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The Active Site for Isoprene Hydrogenation on $MoS_2/\gamma\text{-}Al_2O_3$ Catalysts[1]

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Hydrogenation of 2-methyl-1,3-butadiene (isoprene) at 323 K has been used to probe highly coordinatively unsaturated molybdenum ions on a conventional $MoS_2/\gamma\text{-}Al_2O_3$ hydrotreating catalyst. These unsaturated molybdenum ions have been generated by reduction of the catalyst with H_2 at various temperatures between 293 and 1073 K. In parallel, the amounts of H_2S removed have been measured and the number of vacancies created, or the catalyst stoichiometry, has been deduced. The catalyst has been modeled according to a previously published geometrical model of hydrotreating catalysts [*Appl. Catal.* **13**, 127 (1984)]. Calculated and experimental stoichiometries lead us to identify the sulfur ions removed in the reduction temperature range 293–973 K as edge plane $(\bar{1}010)$ and $(10\bar{1}0)$ ions. A linear correlation has been found between the statistical amount of three-coordinatively unsaturated molybdenum ions in the $(\bar{1}010)$ edge plane of the MoS_2 slabs and hydrogenation activity.

INTRODUCTION

The identification of active sites remains one of the most challenging problems in heterogeneous catalysis. To achieve such a goal a well-known probe reaction and a known catalytic active phase structure, as well as a link between both, are needed. Such a link is provided by the concept developed by Siegel (*1, 2*) in which the number of coordinative unsaturations on a site and the set of elementary reactions involving hydrogen are connected. Thus, as illustrated by the large number of investigated oxides and sulfides (*3–7*), the hydrogenation and/or isomerization of mono- and diolefins appear to be useful probe reactions of different coordinatively unsaturated (cus) sites; however, in many cases, determination of the location of the sites remains difficult because of the complexity of the catalyst surface.

In previous work (*8*) we demonstrated that the $MoS_2/\gamma\text{-}Al_2O_3$ catalytic system, of paramount industrial importance particularly for reactions in which hydrogenation has an important role, can be modeled as small single slabs of MoS_2 dispersed on the alumina surface in accordance with electron micrograph pictures (*8–10*). Interestingly, the two-dimensional nature of MoS_2 and the known unreactivity of the basal plane of the slabs limit the possible site locations to edge or corner molybdenum ions. The reactivity of these sites has been underlined on many occasions such as for the chemisorption of various probe molecules, promoter locations, and catalytic reactions (*3, 11–14*).

In this work hydrogenation of 2-methyl-1,3-butadiene (isoprene) has been used to probe highly coordinatively unsaturated sites in $MoS_2/\gamma\text{-}Al_2O_3$. The hydrogenation activity was measured on a catalyst with controlled stoichiometries obtained by hydrogen reduction at various temperatures. This treatment generates different amounts of various "cus" sites at the periphery of the MoS_2 slabs. The hydrogenation activity has been correlated with the number of three-coordinate unsaturated sites deter-

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mined statistically from the modeling of the MoS_2/γ-Al_2O_3 catalyst structure, and unambiguous identification of the site location has been obtained. In addition, the oxidation number of the active Mo ions can be estimated leading to a fully described active site for isoprene hydrogenation on MoS_2/γ-Al_2O_3 catalysts.

EXPERIMENTAL

The catalyst was prepared by pore-filling impregnation of a γ-Al_2O_3 support (surface area 240 $m^2\ g^{-1}$, pore volume 0.57 $cm^3\ g^{-1}$) with an ammonium heptamolybdate solution, $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$ (from Merck). After digestion the sample was dried at 383 K overnight and calcined at 773 K for 4 h. The loading measured by microanalysis was 9.2 wt% Mo or 13.8 wt% MoO_3.

Isoprene (purum grade from Fluka) was used after purification by distillation under vacuum. All gases were purified by passage through a Pt/zeolite column and trapping of H_2O at 193 K.

Pretreatment and catalytic experiments were carried out at atmospheric pressure in an all-glass grease-free flow apparatus described elsewhere (*15*). The catalyst was sulfided with a H_2/H_2S (90/10) mixture at 623 K for 4 h (a common procedure used industrially and in this laboratory giving fully sulfided samples) and then cooled to room temperature. Then reduction pretreatments were performed under a purified flow at different temperatures (from room temperature up to 1073 K) for 12 h.

