

Quantitative Detection of Reactive Hydrogen on $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ and on $\gamma\text{-Al}_2\text{O}_3$

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Hydrogenation of 2-methyl-1,3-butadiene (isoprene) under helium flow in the absence of gaseous hydrogen is used to titrate reactive hydrogen species present in MoS_2 supported on $\gamma\text{-Al}_2\text{O}_3$ previously submitted to a H_2 treatment at various temperatures T_R . $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ is found to be a hydrogen reservoir and the hydrogen storage depends on the temperature of treatment (T_R) of the solid under H_2 , i.e., on the creation of anionic vacancies on the edges of the supported MoS_2 slabs. A similar result has been obtained on a powdered bulk MoS_2 , which has been investigated by the same dynamic method, but the amount of titrated reactive hydrogen was much lower. Therefore, in the case of $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$, the role of the support in the reactive hydrogen storage is illustrated and also explained by the creation of anionic vacancies in the oxide phase. © 1990 Academic Press, Inc.

During the last 20 years, the determining role of hydrogen in heterogeneous catalysis, energy storage technology, and metallurgy has become widely evident. Consequently, a pronounced interest has developed to understand better the elementary processes involving hydrogen present at the surface or in the bulk of materials and where hydrogen is considered as a chemical reactant, a reaction product, or a structure modifier (1). Transport of hydrogen through the surface from a phase or a complex chemical system to another phase is a phenomenon that can have a determining influence on heterogeneous catalysis (1). Thus, the "spillover" concept gives rise to new perspectives on the interactions between catalytic phases (2).

Some of the properties resulting from a spillover hydrogen phenomenon can be briefly summarized as follows:

1. A lower reduction temperature has been detected for a large number of oxides to which a transition metal has been added (3, 4). Sometimes a new compound can

be obtained by reduction of the initial oxide phase (W, Mo, or V bronze) (3, 5-7).

2. In association with the possible reduction of oxide surfaces, even refractory oxides (SiO_2 , Al_2O_3), it has been shown that these surfaces become catalytically active. Activity obtained on the metallic-doped systems can be important and different from that observed on the pure metals, and depends on the specificity of the system (8-10).

3. Catalytic activity is preserved. The spillover hydrogen can be involved in the elimination of some poisons formed at or adsorbed on the surface, in particular sulfur, which is eliminated by the formation of H_2S (11, 12).

The chemical state of hydrogen involved in the spillover processes is not clear. There is a general agreement in the literature on the dissociative adsorption of hydrogen on metals or surfaces able to adsorb H_2 (ZnO , Cr_2O_3 , Co_3O_4). The problem is the nature of the bond rupture: homolytic or heterolytic. Thus, four different species can be created and/or transported: H^- or H^+ ions, the radical H^\cdot , or the bonded species $\text{H}-$ (1). Hence

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the spillover hydrogen driving forces can be extremely different and depend on the solid involved.

The reaction between hydrogen and transition metal sulfides in hydroprocessing reactions is a very important but complex phenomenon (1) as these reactions involve in part hydrogen transfers. The hydrotreatment catalysts largely used are sulfides (MoS_2 or WS_2) often associated with a promoter (Ni, Co) and usually supported on $\gamma\text{-Al}_2\text{O}_3$. Even if good agreement is obtained in the literature to associate the active sites with the edges of the MoS_2 phase, a complete description should take into account the presence of hydrogen species on or in the MoS_2 structure. Badger *et al.* (13) were the first to explore the change of sorption as a function of temperature in the range 273–673 K. The effect of the time of sorption on the pretreatment under H_2 has been measured (14). On the hydrogen– MoS_2 system (13, 15), measurements at similar temperatures and pressures have shown that the adsorption of hydrogen is dissociative with formation of SH species and also that the adsorbed quantities are much higher than those which could correspond to the accessible surface of the material estimated by N_2 physisorption. Moreover, inelastic neutron scattering measurements have revealed the existence of two sites at which hydrogen may be sorbed in MoS_2 (15, 16): one is the site at which linear SH bonds form; on the second site, sorption occurs at higher temperatures (>423 K) and saturation is obtained only at pressures higher than 50 atm (17). Two binding states were also reported recently by Dianis (18). Theoretical calculations on H_xMoS_2 favor a more stable chemisorption state of heterolytically dissociated hydrogen (19).

