

# Stoichiometry of Reaction between MoO<sub>3</sub> and OH Groups of Alumina

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A series of oxidic MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts with different Mo loading was prepared by reaction of alumina (172 m<sup>2</sup>/g) with aqueous slurry of MoO<sub>3</sub> and by conventional impregnation with ammonium heptamolybdate. Surface concentrations of OH groups on the samples have been determined as a function of pretreatment temperature (160–500°C) and loading (up to 19.3% MoO<sub>3</sub>) by titration with dimethylzinc reagent. It was found that consumption of OH groups of alumina by MoO<sub>3</sub> proceeds during catalyst calcination and is completed already at 315°C. Further thermal treatment led only to dehydroxylation of alumina support. The gradual consumption of OH groups by MoO<sub>3</sub> can be monitored up to saturation loading 14.4% MoO<sub>3</sub>. It was described by a linear decrease of the number of OH groups up to about 7.8% MoO<sub>3</sub>, followed by a nonlinear dependence between 7.8–14.4% MoO<sub>3</sub>. An expression describing the change of OH/Mo stoichiometry (OH consumed per Mo atom) with MoO<sub>3</sub> loading was derived. The OH/Mo value decreased from about 2 for the lowest MoO<sub>3</sub> loadings to about 0.8, close to 14.4% MoO<sub>3</sub>. Above this loading, the content of OH groups decreased to 20–25% of the original value and remained constant irrespective of the excess of MoO<sub>3</sub> added. As a consequence, the OH/Mo stoichiometry approached zero. The residual hydrogen is ascribed mainly to the nonreactive hydroxyls of alumina and probably to a small extent to the Mo–OH groups originating from MoO<sub>3</sub>. © 1997 Academic Press

## INTRODUCTION

The majority of supported Mo catalysts is prepared by deposition of ammonium heptamolybdate (AHM) on alumina support. This salt is transformed partially into molybdate ions by interaction with basic OH groups of the alumina during impregnation. During calcination of the catalyst, molybdate ions react with OH groups under formation of stable Al–O–Mo bonds and release of water (1, 2). Interaction between AHM or molybdate ions with OH groups of the support was the subject of numerous, mostly spectroscopic studies confirming that the formation of an MoO<sub>3</sub> overlayer is accompanied by gradual consumption of free OH groups (3–10). It is believed that the density and availability of OH groups and the MoO<sub>3</sub> loading are

important factors controlling the formation of the resulting surface structures (2, 4). The deeper understanding of this chemistry requires more quantitative information about the mechanism. However, in contrast to a large amount of qualitative data reported in literature, quantitative studies are scarce. The stoichiometry of reaction between the molybdate ion and OH groups of alumina can be calculated from the decrease of the OH groups after deposition of a known amount of Mo atoms and expressed as the ratio OH/Mo (OH removed per Mo atom). The main problem seems to be, in our opinion, the determination of the amount of OH groups. Different methods like H–D exchange (3), chemical methods combined with IR spectroscopy (4, 11), FTIR (6), or NMR spectroscopy (8–10, 12) have been used for this purpose.

Millman *et al.* (3) determined the content of OH groups on  $\gamma$ -alumina (192 m<sup>2</sup>/g) and on the catalyst with 12% MoO<sub>3</sub> loading by means of H–D exchange after pretreatment between 20 and 500°C. The content of OH groups decreased after reaction with AHM at 500°C by about 80% and 20% of OH groups remained on the catalyst. The determined OH/Mo values were about 1.4 and 1.0 at 300 and 500°C, respectively. The mean value calculated for the whole temperature range 20–500°C was 1.7 ± 0.6.

Topsøe and Topsøe studied the consumption of OH groups on the catalysts with 6–18% MoO<sub>3</sub> by FTIR spectroscopy (6). The deposition of 18% MoO<sub>3</sub> removed all free OH groups of  $\eta$ -alumina (230 m<sup>2</sup>/g) after treatment at 450°C leaving behind bulk and H-bonded hydroxyls. The OH/Mo values were calculated from the absolute value of the OH concentration on alumina taken from the literature (4.4 OH/nm<sup>2</sup>) and the relative decrease of the IR absorbances of the reactive hydroxyls. The OH/Mo values decreased progressively from 1.4 to 1.1, when the MoO<sub>3</sub> loading increased from 6 to 15% MoO<sub>3</sub>.

In a similar study, Jacobsen *et al.* (9) found an OH/Mo value equal to about 1.2 by means of <sup>1</sup>H MAS NMR for an amount of MoO<sub>3</sub> between 0 and 15% deposited on  $\eta$ -alumina (230 m<sup>2</sup>/g). The decrease of the total <sup>1</sup>H signal was linear with increasing Mo loading and the OH/Mo value was considered constant in the whole range of loading studied.

