

## Hydrogenation and Isomerization of Alkadienes on Powdered $\text{MoS}_x\text{H}_y$

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Hydrogenation of 2-methyl-1,3-butadiene (isoprene) in the absence of gaseous hydrogen is used to reveal and titrate reactive hydrogen species occluded in powdered  $\text{MoS}_2$  previously reduced under  $\text{H}_2$ . Highly coordinatively unsaturated (cus) Mo ions are generated on  $\text{MoS}_2$  by reduction treatment at various temperatures between 373 and 973 K. After each reduction treatment, the catalyst stoichiometry is measured, so that the values  $x$  and  $y$  in  $\text{MoS}_x\text{H}_y$  can be established. Different compositions where  $x$  is between 1.67 and 2.01 and  $y$  is between 0.002 and 0.12 have been investigated. To probe the unsaturated Mo ions, hydrogenation of isoprene and isomerization of *cis*-1,3-pentadiene are performed at 373 K under 1 atm pressure of hydrogen. Similarly to the case of supported  $\text{MoS}_2$  on  $\gamma\text{-Al}_2\text{O}_3$  catalyst, which has already been investigated, a correlation is proposed between the alkadiene transformation activities and the coordinatively unsaturated (1010) edge Mo ions, viz., hydrogenation and 3 cus ions, isomerization and 2 and 4 cus ions.

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### INTRODUCTION

Sulfide catalysts find extensive use in hydroprocessing reactions and the characterization of the active sites involved in the different reaction paths is of great importance. To identify these active sites and their active species precisely, a link between the phase structure and the catalytic reaction is necessary. Some years ago, a very useful concept was proposed by Siegel, who suggested that the number of coordinative unsaturation positions on a site and the set of elementary reactions involving hydrogen are connected (1, 2). Such a concept has been validated for on nickel sulfide catalysts (3) and has been widely used by Tanaka *et al.* (4-6) to give a careful description of the edge sites on  $\text{MoS}_2$  where coordinatively unsaturated Mo ions are available at various degrees of coordination.

More recently, in our laboratory, activities in hydrogenation and isomerization of

model molecules have been measured on an alumina-supported  $\text{MoS}_2$  catalyst with controlled stoichiometries obtained by hydrogen reduction at various temperatures (7, 8). The structure of the active phase of the  $\text{MoS}_2/\text{Al}_2\text{O}_3$  catalytic system has also been modeled in previous studies (9) as a single slab of  $\text{MoS}_2$  well dispersed on alumina. It was possible to correlate the hydrogenation activity with the edge Mo ions possessing three vacancies and one sulfur present in the (1010) plane of the  $\text{MoS}_2$  slabs (7). On the other hand, the isomerization activity was correlated with the two and/or four coordinatively unsaturated edge Mo ions (8).

A complete description of these sites should take into account the presence of the reactive hydrogen species on or in the  $\text{MoS}_2$  structure. As a matter of fact, the reaction of the sulfide catalysts with hydrogen is complex (10) but of great importance as the hydrotreating reactions involve, in part, hydrogen transfer. There have been several previous works concerning hydrogen sorption or reaction on molybdenum or

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tungsten sulfide. In particular, Badger *et al.* (11) were the first to explore the temperature dependence of the sorption in the range 273–673 K. Other researchers have measured the time dependence of the sorption upon hydrogen pretreatment (12). For the hydrogen– $\text{MoS}_2$  system (11, 13) measurements at various temperatures and pressures showed the existence of dissociative sorption of hydrogen to produce hydrogen–sulfur bonds and uptakes apparently much larger than those that could be accommodated at the accessible surface of the material as determined by nitrogen physisorption (14). Moreover, inelastic neutron scattering measurements have revealed the existence of two sites at which hydrogen may be sorbed on  $\text{MoS}_2$  (13, 15). One site becomes saturated at pressures less than 1 atm and at temperatures less than 473 K and is attributed to the site which forms linear S–H bonds. The second site has been found to be that at which sorption occurs at higher temperatures (>423 K), and which becomes saturated at only 50 atm (16). However, further discrimination between structural models with hydrogen atoms multiply or singly bound at edge or basal positions is not yet possible (13, 15, 16).

