isotope Exchange**

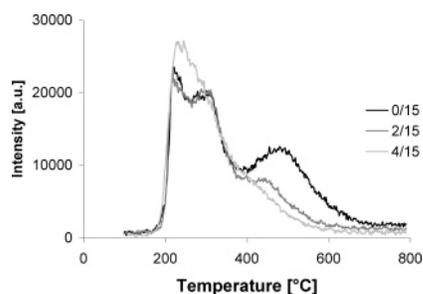
Mo content (wt %)	Si / Al = 15		Si / Al = 40	
	amt of Brönsted acid sites (mmol/g)	no. of Brönsted acid sites consumed per Mo atom (mol/mol)	no. of Brönsted acid sites (mmol/g)	no. of Brönsted acid sites consumed per Mo atom (mol/mol)
0	1.04		0.41	
2	0.61	1.99	0.20	0.94
4	0.18	1.93	0.17	0.53

and zeolite framework. Surprisingly, the peak corresponding to Al<sub>F</sub> was shifted to higher fields: - 2.5 ppm after Mo introduction. This can be due to the modification of the chemical environment of Al<sub>F</sub> atoms, presumably via anchoring of Mo on the neighboring oxygen atom. Recently, Kucera and Nachtigall have proven that such a shift in Al spectrum for high silica zeolites is connected to the extraframework cation coordination as well as on the T-O-T angle distortion.<sup>34</sup> This MAS NMR study confirms that most of the Mo vaporized is linked to a framework oxygen via replacement of a Brönsted acid site.

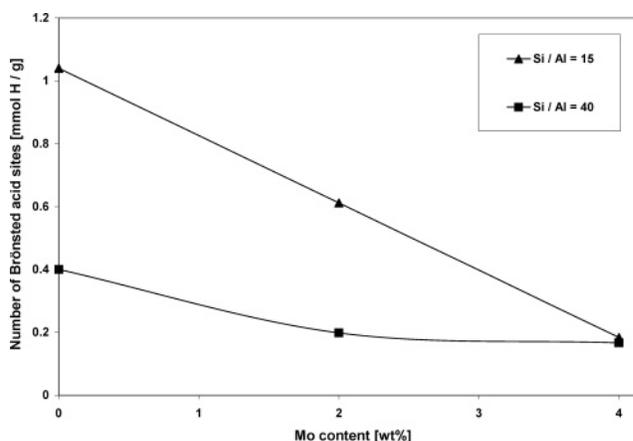
NH<sub>3</sub>-TPD has been used to further investigate the surface acidity of the zeolite. Figure 4 shows the NH<sub>3</sub>-TPD spectra of Mo-ZSM-5 (Si/Al = 15) which are similar to those from the literature.<sup>35-37</sup> Each signal has been deconvoluted in three distinct components. First, a low-temperature peak was attributed to physisorbed ammonia or bonded to terminal silanol groups.<sup>38-40</sup> Second, the peak at about 280 °C has been attributed to ammonia adsorbed on extraframework species.<sup>41</sup> Finally, the high-temperature peak (between 400 and 600 °C) was assigned to chemisorbed ammonia on Brönsted acid sites.<sup>40,42</sup> It is seen that the number of Brönsted acid sites decreases with an increase of the vaporized transition metal oxide, thus confirming the anchoring of MoO<sub>x</sub> species to the zeolite surface via consumption of Brönsted acid sites. The Brönsted acid site decrease was quantitatively estimated via integration of the high-temperature peak. After introduction of 2 wt % Mo, a loss of 2.3 O-H groups per Mo atom introduced has been calculated. This value becomes close to unity after an introduction of 4 wt % Mo. For the zeolite having Si/Al = 40, a consumption of 0.4 and 0.9 hydrons was measured per Mo atom at 2 and 4 wt % loading, respectively. It supposes with increase of the Si/Al ratio, the distance between two Brönsted acid sites was increased and that either polymeric Mo species are formed or the presence of extraframework alumino-molybdate species becomes nonnegligible.

