JOURNAL OF CATALYSIS **147**, 476–483 (1994)

Hydrogen Content and Hydrogenation Activity of $MoS_2/\gamma Al_2O_3$ and γAl_2O_3 Mechanical Mixtures

S. Kasztelan[1] and G. B. McGarvey[2]

Institut Français du Pétrole, Division Cinétique et Catalyse, B.P. 311, 92506 Rueil-Malmaison Cédex, France

Received August 9, 1993; revised December 2, 1993

The hydrogen content and the reactivity of $MoS_2/\gamma Al_2O_3$ catalyst and γAl_2O_3 support mechanical mixtures have been investigated using high pressure toluene hydrogenation, hydrogen temperature programmed desorption (H_2-TPD), and oxygen chemisorption. It has been found by H_2-TPD and confirmed by the oxygen chemisorption that, in the presence of a $MoS_2/\gamma Al_2O_3$ catalyst, the γAl_2O_3 support contains some hydrogen species. These species are therefore provided by spillover from the MoS_2 phase which possesses the active sites able to dissociate molecular hydrogen. However, no cooperative effect of mechanical mixtures on toluene hydrogenation activities obtained in typical hydrotreating conditions, i.e., 6 MPa and 350°C, both in the presence and in the absence of a H_2S partial pressure, has been found.

INTRODUCTION

Alumina supported molybdenum disulfide-based catalysts have demonstrated superior catalytic properties for so-called hydrotreating reactions such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrogenation of olefins and aromatics (HYD) performed under hydrogen pressure and in the presence of H_2S (1, 2). Such catalysts can be considered to be a two-phase system composed of MoS_2 particles in interaction with an alumina support (3–5).

Among the various properties of an oxide support that may influence the catalytic properties of the particles of active phase, its ability to host surface hydrogen species, generated by spillover from an active phase dissociating molecular hydrogen, has attracted a great deal of attention (6–10). The presence of a reactive hydrogen species and its transport on the surface from one phase to another is well documented, in particular for metal-based catalysts (6–25).

The presence of a hydrogen species on alumina and its catalytic effect have been demonstrated in particular by studies of $Pt/Al_2O_3 + Al_2O_3$, Pt/Al_2O_3 + oxide, or $Pd/Al_2O_3 + Al_2O_3$ mechanical mixtures (15–25). The use of mechanical mixtures appears to be of particular interest as it allows one to monitor the amount of surface hydrogen relative to the amount of catalytic phase without modification of the latter. Such an approach has been used by Ceckiewicz and Delmon (15) to show that mechanical mixtures of $Pt/Al_2O_3 + Al_2O_3$ were more active in the benzene hydrogenation reaction at 100–200°C and atmospheric pressure than the geometric sum of the activities of each partner taken separately. These results confirmed earlier observations made by several groups (16–25).

In the case of sulfide catalysts, it is now well established that bulk MoS_2 (26–36) and alumina supported MoS_2 (37–40) contain hydrogen species on the surface after pretreatment under hydrogen. A study of the hydrogen content of $MoS_2/\gamma Al_2O_3 + \gamma Al_2O_3$ mixtures using the hydrogenation of a diene under an inert gas has also shown that hydrogen species generated by the MoS_2 active phase migrate onto the γAl_2O_3 support (40). On the carbon support, direct observation of hydrogen spillover from MoS_2 or iron sulfides by electron microscopy has been recently reported (41).

The use of mechanical mixtures of a MoS_2/Al_2O_3 catalyst and its alumina support appears to be a fruitful means to investigate the potential role of surface hydrogen species that have spilled over onto the support surface from an activating source in reactions involving catalytic hydrotreating. In this work, the hydrogen content of $MoS_2/\gamma Al_2O_3 + \gamma Al_2O_3$ mechanical mixtures has been determined by temperature programmed desorption of hydrogen (H_2-TPD) in order to verify the presence of hydrogen species on the alumina surface. The effect of these species on the activity for toluene hydrogenation performed at operating conditions typical of hydrotreating reactions, i.e., at high hydrogen pressure, reaction temperature higher than 300°C, and both in the presence and in the absence of H_2S, was then investigated.

---

[1] To whom correspondence should be addressed.

[2] Present address: AECL Research, Whiteshell Laboratories, Pinawa, Manitoba R0E 1L0, Canada.