In addition, the effect of hydrogen on catalytic activity during hydrotreating reactions (e.g., hydrodesulfurization) is not perfectly understood. Molybdenum disulfide is able to adsorb a substantial quantity of hydrogen which elevates the hydrogenation activity of  $\text{MoS}_2$  (12, 17). The specific hydrogenation activity increases as nonstoichiometric sulfur is removed (18). The presence of nonstoichiometric  $\text{MoS}_2$ -like species with a high density of anion vacancies and presumably containing appreciable amounts of hydrogen is causally related (18–20). The key factor is the increase in coordinatively unsaturated Mo ions.

As a consequence, the aim of this work is not only to characterize the sites involved in the hydrogenation and isomerization reactions occurring on bulk  $\text{MoS}_2$  by using

probe molecules (isoprene, *cis*-1,3-pentadiene) but also to consider participation of the reactive hydrogen of the solid, the amount of which is titrated by a dynamic method under conditions similar to those of catalytic tests.

#### EXPERIMENTAL

Bulk  $\text{MoS}_2$ (I) with a specific surface area of about  $47 \text{ m}^2 \text{ g}^{-1}$  was obtained by thermal decomposition of ammonium tetrathiomolybdate (ATTM) under a  $\text{H}_2/\text{H}_2\text{S}$  (90–10) flow at 673 K for 4 h. This compound, reduced under  $\text{H}_2$  at 773 K for 4 h and further treated with the  $\text{H}_2/\text{H}_2\text{S}$  mixture under the same conditions as above, is transformed into  $\text{MoS}_2$ (II) with a specific surface area of  $7 \text{ m}^2 \text{ g}^{-1}$ . It must be noted that, for any treatment at temperatures higher than or equal to 723 K, the  $\text{MoS}_2$ (I) and  $\text{MoS}_2$ (II) samples correspond to the same compound. Thus, the differentiation between the two solids, I and II, concerns only the reduction treatments at temperatures lower than 723 K.

The pretreatment and catalytic experiments were carried out at atmospheric pressure in the all-glass grease-free flow apparatus previously described (21). The catalyst was first reduced under a purified hydrogen flow at various temperatures between 293 and 1073 K for 12 h.

After each reduction step by  $\text{H}_2$ , the solid (800 mg) was cooled to room temperature, reactants were introduced at constant pressure (20 or 7 Torr, respectively, with regard to the reactive molecule, isoprene or *cis*-1,3-pentadiene) in a flow of purified hydrogen or helium (1 atm,  $20 \text{ ml min}^{-1}$ ) in an isothermal reactor. Catalytic tests were carried out under hydrogen at 373 K.

The procedure for hydrogen titration of the solids has been largely described previously (22). The reduced catalyst was flushed under helium at 323 K for 15 min, until complete elimination of hydrogen in the gas phase, and consumption of the reactive hydrogen occluded in the solids by iso-

prene (0.5% in helium) was carried out at 423 K.

Isoprene (2-methyl-1,3-butadiene) and *cis*-1,3-pentadiene (purum grade from Fluka) were used after purification by distillation under vacuum. Hydrogen and helium were purified of any traces of oxygen and H<sub>2</sub>O which would have resulted in complete catalyst poisoning. The conversions were measured at the steady state reached after 15 min and were never higher than 30%. Reaction products were analyzed by gas chromatography using a 100-m squalane capillary column operating at 318 K and a flame ionization detector. In parallel, after each reduction treatment, the specific area was determined by the BET method, and microanalyses of the samples were performed by the "Service d'analyses du CNRS" to obtain the S/Mo stoichiometry of the bulk "MoS<sub>2</sub>" (the relative error in the S/Mo ratio is 0.5%).

## RESULTS

### *The Catalyst MoS<sub>x</sub>H<sub>y</sub>*

**Stoichiometry and texture.** After each reduction the catalyst stoichiometry was determined. Figure 1 represents the variation in the S/Mo ratio as a function of treatment under H<sub>2</sub>.

MoS<sub>2</sub>(I) and MoS<sub>2</sub>(II) solids sulfided under H<sub>2</sub>/H<sub>2</sub>S at 673 K show a S/Mo ratio of 2.05. After successive reduction treatments under H<sub>2</sub>, large amounts of H<sub>2</sub>S are removed, leading to various substoichiometric samples from S/Mo 2.01 to S/Mo 1.67. The sulfur ions removed were measured after a sufficiently long reduction time (12 h) to obtain a steady state. At temperatures lower than 373 K, some H<sub>2</sub>S is removed by a simple purge with helium. The sulfur evolution is slight up to 573 K but becomes important above 573 K.