The aim of this work is to contribute to the characterization of the active phase of hydrotreatment catalysts such as $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ by considering the participation of reactive hydrogen species H^* of the solid, the amount of which is titrated by a dynamic

method using isoprene under conditions similar to those of catalytic tests.

EXPERIMENTAL

The catalyst was prepared by pore-filling impregnation of a $\gamma\text{-Al}_2\text{O}_3$ support (pellets, surface area $240 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.57 \text{ cm}^3 \text{ g}^{-1}$) with an ammonium heptamolybdate solution, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (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 .

The pretreatment and catalytic experiments were carried out at atmospheric pressure in an all-glass, grease-free flow apparatus previously described (20). The catalyst (pellets) and the catalyst–support mechanical mixture were first sulfided with a $\text{H}_2/\text{H}_2\text{S}$ (90/10) mixture at 623 K for 4-h and cooled to room temperature. Then the solid was treated under a purified hydrogen flow at various temperatures T_R between 473 and 1073 K for 12 h. It must be noted that the catalyst $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ structure is stable in this range of temperatures (21).

After each treatment step by H_2 , the solid (0.24 g) was cooled to room temperature and reactants (isoprene or *cis*-1,3-pentadiene) were introduced at constant pressure (20 or 7 Torr respectively with regard to the gas phase composition) in a flow of purified hydrogen or helium (1 atm, 20 ml min^{-1}) in an isothermal reactor. The catalytic tests were carried out under a hydrogen/alkadiene (740/20) flow at 373 K. In some experiments *cis*-1,3-pentadiene was used as a probe molecule to determine the isomerization potentiality of the catalyst (*cis*–*trans* conversion).

The procedure for titrating the hydrogen content of the solids has been described previously (22). The H_2 -treated catalyst is flushed under helium at 323 K for 15 min, until complete elimination of hydrogen in the gas phase, and the consumption of the reactive hydrogen present in the solid by isoprene (0.5% in helium) was carried out at

423 K. The complete elimination of H_2 is controlled by inserting a conductivity cell into the flow line. Moreover, this conductivity cell allows one to verify that there is no irreversible adsorption of alkadiene (7 Torr, 20 ml min^{-1}).

Isoprene (2-methyl-1,3-butadiene) or *cis*-1,3-pentadiene, purum grade from Fluka, was used after purification by distillation under vacuum. Hydrogen and helium were purified from any traces of oxygen and H_2O which would result in complete catalyst poisoning. 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 thermogravimetric experiments were carried out under purified hydrogen in a Sartorius balance.

RESULTS

$\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$

After treatment with H_2 at a given temperature T_R , the catalyst $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ contains anionic vacancies produced by the elimination of some sulfur ions, SH groups and also some reactive hydrogen species able to hydrogenate probe molecules (e.g., alkadienes) in the absence of gaseous hydrogen. These species are denoted H^* as we are not considering their exact charge. It is important to note that no H^* species is found after only the sulfiding treatment as no alka-

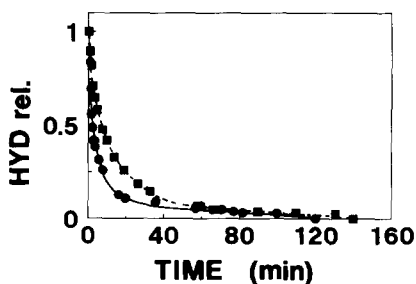


FIG. 1. Relative hydrogenation activity at 423 K under helium + isoprene flow versus time on $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ treated in H_2 at 773 K (■) and 623 K (●).

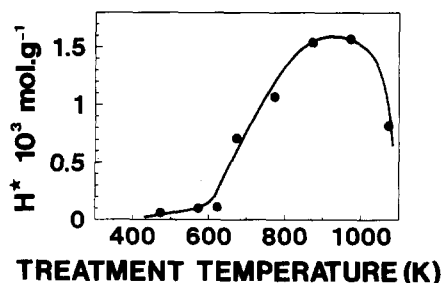


FIG. 2. Variation in the hydrogen H^* species concentration as a function of the treatment temperature T_R of $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$.

diene conversion has been observed. Therefore, these H^* moieties are probably different from SH groups which are known to be present on such catalysts after the classical sulfiding treatment with a $\text{H}_2/\text{H}_2\text{S}$ mixture.

