Effect of Mo Loading of MoS₂/γ-Al₂O₃ on Diene Hydrogenation: Evidence of an "Elementary Ensemble" Site

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Hydrogenation of alkadienes has been performed at relatively low temperature (323 K) and atmospheric pressure on a series of MoS₂/γ-Al₂O₃ catalysts with contents ranging from 2.3 to 15.7 wt% Mo. After sulfidation the solids were treated at various temperatures under H₂ for creating different degrees of unsaturation of the MoS₂ slabs and then tested. The maximum of hydrogenating power is obtained for the same treatment temperature (823 K) under H₂ whatever the Mo loading. As this treatment temperature has been correlated in a previous study on MoS₂/γ-Al₂O₃ (9.2 wt% Mo) (A. Wambeke *et al.*, *J. Catal.* **109**, 320 (1988)) with the presence of a maximum of three coordinatively unsaturated (CUS) Mo ions located in the (1̄010) edge plane of the MoS₂ slab, this correlation applies well whatever the considered Mo loading. Moreover, the product distribution has been analyzed as a function of treatment temperature and Mo loading and attributed to different structures of sites corresponding to "elementary ensembles" constituted by at least two Mo ions with various S and anionic vacancy environments. © 1991 Academic Press, Inc.

INTRODUCTION

Hydrotreatment catalysts based on W or Mo sulfides are widely used because of their application in removal of sulfur (HDS), or of nitrogen (HDN), in hydrogenation of petroleum feedstocks. The characterization of the active sites involved in the different paths is of great importance as the unresolved question is still to know whether these different catalytic functions are due to one or more different kinds of site (*1*, *2*). Another question is to ask what precisely is the role of Mo (with or without promoter) in the successive steps of the hydrotreatment (HDT) reaction, and how structural models can account for the proposed surface state as well as for the selectivity in the products obtained. It is now generally assumed that the active sites are associated with the edge plane of the MoS₂ slabs (*3–5*) as the basal plane is not reactive (*6*, *7*). A modeled MoS₂ slab of regular shape exhibits two different

edge planes (*8–10*) and different degrees of unsaturation at the Mo sites can be obtained depending on the edge plane considered. Only the (1̄010) edge plane can present Mo ions with more than two coordinated unsaturations, from 1 up to 4 (*10*).

Clearly a link between the phase structure and the catalytic reaction is necessary to identify these active sites and their active species. Recently, in our laboratory, activities in hydrogenation and isomerization of model molecules (alkadienes) have been measured on powdered (*11*) and supported (*12*) MoS₂ on γ-Al₂O₃ (9.2 wt% Mo) catalysts with controlled S/Mo stoichiometries obtained by hydrogen treatment at various temperatures. It was possible to correlate the hydrogenation activity with the edge Mo ions possessing three vacancies (³M) and one sulfur present in the (1̄010) edge plane of the MoS₂ slab (*11*, *12*). On the other hand, isomerization activity was correlated with the two (²M) and/or four (⁴M) coordinatively unsaturated (1̄010) edge plane Mo ions (*13*). These results are in agreement with Siegel's

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proposals, which suggest that the number of coordinative unsaturation positions on a site and the set of elementary reactions involving hydrogen are connected (*14, 15*). Such a concept has been validated for nickel sulfide catalysts (*16*) and has been widely used by Tanaka and Okuhara (*17–19*) to give a careful description of the edge sites on MoS_2 where coordinatively unsaturated (CUS) Mo ions are available at various degrees of coordination. Moreover, in the ($\bar{1}010$) edge plane, the sulfur and/or anionic vacancies created are bridged and associated with two Mo ions. In a study where the alkadiene hydrogenated product distribution has been analyzed as a function of the creation of anionic vacancies on the edge of the MoS_2 slab, a better description of the active site has been proposed to correspond to an "elementary ensemble" composed of at least two Mo ions in various environments of S and anionic vacancies which correspond to different site structures $^{X}M–^{Y}M$ (*20*).