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Kraus and Prins (10) found by quantitative analysis of the proton NMR spectra that deposition of 18% MoO<sub>3</sub> on  $\gamma$ -alumina (230 m<sup>2</sup>/g) removed 80% of the total amount of OH groups. Only basic groups were removed at low loading, up to 5% MoO<sub>3</sub> and the OH/Mo value was slightly higher than 1. Acidic OH groups were removed at higher loadings and the total OH/Mo value was about 1.8.

Van Veen *et al.* (11) used the sorption of MoO<sub>2</sub>(acac)<sub>2</sub> for the determination of basic OH groups of alumina. OH/Mo values of about 1.6 and 0.6, corresponding to loadings of 2.6 and 10% MoO<sub>3</sub> on  $\gamma$ -alumina (250 m<sup>2</sup>/g), respectively, can be calculated from the published OH values and relative changes of IR absorbances of the high frequency band after treatment at 450°C.

The common feature of all these OH/Mo stoichiometries is that they represent average values, calculated always for the interval between zero and the given MoO<sub>3</sub> loading. A somewhat different approach was taken in the study of Okamoto and Imanaka (4) who reported OH/Mo values evaluated for discrete intervals of loading. In their study, IR spectroscopy in combination with volumetric CO<sub>2</sub> adsorption was used for the determination of the OH groups. The decrease of the basic and neutral OH groups was linear up to a loading of about 1 Mo/nm<sup>2</sup> and it was less pronounced for higher loadings. The OH groups corresponding to the lowest frequency band, 3590 cm<sup>-1</sup>, were only negligibly consumed and most of them remained intact. Total OH/Mo values decreased in the order 2, 0.6, and 0.2 for increasing Mo loading <1, 1–3, and 3–5 Mo/nm<sup>2</sup>, respectively. Above 5 Mo/nm<sup>2</sup>, the stoichiometry approached zero. The OH/Mo values close to 2 are in good agreement with the formation of tetrahedrally coordinated Mo species (Mo<sub>tet</sub>) at low loading, and the decrease of stoichiometry at higher loadings is explained by the formation of polymolybdate species.

Comparison of all these data suggests that the number of OH groups consumed by one Mo atom seems to be typically in the range 1.1–1.6 and most probably, it decreases with increasing MoO<sub>3</sub> content. However, a more exact quantification is missing up to now. Also, a lack of data concerning the OH group quantity, especially that on highly loaded MoO<sub>3</sub>/alumina catalysts, is apparent from the literature.

The main aim of the present work was to obtain quantitative data about the content of surface OH groups and about the stoichiometry of reaction between MoO<sub>3</sub> and surface OH groups on alumina during catalyst calcination. We attempted to describe the consumption process mathematically and to derive the equation describing the change of OH/Mo stoichiometry as a function of MoO<sub>3</sub> loading. A series of MoO<sub>3</sub>/alumina catalysts with loading up to 19.3% MoO<sub>3</sub> was chosen as a model system. The number of OH groups was determined by a sensitive method based on the reaction with an organometal-

lic reagent, specific for the determination of surface active hydrogen.

## EXPERIMENTAL

$\gamma$ -alumina used in this study was prepared from aluminium hydroxide (Condea Chemie, Germany) which was extruded, grinded and sieved to a 0.16–0.32-mm particle size (13). The fraction was dried at 160°C, calcined in air at 500°C for 2 h and stored. The BET surface area was 172 m<sup>2</sup>/g, pore volume 0.54 ml/g and average pore diameter 11 nm. This support was used for the study of the effects of temperature and time of pretreatment. The support was immersed in water for 2 h and dried in air at 160°C for 2 h in order to obtain the same degree of hydration as that of support in the catalysts when studying the effect of MoO<sub>3</sub> loading. A sample of bulk MoO<sub>3</sub> was prepared by thermal decomposition of ammonium heptamolybdate (AHM) at 450°C for 4 h in air. The BET surface area was 1.2 m<sup>2</sup>/g.

A series of MoO<sub>3</sub>/alumina catalysts containing up to 14.4% MoO<sub>3</sub> (samples 1–6) was prepared by equilibrium adsorption of MoO<sub>3</sub> in the aqueous slurry with alumina at 20°C. This so called “slurry impregnation method” (SIM) procedure was described in detail elsewhere (13). The content of Mo in these catalysts was determined by the inductively coupled plasma (ICP) method. Samples of catalysts were dried in air at 160°C for 2 h and stored. Two additional samples of highly loaded MoO<sub>3</sub>/alumina catalysts containing 13.2 and 19.3% MoO<sub>3</sub> (samples 7, 8) were prepared by the pore filling method using an aqueous solution of AHM at natural pH of the impregnating solution. These catalysts were calcined at 500°C for 2 h to assure complete decomposition of AHM.