The H^* content of the solid can be titrated by using a dynamic method already described (22). At 423 K under a helium + isoprene (0.5% volume) flow, alkadiene hydrogenation occurs on $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ previously treated by H_2 at different temperatures T_R . As a function of time on stream, the isoprene conversion or hydrogenation activity (in $\text{mol g}^{-1} \text{ time}^{-1}$) is measured. The ratio $\text{HYD}_{\text{rel}} = A_{\text{H}_t}/A_{\text{H}_0}$ (where A_{H_0} and A_{H_t} are the initial hydrogenation activity and the hydrogenation at time t) can then be plotted versus time. The relative hydrogenation activity (HYD_{rel}) at 423 K under the helium + alkadiene feed decreases with time and is reported for $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ treated at different T_R in Fig. 1. For each T_R a similar curve is obtained and by integrating this curve the extractable reactive hydrogen H^* content of the solid can be determined if the product distribution is taken into account (2 H^* consumed for monohydrogenation and 4 H^* for complete hydrogenation).

The extractable hydrogen content of the solid is found to be dependent on the temperature T_R . Figure 2 shows a maximum $\text{H}^* = 1.57 \cdot 10^{-3} \text{ mol g}^{-1}$ for $T_R = 973 \text{ K}$. The values obtained are much higher than those observed on the powdered bulk MoS_2 stud-

ied previously for which values between 1×10^{-5} and $7.5 \times 10^{-5} \text{ mol g}^{-1}$ were found (23).

In addition, between t and t_f (time at which the hydrogenation activity is found to be zero) the percentage of reactive hydrogen still present in the solid can be estimated and is reported as a function of time in Fig. 3. A plot of HYD_{rel} versus H^* concentration can be obtained for each T_R . In Fig. 4 the results are reported for the solid $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ treated at 773 and 623 K under H_2 . The curves obtained show clearly that there is no proportionality between the relative hydrogenation rate consuming H^* with the hydrogen content of the solid, and therefore the kinetics of H^* consumption by the alkadiene is a complex phenomenon; in particular, a diffusional process of the H^* species within the solid must be considered (22). A clear analogy exists between these results and those obtained on bulk MoS_2 (23) or with reduced copper oxides (22, 24) which were found to be hydrogen reservoirs.

$\gamma\text{-Al}_2\text{O}_3$

Consumption of reactive hydrogen H^* under helium-isoprene flow has been carried out on pure $\gamma\text{-Al}_2\text{O}_3$ to obtain a reference titration blank: no hydrogenation activity has been found. Yet it must be noted that an isomerization activity is observed with *cis*-1,3-pentadiene under either hydrogen or helium flow. Thus, on the support alone the

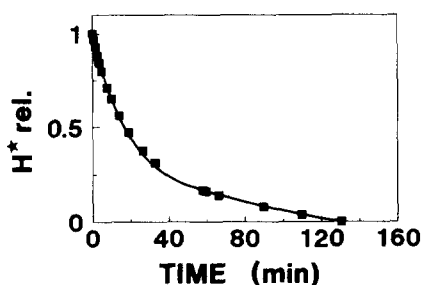


FIG. 3. Relative concentration of hydrogen H^* species versus time under helium + isoprene flow of $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ treated in H_2 at 773 K.

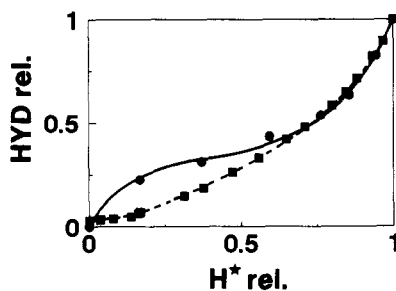


FIG. 4. Relative hydrogenation activity at 423 K under helium + isoprene flow versus the hydrogen H^* species concentration of $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ treated at 773 K (■) and 623 K (●).

direct titration of the reactive hydrogen of the solid by this method makes no sense because such a solid has no hydrogenating function. Extraction and measurement of hydrogen H^* species of the solid are obtained in this study by the use of a hydrogenation reaction, so, even if some reactive hydrogen species are present on or in the support, they cannot be measured by consumption with an alkadiene.