After each reduction, isoprene hydrogenation was performed at 323 K. Fifty milligrams of catalyst was used with a flow rate of 2.8 liters h^{-1} and a HC/H_2 ratio of 20/740. The reaction products were analyzed by gas chromatography using a 100-m squalane capillary column operating at 318 K and a flame ionization detector.

The conversions were measured at the steady state reached after 20 min and were never higher than 30%. A blank run on the sulfided alumina showed no detectable hydrogenation activity. Care was taken to avoid any air leak or oxygen contamination which would have resulted in a complete catalyst poisoning.

In separate experiments, the amounts of H_2S removed from 5 g of catalyst after different reduction pretreatments or purge under Ar were determined by iodometry after trapping in an iodine solution.

Microanalysis of oxides and some sulfided samples were performed by the Service Central d'Analyses CNRS.

RESULTS

The effect of reduction temperature on isoprene hydrogenation activity of MoS_2/γ-Al_2O_3 catalysts is reported in Fig. 1. A volcano-type curve is obtained with no detectable activity for reduction below 298 K or above 1073 K and with maximum activity at 823 K. The main products of this reaction were isopentane, 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene. Their distribution, which also depended on the reduction temperature, is discussed elsewhere (*16*); only the overall hydrogenation activity is considered in this work.

The number of anionic vacancies generated in the MoS_2 active phase was determined by measuring the amounts of sulfur removed at different temperatures of reduction. These amounts and the cumulated amounts versus the reduction temperature are reported in Figs. 2 and 3, respectively. Some of the measurements have been re-

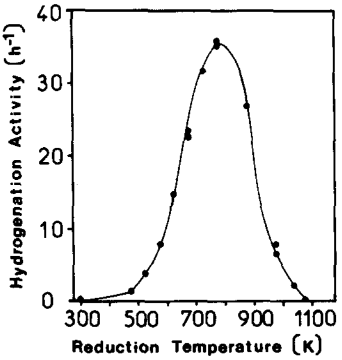


FIG. 1. Isoprene hydrogenation activity at 323 K versus prereduction temperature of MoS_2/γ-Al_2O_3.

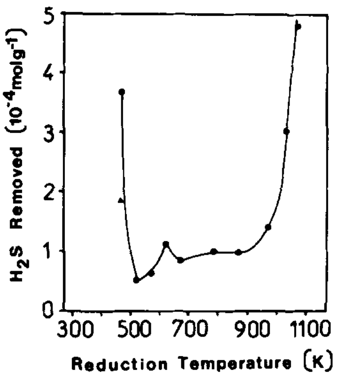


FIG. 2. Amounts of H_2S removed from MoS_2/Al_2O_3 at different reduction temperatures and after purging under Ar at 473 K (▲).

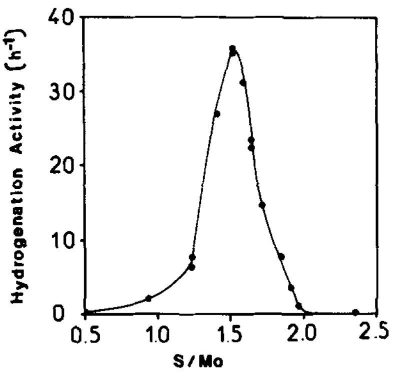


FIG. 4. Isoprene hydrogenation activity at 323 K versus S/Mo stoichiometry after reduction.

peated so that we can assume a reproducibility better than 2.5%.

Three temperature domains can be distinguished in Fig. 2. At temperatures lower than 473 K a large amount of H_2S (ca. 3.5×10^{-4} mol g^{-1}) is removed. Half of this amount (ca 1.8×10^{-4} mol g^{-1}) can, however, be removed by purging with Ar at the same temperature and is therefore not due to a reduction by H_2. Then, from 473 to 973 K, various quantities of H_2S (ca. 0.5 to 1.5×10^{-4} mol g^{-1}) are removed, with a small peak at 623 K. Finally, above 1073 K, a significant increase in H_2S production is observed.