The reduction treatment also leads to an evolution of the texture of the MoS<sub>2</sub>(I) as the specific area, reported by the dashed line in Fig. 1, is modified. For reduction temperatures lower than 573 K the MoS<sub>x</sub>(I) and MoS<sub>x</sub>(II) samples with  $x = 2$  have spe-

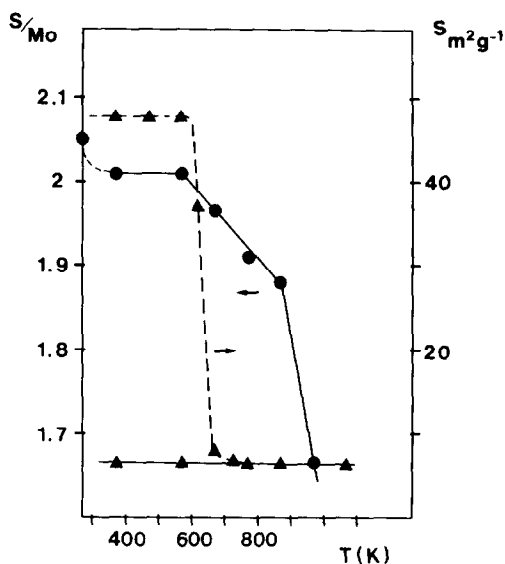


FIG. 1. Stoichiometry and specific surface area variation of bulk MoS<sub>2</sub>(II) versus reduction temperature under hydrogen. The dashed line corresponds to MoS<sub>2</sub>(I) with an initial specific surface area of 47 m<sup>2</sup> g<sup>-1</sup>.

cific areas of 47 and 7 m<sup>2</sup> g<sup>-1</sup>, respectively. For the bulk catalysts treated in the range 573 to 673 K, the S/Mo ratio decreases from 2 to 1.96 and the specific area of MoS<sub>2</sub>(I) decreases from 47 to 8 m<sup>2</sup> g<sup>-1</sup>. Such sintering has often been observed for a treatment temperature close to 673 K (18, 23). For reduction temperatures higher than 673 K, MoS<sub>x</sub> with  $x$  from 1.96 to about 1.7 is formed with a specific area of 6 m<sup>2</sup> g<sup>-1</sup>. It is also interesting to note that the low surface area observed after a high-temperature treatment becomes stable even after further chemical (H<sub>2</sub>/H<sub>2</sub>S) or thermal treatments.

**Reactive hydrogen content.** Bulk MoS<sub>2</sub> contains some occluded hydrogen species able to hydrogenate alkadienes in the absence of gaseous hydrogen. These species are denoted H\* as we are not considering their exact charge.

The H\* content of the solid is varied and controlled by using a dynamic method already described (22). At 423 K under a helium + isoprene (0.5% volume) flow, alkadiene hydrogenation occurs on MoS<sub>2</sub> previously reduced by H<sub>2</sub> at different tem-

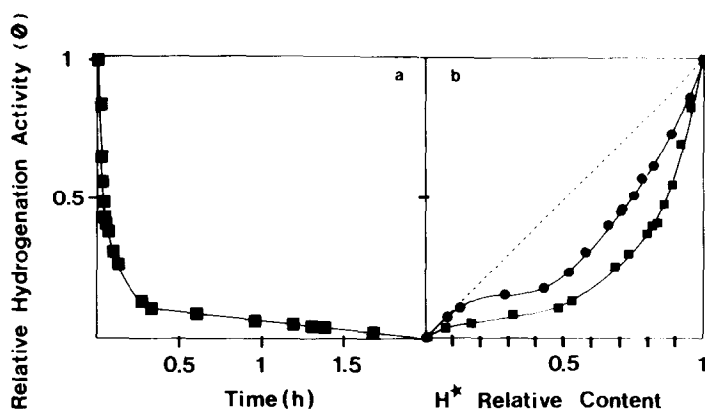


FIG. 2. Relative hydrogenation activity measured at 423 K under a helium + diene flow on bulk  $\text{MoS}_2(\text{I})$  reduced (a) at 773 K versus time and (b) at 673 K (●) and at 773 K (■) versus relative  $\text{H}^*$  content.

peratures. It is important to note that these highly reactive species do not exist after only the sulfiding treatment. A plot of the ratio  $\phi = A_{\text{H}_t}/A_{\text{H}_0}$  (where  $A_{\text{H}_0}$  and  $A_{\text{H}_t}$  are the initial hydrogenation activity and the hydrogenation activity at time  $t$ ) versus time is obtained. In Fig. 2a, the relative hydrogenation activity ( $\phi$ ) versus time under helium + alkadiene flow is reported for  $\text{MoS}_2$  reduced at 773 K. For each reduction temperature a similar curve is obtained, and by integrating this curve the total reactive hydrogen  $\text{H}^*$  content of the solid can be determined.

