JOURNAL OF CATALYSIS **124**, 12–21 (1990)

Site Structure Sensitivity of Diene Hydrogenation and Isomerization Reactions on $MoS_2/\gamma\text{-}Al_2O_3$ Catalysts

S. KASZTELAN,[1,2] A. WAMBEKE,[3] L. JALOWIECKI, J. GRIMBLOT,[1] AND J. P. BONNELLE

Laboratoire de catalyse hétérogène et homogène (U.A. CNRS 402), Université des Sciences et Techniques de Lille, Flandres-Artois, F-59655 Villeneuve d'Ascq, Cedex, France

Received May 25, 1989; revised January 11, 1990

The hydrogenation and isomerization of two diene molecules, *cis*-1,3-pentadiene and 2-methyl-1,3-butadiene (isoprene), have been performed at 50°C on a 13.8 wt% $MoO_3/\gamma\text{-}Al_2O_3$ sulfided hydrotreating catalyst. The alumina support was not active for hydrogenation and its activity for isomerization was found poisoned by the presence of the MoS_2 phase. The observed diene hydrogenation and isomerization activities are therefore attributed to the sulfide phase. Both the activity and the product distribution have been found strongly dependent on the sulfur content of the $(\bar{1}010)$ edge plane of the MoS_2 slabs. In that edge plane all the Mo ions are similar. Therefore the active sites responsible for the various catalytic functions must be distinguished on the basis of the environment of the Mo ions. More precisely hydrogenation has been found sensitive to Mo ions tricoordinatively unsaturated (cus) and isomerization to 2-cus and 4-cus Mo ions. However, as each vacancy or sulfur ion is shared by two Mo ions in the $(\bar{1}010)$ edge plane, a full description of the sites leads us to consider an "elementary ensemble" of two Mo ions and their six associated sulfur ions and/or vacancies. The active sites responsible for the different catalytic functions observed correspond primarily to different configurations of sulfur ions and vacancies in the "elementary ensemble" or, in other words, to different site structures. It is shown that due to its strongly preferred 3-4 hydrogenation, the reaction scheme of isoprene hydrogenation is simple enough to correspond to a catalytic function for each product. It is then shown that different site structures could be assigned to each of these functions and that simple statistical calculations can satisfactorily explain the experimental product distribution. The selectivity and activity of the catalyst for the diene hydrogenation and isomerization reactions studied are therefore dependent on the structure of the sites present in the $(\bar{1}010)$ edge plane of the MoS_2 slabs.

INTRODUCTION

The determination of the nature and number of adsorption and catalytic sites in molybdenum- and tungsten sulfide-based hydrotreating catalysts is a subject of considerable interest in both the academic and the industrial community. This interest appears in the unsolved debate in the literature on the existence of one or several catalytic sites. The latter is however more often claimed as it is well recognized that these catalysts possess various catalytic functions that may result from the existence of different sites, as pointed out by Massoth *et al.* (*1*, *2*). Considerable evidence of the location of the active sites on the edge plane of $MoS_2(WS_2)$ slabs has been gathered recently (*3–5*). The basal plane (0001) of the slab has been shown to be particularly unreactive (*6*, *7*). Thus, this edge sensitivity limits the number of surfaces of interest to the two edge planes, namely the $(10\bar{1}0)$ and $(\bar{1}010)$, present on MoS_2 crystallites with regular shapes (*8–10*).

In previous work from this laboratory it has been reported that the sulfur content of the edge plane can be monitored by reduction of the catalyst in hydrogen at various temperatures (*11*). Three types of sulfur ion

---

[1] To whom correspondence should be addressed.

[2] Present address: Institut Français du Pétrole, B.P. 311, 92506 Rueil-Malmaison, Cedex, France.

[3] Present address: Papeterie de Chantraine, Siège social, 59166 Bousbecque, Cedex, France.

0021-9517/90 $3.00

have been found to be removed for reduction temperature $T < 200°C$, then for $200°C < T < 700°C$ and for $T > 700°C$. These sulfur ions have been assigned to the terminal sulfur ions in the $(10\bar{1}0)$ edge plane, bridged sulfur in the $(\bar{1}010)$ edge plane, and basal sulfur ions, respectively (*11*).

After these reduction pretreatments, the 2-methyl-1,3-butadiene (isoprene) total hydrogenation activity has been measured at low temperature, 50°C, i.e. with a catalyst in a "frozen state" and large variations in the hydrogenation activity have been obtained upon the removal of the bridged sulfur ions in the $(\bar{1}010)$ edge plane of the slab. These variations in total hydrogenation activity have been correlated with the number of three coordinatively unsaturated (CUS) Mo ions in that plane in agreement with Siegel's model (*12*) and the proposals of Tanaka *et al.* (*13–15*). In addition no other edge plane can give three coordinatively unsaturated Mo ions and therefore the hydrogenation sites have been located unambiguously on the $(\bar{1}010)$ edge plane of MoS_2 crystallites (*11*).