From the curve in Fig. 3 and a quantitative analysis of the samples reduced at 473 K (S/Mo = 1.91) and 1038 K (S/Mo = 0.97), the stoichiometry of the sample can be deduced at each reduction temperature. These two reference samples have been chosen as they provide two limiting values. Starting from the 0.97 S/Mo ratio of the 1038 K reduced sample, a 2.00 value for the 473 K reduced sample is computed which can be compared with the 1.91 value obtained elsewhere (Service Central d'Analyses du CNRS) by quantitative analysis. The small difference (less than 5%) observed probably corresponds to the cumulated uncertainties in the amounts of H_2S removed at each reduction temperature. As a basis for the stoichiometric data used later in this work we have chosen for that sample a mean value of 1.96 as reference. The fully sulfided sample therefore has a S/Mo ratio of 2.36, and the Ar-purged sample has a 2.16 stoichiometry. The variation of the stoichiometry versus the temperature of reduction is reported in the right-hand scale of Fig. 3.

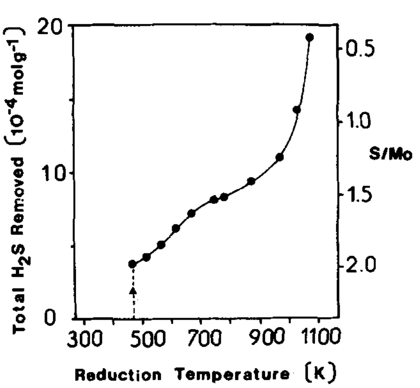


FIG. 3. Cumulated amounts of H_2S removed from MoS_2/Al_2O_3 (left) or S/Mo stoichiometry (right) versus reduction temperature or purge under Ar at 473 K (▲).

The activity variation versus the active phase stoichiometry can therefore be deduced and has been reported in Fig. 4. The maximum activity corresponds to an optimum stoichiometry of 1.53, whereas no activity is obtained for stoichiometry lower than 0.44 (reduction at 1073 K) or higher than 2.36 (evacuation at room temperature).

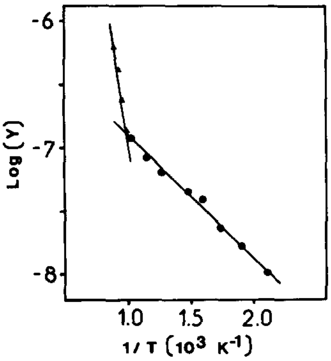


FIG. 5. Log of cumulated amount of H_2S removed upon reduction versus $1/T$. Symbols ● and ▲ represent two separate experiments.

The amount of sulfur ions removed was measured after a long reduction (16 h). Thus, we can assume that a thermodynamic steady state had been reached. A log Y versus $1/T$ plot of the cumulated amounts of H_2S removed (Y) is given in Fig. 5. Two domains of linear variation can be distinguished below and above 1033 K. A third domain, for reduction temperatures lower than 473 K, is also considered. These domains correspond to the removal of three different types of sulfur ions, i.e., S_I, S_{II}, and S_{III}, at increasing temperatures.

The enthalpy variation, ΔH_r, of removal of S_{II} and S_{III} ions was calculated from the respective plots of log $S_{II} = S_t - S_I$ and log $S_{III} = S_t - S_{II} - S_I$ versus $1/T$, where S_t is the total amount of sulfur removed. A value of 11.4 kJ mol^{-1} was obtained for S_{II} whereas 160 kJ mol^{-1} was obtained for S_{III}. The latter value is to be compared with 191 kJ mol^{-1}, the heat of reaction of MoS_2 with H_2 (*17*). Although the same order of magnitude is obtained, the lower value may be the result of the very small size of the slab and/or interactions with the support. It appears therefore that S_{III} is likely to correspond to a bulk-type sulfur ion whereas S_I and S_{II} would be other sulfur ions much less strongly bound and probably located at edge and corner positions.

Thus, from these results the question that arises concerns the relationship among the stoichiometry, number, location, and configuration of the site(s) responsible for the isoprene hydrogenation. After a presentation of the structural description of the catalytic phase this point will be the main object of the discussion.

Modeling of the catalyst structure. In a previous paper (*8*) we described the MoS_2/γ-Al_2O_3 catalyst structure as single MoS_2 slabs of similar shape and size dispersed on the alumina surface. In a MoS_2 slab, different molybdenum ions locations M_x can be found such as internal or basal, corner, and edge Mo ions (x = b, c, and e, respectively) as illustrated in Fig. 6 for a regular hexagonal slab containing 37 Mo ions.