0021-9517/94 $6.00

EXPERIMENTAL

Catalyst

The $MoO_3/\gamma Al_2O_3$ catalyst was prepared by pore-filling impregnation of a γAl_2O_3 support (Rhone-Poulenc, cylindrical pellets, 1.2 mm in diameter, specific surface area 240 m^2/g, pore volume 0.57 cm^3/g) with an ammonium heptamolybdate solution ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Merck). The impregnated solid was then dried at 120°C overnight and calcined at 500°C for 4 h. The Mo loading measured by X-ray fluorescence was 10.2 wt% Mo. The $MoO_3/\gamma Al_2O_3$ + γAl_2O_3 mechanical mixtures were generally made using the catalyst and the γAl_2O_3 support in pellet form. Some experiments were, however, performed using a mixture of ground catalyst and ground γAl_2O_3 support in the particle size range 0.1–0.25 mm.

All catalyst and support samples were calcined at 500°C for 2 h prior to preparing the mechanical mixture and carrying out the catalytic tests. Each mixture was obtained by mixing the components in a flask and shaking them until the catalyst particles appeared to be uniformly distributed in the alumina and vice versa.

Hydrogen Thermodesorption

The hydrogen thermodesorption (H_2-TPD) experiments were carried out using a χ-SORB semiautomatic solid catalyst characterization unit from GIRA. All catalyst sulfidation and pretreatments were performed *in situ* using a bypass gas handling circuit which circumvented the inline traps and detector.

For each experiment, 1 g of catalyst or mechanical mixture of catalyst + alumina support in pellet form was sulfided at 400°C using a H_2/H_2S (85/15 v/v) mixture, from Air Liquide, at atmospheric pressure for 2 h. Then the samples were cooled in the sulfiding mixture and purged in argon for 1 h before switching the flow to the H_2/Ar (5/95 v/v) reduction mixture. The reductive pretreatment was then carried out in the H_2/Ar mixture, using a temperature ramp of 15°C/min, to the desired temperature for 1 h. The samples were then cooled to 50°C before the gas flow was switched to pure argon and the temperature was maintained for 1 h. The H_2-TPD experiments were carried out between 50 and 1000°C using a heating rate of 30°C/min.

The analysis of the sulfided catalyst cooled under H_2/H_2S and then purged under He at 50°C gave 9.4 wt% Mo and 6 wt% S.

Oxygen Chemisorption

The oxygen chemisorption experiments were carried out using the same apparatus employed for the H_2-TPD experiments. Similar quantities and sulfiding procedures were also used. After sulfiding at 400°C for 2 h, the catalyst was cooled under He to reach the temperature of 60°C used for the oxygen chemisorption (42). In another set of experiments, the catalyst was cooled under H_2/Ar after sulfiding to the 300°C reduction temperature and, after standing for 1 h at that temperature, cooled under pure He to 60°C. After purging in pure He, the amount of O_2 chemisorbed by the sample at 60°C was determined by injecting from 30 to 50 pulses of 0.5 ml O_2 onto the catalyst.

Toluene Hydrogenation Tests

Toluene hydrogenation tests were performed in a high pressure continuous flow "catatest" unit from Vinci Technologies, France. For each test, 40 cm^3 of catalyst or catalyst + alumina support mechanical mixture in pellet form or ground in the particle size range 0.1–0.25 mm has been used. Prior to the catalytic tests, the samples were sulfided *in situ* by passing a feed containing 2 wt% dimethyl-disulfide in cyclohexane over the catalyst at 6 MPa, liquid hourly space velocity (LHSV) of 2 h^{-1} from room temperature to 350°C with a ramp of 2°C/min, followed by standing 4 h at 350°C.

All catalytic tests have been performed at a total pressure of 6 MPa, a reaction temperature of 350°C, and a liquid hourly space velocity (LHSV) of 2 h^{-1}. For the tests performed in the presence of H_2S, a liquid feed composed of 20 wt% toluene, 2 wt% thiophene, and 78 wt% cyclohexane was used. For the tests with no H_2S, the following procedure was implemented. After sulfiding, pure cyclohexane was passed over the catalyst for 2 h at 350°C and for 16 h at 150°C. Then the temperature was raised to 350°C under pure hydrogen and maintained 2 h before injection of a liquid feed composed of 20 wt% toluene and 80 wt% cyclohexane. Steady-state activities were determined after 4 h time on stream.

The reaction products were analyzed by gas chromatography using a 50-m PONA column at 60°C and a flame ionization detector.

A first order kinetic law was used to compute the hydrogenation rate coefficient k in mol/kg/h from the conversion of toluene in hydrogenated products.