Similar results have been obtained for the hydrogenation of *cis*-1,3-pentadiene (*16*). In addition this molecule allows the investigation of the diene isomerization function which according to Siegel's model should be sensitive to two coordinatively unsaturated sites. Indeed it was proposed that 2-cus and also 4-cus Mo ions were responsible for the isomerization activity.

We report in this work a full analysis of the product distributions obtained from isoprene hydrogenation and *cis*-1,3-pentadiene isomerization and hydrogenation reaction. The results obtained have been rationalized and a general description of the various active sites leading to the observed catalytic activity and product distribution is proposed and discussed.

EXPERIMENTAL

The experimental methods used in this work have been reported in detail previously (*11, 16*). Briefly, the catalyst studied contained 9.2 wt% Mo (13.8 wt% MoO_3) on $\gamma\text{-}Al_2O_3$ (240 $m^2\ g^{-1}$) and was prepared by pore-filling impregnation of heptamolybdate solution. The catalyst was sulfided with a H_2/H_2S (90/10) mixture at 350°C for 4 h. After sulfidation the catalyst was reduced under purified hydrogen at different temperatures (from 200 to 800°C) for 12 h and the amount of H_2S removed was measured by iodometry after trapping in an iodine solution. The isoprene hydrogenation and *cis*-1,3-pentadiene hydrogenation and isomerization were performed at 50°C and atmospheric pressure after each reduction pretreatment with a 2.8 liter h^{-1} flow rate and 20/740 HC/H_2. The reaction products were analyzed by gas chromatography. Blank runs were performed on the alumina support pretreated under the same conditions as those for the $MoS_2/\gamma\text{-}Al_2O_3$ catalyst.

RESULTS

The dependence of the total hydrogenation (HYD) activities at 50°C for both isoprene and *cis*-1,3-pentadiene with the temperature of reduction of the $MoS_2/\gamma\text{-}Al_2O_3$ catalyst is reported in Fig. 1. Two similar volcano curves were obtained with no detectable hydrogenation activity for a reduction at temperatures lower than 200 or higher than 800°C. For both molecules a maximum of the activities is observed at 550°C. Notably the alumina support is inactive for the hydrogenation reaction. The sulfide phase is therefore responsible for the hydrogenation activity. A slightly higher HYD activity is observed for *cis*-1,3-pentadiene which can be accounted for by a difference in adsorption coefficient.

The effect of the temperature of reduction of the catalyst is to remove sulfur and change the S/Mo ratio of the sulfide, i.e., create coordinatively unsaturated Mo ions. The number of vacancies generated in the MoS_2 active phase has been determined in previous work by measuring the amounts of sulfur removed at the different tempera-

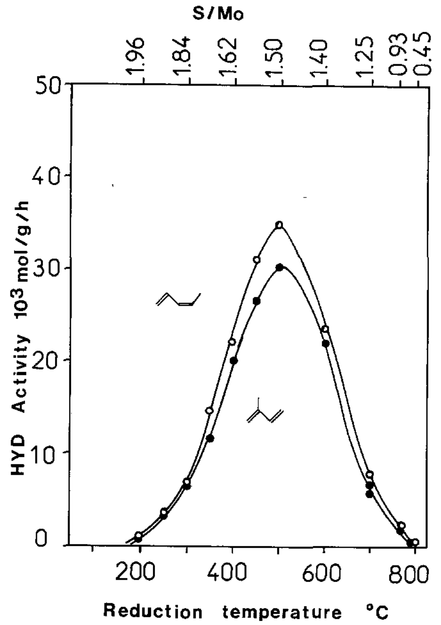

FIG. 1. Isoprene and *cis*-1,3-pentadiene hydrogenation activity at 50°C versus the prereduction temperature of $MoS_2/\gamma\text{-}Al_2O_3$ or the S/Mo ratio of the active phase (upper scale).

tures of reduction (*11*). The S/Mo ratio of the catalyst obtained after each reduction pretreatment is reported in the upper scale of Fig. 1. The low temperature used for the HYD reaction allows us to assume that no change of S/Mo ratio occurred during the reaction. Thus the HYD activities depend primarily on the sulfur unsaturation of the $(\bar{1}010)$ edge plane, the maximum being obtained at S/Mo = 1.5 for the catalyst studied.