When dealing with a system of isolated particles with the same mean size and shape, it can be shown that the nominal specific activity A for a given reaction of one slab of the catalyst can be written as

$$A = (M_x/M)a_x \qquad (1)$$

where M is the mean number of molybdenum ions per slab (hereafter called the slab size), M_x the number of molybdenum ions or active sites at some location (x), and a_x the turnover number of the reaction. With such formalism, the nominal activity of the

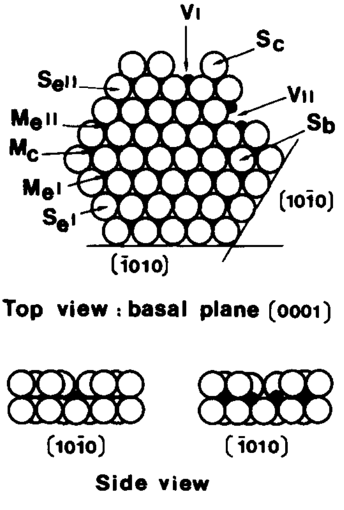


FIG. 6. Top and side views of a hexagonal MoS_2 slab of 37 Mo ions with distinction between the different Mo and sulfur ions and vacancies.

whole catalyst is equivalent to the activity of one slab.

In a single slab different sulfur ions, such as S_b, S_e, and S_c, can be distinguished (see Fig. 6). A basal plane (0001) sulfur ion (S_b), is linked to three molybdenum ions, whereas an edge sulfur ion (S_e) is either terminal (S_{e_I}) on plane (10$\bar{1}$0) or bridged ($S_{e_{II}}$) on plane ($\bar{1}$010). Corner sulfur ions are always terminal (S_{c_I}). The removal of these sulfur ions generates either terminal vacancies (V_I) or bridged vacancies (V_{II}), assuming that no edge reconstruction occurs; the removal of basal plane sulfur ions S_{III} generates V_{III} vacancies.

In addition, different edge Mo ions can be found in MoS_2 as already noted (*8*, *11*, *18*). Those in the (10$\bar{1}$0) plane are bound to two terminal sulfur ions S_{e_I} and will be denoted M_{e_I}, whereas those in the ($\bar{1}$010) plane are linked to four outer bridged sulfur ions $S_{e_{II}}$ and will be denoted $M_{e_{II}}$. Note that corner Mo ions are bound to two terminal sulfur ions and two bridged sulfur ions. Therefore, a M_{e_I} ion can possess up to 2 V_I, whereas both $M_{e_{II}}$ and M_c can possess up to 4 V_I for $M_{e_{II}}$ and 2 V_I + 2 V_{II} for M_c. Thus, these two latter Mo ions can have the same number of vacancies but with different environments in terms of different types of vacancies.

The variations of the numbers of these different Mo ions, S ions, or V vacancies versus different parameters, such as the shape and size of the MoS_2 slabs, have been established previously (*8*). In addition, stoichiometries and oxidation numbers can also be computed. Finally, it must be noted that the above description corresponds to an idealized structure of the catalyst. Evidently a size and shape distribution should be considered for a more accurate evaluation of a real catalyst. For the study of correlation, however, this approach is considered satisfactory.

DISCUSSION

The catalyst used in this study has been previously investigated both alone and after the addition of nickel ions as a promoter (*16*, *19*). A good dispersion of molybdenum in the oxidic and sulfided states, determined by XPS, has been found as well as a good promotion by nickel with a maximum of activity in hydrogenation of toluene (623 K, 60 atm) for the sample with Ni/(Ni + Mo) = 0.3. Therefore this $MoS_2/\gamma\text{-}Al_2O_3$ catalyst appears to be a classical hydrotreating catalyst which can be modeled as described above and in Ref. (*8*).

Such a catalyst structure modeling allows us to study the effect of different parameters on the catalytic activity. In particular, the variation of the activity versus the size of the slabs can be computed. Evidently this activity depends on the locations of the active sites considered. The analogy between the experimental specific activities for propene hydrogenation and thiophene hydrodesulfurization versus the molybdenum loading curve reported by Bachelier *et al.* (*20*) and the model curve for the activity given by all the edge sites versus the regular hexagonal MoS_2 slab size leads us to suggest that these sites were the active ones. All other types or combinations of sites, in particular corner sites, gave different curves.