In addition, between  $t$  and  $t_f$  (time at which the activity is zero) the percentage of reactive hydrogen still present in the solid can be estimated. A plot of  $\phi$  versus  $\text{H}^*$  concentration can be obtained for each reduction temperature. In Fig. 2b the results are reported for the solid  $\text{MoS}_2(\text{I})$  reduced at 673 and 773 K under hydrogen. The curves obtained show clearly that there is no proportionality between the relative hydrogenation rate consuming  $\text{H}^*$  and the hydrogen content of the solid, and that a diffusional process must be considered. A clear analogy exists between these results and those obtained on reduced copper oxides (22, 24, 25) which were found to be hydrogen reservoirs.

The extractable hydrogen content of the

solid is found to depend on the temperature of reduction of the catalyst by  $\text{H}_2$ . Figure 3 shows a maximum  $\text{H}^*$ ,  $7.5 \times 10^{-5} \text{ mol g}^{-1}$ , for a reduction temperature of 723 K. On  $\text{MoS}_2(\text{I})$  (dashed line), which has an initial specific surface area of  $47 \text{ m}^2 \text{ g}^{-1}$ , the hydrogen content is higher than that obtained on stabilized  $\text{MoS}_2(\text{II})$  at identical reduction temperatures.

Finally, the stoichiometries of the  $\text{MoS}_x\text{H}_y$  catalysts obtained by treatments at

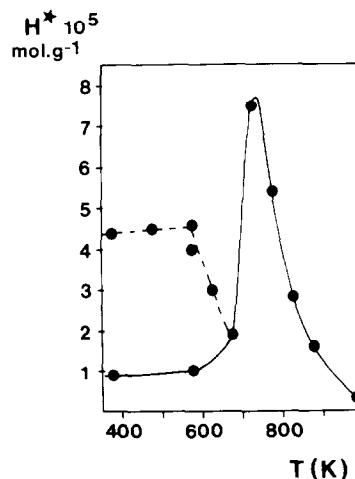


FIG. 3.  $\text{H}^*$  content versus reduction temperature of  $\text{MoS}_2(\text{II})$  ( $7 \text{ m}^2 \text{ g}^{-1}$ ). The dashed line corresponds to  $\text{MoS}_2(\text{I})$  with an initial surface area of  $47 \text{ m}^2 \text{ g}^{-1}$ .

TABLE 1

Specific Surface Areas and Stoichiometries of  $\text{MoS}_2\text{H}_x$  Catalysts after Different Reduction Treatments

Reduction temperature (K)	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	$\text{MoS}_2\text{H}_x$
373 <sup>a</sup>	47	$\text{MoS}_{2.01}\text{H}_{0.007}$
373	7	$\text{MoS}_{2.01}\text{H}_{0.002}$
473 <sup>a</sup>	47	$\text{MoS}_{2.01}\text{H}_{0.007}$
573 <sup>a</sup>	47	$\text{MoS}_{2.01}\text{H}_{0.007}$
573	7	$\text{MoS}_{2.01}\text{H}_{0.002}$
623 <sup>a</sup>	37	$\text{MoS}_{1.99}\text{H}_{0.005}$
623	8	$\text{MoS}_{1.96}\text{H}_{0.003}$
723	7	$\text{MoS}_{1.94}\text{H}_{0.012}^b$
773	6	$\text{MoS}_{1.91}\text{H}_{0.009}$
823	6	$\text{MoS}_{1.90}\text{H}_{0.005}$
873	6	$\text{MoS}_{1.88}\text{H}_{0.003}$

<sup>a</sup>  $\text{MoS}_2(\text{I})$  sample which does not have the specific surface area stabilized.

<sup>b</sup> This value is quite similar to that found by Moyes (10) and is assigned to edge-plane hydrogen.

different reduction temperatures can be reported (Table 1). Evolution of the extractable reactive hydrogen content versus  $\text{MoS}_2(\text{II})$  phase stoichiometry is presented in Fig. 4a, indicative of a "volcano curve" with a maximum S/Mo ratio of 1.93.