Surface concentrations of OH groups of alumina, bulk MoO<sub>3</sub>, and MoO<sub>3</sub>/alumina catalysts were determined by a titration method developed earlier and described in detail elsewhere (14). The samples were titrated by pulses of dimethylzinc-tetrahydrofuranate (DMZ) in a stream of He at 130°C and the methane evolved by reaction with OH groups was detected by TCD. Helium (Messer Griesheim, 99.996%) was purified by passing through a unit with activated molecular sieve (Linde, A5) and a 3-m capillary immersed in liquid nitrogen. Before measurement, samples were pretreated between 160–500°C for 1–6 h in dry He. Pretreatment and the following determination of OH groups was performed *in situ* excluding any contact of sample with ambient atmosphere. The reproducibility of determination was better than 5%. The detection limit of the OH groups was about 2  $\mu$ mol on the catalyst charge used ( $\approx$ 20 mg).

The BET surface area and pore size distribution of the support was measured by nitrogen adsorption on a Micromeritics Digisorb 2600 instrument.

## RESULTS AND DISCUSSION

*Determination of OH Groups by Dimethylzinc—Relation to the Other Methods*

The quantitative determination of surface OH groups by organometals was already reviewed by Boehm (15). The reaction with dimethylzinc tetrahydrofuranate (DMZ), performed in a pulse arrangement in the gas phase has been used for oxides like alumina and silica (16). The method has the advantage of easy determination of the quantity of OH groups and a high sensitivity because of the chromatographic detection of methane, the amount of which is proportional to the concentration of OH groups. This is a significant difference compared to IR or NMR techniques, where quantification of spectra can be complicated by different factors, e.g. by vibrational broadening due to H-bonding, the necessity to use a deconvolution procedure which contributes to uncertainty in the determined values and in some cases can lead to problems to detect all OH groups present (12). The DMZ method is free of these disadvantages, it gives absolute values related to the surface of the catalyst. However, it has a limitation compared to the IR or NMR techniques, because it cannot resolve different forms of hydrogen such as free, H-bonded hydroxyls and physisorbed water, if present.

For alumina supports, the DMZ method gives results very near to those obtained by H-D exchange or gravimetry (16) which are in close agreement with generally accepted values published by Knözinger and Ratnasamy (17). The sensitivity is advantageous when low surface area solids like unsupported MoO<sub>3</sub> are studied. The concentration of OH groups on our MoO<sub>3</sub> sample pretreated at 400°C was about 2.7 OH/nm<sup>2</sup>, i.e., very near the value 2.4 found earlier by the same method by Halász and Gáti (18).

Preliminary experiments with MoO<sub>3</sub>/alumina catalysts confirmed that the course of titration was quite similar to that for alumina support; i.e., the amount of CH<sub>4</sub> evolved by the reaction of OH groups decreased rapidly to zero after each pulse, and a sharp end point of the titration was achieved. This showed that no bulk reaction or catalytic decomposition of DMZ occurs on the catalysts studied.

*Effect of Temperature and Duration of Catalyst Pretreatment*

The temperature of catalyst pretreatment was studied because it is known to affect the OH density significantly. The dependence of the OH surface concentrations on pretreatment temperature for both alumina and a catalyst containing 13.2% MoO<sub>3</sub> (sample 5) is shown in Fig. 1. As expected, the catalyst contained much less OH than the original alumina support. The decrease of the OH concentration of the catalyst was relatively strong up to 315°C and after reaching this temperature it became much smaller, following the trend similar to alumina support. The overall amount of OH

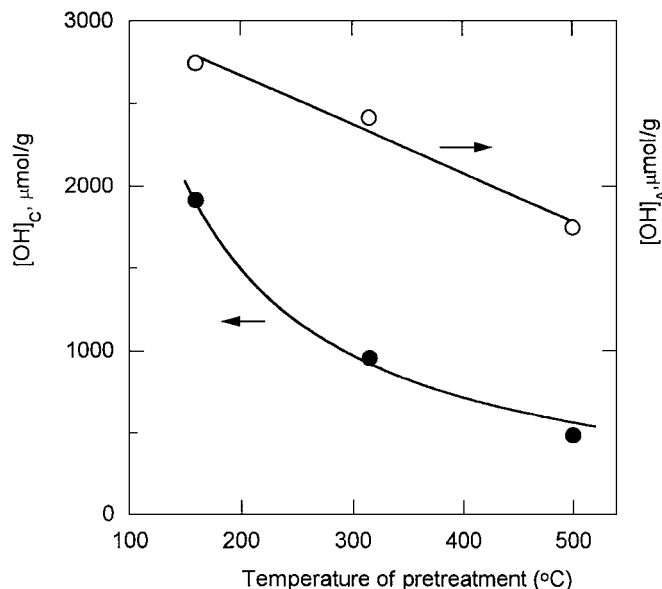


FIG. 1. Effect of temperature of pretreatment on the OH content: ○ alumina; ● sample 5. Time of pretreatment 1 h.