Furthermore, different slab shapes were studied and the hexagonal shape has been proposed to be the most likely. At the maximum of the activity curve the mean size of the hexagonal slab was found to be 27 Mo ions (irregular hexagon), corresponding to a loading of 9 wt% MoO_3. From these results, a regular hexagonal slab size of 61 Mo ions can be deduced for a 14 wt% MoO_3 loading (a size corresponding to a slab length of ca. 30 Å).

Stoichiometry and Oxidation Number

Upon reduction, different types of sulfur ions, in large amounts, are removed from these slabs. To identify the location of these sulfur ions a comparison between calculated and experimental stoichiometry can be made.

The stoichiometry of one MoS_2 slab can

TABLE 1

Experimental and Calculated Stoichiometry of MoS_2/γ-Al_2O_3 Catalyst

	Saturated slab	Unsaturated $(10\bar{1}0)$ edge plane	Unsaturated $(10\bar{1}0)$ + $(\bar{1}010)$ edge plane
Calculated[a]	2.46	1.97	1.57
Measured	2.36[b]	1.96[c]	1.30[d]

[a] For a 61-Mo-ion hexagonal MoS_2 slab.
[b] After sulfurization.
[c] After reduction at 473 K.
[d] After reduction at 973 K.

be easily computed; for example, a 61-Mo-ion regular hexagon contains 150 sulfur ions when it is fully saturated, leading to S/Mo = 2.46. Removal of the 30 S_I ions leads to S/Mo = 1.97, and removal of all 54 peripheral sulfur ions (S_I + S_{II}) leads to S/Mo = 1.57. These calculations clearly demonstrate that without changing the core of the MoS_2 slab, large variations in the S/Mo ratio can result only in the removal of peripheral sulfur ions. These values have been reported in Table 1 with the experimental S/Mo results obtained after sulfurization and reduction at 473 and 973 K.

After sulfurization the experimental stoichiometry is close to the stoichiometry of the fully saturated 61-Mo-ion slab. The removal of sulfur ions by reduction below 973 K corresponds to weakly bound S_I and S_{II} sulfur ions, as shown by the small value found for the enthalpy change of reduction. The S/Mo values reported in Table 1 and the relative differences between experimental and calculated data are close enough so that the amount of sulfur ions removed below 473 K corresponds approximately to the amount of singly bound S_I sulfur ions, whereas from 473 to 973 K doubly bound S_{II} sulfur ions are probably removed. It can therefore be concluded that starting from the completely saturated slab, the reduction leads to the creation of increasingly unsaturated Mo ions, first on the $(10\bar{1}0)$ edge plane and then on the $(\bar{1}010)$ edge plane of the MoS_2 single slab, before reaching destruction of the slab and formation of metallic aggregates at reduction temperatures higher than 973 K.

The oxidation number (ON) of Mo ions is related to the stoichiometry and is computed on the basis of the slab edges and corners saturated by SH groups. In that situation the slab is almost electroneutral (*8*). When these SH groups are removed upon reduction, an equivalent amount of electrons are introduced into the slab according to the global schematic equation

$$nSH^- + n/2H_2 \rightarrow nV + nH_2S + ne^- \quad (2)$$

where V is an anionic vacancy.

In Fig. 7 the variations of the mean oxidation numbers versus the stoichiometry have been reported for the 61-Mo-ion hexagonal slab. Two cases have been considered: (i) all the Mo ions have the same mean oxidation number, and (ii) the internal Mo ions remain in the +4 state whereas the mean oxidation number of the peripheral Mo ions changes upon reduction. In the first case a variation of the mean ON from +4.04 for the saturated slab to +3.1 for the unsaturated slab is obtained, whereas when considering a distribution of the electrons on the peripheral Mo ions alone, lower mean ONs are found with a variation from +4.1 to +1.8.

These simple calculations clearly show that various molybdenum oxidation numbers can be found depending on the slab

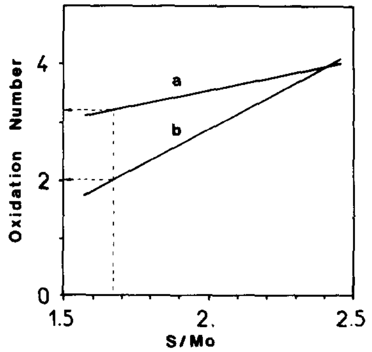


FIG. 7. Calculated mean oxidation number variation versus 61-Mo-ion hexagonal slab stoichiometry. (a) All Mo ions are reduced; (b) Only peripheral Mo ions are reduced with internal Mo ions remaining +4.