Thus, to study the effect of the support, the reactive hydrogen concentration has been measured on mechanical mixtures of $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ with $\gamma\text{-Al}_2\text{O}_3$ for different weight ratios α of $(\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3)/(\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3 + \gamma\text{-Al}_2\text{O}_3)$. These mixtures, after $\text{H}_2/\text{H}_2\text{S}$ treatment, have been treated at $T_R = 773 \text{ K}$ and the total weight used for the titration experiments has been always chosen constant. In this study, only one T_R has been applied, in such a way that the maximum alkadiene hydrogenation activity is observed on $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ (21). The results obtained are presented in Fig. 5.

The variation of the relative content of the reactive hydrogen H^* is linear as a function of the ratio α . The line obtained is located above the straight line of slope unity, and the extrapolation of the ratio α to zero gives a value H_A^* which corresponds to 30% of the total concentration of reactive H^* found in $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$. Indeed, $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ treated at 773 K contains $1.07 \times 10^{-3} \text{ mol g}^{-1}$ of H^* species, and the value ob-

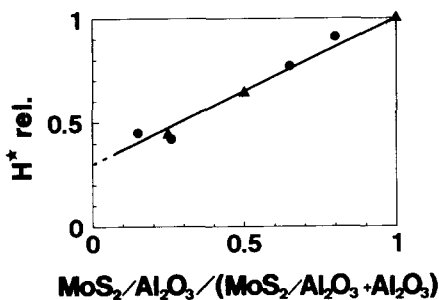


FIG. 5. Relative concentration of hydrogen H^* species versus the relative proportion (α) of the catalyst $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ in the mixture $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3 + \gamma\text{-Al}_2\text{O}_3$ reduced at 773 K.

tained for H_A^* is $0.33 \times 10^{-3} \text{ mol g}^{-1}$. Considering the method used to obtain this latest value (mechanical mixing with pure $\gamma\text{-Al}_2\text{O}_3$) this H_A^* concentration can be attributed to the support $\gamma\text{-Al}_2\text{O}_3$.

After the tests, the $\gamma\text{-Al}_2\text{O}_3$ pellets have been isolated, then analyzed by XPS and tested again in the hydrogenation reaction. In this way, it has been verified that there was no migration of Mo atoms from $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ to $\gamma\text{-Al}_2\text{O}_3$ (no Mo signal is found on $\gamma\text{-Al}_2\text{O}_3$ by XPS), and used $\gamma\text{-Al}_2\text{O}_3$ had no hydrogenating function only using the catalytic tests.

Moreover, the variation of the relative hydrogenation activity under helium at 423 K is close to being a linear relationship as a function of the concentration of hydrogen H^* species in the mixture $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3 + \gamma\text{-Al}_2\text{O}_3$ (50:50) treated at 773 K (Fig. 6). This kinetic variation is very different from that obtained on the catalyst $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ alone (Fig. 4) but close to a kinetic model proposed in a previous study involving a slow migration of the H^* species (22) and consistent with a hydrogen migration (spillover) from grain to grain in the support.

DISCUSSION

The effect of treatment of the $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ with H_2 has been previously analyzed (21). After the treatment by H_2 at a given temperature T_R some SH groups are formed

and simultaneously, by the elimination of H_2S , anionic vacancies are created on the MoS_2 phase. The amount of H_2S removed has been measured and the number of vacancies created has been deduced. According to a geometrical model of the catalyst $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ (25) the sulfur ions removed have been identified and located. It has been concluded that highly coordinatively unsaturated molybdenum ions are generated on the (1010) edge plane of the MoS_2 phase during the treatment under H_2 at various T_R (21). On the other hand, a powdered bulk MoS_2 sample has been also investigated in similar ways and the composition of the active phase has been defined as a MoS_xH_y compound (x between 1.67 and 2.01 and y between 0.002 and 0.12). Reactive hydrogen species, correlated with the presence of anionic vacancies located on the (1010) edge plane of MoS_2 slabs, have been titrated (23). Furthermore, a diffusional process of the hydrogen species from the "bulk" to the "surface" of the solid has been reported. The bulk and surface differentiation has been attributed to the existence of some edge planes of the MoS_2 slabs which could be accessible to hydrogen only by diffusion but not to the alkadiene molecules. Moreover, on bulk (23) or supported MoS_2 on alumina (21, 26), alkadiene hydrogenation (isoprene, *cis*- or *trans*-1,3-pentadiene) and isomerization (*cis* \leftrightarrow *trans*-1,3-pentadiene) activities have been correlated respectively

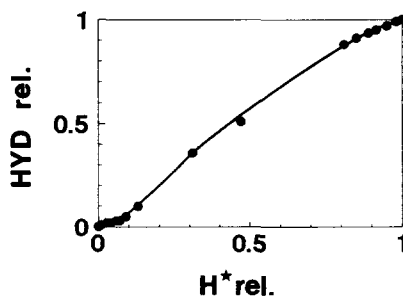


FIG. 6. Relative hydrogenation activity under helium at 423 K versus the hydrogen H^* species concentration of the mixture $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ (50:50) treated at 773 K.