The quantities obtained in this study are much lower than those reported by other authors (10, 14, 26, 27). For example, the compound  $\text{H}_{0.37}\text{MoS}_2$  was found by Badger *et al.* (11). It is well known that the amount of hydrogen depends largely on the preparation method (10, 11), but generally the amount of hydrogen is correlated to SH species (10, 11, 13, 15, 28). The  $\text{H}^*$  titrated in this work is different in nature from the SH group, as no  $\text{H}^*$  is found on a completely sulfided solid.

#### Hydrogenation and Isomerization Activities

The effect of the temperature of reduction on isoprene hydrogenation activity (HYD) at 373 K of bulk  $\text{MoS}_2$  catalyst is reported in Fig. 5a. A volcano curve is obtained with no detectable activity for reduction at temperatures lower than 373 K and maximum activity for reduction at 673 K. The main products of this reaction are 2-

methyl-1-butene, 2-methyl-2-butene, isopentane, and 3-methyl-1-butene; only the overall hydrogenation activity is considered in this work.

A similar curve is obtained for *cis*-1,3-pentadiene hydrogenation activity (Fig. 5b). The main products of the hydrogenation reaction are 1-pentene, *cis*-2-pentene, *trans*-2-pentene, and pentane. Moreover, *cis*-1,3-pentadiene is a convenient molecule as, by the formation of *trans*-1,3-pentadiene, the evolution of isomerization activity (ISOM) with reduction temperature is also observed (right-hand scale of Fig. 5b). The isomerization activity is always higher than the hydrogenation activity, except for a small reduction temperature range close to 673 K.

The results obtained on bulk  $\text{MoS}_2(\text{I})$ , whose initial specific surface area is  $47 \text{ m}^2 \text{g}^{-1}$ , are represented by the dashed lines in Fig. 5, and the intrinsic activities observed on each  $\text{MoS}_2$  are similar. A linear dependence of specific activity on specific surface area has often been observed for catalysts

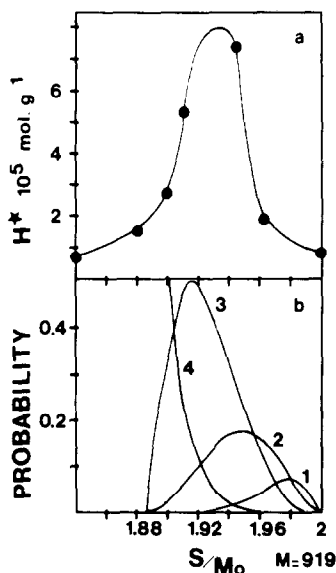


FIG. 4. (a)  $\text{H}^*$  content versus  $\text{MoS}_2(\text{II})$  stoichiometry. (b) 1, 2, 3 and 4 cus edge Mo ions versus the stoichiometry for a modeled hexagonal slab having  $n = 18$  Mo ions per side ( $M = 919$ ).

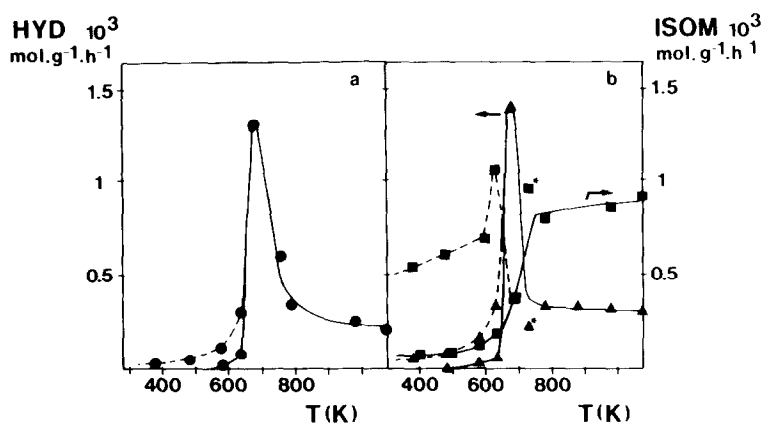


FIG. 5. (a) Isoprene hydrogenation activity at 373 K versus reduction temperature. (b) *cis*-1,3-Pentadiene hydrogenation and isomerization activities at 373 K versus reduction temperature. The dashed lines correspond to  $\text{MoS}_2(\text{I})$  which has an initial specific surface area of  $47 \text{ m}^2 \text{ g}^{-1}$ .  $\blacktriangle^*$ ,  $\blacksquare^*$ : Obtained with  $\text{MoS}_2$  from a different batch of ammonium tetrathiomolybdate.

prepared with the same procedure and with equivalent stoichiometries (29–31). When no correlation has been observed, the solids used presented a large variation of stoichiometries (32, 33).