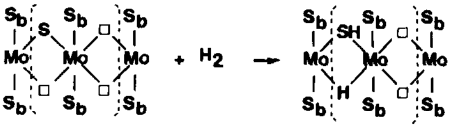
stoichiometry and size. Interestingly the ONs obtained are lower than +4 and experimental support for this is provided by several recent IR studies of CO chemisorbed on $MoS_2/\gamma\text{-}Al_2O_3$ demonstrating the presence of highly reduced Mo ions, in particular Mo^{2+} (*20–22*). The detection of such low ONs would suggest that mainly peripheral Mo ions are reduced whereas internal Mo ions remain +4, as considered above in case ii. Indeed, the known unreactivity of the basal sulfur ions and, conversely, the high reactivity of the edge sulfur ions (illustrated above) support this idea of a reduction limited to the peripheral Mo ions.

Active Sites for Isoprene Hydrogenation

The hydrogenation of isoprene is a useful test reaction for probing sites that are at least three-coordinatively unsaturated (3-cus), as the isoprene molecule requires two vacancies to be fully adsorbed and a H* species (the star indicates that we are not considering the exact charge on this species) will fill up the remaining available vacancy (formation of a Mo–H* group). In addition, an adjacent SH group will complete the site configuration in the case of heterolytic dissociation of H_2.

This configuration has already been suggested for the hydrogenation of dienes on different oxide or sulfide catalysts (*3–7*). Furthermore, previous work from this laboratory on diene hydrogenation on copper-based catalysts has shown that the 3-cus Cu^+ ion, leading to the generation of a Cu^+–H^- pair upon hydrogenation, was the active site (*23–26*).

The volcano-shaped curve of hydrogenation activity versus the active phase stoichiometry (or reduction temperature) in Fig. 4 is related to the variation of the number of the active sites. The shape of the curve already indicates that these active sites are three-coordinatively unsaturated and probably not four- or more coordinatively unsaturated because no activity has been detected at a high unsaturation level. Such a result would not occur if 4-cus or metallic aggregates were active.



SCHEME 1

These considerations alone can lead to determination of the isoprene hydrogenation active site location because only $M_{e_{II}}$ and M_c ions can be three-coordinatively unsaturated on a MoS_2 slab. As M_c ions are not active, the $3M_{e_{II}}$ ion remains the only possible hydrogenation site of isoprene. This type of site is located on the $(\bar{1}010)$ plane of the MoS_2 slab and can be described in the original and hydrogenated form as shown in Scheme 1. It can be seen that the site within the dashed brackets corresponds respectively to the C and CH sites symbolized by Siegel (*1*).

To check this point, the number of $3M_{e_{II}}$ sites can be statistically evaluated. Such a calculation is made possible because first the mean size of the MoS_2 slabs is known (61 Mo ions), and therefore the number of different Mo and S ions can be computed, and second, the reduction process in the temperature range 473 to 973 K corresponds to the removal of S_{II} edge sulfur ions as discussed above. Thus, the probability and hence the number of $3M_{e_{II}}$ sites can be computed versus the slab stoichiometry variation when peripheral S_{II} sulfur ions are removed. The probability of having three vacancies simultaneously on one $M_{e_{II}}$ edge site is

$$P(3) = 4q^3(1 - q) \qquad (3)$$

$$q = V_{II}/S_{II} \qquad (4)$$

where q is the fraction of vacancies on the $(\bar{1}010)$ edge plane. The number of sites, therefore, is

$$3M_{e_{II}} = M_{e_{II}}P(3) \qquad (5)$$

and the stoichiometry is computed as

$$S/Mo = (S - S_I - qS_{II})/M. \qquad (6)$$

The variation of the ratio $3M_{e_{II}}/M$, proportional to the activity according to Eq. (1), versus the stoichiometry has been reported in Fig. 8 for different hexagonal slab sizes. These curves have very similar shapes when compared with the experimental results. Clearly the slab size has a strong effect on the curve width, intensity, and optimum stoichiometry position. This effect is a consequence of the nonlinear dependence of both the number of $M_{e_{II}}$ ions and the stoichiometry on slab size. The relative experimental activity correlates almost linearly with the relative model $3M_{e_{II}}$ activity obtained for the 61-Mo-ion slab (Fig. 9). In Fig. 9, it can be checked that smaller or larger slabs give nonlinear correlation on both sides of the 61-Mo-ion slab curve, favoring the conclusion that this slab size is the more appropriate to account for the results; however, a shift in stoichiometry exists between the model (S/Mo $\simeq$ 1.68 at the maximum) and the experimental results (S/Mo $\simeq$ 1.53 at the maximum). This probably results from a slab size distribution around 61 Mo ions. In particular, slabs smaller than 61 Mo ions give larger S/Mo variations. The experimental curve is therefore the sum of the model curve over all the slabs of different sizes.