This previous work was performed with a constant Mo loading (9.2 wt% Mo) catalyst. The aim of the present study was to analyze the influence of the Mo loading on the distribution of alkadiene hydrogenated products. Indeed, the Mo loading may influence the MoS_2 crystallite size or dispersion on the γ-Al_2O_3 support. It is generally accepted that in the oxidic precursor of monolayer-like coverage composed of polyoxomolybdate species interacting with the support is obtained (*21–23*) up to ~20 wt% MoO_3. Upon sulfidation, strong experimental evidences by EXAFS (*24, 25*) and electron microscopy (*26*) indicate the presence of MoS_2 as small single slabs. The mean stacking on MoS_2/γ-Al_2O_3 (9.2 wt% Mo) has been proposed to be of 1.5 (*12, 27, 28*). The effect of the Mo loading on some catalytic tests such as thiophene HDS or alkane hydrogenation obtained by Bachelier *et al.* (*29*) has been explained with the help of a geometrical model: the increase of the Mo loading mainly influences the mean slab size (*10, 30*). It is therefore inferred that the ensemble effect previously mentioned will be clearly detected within the context of the present study. This approach is very similar to those conducted on the catalytic properties of metal particles of various dispersion.

EXPERIMENTAL

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

The pretreatment and catalytic experiments were carried out at atmospheric pressure in an all-glass, grease-free flow apparatus previously described (*31*). The catalysts (pellets) were first sulfided with a H_2/H_2S (90–10) mixture at 623 K for 4 h and then cooled to room temperature. The solid was then treated under a purified hydrogen flow at various temperatures T_R between 473 and 1073 K for 12 h. It should be noted that the catalyst MoS_2/γ-Al_2O_3 structure is stable in this range of temperatures (*12*).

After each treatment step by H_2, the solid (50 mg) was cooled to room temperature, reactants (isoprene, *trans*- or *cis*-1,3-pentadiene) were introduced at constant pressure (20 Torr) in a flow of purified hydrogen (1 atm, 20 ml min^{-1}) in an isothermal reactor. The catalytic tests were carried out under hydrogen–alkadiene (740–20) flow at 323 K.

Isoprene (2-methyl-1,3-butadiene), *trans*- or *cis*-1,3-pentadiene, purum grade from Fluka, were used after purification by distillation under vacuum. Hydrogen was purified from any traces of oxygen and H_2O that would result in a complete catalyst poisoning. The reaction products were analyzed by gas chromatography using a 50-m PLOT Al_2O_3/KCl capillary column (ϕ 32 mm) operating at 398 K and a flame ionization detector.

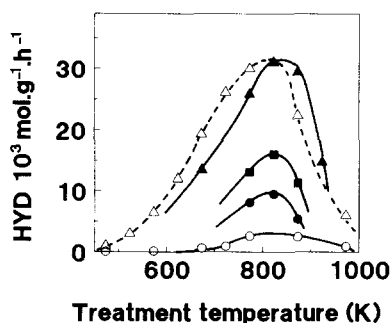FIG. 1. Isoprene hydrogenation activity measured at 323 K as a function of treatment temperature under H$_2$ of MoS$_2$/γ-Al$_2$O$_3$ containing (○) 2.3 wt% Mo, (●) 2.9 wt% Mo, (■) 4 wt% Mo, (△) 9.2 wt% Mo (from Ref. (12)), and (▲) 10 wt% Mo.

RESULTS

I. Hydrogenation Activity

In order to be active in hydrogenation, these solids must be treated under H$_2$ at various temperatures T_R. This treatment leads to the elimination of S ions and to the creation of anionic vacancies on the MoS$_2$ phase (12). Based on the Siegel concept which proposes that a type of reaction is associated with a cation with a defined number of coordinated unsaturation positions (14, 15), hydrogenation of model molecules at low temperature and atmospheric pressure has been largely used previously to characterize active sites on these MoS$_2$-based catalysts (11–13, 20).

It has been previously reported that isoprene as well as cis-1,3-pentadiene hydrogenation activity on a MoS$_2$/γ-Al$_2$O$_3$ (9.2 wt% Mo) catalyst is dependent on the treatment temperature T_R under H$_2$ (12). The variation of activity observed corresponds to a volcano curve with a maximum for T_R of about 823 K.