RESULTS

Hydrogen Content of Mechanical Mixtures

Hydrogen desorption profiles were measured for a series of $MoO_3/\gamma Al_2O_3$ catalyst and γAl_2O_3 support mechanical mixtures which had been sulfided at 400°C and had undergone reductive treatment in hydrogen at 300 or 500°C. Desorption profiles for the sulfided catalysts, the sulfided alumina support, and various mechanical mixtures (in wt% of catalyst in mixture) are shown in

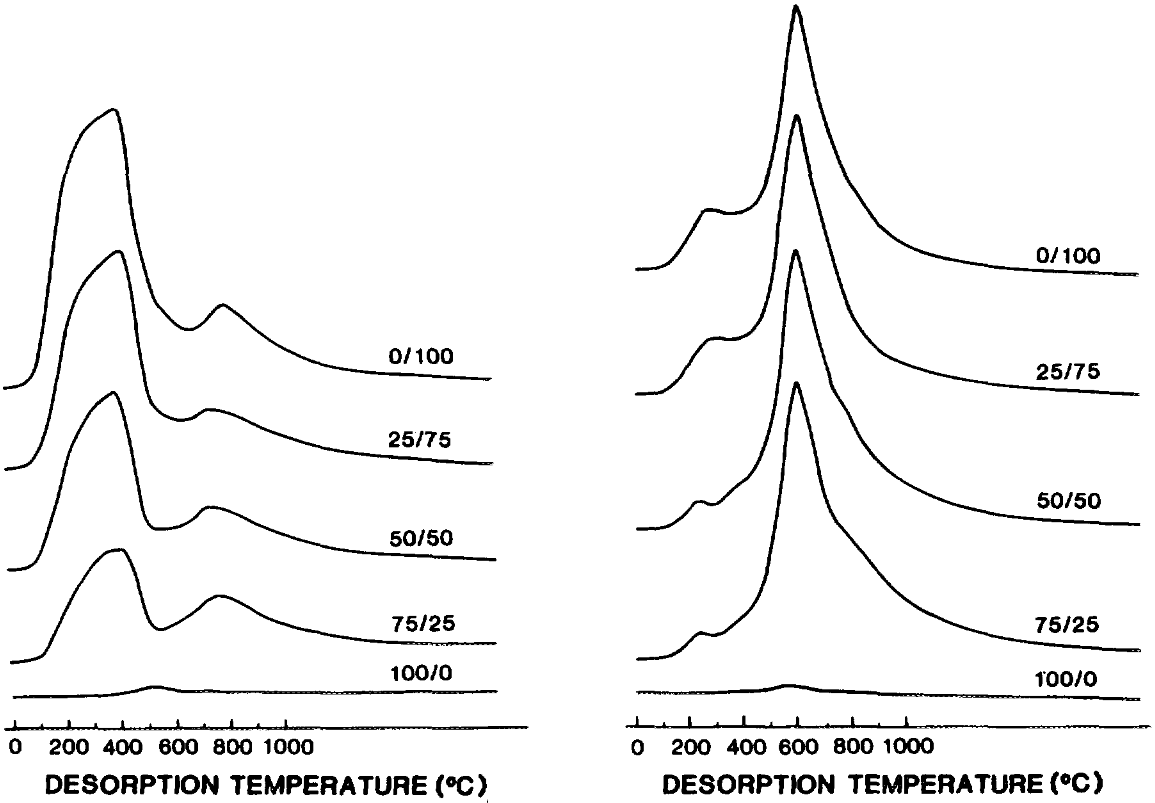

FIG. 1. H_2-TPD profiles of sulfided mechanical mixtures of $MoO_3/\gamma Al_2O_3$ catalyst and γAl_2O_3 support (in wt% support/wt% catalyst) pretreated under H_2 at 300°C (left) or 500°C (right) after sulfidation at 400°C and before TPD.

Fig. 1. In this figure, it can be seen that the alumina sample had an almost featureless H_2-TPD profile compared to the samples containing a portion of the MoS_2/Al_2O_3 catalyst. All samples containing some MoS_2/Al_2O_3 catalyst show features similar to the MoS_2/Al_2O_3 catalyst alone.

The H_2-TPD desorption profiles for mixtures reduced at 300 and 500°C are characterized by a low temperature and a high temperature peak. In Fig. 1, the low temperature peak dominates for the samples reduced at 300°C, whereas the high temperature peak dominates for the samples reduced at 500°C. The relative intensities of these two peaks have been found to depend strongly on the reduction temperature with the low temperature peak centered at approximately 400°C decreasing in intensity and the high temperature peak at about 500°C increasing in intensity as the reduction temperature increases (38).

In Fig. 2, plots of the amount of H_2 desorbed per gram of sample versus the weight percent of catalyst in the sample for the two reduction temperatures reveal two linear relationships. Pure alumina does not desorb a detectable amount of H_2 for either reduction temperature. Extrapolation of the straight lines of Fig. 2 to the pure alumina sample leads to a value of 40 μmol H_2/g (0.2 H/nm^2) and 55 μmol H_2/g (0.27 H/nm^2) of hydrogen present on the Mo–free-alumina support in the presence of the catalyst after reduction at 300 and 500°C, respectively.