groups of the support consumed by reaction with MoO<sub>3</sub> was calculated for all three temperatures according to Eq. [1],

$$\sum \text{OH} = [\text{OH}]_A (1 - [\text{Mo}]/6945) - [\text{OH}]_C, \quad [1]$$

where [OH]<sub>A</sub> and [OH]<sub>C</sub> stand for the amounts of OH groups (μmol/g) on alumina and the catalyst, respectively. The term [Mo] corresponds to the MoO<sub>3</sub> loading in μmol/g and the ratio [Mo]/6945 expresses the weight fraction of MoO<sub>3</sub> in the catalyst. The amounts of consumed OH groups were 470, 1130, and 1030 μmol/g for pretreatment temperatures of 160, 315, and 500°C, respectively. This suggests that the reaction between MoO<sub>3</sub> and the OH groups of the alumina proceeds during thermal treatment and is already completed below 315°C, since the amount of OH consumed did not increase by treatment at higher temperatures. The decrease of the OH concentration above this temperature, apparent in Fig. 1, is caused only by dehydroxylation of the alumina support. This interesting result shows that the temperature which is required for the condensation reaction of MoO<sub>3</sub> is in fact much lower than temperatures usually used to prepare catalysts from AHM, i.e. about 500°C. However, in the latter case, the higher temperature is needed for decomposition of the ammonium salt, which only proceeds above 350°C (1).

The second parameter studied was the duration of catalyst pretreatment. The effect of time of drying for alumina and two catalysts with different Mo loading is shown in Fig. 2. A smaller decrease in OH concentration was observed within the interval 1–2 h of drying, further prolongation up to 6 h usually caused a change below 10%. This difference was considered to be within the limits of

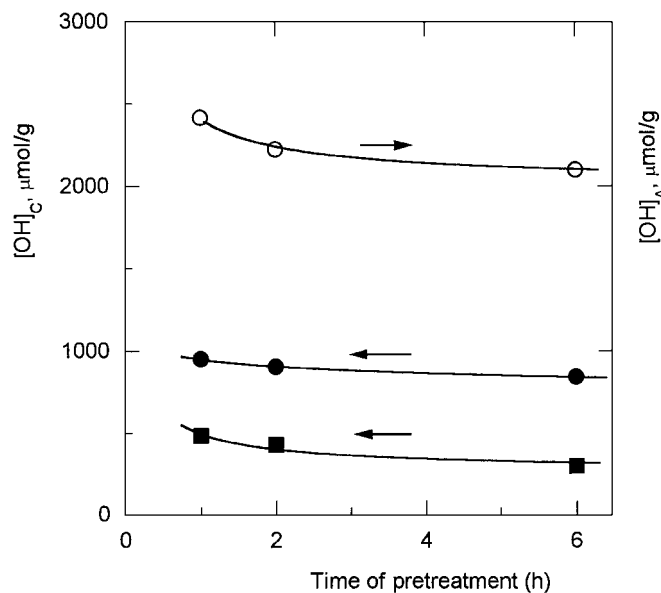


FIG. 2. Effect of time of pretreatment on the OH content: ○ alumina, 315°C; ● sample 5, 315°C; ■ sample 8, 500°C.

experimental error and the values obtained after 2 h of pretreatment have been considered as representative to distinguish differences among the catalysts studied.

#### Effect of Loading—Stoichiometry of Reaction between MoO<sub>3</sub> and OH Groups of Alumina

Table 1 summarizes the values of OH concentrations of alumina support, bulk MoO<sub>3</sub>, and all the prepared catalysts. Because the condensation reaction between OH groups of alumina and MoO<sub>3</sub> was completed already at 315°C, the effect of loading on samples 1–6 was studied also at this

TABLE 1  
MoO<sub>3</sub> and OH Contents in Catalysts after Treatment at a Given Temperature

Sample	Preparation <sup>a</sup>	[Mo] (μmol/g)	[OH] (μmol/g)	
			315°C	500°C
Alumina <sup>b</sup>	—	0	2510	1745
MoO <sub>3</sub>	—	—	—	5.4 <sup>c</sup>
1	2.0-MoO <sub>3</sub> /SIM	139	2250	—
2	4.8-MoO <sub>3</sub> /SIM	333	1630	—
3	7.8-MoO <sub>3</sub> /SIM	542	1265	—
4	11.0-MoO <sub>3</sub> /SIM	764	1095	—
5	13.2-MoO <sub>3</sub> /SIM	917	905	485
6	14.4-MoO <sub>3</sub> /SIM	1000	715	—
7	13.2-AHM/Pore filling	917	—	450
8	19.3-AHM/Pore filling	1340	—	430

<sup>a</sup> Numbers correspond to wt% MoO<sub>3</sub>.

<sup>b</sup> Hydrated and dried at 160°C for 2 h.