In this study, a series of MoS$_2$/γ-Al$_2$O$_3$ catalysts with various Mo contents from 2.3 to 16 wt% has been investigated. It is found that the isoprene hydrogenation activity of the catalyst depends on the Mo content of MoS$_2$/γ-Al$_2$O$_3$ as reported in Fig. 1. For solids prepared in the same conditions and us-

ing the same support, a volcano curve is obtained with different intensities. The position of the maximum corresponds to the same treatment temperature T_R (823 K). The results obtained previously (12) on MoS$_2$/γ-Al$_2$O$_3$ (9.2 wt% Mo) are also presented; globally the same shape of curve is obtained. A very different result has been obtained on a bulk powdered MoS$_2$ for which a maximum of alkadiene hydrogenation activity was observed after a treatment at T_R = 673 K (11). Thus when exactly the same support and the same operating and preparation conditions are used, the optimum hydrogenating power is obtained at the same treatment temperature T_R.

In Fig. 2a the evolution of isoprene hydrogenation activity is reported as a function of Mo concentration of MoS$_2$/γ-Al$_2$O$_3$ pretreated at T_R = 773 or 823 K. For the different treatment temperatures, different curves with a similar shape are obtained,
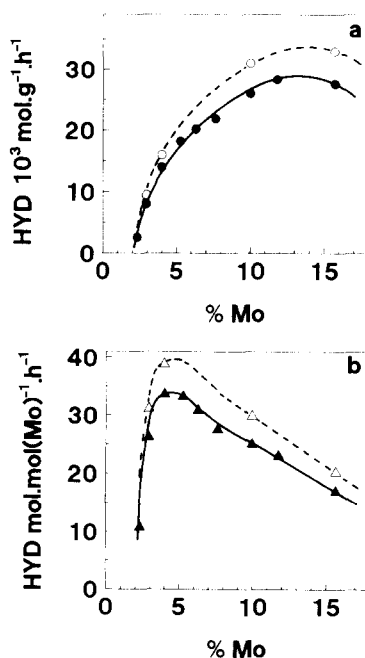

FIG. 2. Isoprene hydrogenation activity measured at 323 K as a function of Mo concentration of MoS$_2$/γ-Al$_2$O$_3$ treated at (●, ▲) 773 K and (○, △) 823 K under H$_2$.

and the highest values are observed for $T_R =$ 823 K as already noted in Fig. 1. Alkadiene hydrogenation activity increases with Mo content up to a value of about 33 10^{-3} mol $g^{-1} h^{-1}$ corresponding to a Mo concentration of about 13.5 wt%. When the isoprene HYD is reported in mol $mol(Mo)^{-1}h^{-1}$ as in Fig. 2b (which corresponds to the HYD in mol $g^{-1} h^{-1}$ divided by the Mo content of the solid), a maximum is observed for 4.5 wt% Mo. So the optimum ratio of active Mo compared to total Mo content is obtained for a MoS_2/γ-Al_2O_3 catalyst with 4.5 wt% Mo (7 wt% MoO_3). A similar trend was already observed by Bachelier *et al.* (29) for thiophene HDS but the position of the maximum was not exactly the same (10 wt% MoO_3 instead of 7 wt% MoO_3 in our case). However, it is difficult to know whether this difference is really significant when various parameters involved in the catalyst preparation and activation are different. The important result is that the same shape of curve is obtained, attributed to the activity of edge plane Mo ions (10, 29).

II. Distribution of Products

The hydrogenation activity takes into account all the hydrogenated products, which are isopentane (dihydrogenated), 2-methyl-1-butene, 3-methyl-1-butene and 2-methyl-2-butene (monohydrogenated) for isoprene and pentane (dihydrogenated), *cis*-2-pentene, *trans*-2-pentene, and 1-pentene (monohydrogenated) for *trans*- or *cis*-1,3-pentadiene.

The distribution of these different products has been found to depend on the pretreatment temperature T_R of MoS_2/γ-Al_2O_3 (9.2 wt% Mo) and has been attributed to different types of sites (20). In Fig. 3a the observed variations are reported: the dihydrogenated product concentration (isopentane, pentane) is found to be the highest for T_R between 673 and 973 K.