The presence of hydrogen species on the alumina sur-

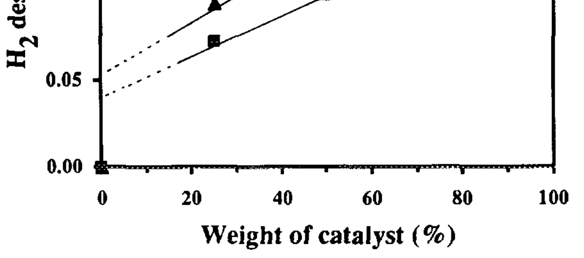

FIG. 2. Amount of H_2 desorbed versus the composition of sulfided $MoO_3/\gamma Al_2O_3$ and γAl_2O_3 mechanical mixtures reduced at (■) 300°C and (▲) 500°C.

face in the presence of the active phase must be taken into account to estimate the amount of hydrogen on the MoS_2 phase. In Table 1, two cases have been considered in computing a H/Mo ratio. In the first case (H/Mo[b]), it is assumed that no hydrogen is present on the alumina surface of the catalyst. In the second case (H/Mo[c]), it is assumed that the alumina surface of the catalyst contains the same amount of hydrogen per nm^2 as the Mo-free-alumina support. As the mechanical mixtures have always been pretreated and analyzed by H_2-TPD using the same conditions, the MoS_2 phase should always contain the same amount of hydrogen, which is well verified in Table 1 in the two cases. The differences in terms of H/Mo ratio between the two modes of calculation are not negligible and indicate that the H/Mo ratio can be overestimated if the presence of hydrogen species on the support surface is not taken into account.

Oxygen Chemisorption

The results obtained from oxygen chemisorption are qualitatively very similar to the H_2-TPD results. The plots of the amount of oxygen chemisorbed versus the composition of the mechanical mixture are reported in Fig. 3. Straight lines are obtained which, by extrapolation, allow us to determine that in the presence of the catalytic phase, the free-alumina support is able to chemisorb about 17 μmol O_2/g after cooling under He and 22 μmol O_2/g after reduction at 300°C and cooling under He. Clearly, not much difference in the amount of O_2 chemisorbed is induced by the reduction pretreatment at 300°C. The alumina alone led only to traces of chemisorbed oxygen for both types of pretreatment.

TABLE 1

Amount of H_2 Desorbed in H_2-TPD Experiments by Mechanical Mixtures of $MoS_2/\gamma Al_2O_3$ + γAl_2O_3 Pretreated under H_2 at (A) 300°C and (B) 500°C

	Amount of hydrogen desorbed			
Weight of catalyst (%)	mol H_2/kg mixt.	mol H_2/kg cat.	H/Mo[b]	H/Mo[c]
(A) 0	0 (0.04)[a]	—	—	—
25	0.072	0.168	0.34	0.27
50	0.099	0.158	0.32	0.25
75	0.120	0.147	0.30	0.23
100	0.158	0.158	0.32	0.25
(B) 0	0 (0.055)[a]	—	—	—
25	0.094	0.211	0.44	0.34
50	0.128	0.201	0.42	0.32
75	0.169	0.207	0.43	0.33
100	0.204	0.204	0.42	0.32

[a] Extrapolated from Fig. 2.
[b] No H on alumina surface of catalyst.
[c] H on alumina surface of catalyst.

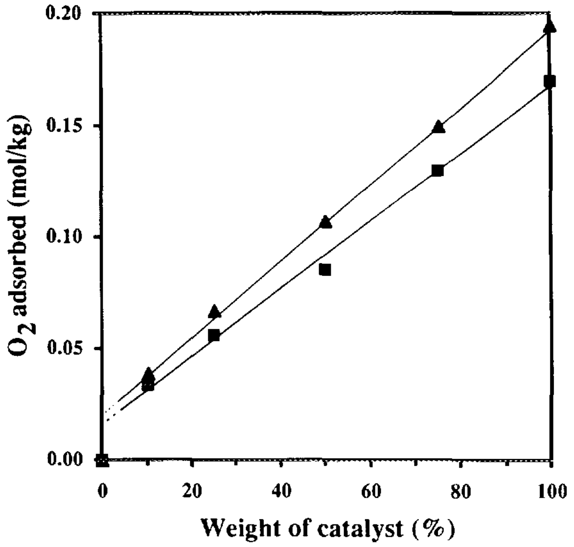

FIG. 3. Variation of the amount of O_2 chemisorbed at 60°C versus the composition of the $MoO_3/\gamma Al_2O_3$ and γAl_2O_3 mechanical mixture sulfided at 400°C and (■) cooled under He, (▲) reduced under H_2 at 300°C and cooled under He.