The Mo-ZSM-5 zeolites were characterized by means of different bulk and surface techniques. The later methods allowed following the perturbation of surface acidity (<sup>27</sup>Al MAS NMR) or its decrease (NH<sub>3</sub>-TPD) and will serve as a basis for comparison with the H/D exchange method which permits titration to determine the total number of Brönsted acid sites of many solid acids.<sup>14</sup>

**3.3. Brönsted Acid Sites Titration via H<sub>2</sub>O/D<sub>2</sub>O Isotope Exchange.** This isotope exchange technique has been proven

**Figure 4.** NH<sub>3</sub>-TPD spectra of Mo-ZSM-5 (Si/Al = 15).

to be an efficient tool for the quantification of Brönsted acid sites of different kind of solid acids: zeolites, heteropolyacids, sulfated zirconia,<sup>14</sup> as well as mesoporous materials such as SBA-15 and Ga-promoted SBA-15.<sup>43</sup> Figure 5 shows the

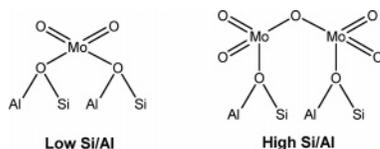
**Figure 5.** Dependence between the amount of number of Brönsted acid sites and the Mo content.

dependence between the number of Brönsted acid sites measured via this method and the Mo content of the two zeolites. The number of Brönsted acid sites decreases while raising the Mo content in both MFI zeolites, thus indicating the anchoring of Mo species on surface OH groups. It is noteworthy that the OH groups consumption was more pronounced on the zeolite having the higher Brönsted acid sites density (Si/Al = 15). Table 3 expresses this trend via the number of Brönsted acid sites consumed per Mo atom. In the zeolite having a Si/Al = 15, a molybdenum atom was found to replace two hydrons whatever the Mo loading (2 or 4 wt %). Unlike this zeolite, the amount of hydrons consumed was only close to unity for the zeolite having a Si/Al = 40 at 2 wt % Mo loading. The ratio O-H loss/Mo was further reduced to 0.53 with an increase to 4 wt % of Mo. Consequently it appears that either the bonding mode or the nature of the Mo species are different for both zeolites. In fact, it appears that the density of OH groups (their proximity) has an influence on the metal introduction inside the zeolite channels. This suggests that the interaction between the Mo species and the Brönsted acid sites is closely related to the amount of those sites per unit cell.

#### 4. Nature and Location of Mo Complexes in the Zeolitic Environment

It has been demonstrated in the last section that 2 and 4 wt % of Mo can be introduced in the zeolite channels via vaporization reaction of MoO<sub>3</sub> with the surface OH groups at 700 °C.

Higher Mo loading (6 wt %) led to an extensive dealumination of the zeolite framework, accompanied by a decrease in crystallinity, and thus to the loss of the confinement effect<sup>44-47</sup> created by the framework. It has been proven that the bifunctional site created in this confined environment via the presence



**Figure 6.** Proposed anchoring modes for the Mo on Brønsted acid sites.

of Brønsted acidity in the vicinity of a Mo center is the active site for natural gas conversion into aromatics.<sup>18,22,23</sup> During the catalyst synthesis, MoO<sub>3</sub> crystallites were first dispersed on the zeolite outer surface and then migrated as (MoO<sub>3</sub>)<sub>n</sub> oligomers into the zeolite channels.<sup>48</sup> By performing infrared studies, these authors came to the conclusion that MoO<sub>x</sub> interacts with framework oxygens to form isolated monomolybdate species (MoO<sub>4</sub><sup>2-</sup>).<sup>48</sup> As isolated MoO<sub>4</sub><sup>2-</sup> species migrate via surface or gas-phase diffusion, they react with H atoms at exchange sites to form (MoO<sub>2</sub>(OH))<sup>+</sup> species, which can condense to produce a (Mo<sub>2</sub>O<sub>5</sub><sup>2+</sup>) dimer.<sup>18</sup> Nevertheless, free cations do not exist inside zeolites.<sup>6</sup> So these species are rather in a (Mo<sub>2</sub>O<sub>7</sub>) form via stabilization by two nucleophilic oxygens from the framework. The effective mode of coordination between molybdenum species and the Brønsted acid sites is crucial to activate the stable C–H bonds from methane.<sup>22</sup> In this work, we have observed by <sup>27</sup>Al MAS NMR, NH<sub>3</sub>-TPD, and H/D exchange that the way of bonding differs either with a change in the density of Brønsted acid sites or with the Mo loading (see section 3).