Completely different is the product distribution obtained with the 2.3 wt% Mo catalyst, since the major product is never the dihydrogenated compound but a monohy-
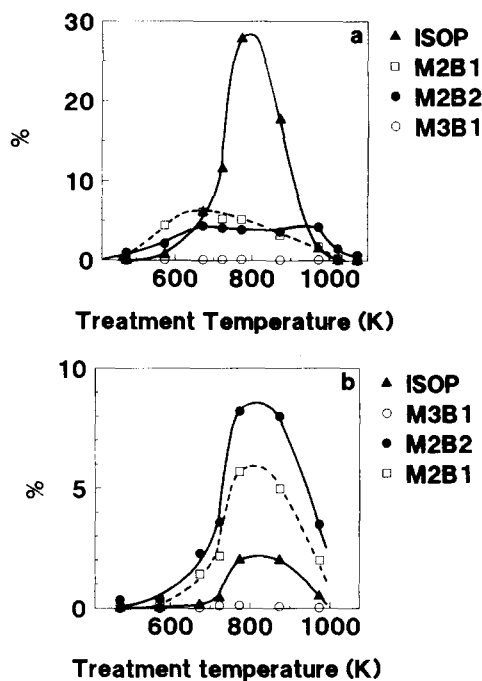

FIG. 3. Isoprene product distribution measured at 323 K as a function of treatment temperature under H_2 of MoS_2/γ-Al_2O_3 containing (a) 9.2 wt% Mo (from Ref. (20)) and (b) 2.3 wt% Mo.

drogenated molecule (2 methyl-2-butene) (Fig. 3b). As can be seen in Fig. 4, where the isoprene hydrogenation product distribution has been reported as a function of the Mo concentration of MoS_2/γ-Al_2O_3 treated at $T_R =$ 823 and 773 K, the dihydrogenated product disappears for a Mo content lower than ~5 wt% Mo. The same result has been obtained with another alkadiene molecule, the *trans*-1,3-pentadiene (Fig. 5). Hence, the Mo concentration plays a crucial role in the product distribution: for Mo content lower than 5 wt%, major changes occur; for Mo concentrations higher than 5 wt% up to 16 wt% Mo, the upper limit explored, the same product distribution is obtained.

Some differences are observed in the monoenes distribution obtained from *cis*-1,3-pentadiene compared to *trans*-1,3-pentadiene; this can be explained by the difference of adsorption (conformation and ad-
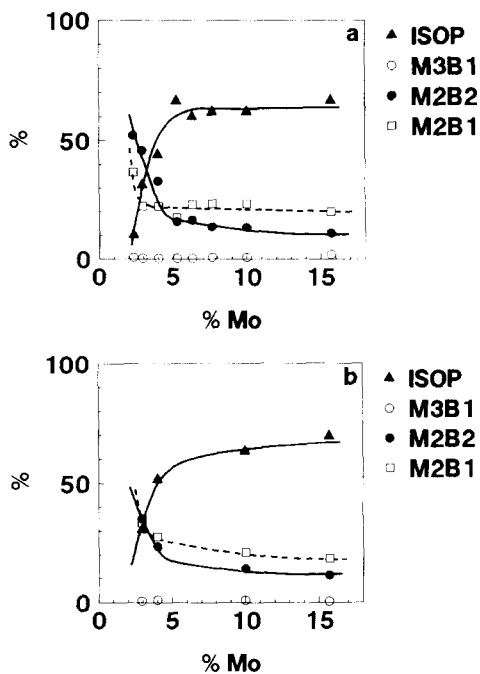
FIG. 4. Isoprene product distribution measured at 323 K as a function of Mo concentration of MoS_2/γ-Al_2O_3 treated at (a) 773 K and (b) 823 K under H_2.

sorption strength) of these two molecules (32).

DISCUSSION

The effect of treatment temperature under H_2 on MoS_2/γ-Al_2O_3 (9.2 wt% Mo) has been studied previously (12). Some anionic vacancies are created at the edge planes of the MoS_2 slabs by the elimination of H_2S during the H_2 treatment at various temperatures T_R. By comparison to a modeled MoS_2 phase, it was possible to localize the different types of S ion removed as a function of the range of treatment temperatures applied. For treatment temperatures lower than 473 K a large amount of H_2S is eliminated and corresponds to the removal of (10$\bar{1}$0) edge plane terminal S ions; for temperatures between 473 and 973 K the (1$\bar{0}$10) edge plane bridge S ions are eliminated and for higher treatment temperatures the basal plane S ions are removed with the destruction of the MoS_2 slab.