These results suggest that the hydrogen species present on the alumina support surface generated by spillover plays a role in the oxygen chemisorption, a possibility that has seldom been emphasized in the literature. In this respect, an interesting, although qualitative, observation must be reported, namely, the detection of water condensation on the wall of the cell containing the catalyst following O_2 chemisorption, whereas before O_2 chemisorption or in the presence of the alumina support alone, the wall showed no evidence of water condensation. This suggests that a portion of the chemisorbed oxygen molecules has reacted with some adsorbed hydrogen species to form water.

Using the amount of O_2 chemisorbed on the alumina support extrapolated from the straight lines of Fig. 3, it is possible to verify in Table 2 that an approximately constant amount of oxygen is adsorbed by the MoS_2 phase in the various mechanical mixtures. In this quantity of O_2 chemisorbed by MoS_2, there will, however, be a fraction consumed by reaction with the MoS_2 hydrogen surface species.

Toluene Hydrogenation Activity of Mechanical Mixtures

The catalytic properties of the mechanical mixtures have been determined for toluene hydrogenation, i.e., a demanding reaction for sulfide catalyst, using experimen-

TABLE 2

Amount of O_2 Chemisorbed at 60°C by Mechanical Mixtures of $MoS_2/\gamma Al_2O_3$ + γAl_2O_3 Sulfided at 400°C and (A) Cooled under He, (B) Reduced at 300°C and Cooled under He

Weight of catalyst (%)	Amount of O_2 adsorbed		
	mol O_2/kg mixt.	mol O_2/kg cat.	O/Mo
(A) 0	Trace (0.017)[a]	—	—
10	0.034	0.19	0.35
25	0.056	0.17	0.32
50	0.085	0.15	0.35
75	0.13	0.16	0.305
100	0.17	0.17	0.32
(B) 0	Trace (0.022)[a]	—	—
10	0.039	0.19	0.35
25	0.067	0.20	0.37
50	0.107	0.19	0.35
75	0.150	0.19	0.35
100	0.195	0.195	0.36

[a] Extrapolated from Fig. 3.

tal conditions close to those used in hydrotreating. The toluene hydrogenation activities obtained at 6 MPa and 350°C in the presence of H_2S generated by the decomposition of thiophene or in the absence of H_2S versus the composition of the mechanical mixture are shown in Fig. 4. Linear relationships are clearly obtained for the tests in the presence or in the absence of H_2S which pass through the zero activity determined for the alumina support alone. Mixtures of ground catalyst and ground alumina have also been tested in the presence of H_2S and no differences with the mixture of pellets have been detected. The computation of the hydrogenation rate coefficient for the catalyst is reported in Table 3 and gives a constant value, indicating that only the MoS_2 phase is responsible for the catalytic activity in toluene hydrogenation under these conditions.

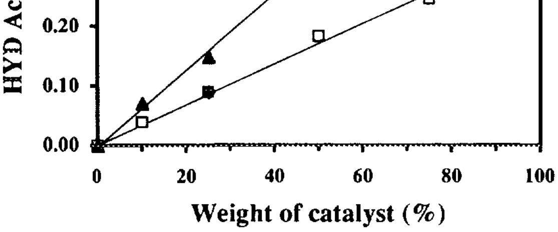

FIG. 4. Variation of toluene hydrogenation activity of 6 MPa and 350°C versus the composition of sulfided $MoO_3/\gamma Al_2O_3$ and γAl_2O_3 mechanical mixtures tested in the presence of H_2S ((□) pellets, (◆) powder) or tested in the absence of H_2S ((▲) pellets).

DISCUSSION

Of initial interest in the present discussion is the observation that both H_2-TPD and O_2 chemisorption results lead to the same conclusion, i.e., the presence of hydrogen species on the Mo–free-alumina support when it has been mechanically mixed with a MoS_2/Al_2O_3 catalyst. This is indicated by the fact that the reduced alumina support alone led to traces of H_2 desorption and traces of O_2 adsorption when compared to the MoS_2/Al_2O_3 catalyst, whereas the reduced mechanical mixtures desorbed more hydrogen than would be expected if only the MoS_2 phase were considered.

These results are in good agreement with those reported by Jalowiecki *et al.* (40) for MoS_2/Al_2O_3 + Al_2O_3 mechanical mixtures using a different technique, namely, hydrogen titration by 2-methyl-1,3-butadiene hydrogenation in He and with those for noble-metal-based mechanical mixtures reported by several authors (14–22).