It has been shown previously that the range of S/Mo leading to the observed variation in HYD activity corresponds to the removal of a particular type of sulfur ion which has been identified as the bridging sulfur ions of the $(\bar{1}010)$ edge plane of the slab (*11*). In addition, this edge plane is the only one that can give 3-cus Mo ions which are required to create a HYD site according to Siegel's model (*12*). This has been further supported by finding a linear correlation between the statistical number of 3-cus Mo ions present in an hexagonal slab containing 61 Mo ions and the isoprene HYD activity. The 61 Mo ion hexagonal slab is the mean slab size expected from the loading of the catalyst (*10, 11*). Notably the two curves of Fig. 1 correlate linearly, which allows us to state that both molecules need the same 3-cus Mo ions in the $(\bar{1}010)$ edge plane to be hydrogenated.

Using the *cis*-1,3-pentadiene molecule has an advantage over isoprene since it allows the observation of both the diene isomerization (ISOM) and hydrogenation reactions. However, the alumina support has been found active for the ISOM reaction as is well known (*17, 18*). The variation both in the isomerization activity versus the reduction temperature of the support alone and in the $MoS_2/\gamma\text{-}Al_2O_3$ catalyst is reported in Fig. 2. Clearly the ISOM activity variations of each catalyst are very different. For alumina, the ISOM activity increases drastically between 400 and 500°C to reach a plateau for reduction tem-

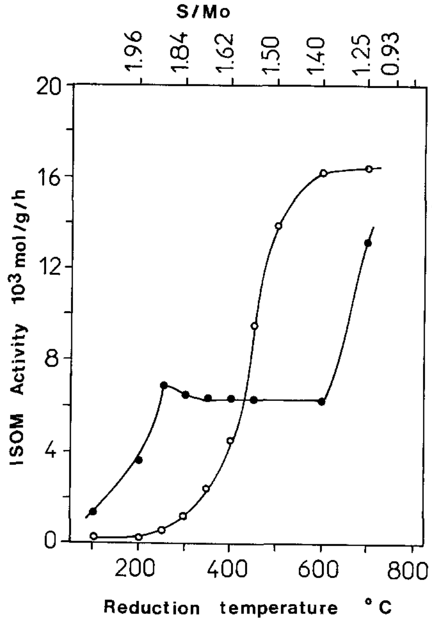

FIG. 2. *cis*-1,3-Pentadiene isomerization activity at 50°C versus the prereduction temperature of (●) $MoS_2/\gamma\text{-}Al_2O_3$ and of (○) the $\gamma\text{-}Al_2O_3$ support. The upper scale reports the variation in the S/Mo ratio in the case of the MoS_2/Al_2O_3 catalyst.

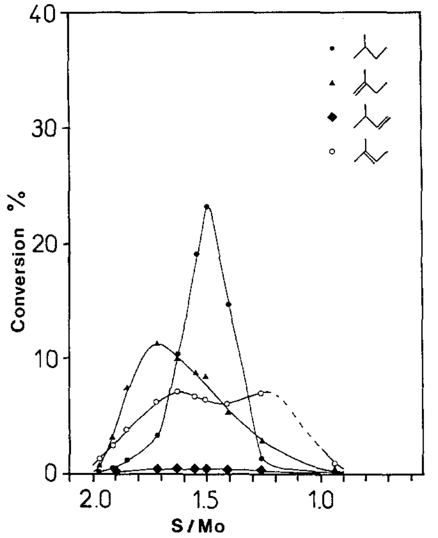

FIG. 3. Conversion (%) into product from isoprene hydrogenation versus the S/Mo ratio of the active phase.

peratures higher than 600°C. On the contrary, for $MoS_2/\gamma\text{-}Al_2O_3$, the ISOM activity appears at much lower temperature of reduction and there is no dramatic increase in the ISOM activity between 400 and 500°C as would be expected from the contribution of the alumina support. In fact, the ISOM activity starts to increase only after a reduction at 600°C. Thus it appears that in the presence of the MoS_2 phase the isomerization sites of the alumina support have been poisoned at least up to 600°C. This can be understood if it is considered that the MoS_2 slabs are fixed at the location of the diene ISOM sites of alumina, the nature of which cannot be determined from these results. At reduction temperature higher than 600°C, the increase in the ISOM activity may be due to the release of alumina ISOM sites or to the generation of ISOM sites on the MoS_2 phase. Although we cannot reach a conclusion on this point, we shall choose the second hypothesis in the following and consider that the measured ISOM activity of the $MoS_2/\gamma\text{-}Al_2O_3$ catalyst results only from the activity of the MoS_2 phase.