<sup>c</sup> After pretreatment at 400°C for 2 h in He.

temperature. On the other hand, catalysts prepared from AHM were treated at 500°C in order to fully decompose the ammonium salt and they were compared with alumina and sample 5 after treatment at 500°C. The OH content of alumina, given in Table 1, corresponds to a sample which was hydrated in water and dried at 160°C, i.e. treated in the same way as the support in the catalyst. Alumina and the catalysts prepared from MoO<sub>3</sub> (samples 1–6) represent a set with loading between zero and 14.4% MoO<sub>3</sub>. The value of 14.4% MoO<sub>3</sub> is the saturation loading which was obtained by the slurry impregnation method and corresponds to a coverage of 4.1 Mo/nm<sup>2</sup>. The MoO<sub>3</sub> phase in these catalysts is present in a well-dispersed state, as was proved by XPS and XRD measurements (13). Sample 8 prepared from AHM by pore filling represents a catalyst with MoO<sub>3</sub> loading substantially exceeding the adsorption capacity of our alumina used.

Table 1 shows that deposition of MoO<sub>3</sub> up to 14.4% (samples 1–6) was accompanied by a gradual decrease of the OH concentration by roughly 72% after treatment at 315°C. A similar decrease was caused by deposition of 13.2% MoO<sub>3</sub> in the form of AHM, followed by treatment at 500°C. This change is in good agreement with similar data concerning interaction in the AHM–alumina system (3, 4, 6–11). Because a catalyst prepared from AHM (sample 7) treated at 500°C was available, we estimated the mean OH/Mo stoichiometry for comparison with values published by other authors by the formula OH/Mo<sub>mean</sub> = ΣOH/[Mo], in which ΣOH was calculated according to Eq. [1]. The value of 1.16 obtained is practically identical to the values 1.0–1.2 obtained by other methods for catalysts of approximately the same MoO<sub>3</sub> loading pretreated at 450–500°C (3, 6, 9). This suggests that data obtained in this work are comparable to those obtained by means of <sup>1</sup>H NMR or FTIR.

One additional conclusion follows from the data in Table 1 and should be mentioned in this connection; this is the effect of the Mo precursor. The OH content of the catalyst prepared from AHM (sample 7) was practically the same as that of the catalyst prepared directly from MoO<sub>3</sub> (sample 5) and, consequently, the mean OH/Mo value calculated for sample 7 was practically the same as that for sample 5 (OH/Mo = 1.12). This shows that there is not a substantial difference between the extent of interaction of both Mo precursors with the alumina support. This behavior can easily be understood, taking into account that AHM is transformed into molybdate ion or thermally decomposed to MoO<sub>3</sub> during catalyst heating, followed by a condensation reaction, as in the case of direct deposition of MoO<sub>3</sub>.

The OH/Mo value mentioned above was calculated from one value of OH concentration only and for a broad range of MoO<sub>3</sub> loading. It represents the average value and it is logical that it can differ considerably from the value

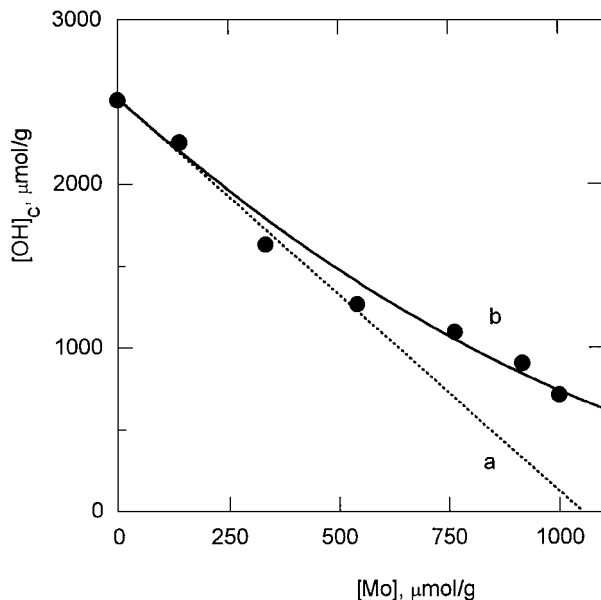


FIG. 3. The OH content as a function of MoO<sub>3</sub> loading after pretreatment at 315°C for 2 h: (a) fit by Eq. [2]; (b) fit by Eq. [3].

calculated for a smaller interval. This was the reason why we attempted to obtain more exact description, as demonstrated in the following.

The OH concentrations of catalysts prepared from MoO<sub>3</sub> are plotted against the MoO<sub>3</sub> content in Fig. 3. The decrease of OH concentration was linear up to a loading of about 500 μmol/g (≈7.8% MoO<sub>3</sub>) followed by a nonlinear decrease up to 1000 μmol/g (14.4% MoO<sub>3</sub>). The part of the data concerning samples 1–3 was described by Eq. [2],

$$[\text{OH}]_c = 2520 - 2.39 [\text{Mo}], \quad [2]$$

and the corresponding fit is shown by line a. Data in the whole range of Mo loading were fitted by a function derived from Eq. [2] by addition of a nonlinear term,

$$[\text{OH}]_c = 2520 - 2.39 [\text{Mo}] + K [\text{Mo}]^2. \quad [3]$$

The value of constant  $K$  was found to be  $6 \times 10^{-4} \text{ g}^2 \mu\text{mol}^{-2}$  by an optimisation procedure and the fit of the data is shown by curve b. Equation [3] allows us to monitor the continuous change between the linear and nonlinear parts. At low MoO<sub>3</sub> loadings, the value of the nonlinear term is small and the function approaches a straight line.