Oxygen chemisorption has been employed previously to investigate the number of active sites on MoS_2-based catalysts (42–44). One drawback of the technique has

TABLE 3

Toluene Hydrogenation Activity in (A) the Presence of H_2S and in (B) the absence of H_2S, at 6 MPa, 350°C, LHSV = 2 h^{-1} of Mechanical Mixtures of $MoS_2/\gamma Al_2O_3$ + γAl_2O_3 Support

Weight of catalyst (%)	*k* hydrogenation	
	mol tol/kg mixt./h	mol tol/kg cat./h
(A) 0[a]	0	—
10[a]	0.026	0.26
25[a]	0.070	0.28
25[b]	0.066	0.26
50[a]	0.14	0.27
75[a]	0.19	0.25
100[a]	0.26	0.26
100[b]	0.26	0.26
(B) 0[a]	0	—
10[a]	0.055	0.55
25[a]	0.11	0.46
50[a]	0.25	0.50
75[a]	0.35	0.47
100[a]	0.50	0.50

[a] Pellets, 1.2 mm in diameter.

[b] Particle size, 0.1–0.25 mm.

been the fact that it is a rather nonspecific technique and hence, discriminating between different sites based on the O_2 adsorption data has proven to be difficult. This is particularly evident for two-phase systems such as supported catalysts, where contributions from both the sulfide and the support phases are difficult to separate. O_2 chemisorption on the pure alumina was negligible, suggesting that no active O_2 chemisorption sites were present on the alumina surface. The excess of O_2 chemisorbed can be related to the presence of hydrogen species on the alumina surface and it can be concluded that the contribution of the support to the total quantity of O_2 chemisorption by the mixture is a result of the reaction of oxygen with spilled over hydrogen to form water.

It is interesting to note that the intercepts of Figs. 2 and 3 yield the values of 40 μmol H_2/g and 22 μmol O_2/g, respectively, when the sulfided sample was reduced at 300°C. The H_2/O_2 ratio of 1.9 confirms that water formation does occur on the alumina support from the interaction of oxygen with spilled over hydrogen. It is also significant to note that as the quantity of the catalytic phase increases, the quantity of desorbed hydrogen and adsorbed oxygen does not increase in a parallel manner. Rather, the slope of the O_2 chemisorption plot increases more rapidly (1.53 μmol O_2/wt% cat.) than the corresponding slope for the quantity of desorbed hydrogen (versus 1.18 μmol H_2/wt% cat.). The ratio $H_2/O_2 = 0.75$ is found for the pure MoS_2/Al_2O_3 catalyst. This ratio indicates that there is more O_2 chemisorbed than is required to react with MoS_2 surface hydrogen. Thus, after the reaction of O_2 with the surface hydrogen, MoS_2 surface sites are left free for O_2 adsorption.

In the H_2-TPD and O_2 chemisorption experiments described in this work, pellets of a large size (1.2-mm diameter and about 5-mm length) have been used. The presence of hydrogen species on the Mo–free alumina shows that long range migration of hydrogen has occurred from the MoS_2 active phase to the alumina and vice versa during the H_2 desorption.

The techniques used to probe the hydrogen content of the mechanical mixtures provide complementary information on the location of sites for the hydrogen activation. Both alumina sites or MoS_2 sites could dissociate molecular hydrogen, but the lack of noticeable hydrogen desorption from Mo–free-alumina pretreated at 300°C rules out the ability of alumina to dissociate hydrogen for these H_2 pretreating conditions. H_2 dissociation on alumina has, however, been proposed in the literature (45) and may occur at higher reduction temperatures. Nevertheless, when hydrogen species are supplied by the hydrogen activating phase, MoS_2, or a noble metal, it might be possible that alumina sites allow hydrogen desorption. The lack of change of the shape of the H_2-TPD profiles of mixtures suggests that this is not the case unless hydrogen desorbed in the same temperature range. It is worth recalling, however, that H_2 pretreated alumina (usually at temperatures higher than 300°C) and also calcined alumina have been found to be able to isomerize olefins, a reaction associated with the presence of Lewis acid sites (46, 47). In addition, alumina and silica activated by spillover hydrogen are known to hydrogenate various hydrocarbons (6, 48), indicating that these supports can possess catalytic hydrogenation sites.

The hydrogenation activity of the MoS_2 phase determined in experimental conditions to be typical of hydrotreating reactions, and in particular in the presence of H_2S, has not been perturbed by the presence of various amounts of alumina, as shown in Fig. 4 and Table 3. It is puzzling that no cooperative effect is found in this work when a cooperative effect has been found for benzene hydrogenation at less than 200°C over $Pt/Al_2O_3 + Al_2O_3$ by Ceckewicz and Delmon (15). It can be argued that the presence of H_2S could offset the effect because of the strong adsorption of this reactant on the alumina and MoS_2 surface sites. Indeed, the results of Ceckewicz and Delmon (15) indicate that the cooperative effect occurs only in very clean conditions, which is usually not the case for hydrotreating reactions. The test performed without any sulfur in the feed also showed no cooperative effect, suggesting that H_2S is not the cause of the lack of cooperative effect, although trace impurities of sulfur may not have permitted the detection of the effect if any were present.