The very different variations between *cis*-1,3-pentadiene HYD and ISOM activity clearly demonstrate that these reactions involve different catalytically active sites and that ISOM sites are not 3-cus Mo ions. However, the range of S/Mo ratio in which the variation of ISOM activity occurs is the same as that for HYD activity. Therefore we can conclude that the ISOM sites are located on the same edge plane as the HYD site, i.e., the $(\bar{1}010)$ edge plane.

The distribution of the hydrogenated products of both molecules has been obtained at steady state, which leads us to use the term product distribution rather than selectivity in the following. In Fig. 3 the variation in the conversion for each product from isoprene hydrogenation has been reported versus the variation in the S/Mo ratio. The products obtained were either monohydrogenated (2-methyl-1-butene, 3-methyl-1-butene (in very small amounts), 2-methyl-2-butene) or dihydrogenated (isopentane).

In Fig. 4 the variation in the conversion for each product from *cis*-1,3-pentadiene HYD and ISOM versus the S/Mo ratio is also reported. The products obtained were *cis*-1,3-pentadiene isomerized into *trans*-

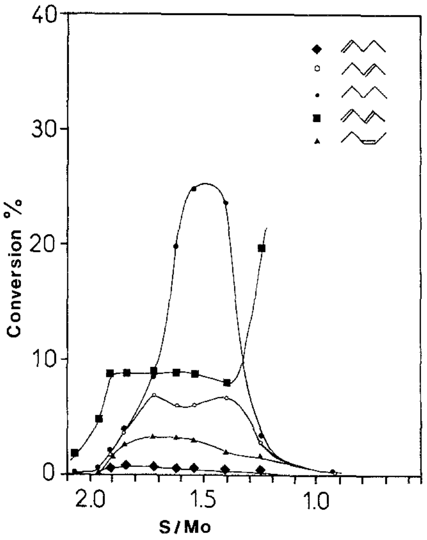

FIG. 4. Conversion (%) into product from *cis*-1,3-pentadiene versus the S/Mo ratio of the active phase.

1,3-pentadiene and either monohydrogenated (1-pentene, *cis*-2-pentene, and *trans*-2-pentene) or dihydrogenated (*n*-pentane). As previously indicated, the interest in using *cis*-1,3-pentadiene lies in the possibility of getting information about the ISOM function which is not given by isoprene. Nevertheless for HYD the reaction scheme of isoprene is less complicated than that for *cis*-1,3-pentadiene, as the presence of the methyl group on the 2 position of the molecule is known to limit drastically the 1-2 and 1-4 HYD (*14, 15, 19, 20*). Thus in comparison with *cis*-1,3-pentadiene the products of isoprene HYD come mainly from 3-4 hydrogenation, making the interpretation of the product distribution easier.

Clearly in Figs. 3 and 4 the distribution of the hydrogenated products depends strongly on the reduction temperature, i.e., on the sulfur unsaturation of the $(\bar{1}010)$ edge plane. Interestingly in the case of isoprene HYD, each product of the reaction has a very different curve for percentage of conversion versus the S/Mo ratio, neglecting the case of 3-methyl-1-butene which is detected in low amounts. For *cis*-1,3-pentadiene, the curves obtained for the various hydrogenated products are rather similar, likely as a result of the superposition of 1-2, 1-4, and 3-4 hydrogenation pathways. However, the curve obtained for *trans*-1,3-pentadiene, the isomerized product of *cis*-1,3-pentadiene, has a shape completely different from that of the total hydrogenation curve.

Thus by taking into consideration the *cis*-1,3-pentadiene ISOM activity and the isoprene HYD activity variation versus the S/Mo ratio, the different curve shapes obtained lead to the apparent contradiction that the same structural type of Mo ions present in the $(\bar{1}010)$ edge plane performs all the different catalytic functions that would be expected to result from the presence of different catalytic sites. This question is related to the nature of the catalytic sites and will be the main subject of the discussion.

DISCUSSION

All the results reported above strongly suggest that the sulfur unsaturation of one particular edge plane of the MoS_2 slabs is the key factor influencing both activity and product distribution of diene HYD and ISOM. Since all the Mo ions are similar in the $(\bar{1}010)$ edge plane, different environments or site structures must be responsible for these activity and selectivity variations (*15*).

It has been shown by Siegel that there is a connection between the "elementary reaction" involving hydrogen (such as HYD and ISOM) and the number of coordinative unsaturation of the metal ion. In particular Siegel concluded that HYD would require 3-cus metal ions whereas ISOM would require 2-cus metal ions (*12*). Such an approach has been developed by Tanaka *et al.* in the case of sulfides (*14, 15*). These numbers of coordinative unsaturation are in fact the number of anions missing in the coordination sphere of the metal ion. These vacancies may then accommodate reactive species so that the metal ion will be formally less coordinatively unsaturated. However, in the following, the cus number referred to will be the original one, i.e., the number of sulfur species missing.