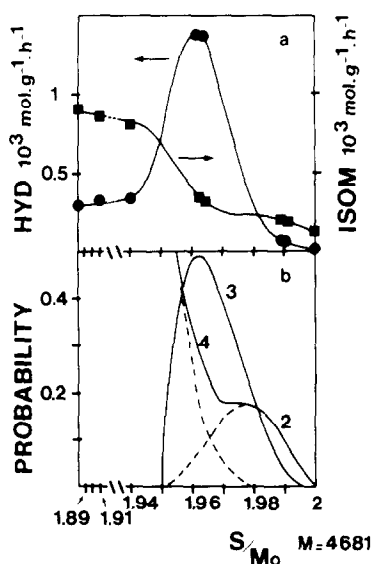


FIG. 6. (a) *cis*-1,3-Pentadiene hydrogenation and isomerization activities at 373 K versus  $\text{MoS}_2(\text{II})$  stoichiometry. (b) 2, 3, 4 cus edge Mo ion probabilities versus  $\text{S}/\text{Mo}$  stoichiometry of a modeled hexagonal  $\text{MoS}_2$  slab having  $n = 40$  Mo ions per side. [The total number of molybdenum atoms  $M$  in the slab is therefore 4681: see Refs. (6–8) for modeling and calculations.]

It must be noted also that after high-temperature treatment ( $>723 \text{ K}$ ), the *cis*-1,3-pentadiene HYD and ISOM activities remain constant, whereas  $\text{S}/\text{Mo}$  stoichiometry decreases. It is possible that the degree of unsaturation at the surface after reduction at temperatures higher than 723 K remains unchanged as long as there is enough sulfur in the bulk to ensure a steady state at the surface, but we have no direct evidence to demonstrate this point.

The variation in the activities versus  $\text{MoS}_2(\text{II})$  phase stoichiometry can therefore be deduced and is presented in Fig. 6a. HYD and ISOM functionalities are strongly dependent on the  $\text{S}/\text{Mo}$  ratio. Interestingly, after sulfidation, the catalyst has been found to be inactive for both ISOM and HYD, whereas significant activity appears only for  $\text{S}/\text{Mo} < 2$ . The maximum HYD activity is obtained at an  $\text{S}/\text{Mo}$  ratio of 1.96. ISOM activity increases with decreasing  $\text{S}/\text{Mo}$  ratio in a similar way, as already observed for the supported catalyst (8).

## DISCUSSION

### *Hydrogenation and Isomerization Active Sites*

In previous works on the  $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$  catalyst, the active phase was described

and modeled as single  $\text{MoS}_2$  slabs of similar shape and size well dispersed on the alumina surface (9). Bulk  $\text{MoS}_2$  also contains  $\text{MoS}_2$  slabs of larger size but with an important stacking as no support is present (34–36). Nevertheless, the structure of a slab is always the same with different molybdenum ion locations at internal or basal (b), corner (c), and edge (e) positions. Different sulfur ions can be also distinguished such as  $\text{S}_b$ ,  $\text{S}_c$ , and  $\text{S}_e$ .

Highly coordinatively unsaturated Mo ions have been generated by reduction of the bulk  $\text{MoS}_2$  we have prepared under hydrogen at different temperatures. Lo Jacono and Hall have already observed that the concentration of anionic vacancies increases with the reduction temperature (37).

Without changing the core of the  $\text{MoS}_2$  slab, large variations in the S/Mo ratio can result only in the removal of peripheral sulfur ions. Such a possibility was proposed in a previous study as a function of crystallite size (9). With the  $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$  (9.2 wt% Mo) catalyst, the stoichiometry variations were observed in a markedly broader range (from 2.3 to 0.5) with reduction temperatures from 473 to 1100 K. In that particular case, this evolution has been well correlated to the removal of peripheral sulfur ions of a 61-Mo-ion mean size  $\text{MoS}_2$  slab (17) starting schematically from the terminal sulfur ions [ $(10\bar{1}0)$  edge plane], whereas bridged S ions [ $(\bar{1}010)$  edge plane] are further removed at higher reduction temperatures. The low S/Mo stoichiometries obtained at the highest temperatures are due to the beginning of destruction of the  $\text{MoS}_2$  structure.