In this work, tests with ground particles in the range 100–250 μm, i.e., the same size as used by Ceckiewicz and Delmon (15), also showed no cooperative effect. Thus, differences in particle size cannot be advocated. In addition, both the TPD and O_2 chemisorption were performed with extrudates and showed the effect.

Impurities on the alumina or the catalysts are also a possible factor of discrepancy. Fe impurities on the alu mina cannot really be suspected, as it has been shown that a large amount of Fe has a limited effect (15). The amount of carbon on the used catalysts has been found to be small at 0.5 wt%. This might be a cause for the lack of effect as reported in Ref. (15), but one has to remember that coke deposits are always present on hydrotreating catalysts.

The 350°C reduction temperature used in this work may not have been high enough to efficiently activate the alumina surface compared to the 450°C used in Ref. (15) and 430°C in Ref. (48). However, this may be compensated by the high hydrogen pressure employed. This high hydrogen pressure is the major experimental difference with the work of Ceckiewicz and Delmon (15). It is not certain that in such conditions the spillover hydrogen is provided to the alumina support with a rate sufficient to allow an increase of the hydrogenation activity compared to the high intrinsic activity of the MoS_2 phase.

The existence of a cooperative effect in MoS_2/Al_2O_3 + Al_2O_3 mechanical mixtures for aromatic hydrogenation cannot be completely ruled out on the ground of the experiments reported in this work. However, as far as a typical reaction of hydrotreating catalysis is concerned, no cooperative effect is detectable. In these conditions, either there is no hydrogen species on the Mo-free-alumina surface and therefore no hydrogenating sites (48), or the presence of hydrogen species on the alumina surface has no direct effect on the hydrogenation activity of the MoS_2 active phase.

MoS_2/alumina catalysts are usually promoted by cobalt or nickel. The promoter may produce or accept spillover hydrogen (41) and possibly modify the observations made for the MoS_2 alone. Work is in progress to address the effect of the presence of a promoter on the hydrogen content and hydrogenation activity in hydrotreating conditions of mechanical mixtures.

CONCLUSION

Both the H_2-TPD and O_2 chemisorption experiments performed on mechanical mixtures of a MoS_2/alumina catalyst and its alumina support demonstrate that in the presence of the catalyst, some hydrogen has spilled over to the alumina support surface. The presence of such surface hydrogen species influences the amount of oxygen chemisorbed at 60°C, as some reaction between adsorbed oxygen and surface hydrogen species to form water seems to occur.

No detectable cooperative effect of the mechanical mixture on the toluene hydrogenation activity at high pressure was found, whether the feed contained sulfur or not. Although the experiments do not rule out the existence of such an effect under very clean conditions, this suggests that under typical hydrotreating conditions, either there are no hydrogen species present on the alumina surface or the presence of hydrogen species on the alumina surface has no direct effect on the catalytic activity of the MoS_2 phase.

ACKNOWLEDGMENTS

We are indebted to A. Fauchon, B. Betro, and H. Deschamps for their experimental assistance.