The comparison of these results with the evolution of alkadiene hydrogenation and isomerization activities as a function of treatment temperature allow us to attribute hydrogenation activity to the three CUS Mo ions located in the (1$\bar{0}$10) edge plane of the MoS_2 phase (^3M) whereas isomerization activity depends on the presence of two and/or four CUS Mo ions (^2M and/or ^4M) located in the same plane in agreement with the literature (14–19) as well as with a statistical model giving the evolution of the ^2M, ^3M, and ^4M sites as a function of the removal of S ions (13). In Fig. 1 the maximum of isoprene hydrogenation (HYD) activity measured at 323 K for a specific treatment temperature under H_2 of MoS_2/γ-Al_2O_3 catalysts with various Mo concentrations corresponds to the presence in each case of a maximum of ^3M sites in the edge plane of the MoS_2 slab (12). The difference between the hydrogenating power of each solid can be explained by the difference in the size of the MoS_2 crystallites (10). As a matter of fact, Fig. 2b shows that an optimum ratio $^3M/M$ is obtained for the solid MoS_2/γ-Al_2O_3 with 4.5 wt% Mo which is in agreement with the existence of an optimum ratio between edge Mo ions compared to the total (M) Mo ions of the MoS_2 slab (10). One can therefore estimate a "turnover" of a ^3M site by dividing the HYD activity in mol mol(Mo)$^{-1}$ h^{-1} as presented in Fig. 2b by the $^3M/M$ ratio of
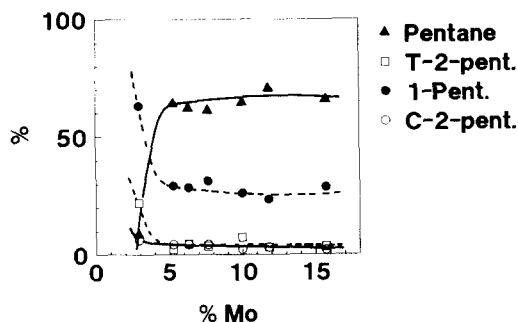

FIG. 5. Cis-1,3-pentadiene product distribution measured at 323 K as a function of Mo concentration of MoS_2/γ-Al_2O_3 treated at 773 K under H_2.
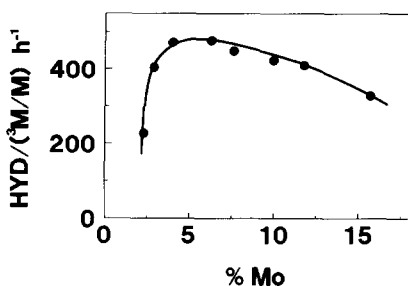
FIG. 6. Isoprene hydrogenation activity measured at 323 K of a ^3M site as a function of Mo loading of MoS_2/ γ-Al_2O_3.

modeled hexagonal slabs (12). The average value obtained is 440 h^{-1} and remains quite constant for Mo loadings varying from 2.9 to 10 wt% Mo (Fig. 6). For higher Mo loading it is probable that the stacking of MoS_2 slabs is not as low as we have supposed and a decrease of the accessible ^3M sites could explain the decrease of the turnover value observed. For Mo loading lower than 2.9 wt% Mo a sharp decrease is observed; the turnover value obtained for 2.3 wt% Mo is 227 h^{-1}.

The crystallite size of MoS_2/γ-Al_2O_3 9.2 wt% Mo has been proposed to be 30 Å with an average stacking of 1.5 (31,32), which corresponds to modeled hexagonal MoS_2 slabs of $M = 61$ total Mo ions with $n = 5$ Mo ions per side (the side includes the edge and corner sites) (10, 12). Assume that:

—the number of "anchoring" sites of MoS_2 on γ-Al_2O_3 (if they exist) do not vary as a function of Mo content as long as exactly the same γ-Al_2O_3 is used;

—the MoS_2 crystallite size increases as a function of Mo content and not the stacking (which is certainly true for the range of Mo content below 9.2 wt% and which can vary as Mo content increases — at first slowly and possibly more and more sharply for higher Mo concentrations).

The value for 3 wt% Mo corresponds to a modeled hexagonal MoS_2 slab with M = 19 total Mo ions so $n = 3$ Mo ions per side which is the limit to obtain at least one edge Mo ion. For lower Mo loading the edge Mo

ion disappears and the activity decreases as expected because of the well known correlation between edge Mo ions and activity (3–5), confirmed here using the hydrogenation reaction of alkadiene molecules.