Thus, the hydrogen reduction pretreatment allows us to scan the entire S/Mo ratio range, from the completely saturated slab to the completely unsaturated slab at the edges. The experimental values obtained on bulk  $\text{MoS}_2$  after sulfurization (S/Mo = 2.05) and reduction at 373 K (S/Mo = 2.01) and at 873 K (S/Mo = 1.88) can result from the loss of peripheral sulfur

ions of  $\text{MoS}_2$  crystallites larger than those of the  $\text{MoS}_2$  slab supported on alumina (slab length of about 30 Å) (9). Such a hypothesis is highly probable and supported by results in the literature (35, 36). Thus, by comparison with the supported catalyst, the evolution of the sulfur stoichiometry can be explained by the removal of terminal S ions at reduction temperatures lower than 373 K, whereas bridged S ions are removed mainly above 573 K. Evidently, for reduction temperatures higher than 873 K, the attack on the basal sulfur ions probably begins to occur with the destruction of the  $\text{MoS}_2$  slab.

Consequently, the activity results from the generation of coordinatively unsaturated (cus) sites, as has often been pointed out (1–6, 38–40). Furthermore, it must be noted that each functionality follows very different behavior as a function of the extent of reduction.

Siegel proposed that the HYD reaction occurs on 3 cus ions, whereas ISOM would occur on 2 cus ions (1, 2) a formalism which was demonstrated by Tanaka *et al.* on  $\text{MoS}_2$  (41) and also extensively reported on other catalysts (4–6, 24, 42). In particular, on  $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$  it has been shown that the statistical number of 3 cus sites in the  $(\bar{1}010)$  edge plane could be computed versus the S/Mo ratio and that the model curve fitted quite well with the experimental isoprene hydrogenation activity results for a model hexagonal slabs of 61 Mo ions (7). Moreover, the theoretical curves can be computed versus the S/Mo ratio for any crystallite size (7, 9). In the same way, evolution of the statistical number of 2 and 4 cus sites can also be computed and was presented previously (8).

As a first step, qualitative comparison of the experimental and model curves is proposed (Figs. 6a,b) *only for S/Mo ratios higher than 1.95*. This comparison is based on calculations performed with a modeled hexagonal slab containing  $n = 40$  Mo ions per side (or total Mo content  $M = 4681$  Mo per slab) for which the best fit was obtained between the results of *cis*-1,3-pentadiene

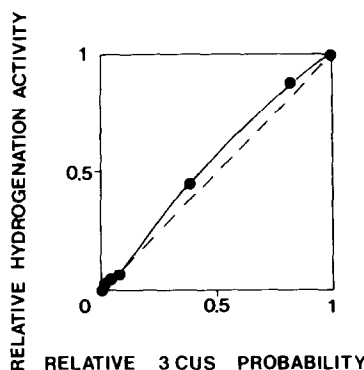


FIG. 7. Relative *cis*-1,3-pentadiene hydrogenation activity versus the relative 3 cus Mo ion probability for a modeled hexagonal slab having  $n = 40$  Mo ions per side ( $M = 4681$ ).

HYD activity and the statistical amount of 3 cus edge Mo ions (Fig. 7). Hence we can conclude and it is not so surprising that the structures of the active sites for bulk  $\text{MoS}_2$  and alumina-supported  $\text{MoS}_2$  are the same; i.e., the 3 cus edge Mo ions are a prerequisite condition for the HYD reaction, whereas the 2 and/or 4 cus Mo edge ions are responsible for ISOM activity. One may note that the participation of 4 cus ions in the ISOM reaction was not envisaged by Siegel.

The distinction of Mo ions on the basis of the number and nature of the vacancies previously made (9) is important in locating and distinguishing between different sites. These active sites are located in the  $(\bar{1}010)$  edge plane of the  $\text{MoS}_2$  slab as only these edge Mo ions can be 3 or 4 cus, and depending on the degree of unsaturation the same Mo ions can have different functionalities. Furthermore, the vacancies in the  $(\bar{1}010)$  edge plane are bridged and the active site cannot be described by an isolated Mo ion and must be considered as an "elementary ensemble" composed of at least two edge Mo ions (8).

Moreover, as the maximum HYD activity corresponds to the maximum of 3 cus Mo ions, it appears that the rupture of molecular hydrogen is heterolytic. A sulfur ion

is necessary to dissociate the hydrogen molecule with the formation of S-H and Mo-H entities; Wright *et al.* (13, 14) have already identified a site where S-H bonds are formed and have shown that there were at least two sites for hydrogen sorption (15, 16). Furthermore, Anderson *et al.* (43) have recently calculated that the heterolytic chemisorption of hydrogen at the edges of crystal layers is the most stable form.