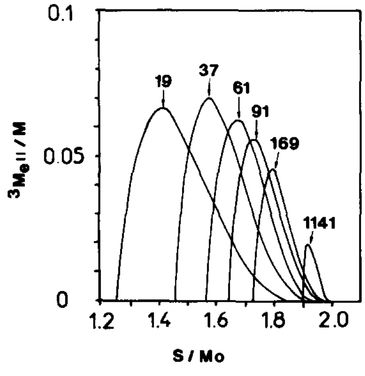


FIG. 8. Statistical fraction of three-coordinatively unsaturated $M_{e_{II}}$-type Mo ions versus stoichiometry of MoS_2 hexagonal slabs of different sizes expressed in number of Mo ions.

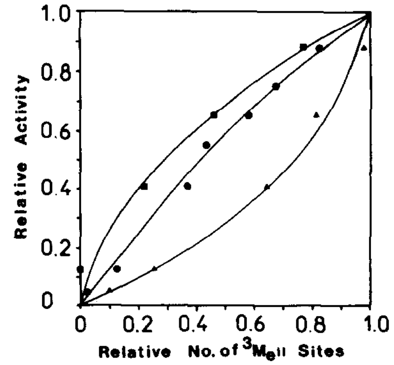


FIG. 9. Relative isoprene hydrogenation activity versus relative number of three-coordinatively unsaturated $M_{e_{II}}$ edge ions of hexagonal MoS_2 slabs containing 37 (▲), 61 (●), or 91 (■) Mo ions. The values have been normalized relative to the maximum of the curves.

The results in Fig. 9 demonstrate clearly that the presence of $3M_{e_{II}}$ centers on the $(\bar{1}010)$ plane of MoS_2 is a prerequisite for the active sites for isoprene hydrogenation. Moreover, a sulfur ion adjacent to three vacancies seems necessary. Although 4-cus sites have adjacent basal sulfur ions (S_b) linking these Mo ions to the slab, these sulfurs are saturated, being linked to 3Mo. Therefore, the presence of unsaturated sulfur ions also seems to be a prerequisite, likely to allowing heterolytic hydrogen dissociation with formation of a SH group.

To complete the description of this site the ON of the $3M_{e_{II}}$ molybdenum ion can be determined from the model curve in Fig. 8 (established for a 61-Mo-ion slab), using the value of stoichiometry leading to the maximum number of 3-cus Mo ions, i.e., S/Mo = 1.675. As we previously considered that the reduction of peripheral Mo ions occurs preferentially, a mean on value of +2.04 is obtained. In view of recent IR studies of CO adsorption (*21*, *22*) confirming the existence of such low ONs, +2 is likely to be the ON of the $3M_{e_{II}}$ site.

Clearly this site configuration is the minimum requirement to obtain monohydrogenation of the diene molecule. Double hydrogenation of the diene molecule may also occur if other vacancies exist close to that site on the neighboring molybdenum ions as can be seen in Scheme 1 and in Fig. 6. This is possible as all vacancies on that MoS_2 edge plane are shared by two Mo ions. As double hydrogenation is experimentally observed and is likely to be simultaneous because monoenes are very much less reactive at these temperatures (*20*), further constraints on the site environment, such as the number of vacancies in the neighborhood of the $3M_{eII}$ site, should be assumed to take into consideration the double hydrogenation. This important point, relevant to the role of catalyst structure in selectivity, is discussed in a forthcoming paper (*16*); however, this consideration does not modify the conclusion reached in this work which deals with the total hydrogenation properties of $MoS_2/\gamma\text{-}Al_2O_3$ catalysts.