The overall amounts of OH groups consumed by MoO<sub>3</sub> were calculated according to Eq. [1] and plotted against the MoO<sub>3</sub> content in Fig. 4. The amount of OH groups increased linearly up to MoO<sub>3</sub> loading of about 500 μmol/g, and after that the slope decreased, indicating that the stoichiometry changes. The slope of the curve fitting the experimental points gives information about the reaction stoichiometry. The experimental points corresponding to the low range

of loading (samples 1–3) were treated by linear regression (line a) and the value of the slope found by this procedure was 2.01. This means that the number of OH groups consumed by one Mo atom is near 2, in excellent agreement with the generally accepted idea of the reaction of two OH groups with one Mo atom in tetrahedral coordination at low MoO<sub>3</sub> loading. Data in Fig. 4 suggest that this situation lasts more or less up to loading about 500 μmol/g. The expression describing the experimental data in the whole range of MoO<sub>3</sub> loading was obtained by the following procedure. Combining Eqs. [1] and [3] led to Eq. [4], the course of which is shown by curve b,

$$\sum \text{OH} = 2.03 [\text{Mo}] - 6 \times 10^{-4} [\text{Mo}]^2. \quad [4]$$

This expression allows us to obtain the equation describing the change of the OH/Mo stoichiometry as a function of MoO<sub>3</sub> loading by taking its derivative against [Mo]. This procedure led to Eq. [5],

$$\text{OH/Mo} = \frac{d \sum \text{OH}}{d [\text{Mo}]} = 2.03 - 1.2 \times 10^{-3} [\text{Mo}]. \quad [5]$$

The curve calculated according to Eq. [5], together with points corresponding to catalysts 1–6, is shown in Fig. 5. This figure shows that the OH/Mo stoichiometry approaches 2 close to zero loading and decreases to about 0.8 at a loading of 14.4% MoO<sub>3</sub>. This supports strongly the assumption about the bonding of one Mo atom via two oxygen bridges to the alumina surface at the first stage of MoO<sub>3</sub> deposition. At the same time, the decrease of stoichiometry at higher loadings is in accordance with most earlier

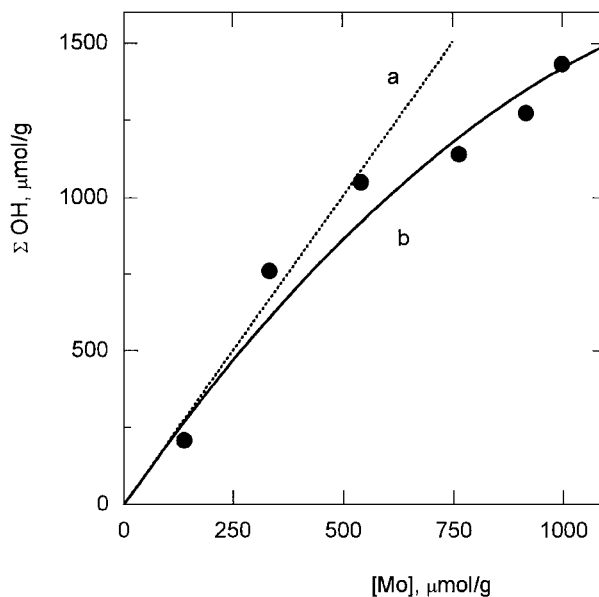


FIG. 4. Overall amount of consumed OH groups as a function of MoO<sub>3</sub> loading: (a) fit by linear regression; (b) fit by Eq. [4].

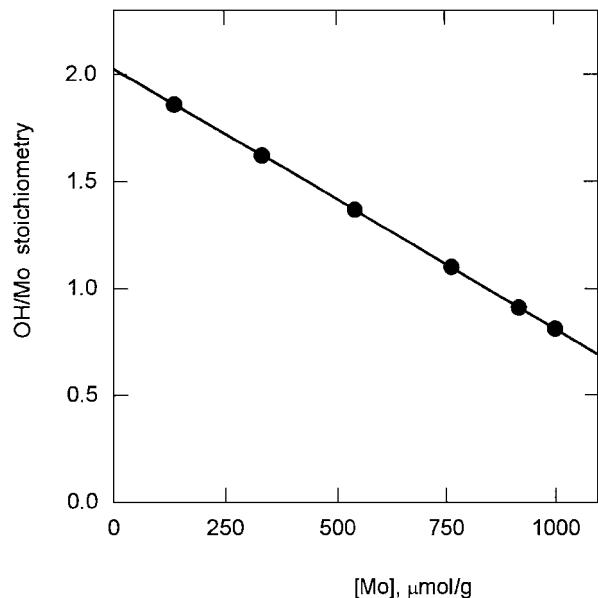
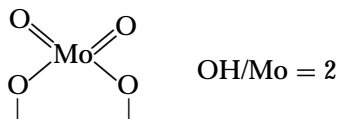


FIG. 5. Stoichiometry OH/Mo as a function of MoO<sub>3</sub> loading: calculation according to Eq. [5].