As discussed previously (*11*), the HYD activity of dienes is related to 3-cus Mo ions on MoS_2, giving strong support to Siegel's model. Thus, based on this model we shall assign the HYD activity to 3-cus Mo ions and the ISOM activity to 2-cus Mo ions. This latter assignment takes into account the ISOM activity at high S/Mo ratios. However, to include the large increase in the ISOM at low S/Mo ratio in this context, we shall postulate that 4-cus Mo ions are also ISOM sites (*16*). Let us recall that in the $(\bar{1}010)$ edge plane Mo ions can be up to 4-cus. Thus, starting from a completely saturated $(\bar{1}010)$ edge plane, the gradual removal of sulfur ions upon reduction will lead to the generation of 2-cus, then 3-cus, and finally 4-cus Mo ions, i.e., to the corresponding sequence ISOM, HYD, and ISOM as observed experimentally in Figs. 1 and 2.

Thus, as a necessary condition to obtain isomerization or hydrogenation, the number of cus is a satisfactory concept. However, it is not sufficient to understand the dependence of the hydrogenation product distribution upon the sulfur unsaturation. Indeed, all the hydrogenated products are derived through reaction with a 3-cus Mo ion, but different products are obtained. To understand this point we must consider more carefully the environment of the Mo ions in the $(\bar{1}010)$ plane.

In the $(\bar{1}010)$ edge plane each sulfur ion or vacancy is shared by two Mo ions. Thus, at such a vacancy an adsorbed molecule will interact with two molybdenum ions. We have therefore to consider a pair of molybdenum ions with their six neighbor sulfur ions and/or vacancies as the "elementary ensemble" interacting with the molecule. Note that if we consider the other edge plane $(10\bar{1}0)$ and the intersection of both edge planes, four different elementary ensembles can be defined (*21*).

Depending on the amount of sulfur ions present in the $(\bar{1}010)$ edge plane, different configurations of the elementary ensemble can be found. A number of 32 configurations can be obtained by creating one, two, three, four, or five vacancies in the elementary ensemble and arranging them differently around the central vacancy specified for adsorption of the molecule (*21*). These configurations can be classified into 12 different configurations sorted out in Table 1 and corresponding to the combination of the number of cus of each Mo ion of the elementary ensemble, i.e., ${}^{x}M\text{–}{}^{y}M$ with x, $y = 1$ to 4 according to the notation recommended by Tanaka *et al.* (*14, 15*). Evidently these are the configurations obtained by considering only sulfur ions and vacancies. The presence of SH^- or H^* as well as an adsorbed molecule will significantly increase the number of combinations.

Each of these configurations will be considered as a catalytically active site except the trivial case of one vacancy in the ensemble ${}^{1}M\text{–}{}^{1}M$ which is only able to adsorb (ADS) a molecule (see Table 1). These sites are therefore not distinguishable on the basis of different Mo ions but on the basis of different structures or environments of the adsorbed molecule.

As each vacancy in the $(\bar{1}010)$ edge plane is shared by two Mo ions so will be the molecule adsorbed at that vacancy. Therefore it can be proposed as a rule that in the ensemble each metal ion interacting with the adsorbed molecule will perform the elementary reaction authorized by the number of cus it possesses. Thus the combination of elementary reactions occurring in a concerted way will result in a certain function which each configuration or site will perform. In this work we are considering two elementary reactions, HYD and ISOM. Therefore the possible combinations will be HYD–ISOM, HYD–HYD, and ISOM–ISOM.

Interestingly, the hydrogenated products obtained experimentally allow us to characterize these functions especially in the case of isoprene HYD. Considering the molecule in the adsorbed state and the various functions involving one or two elementary reactions, we have reported the simplified reaction schemes for isoprene in Fig. 5 and for *cis*-1,3-pentadiene in Fig. 6. Since the 3-4 hydrogenation reaction of isoprene is preferred, isopentane will characterize the HYD–HYD function, 2-methyl-1-butene and 3-methyl-1-butene the HYD function, and 2-methyl-2-butene the HYD–ISOM function as can be seen in Fig. 5. This is different in the case of *cis*-1,3-pentadiene as shown in Fig. 6 where one product can be produced by several reaction pathways, i.e., different functions. For example *trans*-2-pentene can be the product of the 1-2 HYD or of the 3-4 HYD followed by ISOM.