CONCLUSION

The results reported in this study, combined with an analysis of the data using a model of the catalyst structure, demonstrate that the isoprene hydrogenation reaction on alumina-supported MoS_2 catalyst occurs on Mo edge sites in the $(\bar{1}010)$ plane of MoS_2 slabs possessing three vacancies and one sulfur.

Although such a conclusion is obtained unambiguously because of the relative simplicity of the MoS_2 structure, the concept of a connection between number of vacancies and type of reaction, as proposed by Siegel (*1*), is demonstrated to be valid. This concept provides a link between the mechanistic and structural criteria needed for the catalytic reaction to occur.

These results also suggest that it is possible to choose the appropriate model molecule to characterize the structure of the active site for different reactions such as hydrodesulfurization, hydrodenitrogenation, isomerization, and hydrogenation involved in the hydrotreatment of oil fractions by $MoS_2/\gamma\text{-}Al_2O_3$ catalysts.

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REFERENCES

1. Siegel, S., *J. Catal.* **30,** 139 (1973).
2. Siegel, S., Outlaw, J., and Garti, N., *J. Catal.* **52,** 102 (1978).
3. Tanaka, K. I., and Okuhara, T., *Catal. Rev. Sci. Eng.* **15,** 24 (1977).
4. Tanaka, K. I., *Adv. Catal.* **33,** 99 (1985).
5. Imizu, Y., Sato, K., and Hattori, H., *J. Catal.* **76,** 65 (1982) and references therein.
6. Hattori, H., Tanaka, Y., and Tanabe, K., *J. Amer. Chem. Soc.* **98,** 4652 (1976).
7. Lombardo, E. A., Houalla, M., and Hall, W. K., *J. Catal.* **51,** 256 (1978).
8. Kasztelan, S., Toulhoat, H., Grimblot, J., and Bonnelle, J. P., *Appl. Catal.* **13,** 127 (1984); *Bull. Soc. Chim. Belg.* **93,** 807 (1984).
9. Sanders, J. V., *Chem. Scr.* **14,** 141 (1979).
10. Candia, R., Sørensen, O., Villadsen, J., Topsøe, N. Y., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **93,** 763 (1984).
11. Ratnasamy, P., and Sivasanker, S., *Catal. Rev. Sci. Eng.* **22,** 401 (1980).
12. Chianelli, R., "Surface Properties and Catalysis by Non-metals" (J. P. Bonnelle, B. Delmon, and E. Derouane, Eds.), p. 361. Reidel, Dordrecht, 1983.
13. Topsøe, H., Candia, R., Topsøe, N. Y., and Clausen, B. S., *Bull. Soc. Chim. Belg.* **93,** 783 (1984) and references therein.
14. Muralidhar, G., Massoth, F. E., and Shabtai, J., *J. Catal.* **85,** 44 (1984); **85,** 53 (1984).
15. Garin, F., and Gault, F. G., *J. Amer. Chem. Soc.* **97,** 4466 (1975).
16. Wambeke, A., to be published.
17. This value is calculated from data obtained in the "CRC Handbook of Chemistry and Physics" (R. C. Weast, Ed.), p. D58. CRC Press, Boca Raton, FL, 1978.
18. Schuit, G. C. A., *Int. J. Quantum Chem.* **12,** 43 (1977).
19. Wambeke, A., Toulhoat, H., Boutrois, J. P., Grimblot, J., and Bonnelle, J. P., *in* "Preparation of Catalysts IV" (B. Delmon *et al.*, Eds.), p. 581. Elsevier, Amsterdam, 1987.
20. Bachelier, J., Tilliette, M. J., Duchet, J. C., and Cornet, D., *J. Catal.* **76,** 300 (1982).
21. Valyon, J., and Hall, W. K., *J. Catal.* **84,** 216 (1983).
22. For a recent review, see Zaki, M. I., Vielhaber, B., and Knözinger, H., *J. Phys. Chem.* **90,** 3716 (1986) and references therein.
23. Jalowiecki, L., Daage, M., Bonnelle, J. P., and Tchen, A., *Appl. Catal.* **16,** 1 (1985).
24. Béchara, R., Wrobel, G., Daage, M., and Bonnelle, J. P., *Appl. Catal.* **16,** 15 (1985).
25. Daage, M., and Bonnelle, J. P., *Appl. Catal.* **16,** 355 (1985).
26. Jalowiecki, L., Wrobel, G., Daage, M., and Bonnelle, J. P., *J. Catal.* **107,** 375 (1987).