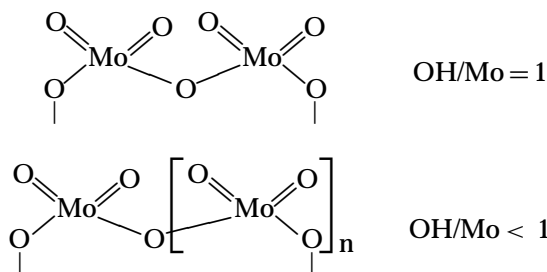
observations made on the AHM-alumina system (2, 4, 6, 11). The stoichiometry values found in this work are close to those reported by Okamoto and Imanaka (4) for the range of the lowest Mo loading (OH/Mo = 2). In the middle range, 1–3 Mo/nm<sup>2</sup>, our values (1.8–1) seem to be somewhat higher than those reported in Ref. (4), i.e. >0.6.

The decrease of OH/Mo stoichiometry can be explained considering both the ratio between the numbers of Mo atoms and OH groups in contact, together with the accessibility of OH groups (2). During preparation of a catalyst with a small loading, for example below 8%, a relatively small portion of MoO<sub>3</sub> interacts with an excess of support having a rather high density of OH groups. The distance between the free OH groups is short and the conditions are therefore favorable for an almost selective reaction, keeping the OH/Mo stoichiometry close to 2.



During deposition of larger amounts of MoO<sub>3</sub> (8–14%), the first portion reacts according to the stoichiometry shown above and the concentration of the free OH groups decreases rapidly, i.e. almost two times faster than the increment in deposited Mo atoms. As the condensation reaction continues, the remaining part of MoO<sub>3</sub> will be in excess to the unreacted OH groups. This, together with the lower density of available OH groups, increases the probability for mutual condensation of MoO<sub>3</sub> into dimeric or different

polymeric structures for simplicity shown as



Formation of dimeric or polymeric structures is obviously accompanied by lower stoichiometry OH/Mo < 2, because only part of the OH groups of MoO<sub>3</sub> is consumed by reaction with alumina (2, 4). Our value of OH/Mo ≈ 0.8, corresponding to the loading of 1000 μmol/g (14.4% MoO<sub>3</sub>) shows that the presence of such structures is very probable. Nevertheless, catalysts 5 and 6 with a high MoO<sub>3</sub> loading represent still a well-dispersed state of molybdenum. Previous XPS measurements of these catalysts showed that the ratio  $I_{\text{Mo}}/I_{\text{Al}}$  did not deviate markedly from the line corresponding to monomolecular dispersion (13). This high Mo dispersion is evidently maintained after catalysts sulfidation. Tests of catalytic activity in HDS of thiophene performed previously showed that the activity of samples 1–6 increased linearly with MoO<sub>3</sub> loading and a change in catalytic behavior, which could be related to a decrease of stoichiometry, was not observed (13).

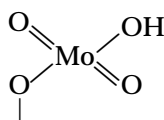
OH/Mo values shown in Fig. 5 and also those reported by Okamoto and Imanaka (4) suggest a continuously decreasing trend with increasing MoO<sub>3</sub> loading above 1000 μmol/g. In attempts to obtain more information, we included a sample with 19.3% MoO<sub>3</sub> (1340 μmol/g) in the set of catalysts studied. The OH concentration of this catalyst pretreated at 500°C is given in Table 1. In contrast to expectation, the increase of MoO<sub>3</sub> loading up to 19.3%, which is substantially above the adsorption capacity of our alumina used, did not lead to a decrease of the OH concentration. Its content was practically the same as that of the catalyst with a lower MoO<sub>3</sub> loading. Moreover, Fig. 2 shows that it decreased only negligibly after prolonged heat treatment to about 350 μmol/g. This result shows clearly that this catalyst contains still a certain fraction of hydrogen, in this case about 20% of original value, which seems to be very resistant to removal. The presence of such a fraction of hydrogen detected by DMZ is not very surprising in the light of recent findings. It was observed that a catalyst with 25% MoO<sub>3</sub> on alumina (180 m<sup>2</sup>/g) possesses still hydrogen detected by <sup>1</sup>H NMR (8). Also catalysts with 12–18% MoO<sub>3</sub> display a broad IR band centered at about 3600 cm<sup>-1</sup>, related usually to bulk hydroxyls and H-bonded structures (6), possess Brønsted acidity (19) or about 500 μmol/g acidic hydroxyls (10).