REFERENCES

1. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Process." McGraw-Hill, New York, 1979.
2. Girgis, M. J., and Gates, B. C., *Ind. Eng. Chem. Res.* **30,** 2021 (1991).
3. Delmon, B., *Stud. Surf. Sci. Catal.* **53,** 1 (1990).
4. Topsoe, H., Clausen, B. S. Topsoe, N., and Zeuthen, P., *Stud. Surf. Sci. Catal.* **53,** 77 (1990).
5. Chianelli, R. R., and Daage, M., *Stud. Surf. Sci. Catal.* **50,** 1 (1989).
6. Conner, W. C., Pajonk, G. M., and Teichner, S. J., *Adv. Catal.* **34,** 1 (1986).
7. Sermon, P. A., and Bond, G. C., *Catal. Rev.* **8,** 211 (1973).
8. Dowden, D. A., *in* "Specialist Periodical Reports: Catalysis," Vol. 8, p. 6. Chemical Society, London, 1980.
9. Khoobiar, S., *in* "Catalyst Supports and Supported Catalysts" (A. B. Stiles, Ed.), p. 201. Butterworths, London, 1987.
10. Delmon, B., *J. Mol. Catal.* **59,** 179 (1990).
11. Delmon, B., *React. Kinet. Catal. Lett.* **13,** 203 (1980).
12. Pirote, D., Grange, P., and Delmon, B., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 1422. Elsevier, Amsterdam, 1981.
13. Teichner, S. J., Mazarbrard, A. R., Pajonck, G., Gardes, G. E., and Hoang-Van, C., *J. Colloid Interface Sci.* **58,** 88 (1977).
14. Lacroix, M., Pajonk, G. M., and Teichner, S. J., *Bull. Soc. Chim. Fr.* **94** (1981).
15. Ceckiewicz, S., and Delmon, B., *J. Catal.* **108,** 294 (1987).
16. Augustine, R. L., Kelly, K. P., and Warner, R. W., *J. Chem. Soc., Faraday Trans. 1* **79,** 2639 (1983).
17. Antonucci, P., Van Truong, N., Giordano, N., and Maggiore, R., *J. Catal.* **75,** 140 (1982).
18. Sancier, K. M., *J. Catal.* **20,** 106 (1971).
19. Sinfelt, J. H., and Lucchesi, P. J., *J. Am. Chem. Soc.* **85,** 3365 (1963).
20. Musso, J. C., and Parera, J. M., *Appl. Catal.* **30,** 81 (1987).
21. Vannice, M. A., and Neikam, W. C., *J. Catal.* **23,** 401 (1971).
22. Lenz, D. H., and Conner, W. C., *J. Catal.* **104,** 288 (1987).
23. Sermon, P. A., and Bond, G. C., *J. Chem. Soc., Faraday Trans. 1* **72,** 730 (1976).
24. Gerand, B., and Figlarz, M., *in* "Specialist Periodical Reports: Catalysis," Vol. 8, p. 275. Chemical Society, London, 1980.
25. Tinet, D., Estrade-Szwarckopf, H., and Fripiat, J. J., *in* "Metal–Hydrogen Systems" (T. N. Verizoglu, Ed.). Pergamon, Oxford, 1982.
26. Moyes, R. B., *in* "Hydrogen Effects in Catalysis" (Z. Paal and P. G. Menon, Eds.), p. 585. Dekker, New York, 1988.
27. Badger, E. H. M., Griffith, R. H., and Newling, W. B. S., *Proc. R. Soc. London A* 184, (1949).
28. Donath, E. E., *Adv. Catal.* **8,** 245 (1956).
29. Wright, C. J., Sampson, C., Fraser, D., Moyes, R. B., Wells, P. B., and Riekel, C., *J. Chem. Soc., Faraday Trans. 1* **76,** 1588 (1980).
30. Vasudevan, S., Thomas, J. M., Wright, C. J., and Sampson, C., *J. Chem. Soc. Chem. Commun*, 418 (1982).
31. Sampson, C., Thomas, J. M., Vasudevan, S., and Wright, C. J., *Bull. Soc. Chim. Belg.* **90,** 1215 (1981).
32. Dianis, W. P., *Appl. Catal.* **30,** 99 (1987).
33. Li, X. S., Xin, Q., Guo, X. X., Grange, P., and Delmon, B., *J. Catal.* **137,** 385 (1992).
34. Komatsu, T., and Hall, W. K., *J. Phys. Chem.* **95,** 9966 (1991).
35. Komatsu, T., and Hall, W. K., *J. Phys. Chem.* **96,** 8131 (1992).
36. Jalowiecki, L., Aboulaz, A., Kasztelan, S., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **120,** 108 (1989).
37. Vasudevan, P. T., and Weller, S. W., *J. Catal.* **99,** 235 (1986).
38. McGarvey, G. B., and Kasztelan, S., *in* "Progress in Catalysis" (K. J. Smith and E. C. Sanford, Eds.), Studies in Surface Science and Catalysis, Vol. 73, p. 1. Elsevier, Amsterdam, 1992.
39. Polz, H., Zeilinger, H., Muller, B., and Knözinger, H., *J. Catal.* **120,** 22 (1989).
40. Jalowiecki, L., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **126,** 101 (1990).
41. Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **140,** 287 (1993).

42. Bachelier, J., Duchet, J. C., and Cornet, D., *Bull. Soc. Chim. Belg.* **90,** 1301 (1981).
43. Burch, R., and Collins, A., *Appl. Catal.* **17,** 273 (1985).
44. Tauster, S. J., and Riley, K. L., *J. Catal.* **67,** 250 (1981); **70,** 230 (1981).
45. Mardilovic, P. P., Zelenskovskii, V. N., Lysenko, G. N., Trokhimetz, A. I., and Zhidomirov, G. M., *React. Kinet. Catal. Lett.* **36,** 107 (1988).
46. Peri, J. B., *J. Phys. Chem.* **69,** 220 (1965).
47. Gerberich, H. R., and Hall, W. K., *J. Catal.* **5,** 99 (1966).
48. Willey, R. J., Teichner, S. J., and Pajonck, G. M., *J. Mol. Catal.* **77,** 201 (1992).