Such identification can be done in the case of isoprene as the hydrogenated products have been found to be primary products. In addition it is known that monoenes

TABLE 1

Schematic Diagram of the Different Sites Generated on the $(\bar{1}010)$ Edge Plane of MoS_2 Slabs and Their Associated Functions and Probability of Existence

Site	Couple of cus	Function	Probability
	1 - 1	ADS	qp^5
	1 - 2	ISOM	$5q^2p^4$
	2 - 2		
	1 - 3	HYD	$2q^3p^3$
	2 - 2	ISOM	$4q^3p^3$
	2 - 3	HYD-ISOM	$4q^3p^3$
	2 - 3		$4q^4p^2$
	2 - 4	ISOM	$2q^4p^2$
	3 - 3	HYD-HYD	$4q^4p^2$
	3 - 3		q^5p
	3 - 4	HYD-ISOM	$4q^5p$
	4 - 4	ISOM	q^6

Note. (▨) Sulfur, (☐) vacancy, (⊞) central vacancy, (●) Mo ion.

are less reactive than conjugated dienes and therefore we can consider that readsorption of monoenes followed by another reaction at the low temperature used is negligible.

We have now to assign a function to each of the configurations (or sites) of Table 1 using the criteria defined above. For example configurations where one Mo ion is 1-cus and the other is 2-cus (^1M–^2M) will perform only a simple ISOM. The configurations with one Mo ion 1-cus and one Mo ion 3-cus (^1M–^3M) will lead to monohydrogenation (HYD) whereas sites with both Mo ions 2-cus (^2M–^2M) will lead to ISOM–ISOM which we shall not distinguish from ISOM in the following. For the configurations possessing four vacancies each Mo ion is 3-cus (^3M–^3M)—therefore double hydrogenation (HYD–HYD) should be obtained—whereas the sites with one Mo ion 2-cus and the other 3-cus (^2M–^3M) will give hydrogenation followed by isomerization (HYD–ISOM). Accordingly, a catalytic function can be attributed to each of the

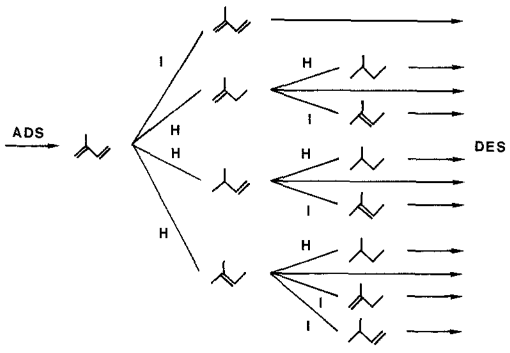

FIG. 5. Simplified reaction scheme of isoprene hydrogenation and isomerization in the adsorbed state (I, ISOM; H, HYD, ADS, adsorption, DES, desorption).

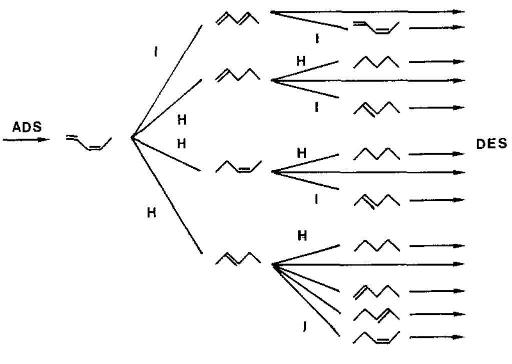

FIG. 6. Simplified reaction scheme of the *cis*-1,3-pentadiene in the adsorbed state (I, ISOM; H, HYD; ADS, adsorption; DES, desorption).

combination of pairs of cus Mo ions in Table 1. Strikingly, it is observed that one type of catalytic function can eventually be performed by several different site structures.

During the experiments performed, the variation in the sulfur content in the $(\bar{1}010)$ edge plane led to a variation in the distribution of the site structures and, if our hypothesis is correct, to a variation in the functions leading to the observed product distribution. In order to check the validity of this approach, a statistical computation based on combinatorial analysis has been attempted. For each configuration we have postulated a vacancy at the central position with probability q, around which the probability of a given combination of sulfur ions and vacancies is

$$P(k)= C_k^n \cdot q^k \cdot p^{(n-k)}, \qquad (1)$$

with q representing the probability of a vacancy being created or sulfur removed; $p = 1 - q$, representing the probability of a nonvacancy; n representing the maximum number of sulfur anions that can be removed, i.e., $n = 5$; and k representing the number of sulfur anions actually removed, $k = 0$ to 5. Hence the probability of existence of a configuration is

$$q \cdot P(k). \qquad (2)$$

Thus in Table 1 one can now compute the probability corresponding to each of the 12 configurations to which a function has been previously assigned. Then we can sum the probability to obtain the catalytic function. For the total isomerization one obtains

$$\text{ISOM} = 5q^2p^4 + 4q^3p^3 + 2q^4p^2 + q^6; \qquad (3)$$

for the monohydrogenation there is only one configuration, thus:

$$\text{HYD} = 2q^3p^3; \qquad (4)$$

for dihydrogenation one obtains

$$\text{HYD–HYD} = 4q^4p^2 + q^5p; \qquad (5)$$

for HYD–ISOM

$$\text{HYD–ISOM} = 4q^3p^3 + 4q^4p^2 + 4q^5p; \qquad (6)$$

and for the total hydrogenation the sum is

$$\text{Total HYD} = 6q^3p^3 + 8q^4p^2 + 5q^5p. \qquad (7)$$

The variation in the probability versus the fraction of sulfur removed for the isomerization and for the total hydrogenation reactions is reported in Fig. 7. Both curves are in reasonable agreement with the experimental results of Figs. 1 and 2. Then the variation in the probability versus the fraction of sulfur removed for the different hydrogenation functions is reported in Fig. 8 with a separation between the two parts of the HYD–ISOM function, i.e., config-

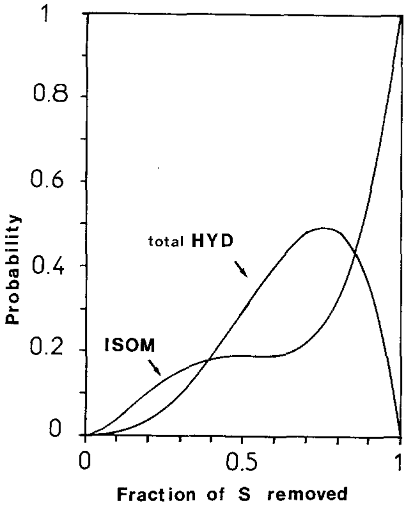

FIG. 7. Probability curve versus the fraction of sulfur removed for the total hydrogenation and isomerization functions.

urations corresponding to $(^2M–^3M)$ and $(^4M–^3M)$, respectively. In Fig. 8 the different curves obtained for each function have their maximum at S/Mo ratio in the same order as observed experimentally, i.e., mono-HYD, HYD–ISOM, HYD–HYD, HYD–ISOM, as the unsaturation of the $(\bar{1}010)$ edge plane increases.

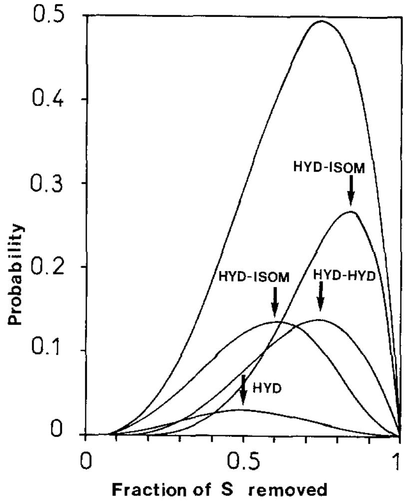

FIG. 8. Probability curve versus the fraction of sulfur removed for the different hydrogenation functions.

There are however two major discrepancies between the experimental and the calculated curves. The first one already noted (*11*) is the difference between the calculated S/Mo ratio and the observed ratio. This is likely a result of the crystallite size distribution since smaller sizes, in particular, will give lower S/Mo ratios. The other main discrepancy is the difference in the curve intensities. In particular in Fig. 7 the ISOM curve is more intense than the HYD curve. In Fig. 8 the various curves for hydrogenation do not have the same relative intensity as the experimental results of Fig. 3. Several reasons can be proposed to explain this discrepancy. First it must be pointed out that for these calculations it is implicitly assumed that: (i) each sulfur is removed with the same energy or probability, (ii) each configuration has the same probability of existence, and (iii) as we have summed probabilities we assume that each configuration has the same turnover number. It is evident that these assumptions are very crude. Clearly it can be expected that the energy to remove one sulfur ion changes as the sulfur ion unsaturation increases. Then some site structures are likely to be more stable than others, and the reactivity of the configurations may be different and change when the S/Mo ratio changes. However, as a first approximation this approach appears successful to check qualitatively the experimental observations.

Another point to consider is the crude description of the site structure made in this work where only sulfur and vacancies have been considered. To be complete one must in fact consider the elementary ensemble with all the possible species involved such as $S^=$, SH^-, H^*, the adsorbed molecule and vacancy (*21*). As sulfur ions are removed, it does not in fact mean (as is implicitly stated above) that the number of vacancies increases. In fact more hydrogen and reactant molecules will be adsorbed, limiting particularly the number of $(^3M–^4M)$ and $(^4M–^4M)$ sites and therefore decreasing the corresponding curve intensities in Fig. 8. In view of the great number of site structures involved when considering all the species, the task of identifying the relationship between structure and catalytic function is difficult.