Table 3 presents the number of hydrons consumed per Mo introduced. It shows that 2 H atoms are replaced by one Mo atom after the introduction of 2 and 4 wt % of Mo in the zeolite presenting the highest number of Brønsted acid sites (Si/Al = 15). In other words, a monomeric (MoO<sub>2</sub>)<sup>2+</sup> species is bonded to two framework oxygens, thus forming a bidentate species as presented in Figure 6. The number of anchoring sites is high enough (1.04 mmol of OH/g) to disperse those species (4 wt % Mo corresponds to 0.40 mmol of Mo/g). Howe et al. have proposed the formation of the same Mo complex on the surface of the FAU zeolite.<sup>49</sup>

When the Si/Al = 40 (0.41 mmol of OH/g), it appears that the number of hydrons replaced by Mo is for each loading below unity (0.94 for 2 wt % and 0.53 for 4 wt %). This indicates that the mode of bonding is completely different. The consumption of close to one hydron per Mo, when the loading is 2 wt %, suggests that in this case, dimeric Mo species are connected to two distinct acid sites (see Figure 6) as proposed by Iglesia<sup>18</sup> or Bao.<sup>56</sup>

Studies from the group of Bell devoted to the occupation of T sites by Al as a function of the Si/Al ratio further support the necessity of forming a dimer to overcome the long distance between two Al when Si/Al > 25.<sup>50</sup> On the contrary to (MoO<sub>2</sub>)<sup>2+</sup>, the dimer (Mo<sub>2</sub>O<sub>5</sub>)<sup>2+</sup> can be grafted to two sites where the second Al belongs to the NNN or even NNNN (next next nearest neighbor) site. The relatively high probability of having a second Al atom in the same unit cell has been further evidenced by different groups.<sup>51–53</sup> However, when the loading was increased to 4 wt %, the number of grafting sites becomes too low to allow all the Mo species to adopt their dimeric geometry. The formation of extraframework polymolybdates or alumino-molybdate species cannot be avoided in this case as evidenced by BET (cf. Table 2). In summary, from our data, one can propose the formation of a monomeric bidentate species when the Si/Al is low (high Al content), similar to the structure observed in HY zeolite.<sup>49</sup> When the Si/Al ratio is higher (low Al content), the distance between two Brønsted acid sites

becomes too high for the formation of such bidentate complex. Therefore, a dimeric Mo complex is formed via condensation of two monomeric species to overcome the distance between the two grafting sites. By choosing the MFI zeolite having an appropriate density of OH groups to suit the desired Mo loading, one should be able to tailor the type and nature of Mo–oxo cations formed and thus to modify the catalytic properties of the material. Early results obtained in our group for the dehydroaromatization reaction of methane performed with the 2/15 (monomeric bidentate species) and the 2/40 (dimeric monodentate species) catalysts conducted to aromatic yields of 17% and 10%, respectively.<sup>26</sup>

In addition to allowing the definition of the chemical formula of zeolites (especially the Si/Al ratio), this method also permits investigation of the nature and mode of bonding of transition metal complexes via the quantification of Brønsted acid sites consumed per metal–oxo cation introduced. This opens new routes for the preparation of either single-site heterogeneous catalysts<sup>19</sup> or bifunctional materials with optimal loading and site geometry.

## 5. Conclusions

Unlike many other methods which are mainly destructive and hence limited by mass transfer constraints, the shape of the catalytic bed, and the need to reach a thermodynamic equilibrium between a basic probe and the solid surface, this H<sub>2</sub>O/D<sub>2</sub>O isotope exchange technique counts the total number of Brønsted acid sites in solid acids. Furthermore, this “anhydride method” can also be applied to characterize the nature and bonding of transition metal complexes in their zeolite host. In the present work, this new method was applied to get more insight about the grafting of molybdenum inside the channels of ZSM-5 zeolites with different Si/Al ratios. Thanks to this method, used in combination with <sup>27</sup>Al MAS NMR and NH<sub>3</sub>-TPD, we were able to show that the anchoring mode of the molybdenum is strongly linked with the Si/Al ratio of the starting ZSM-5 zeolite: monomeric bidentate species at low Si/Al ratio and dimeric monodentate species at high Si/Al ratio. So, we were able to develop a useful tool to characterize new tailor-made Mo-ZSM-5 catalysts possessing an optimized amount and distance between the active sites for methane conversion into aromatics. In conclusion, this strategy opens a new route for the investigation of one of the major problems in catalysis which is the relationship between structure and reactivity of a catalytic material.

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