TABLE 1

Relative H* Content of the MoS₂/γ-Al₂O₃ Catalyst Submitted to Different Treatment Temperatures T_R

Treatment temperature (K)	H*/Mo
473	0.06
573	0.12
623	0.12
673	0.75
773	1.13
873	1.62
973	1.65
1073	0.86

with the 3 and 2 and/or 4 coordinatively unsaturated (cus) Mo ions located on the (1010) edge plane of the MoS₂ slab.

In Table 1 the amount of hydrogen H*, titrated by the dynamic procedure using isoprene, is reported relative to the atomic content of Mo in the catalyst. For each T_R, a different ratio is obtained. The highest value found corresponds to a H*/Mo ratio obtained after H₂ treatment of the solid at 973 K. These values are in good agreement with some results already published (27) and much higher than those we have obtained on powdered bulk MoS₂ (H_{0.012}MoS_{1.94} was the bulk compound presenting the highest H* amount stored) (23). We will further discuss that the total amount of reactive hydrogen H* is due not only to the MoS₂ phase but to the properties of the MoS₂/γ-Al₂O₃ system considered as a whole. In fact, a diffusion process of the reactive hydrogen species is pointed out in the case of the MoS₂/γ-Al₂O₃ catalyst; the highly probable participation of the support in this phenomenon must be considered.

The catalyst MoS₂/γ-Al₂O₃ (9.2 wt% Mo) is composed of MoS₂ slabs well dispersed on the γ-Al₂O₃ support with an average mean stacking of 1.5 (28, 29). Hence it would be difficult to justify diffusion as a bulk phenomenon considering only the MoS₂ phase.

Furthermore, such high H*/Mo stoichiometries obtained in the MoS₂/γ-Al₂O₃ system cannot be explained by or correlated only with the number of anionic vacancies created at the edges of the MoS₂ slabs; for example, the MoS₂/γ-Al₂O₃ catalyst treated by H₂ at 973 K has a S/Mo stoichiometry of 1.3, whereas the H* content relative to Mo is 1.65. Vasudevan and Weller (27) have observed that the amount of hydrogen consumed to reduce MoS₂/γ-Al₂O₃ at 723 K is 2.5 times higher than the theoretical quantity necessary. Polz *et al.* also reported recently a fourfold higher value of hydrogen adsorbed on supported MoS₂ on γ-Al₂O₃ compared to bulk MoS₂ (30). The effect of hydrogen spillover was also involved when a fourfold increase in specific hydrogenation activity has been mentioned when an alumina-supported Pt catalyst was diluted with alumina in the ratio 1 : 20 (31).

On the other hand, in thermogravimetric experiments, the thermal treatment under H₂ of pure γ-Al₂O₃ (Fig. 7) shows a higher dehydroxylation rate with a different slope in the curve for treatment temperatures higher than 573 K where the hydrogen H* concentration of MoS₂/γ-Al₂O₃ starts to increase (Fig. 2). Thus it is highly probable that a part of the total amount of hydrogen H* species is correlated with the creation of anionic vacancies in γ-Al₂O₃ obtained by the desorption of water from OH groups. This did not imply that some surface or even bulk

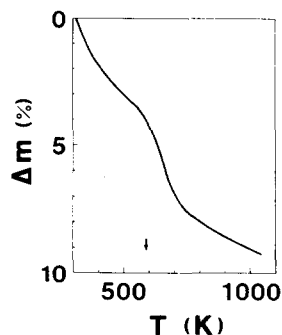


FIG. 7. Thermal treatment under H₂ of γ-Al₂O₃ followed by thermogravimetry.

Al^{3+} ions are reduced. For treatment temperatures higher than 973 K the structure of $\gamma\text{-Al}_2\text{O}_3$ begins to transform to finally lead to $\alpha\text{-Al}_2\text{O}_3$ and the amount of H^* species decreases.