Finally it is shown that within the limitations of the model the general features of the observations are reproduced and validate the importance of considering the site structure as one of the keys to understanding the activity and selectivity properties for diene HYD and ISOM reactions on $MoS_2/\gamma\text{-}Al_2O_3$ catalysts.

CONCLUSION

The results reported in this study demonstrate that both the activity and product distribution for hydrogenation and isomerization reactions on alumina-supported MoS_2 catalysts depend primarily on the sulfur content of the $(\bar{1}010)$ edge plane of MoS_2 slabs. This dependence can be rationalized by considering that the active sites consist of an elementary ensemble of two Mo ions and their six surrounding sulfur anions or vacancies with the adsorbed molecules interacting with the two Mo ions where each vacancy or sulfur ion is bridged in the edge plane. Many different configurations of the elementary ensemble can be found by changing the number of sulfur anions or vacancies in it. To each configuration or site structure a function is assigned resulting from the combination of two elementary reactions (HYD or ISOM) each performed by one of the Mo ions of the elementary ensemble. While the HYD reaction has been shown to need 3-cus Mo ions, it appears that ISOM needs Mo ions possessing 2 or 4-cus. The functions are therefore HYD–ISOM, HYD–HYD, and ISOM–ISOM corresponding to $({}^3M\text{–}{}^2M)$, $({}^3M\text{–}{}^3M)$, and $({}^2M\text{–}{}^2M)$ or $({}^4M\text{–}{}^4M)$ cus combinations, respectively. Simple statistical computations are in reasonable agreement with the experimental observations.

ACKNOWLEDGMENTS

The experimental work is part of the thesis of A. Wambeke. We are indebted to the Institut Français du Pétrole for the preparation of the samples. The comments of the referees have been very fruitful and much appreciated.

REFERENCES

1. Muralidhar, G., Massoth, F. E., and Shabtai, J., Preprint of ACS Div. Petr., Kansas, p. 722 (1982).
2. Muralidhar, G., Massoth, F. E., and Shabtai, J., *J. Catal.* **85,** 44 (1984); *J. Catal.* **85,** 53 (1984).
3. Chianelli, R. R., Ruppert, A. F., Behal, S. K., Kear, B. H., Wold, A., and Kershaw, R., *J. Catal.* **92,** 56 (1985).
4. Topsøe, H., and Clausen, B. S., *Appl. Catal.* **25,** 273 (1987).
5. Roxlo, C. B., Daage, M., Ruppert, A. F., and Chianelli, R. R., *J. Catal.* **100,** 176 (1986).
6. Farias, M. H., Gellman, A. J., Somorjai, G. A., Chianelli, R. R., and Liang, K. S., *Surf. Sci.* **140,** 181 (1984).
7. Salmeron, M., Somorjai, G. A., Wold, A., Chianelli, R. R., and Liang, K. S., *J. Catal.* **90,** 105 (1982).
8. Schuit, G. C. A., *Int. J. Quantum Chem.* **12,** 43 (1977).
9. Ratnasamy, P., and Sivasanker, S., *Catal. Rev. Sci. Eng.* **22,** 401 (1980).
10. Kasztelan, S., Toulhoat, H., Grimblot, J., and Bonnelle, J. P., *Appl. Catal.* **13,** 127 (1984); *Bull. Soc. Chim. Belg.* **93,** 807 (1984).
11. Wambeke, A., Jalowiecki, L., Kasztelan, S., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **109,** 320 (1987).
12. Siegel, S., *J. Catal.* **30,** 139 (1973).
13. Okuhara, T., Itoh, H., Miyahara, K., and Tanaka, K., *J. Phys. Chem.* **82,** 678 (1978).
14. Tanaka, K. I., and Okuhara, T., *Catal. Rev. Sci. Eng.* **15,** 249 (1977).
15. Tanaka, K. I., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 33, p. 99. Academic Press, San Diego, 1985.
16. Kasztelan, S., Jalowiecki, L., Wambeke, A., Grimblot, J., and Bonnelle, J. P., *Bull. Soc. Chim. Belg.* **96,** 1003 (1987).
17. Imizu, Y., Sato, K., and Hattori, H., *J. Catal.* **76,** 65 (1982) and references therein.
18. Lombardo, E. A., Houalla, M., and Hall, W. K., *J. Catal.* **51,** 256 (1978).
19. Daage, M., and Bonnelle, J. P., *Appl. Catal.* **16,** 355 (1985).
20. Masclet, P., Mouvier, G., Bocquet, J. F., *J. Chim. Phys., Paris* **78,** 99 (1981).
21. Kasztelan, S., *C.R. Acad. Sci. Paris Ser. 2* **307,** 727 (1988).