Moreover, as the S ions and/or vacancies are shared by two Mo ions in the ($\bar{1}010$) edge plane of the MoS_2 slab, a more realistic description of the active site should consider an elementary ensemble of two Mo ions and their six S ions and/or vacancies. The analysis of the alkadiene product distribution obtained as a function of treatment temperature on MoS_2/γ-Al_2O_3 (9.2 wt% Mo) was attributed to the different configurations of S ions and anionic vacancies in this elementary ensemble (i.e., different type structures). A modeling of the MoS_2 phase allowed us to calculate a statistical evolution of the different types of site and a good correlation has been obtained between these theoretical variations and the experimental variations of the products obtained (20). In particular the dihydrogenated product such as isopentane or pentane was correlated to the ^3M–^3M association in which each Mo ion is three CUS. The monoenes formed were associated with ^3M–^1M sites when only monohydrogenation was obtained (for example, 2-methyl-1-butene), whereas ^3M–^2M and ^3M–^4M sites were associated with a monohydrogenation + isomerization reaction (for example, 2-methyl-2-butene).

The results presented on MoS_2/γ-Al_2O_3 (2.3 wt% Mo) in Fig. 3 as well as the variation of isopentane or pentane as a function of the Mo content (Figs. 4 and 5) clearly show that the site associated with the formation of the dihydrogenated product does not exist on MoS_2/γ-Al_2O_3 for very low Mo content, in other words, when the crystallite size of MoS_2 is too small.

The values between 4 and 5 wt% Mo correspond to a modeled hexagonal MoS_2 slab with $M = 26$–32 total Mo ions so, $n = 3$–4 Mo ions per side. Less than four Mo ions per side means less than two edge Mo ions known to be the active sites (3–5). Thus the results obtained are in good agreement with

the elementary ensemble proposition, which associates dihydrogenation with ^3M–^3M site. As the crystallite size decreases the existence of ^3M–^3M sites located in the ($\overline{1}010$) edge plane of the MoS$_2$ slab is perturbed and becomes impossible.

However, one must note that for very low Mo loading (2.3 wt% Mo) the major hydrogenated product obtained from isoprene is 2-methyl-2-butene associated with a ^3M–^2M (or ^3M–^4M) ensemble performing a hydrogenation + isomerization reaction (20). While the ^3M–^3M ensembles disappear the ^3M–^2M (or ^3M–^4M) still exist at very low Mo loading. This apparent contradiction can find different explanations:

—Mo ions at corner sites can participate in the composition of ^XM–^YM elementary ensembles.

—the ^XM–^YM site can be constituted of a mixed Mo–Al pair which could give the selectivity observed. This supposition is based on various results such as the probable isomerization activity of Al^{3+} ions on γ-Al$_2$O$_3$ (33), and the possible existence of Mo-O-Al species at the interface of MoS$_2$ and γ-Al$_2$O$_3$ (34, 35).

The turnover of this type of site is, however, much lower compared with the turnover obtained for the elementary ensemble consisting of two edge Mo ions as presented before.

The results obtained in this study are therefore consistent with the attribution of the activity to the edge Mo ions and moreover confirm the description of the active sites as being elementary ensembles as proposed before (20). For very low Mo loading catalysts this elementary ensemble may be a Mo(edge)–Mo(corner) pair or even a Mo(edge)–Al pair. By changing the environment of edge Mo ions (S and anionic vacancies), different reactions like isomerization or hydrogenation can be obtained, and the selectivities in hydrogenated products can be varied. This can be obtained either by changing the treatment temperature T_R (creation of anionic vacancies) or the Mo loading only on a MoS$_2$/γ-Al$_2$O$_3$ catalyst. More-

over, some other parameters can play a role, like reactive hydrogen species which have been found to depend on the creation of anionic vacancies on the edges of the MoS$_2$ slabs as well as in the γ-Al$_2$O$_3$ support (33). Added to that, the promoter effect was not yet taken into account and its influence on all of these parameters (environment, unsaturations, reactive hydrogen of the solid) with a probable electronic effect should be now analyzed.

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