In our case, the origin of the residual fraction of hydrogen cannot be unambiguously specified because DMZ

cannot differentiate between its different forms. Nevertheless, some conclusions can be drawn. First, the presence of physisorbed water as a possible source can almost certainly be excluded because of our treatment at 500°C for 6 h. Second, it is clear that this hydrogen corresponds only to the surface of the catalyst, because DMZ cannot enter the bulk. Two possible explanations seem to be much more probable. The first can be the presence of a smaller fraction of OH groups of support which react easily with DMZ but not with MoO<sub>3</sub>. This could be the relatively most acidic free hydroxyls of alumina (4, 10) or different H-bonded structures, which are known to remain on the catalyst after consumption of reactive OH groups (6). These forms of hydrogen are always present on alumina and we suppose that this effect occurs also in our case. The concentration of residual acidic hydroxyls found by proton NMR on a catalyst with a MoO<sub>3</sub> coverage of 3.9 Mo/nm<sup>2</sup> was about 1.7 OH/nm<sup>2</sup> (10). The hydrogen content of our sample 7, prepared from the same type of alumina support and having a similar MoO<sub>3</sub> coverage (3.7 Mo/nm<sup>2</sup>), was 1.8 OH/nm<sup>2</sup>. This value is practically identical to that found by proton NMR. Then it is logical to assume that the majority of residual hydrogen present on our highly loaded catalyst is formed by nonreactive acidic hydroxyls of the support.

The second possibility could be the presence of residual Mo–OH groups originating from the excess of MoO<sub>3</sub>. The presence of OH groups on bulk MoO<sub>3</sub> was confirmed by reaction with DMZ earlier (18) and also in the present work. We assume that on the highly loaded sample 8, some part of MoO<sub>3</sub> is present as a bulk phase carrying some residual Mo–OH groups. This effect can occur only in the range of the highest MoO<sub>3</sub> loading, whereas on the samples 1–6 it can be excluded because of the absence of bulk MoO<sub>3</sub> (13).

Another question is the presence of terminal Mo–OH groups bonded via an oxygen bridge to the aluminium atoms and their possible effect on calculated values of OH/Mo stoichiometry:



Direct spectroscopic evidence for this structure does not exist up to now and also our data cannot confirm its existence. Nevertheless, its formation was postulated recently on the basis of the generation of Brønsted acidity on alumina supported Mo catalysts (19) and we do not rule out its presence on samples with higher MoO<sub>3</sub> loading. The concentration of Brønsted acidic sites of catalysts containing 8 and 12% MoO<sub>3</sub> was reported to be about 80 and 150 μmol/g, respectively (19). However, these values are relatively low and comparison with data in Table 1 reveals that they represent about 7–17% of the OH groups of our catalysts with similar MoO<sub>3</sub> loading. We assume that calculated values of

OH/Mo stoichiometry cannot be affected to a large extent by the presence of such species.

The above-mentioned effect of nonreactive OH groups of support and also probably that of Mo–OH groups are obvious reasons why the overall concentrations OH groups does not decrease in the range of highest loading, i.e. above 14.4% MoO<sub>3</sub>. After consumption of the reactive hydroxyls, the residual amount of hydrogen is represented by nonreactive OH groups the amount of which remains constant. Under such conditions, the stoichiometry OH/Mo approached zero.

## CONCLUSIONS

1. Reaction of MoO<sub>3</sub> with OH groups of alumina proceeds during catalyst heating and is completed already at 315°C. There is no substantial difference in the extent of interaction between MoO<sub>3</sub> or AHM with OH groups of alumina.

2. The OH groups are gradually consumed by an increasing amount of MoO<sub>3</sub> up to saturation loading of 14.4% MoO<sub>3</sub> (4.1 Mo/nm<sup>2</sup>). This can easily be monitored by their decrease, and a model describing the change of OH/Mo stoichiometry with MoO<sub>3</sub> loading was derived. The model is based on the linear decrease of OH groups concentration at the lower MoO<sub>3</sub> loading (<7.8% MoO<sub>3</sub>) followed by a nonlinear decrease between 7.8–14.4% MoO<sub>3</sub>.

3. This process can be considered as a well-defined stoichiometric reaction only in the region of low MoO<sub>3</sub> loading, where the stoichiometry is close to 2 in accordance with the formation of Mo<sub>tet</sub> species. The process becomes more complex as the loading increases. The formation of Mo<sub>tet</sub> diminishes while the condensation of MoO<sub>3</sub> becomes dominating. This is accompanied by a decrease of the stoichiometry because of lower density of OH groups of the support and a higher probability for condensation of MoO<sub>3</sub> into polymeric structures.

4. Above the saturation loading, the overall concentration of OH groups decreased to 20–25% of the original value which remains constant irrespective of the excess of MoO<sub>3</sub> added. As a consequence, the OH/Mo stoichiometry approached zero. The residual hydrogen is ascribed mainly to the nonreactive hydroxyls of the alumina and, probably, to a small extent to the Mo–OH groups originating from MoO<sub>3</sub>.

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