#### *Localization of the Extractable Hydrogen Species*

The trend of extractable hydrogen content versus the S/Mo ratio is presented in Fig. 4a as a curve that looks like that for HYD activity, but the width is more important, the maximum is shifted to a lower stoichiometry, and the  $\text{H}^*$  content still decreases at S/Mo ratios lower than 1.9.

The  $\text{H}^*$  species appear at temperatures sufficiently high that some of the sulfur ions at the edge sites are already removed. Thus, the  $\text{H}^*$  content depends also on the presence of anionic vacancies created on the edge of the  $\text{MoS}_2$  slab. Lo Jacono and Hall (37) have already proposed that a reversible hydrogen species is associated with the anionic vacancies and Moyes (10) attributed to the edges of the slab amounts of hydrogen similar to those found in this study. In his material, which had the stoichiometry  $\text{MoH}_{0.067}\text{S}_2$ , 0.011 mol of hydrogen per mole of  $\text{MoS}_2$  was established as the "edge-plane hydrogen" (10).

Considering the shape of the experimental curve (Fig. 4a) it is impossible to know exactly whether all types of cus sites (Fig. 4b) or only a few of them are involved in the hydrogen storage. Only the participation of 4 cus Mo ions can be eliminated as in this case a linear correlation with the creation of anionic vacancies would be observed. Moreover, if different kinds of cus sites are involved (this hypothesis seems to be the most probable), a complementary study involving different parameters, such as the occupation coefficient of the different cus sites by  $\text{H}^*$ , would be necessary. At this



stage of the study a correlation is difficult and only a qualitative comparison can be proposed.

The S/Mo stoichiometry at maximum H\* concentration (1.93) is lower than that observed at maximum HYD activity (1.96, Fig. 6a). Therefore, to establish comparison between the variation in the content of the hydrogen species and the modeled curves, MoS<sub>2</sub> of a smaller size has been considered. In Fig. 4b are shown results of calculations which have been carried out on a modeled hexagonal MoS<sub>2</sub> slab containing M = 919 Mo instead of M = 4681 ions. Such an apparent contradiction in the use modeling curves may be explained by the different nature of the information given by the experiments:

1. The catalytic activity is a surface phenomenon and is proportional to the number of active sites accessible to the alkadienes.
2. The reactive hydrogen species are consumed by diffusion from bulk to surface and by surface reaction.

Thus, the results obtained in this study can be explained if a large majority of the edge Mo ions are accessible only to the hydrogen species by diffusion and not to the alkadiene; the conclusion is that surface slabs are larger ( $\approx 240$  Å) than bulk slabs ( $\approx 120$  Å), as suggested by the modeling curves.

In fact, estimation of the mean size of the bulk MoS<sub>2</sub> crystallites is a problem in itself because of the "rag" structure of this solid (35, 36). It is highly probable that the crystallites are in reality smaller, but sufficiently joined to give perturbations in the average size estimation.

Electron microscopy experiments on our evolving solids should help to establish correlations between real crystallite sizes and those estimated from the catalytic experiments (HYD and/or ISOM activities or measurement of hydrogen content), but this would involve a complementary and different study. For alumina-supported MoS<sub>2</sub> the correlation between the theoretical size es-

tablished from the HYD reaction and MoS<sub>2</sub> stoichiometry and the real size was found to be satisfactory. However, in this case the slabs were well dispersed on the support (7).

## CONCLUSIONS

On bulk MoS<sub>2</sub>, the HYD and ISOM sites are found to be respectively the 3 and 2 and/or 4 coordinatively unsaturated (1010) edge plane Mo ions. The same results were obtained previously on MoS<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Moreover, some reactive hydrogen species different from S-H groups and associated with the same anionic vacancies are shown to exist and are measured by a dynamic method. These highly reactive species are also located on the (1010) edge plane of the MoS<sub>2</sub> slab which constitutes hydrogen reservoir.

Moreover, it is highly probable that the active surface corresponds to the portion of unsaturated edge Mo ions that are accessible to the alkadiene molecule, whereas a large majority of unsaturated edge Mo ions remain inaccessible to the alkadiene and constitute the bulk accessible only to hydrogen species. In this description, the bulk slabs are found to be smaller than the surface slabs.

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