As a complementary argument to this analysis, it is worth mentioning that the supports are not inert in the migration or diffusion of hydrogen species; the spillover process has very often been discussed in that context in the literature (1–10). There are also some publications dealing with the direct heterolytic dissociation of hydrogen on refractory oxides such as MgO (32, 33). Finally, it has been proposed on $\gamma\text{-Al}_2\text{O}_3$ that, after dehydroxylation, the dissociative chemisorption of hydrogen could exist with formation of $\text{Al}^{3+}\text{-H}$ and OH species (34).

In a previous study from this laboratory, copper oxide-based catalysts were reported to be hydrogen reservoirs (24), and the concentration of reactive hydrogen H^* was correlated with the presence of anionic vacancies created after reduction of the solid under H_2 . Moreover, during the alkadiene hydrogenation reaction, the nature of the H^* species has been proposed to be hydridic (35). In particular, $0.34 \times 10^{-3} \text{ mol g}^{-1}$ of hydrogen H^* was found in a cupric aluminate of spinel structure reduced at 523 K (24) and the isomerization site has been defined as an Al^{3+} cation surrounded by two vacancies, one being filled with an H^- species (24, 36, 37). In the present study, a value of the same order of magnitude ($0.33 \times 10^{-3} \text{ mol g}^{-1}$ of hydrogen H^*) is attributed to direct coverage by hydrogen of $\gamma\text{-Al}_2\text{O}_3$ treated by H_2 at $T_R = 773 \text{ K}$. Let us recall that $\gamma\text{-Al}_2\text{O}_3$ is a spinel oxide which may contain anionic vacancies produced by thermal treatment with H_2 . In fact, the H^* concentration in $\gamma\text{-Al}_2\text{O}_3$ will certainly depend on the temperature T_R , i.e., on the creation of anionic vacancies, as was the case for the oxides or sulfides studied (this study is currently in progress and will be discussed in a future publication). It is well known (38, 39) that $\gamma\text{-Al}_2\text{O}_3$ has potentially an isomerization function which is often cor-

related with the presence of Lewis acid sites. As the $\text{Al}^{3+}\text{-H}^-$ ($\text{Cr}^{3+}\text{-H}^-$) pair has been defined to be the alkadiene isomerization site on reduced copper mixed oxides (Cu-Al-O or Cu-Cr-O), it certainly has the same function on $\gamma\text{-Al}_2\text{O}_3$.

On bulk MoS_2 (23) or on the $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ system (26), the alkadiene isomerization activity has been well correlated with the presence of two and/or four coordinatively unsaturated edge Mo ions. It also appeared that the isomerization sites of $\gamma\text{-Al}_2\text{O}_3$ gave little or no perturbation in the isomerization activity of $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$, at least for treatment temperatures lower than 873 K. Hence it seems that the presence of the MoS_2 phase on $\gamma\text{-Al}_2\text{O}_3$ modifies the activity of the support in such a way that it can cover the active sites relative to $\gamma\text{-Al}_2\text{O}_3$. It also appears clear that the storage capacity of the support $\gamma\text{-Al}_2\text{O}_3$ depends not only on the presence and stability of anionic vacancies in $\gamma\text{-Al}_2\text{O}_3$ but also on the presence of the hydrogenating phase MoS_2 which permits the entry/exit of the reactive hydrogen H^* species. The MoS_2 phase plays a role in the reservoir capacity of the $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ system: the adsorption of H_2 takes place only at the MoS_2 phase; then the H^* species may diffuse at any available sites which then store hydrogen. Upon consumption, the reverse process takes place: the H^* species are consumed at hydrogenation sites (3-cus of MoS_2) with, simultaneously, a diffusional driving force from the reservoir to the "exit" gate.

The hydrogen reservoir depends on the existence and concentration of anionic vacancies which are created during the treatment under H_2 on the MoS_2 phase as well as in the $\gamma\text{-Al}_2\text{O}_3$ support. The presence of the MoS_2 phase certainly plays a role in the quantity of hydrogen stored in the support as the hydrogenating phase MoS_2 constitutes the entry/exit gates for the reactive hydrogen species H^* . This concept can be generalized to any kind of support: supports can be differentiated by their ability to favor or not this aptitude depending on the pre-

treatment conditions which may affect the nature and content of defects interacting with the reactive H* species.

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