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Role of the Support in the Skeletal Isomerization of 3,3-Dimethyl-1-Butene on Oxided and Sulfided CoMo/Al_2O_3 Catalysts

S. KARMAL, G. PEROT, AND D. DUPREZ[1]

Laboratoire de Catalyse en Chimie Organique, URA CNRS 350, Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

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The skeletal isomerization of 3,3-dimethyl-1-butene (33DMB1), a typical test for the Brønsted acidity, was carried out at 200°C on a series of CoMo/Al_2O_3 catalysts with a variable atomic ratio $r = \%$ Co/(Co + Mo). This series of catalysts was completed by an unsupported catalyst with $r = 30\%$. On oxided catalysts, a significant decrease of the activity can be observed for low cobalt contents, which shows that the Mo/Al_2O_3 catalyst possesses the greatest number of Brønsted sites. There is a slight linear decrease of the total acidity (determined by temperature-programmed desorption of ammonia) when the cobalt content decreases. A maximum of the Lewis acidity is thus obtained for the promoted catalysts with about 30% cobalt content. On sulfided catalysts (10% H_2S in H_2, 300°C), a similar trend can be observed, the activities remaining close to those measured on oxided precursors. The most striking feature is that promoted catalysts have practically the same initial activity as the bare support. Yet, whereas the CoMo/Al_2O_3 catalysts are very stable, the activity of Al_2O_3 decreases rapidly when the sulfidation state of catalyst is maintained by dimethyldisulfide (DMDS) added to 33DMB1. On the contrary, the support is quite stable when the reaction is carried out in the presence of H_2S. Isomerization most probably occurs on the support which possesses Brønsted sites stable only under a partial pressure of H_2S. Except for Mo/Al_2O_3, there is practically no acid site active in 33DMB1 isomerization on the sulfide phases. Brønsted sites present on molybdenum are rapidly deactivated. © 1991 Academic Press, Inc.

1. INTRODUCTION

During the last decades, the role of cobalt–mobybdenum catalysts in the hydrodesulfurization (HDS) of sulfur compounds has been studied extensively. The kinetics and mechanisms of isomerization reactions which are theoretically linked to the catalyst acidity are not as well known with sulfided catalysts as with the oxided precursors and in particular MoO_3/Al_2O_3 (*1*, *2*). Except for double-bond isomerizations (butene-1 → butenes-2) which intervene in hydrotreatment as secondary reactions of HDS (*3–7*) and for skeletal isomerizations of cyclenes which occur in parallel with hydrogenation (*8–12*), isomerization of hydrocarbons has not been systematically studied. The skeletal isomerization of 3,3-dimethyl-1-butene (33DMB1) into 2,3-dimethyl-1-butene (23DMB1) and 2,3-dimethyl-2-butene (23DMB2) is a reaction well adapted for the study of the isomerization properties of hydrotreatment catalysts in their oxided and sulfided form. First the reaction occurs at temperatures relatively close to those used for thiophene hydrogenolysis: Bourdillon (*13*) showed that the reaction occurred over acid centers of medium strength, desorbing pyridine at 220°C. Second, the reaction scheme is relatively "clean" with only two major products. Methylpentenes appear at higher temperatures (>300°C) and their formation requires relatively strong acid sites (*14*). Third, the mechanism is rather simple since this isomerization reaction is probably the one for which the mechanism via secondary carbenium ions on Brønsted sites is the most likely (*14*):

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[1] To whom correspondence should be addressed.

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$$\mathrm{Me_3C{-}CH{=}CH_2 \xrightarrow{H^+} Me_3C{-}\overset{+}{C}H{-}CH_3}$$

$$\xrightarrow[\text{migration}]{\text{Me}} \mathrm{Me_2\overset{+}{C}{-}CHMe_2}$$

$$\rightarrow \mathrm{23DMB1 + 23DMB2}$$

The slow step of the reaction is probably the isomerization of the carbocation intermediate through the methyl group migration. Kemball *et al.* (*15–17*) who studied the effect of hydrogen, water, and hydrogen sulfide on the reaction rate concluded that, most likely, 33DMB1 isomerization did not occur on Lewis centers of alumina. The most convincing result obtained was that the reaction was not poisoned by H_2O or H_2S. Moreover, it can be noted that the mechanism through the π-allylic intermediate which has often been proposed to explain alkene isomerization, is not possible in the case of 33DMB1 which has a quarternary carbon atom in the β position to the double bond. Even if this mechanism had been possible, it would have required acid–base centers containing Lewis sites very sensitive to the dehydroxylation state of the catalyst and totally poisoned by H_2S. The proposition therefore that 33DMB1 isomerization occurs through a pure protonic mechanism is most likely. However, all the results concerning this reaction were obtained on oxided catalysts. We report here a comparative study of the 33DMB1 isomerization on oxided and sulfided cobalt–molybdenum/alumina catalysts.

2. EXPERIMENTAL

Preparation of Catalysts

The supported cobalt–molybdenum catalysts were prepared by successive impregnation of Rhône-Poulenc GFS C gamma-alumina (210 m^2g^{-1}, particle size 1.1 mm, mean pore radius 4 nm, main impurities Fe, Ti, Na, Fe < 400 ppm) with aqueous solutions of ammonium heptamolybdate and cobalt nitrate. The solids were dried at 120°C and calcined under an air flow at 450°C after each impregnation. In the series of catalysts, the amounts of molybdenum and cobalt salts were adjusted so as to obtain a constant number of transition metal atoms per gram of catalyst, while varying the atomic percentage of cobalt $r = \%$ Co/(Mo + Co). These catalysts are referred to as CoMo-*r*, *r* being the nominal atomic percentage of cobalt. An unsupported CoMo catalyst was also prepared by homogeneous precipitation of an aqueous solution of ammonium heptamolybdate and cobalt nitrate (2 M) with an aqueous solution of ammonium sulfide at 70°C. The solid was washed, dried, and stored in argon. The atomic percentage of cobalt was 30% and this catalyst was designated CoMo-30ns.

Sulfidation

The catalyst samples were sulfided "*in situ*" in a stream of 10% H_2S in H_2. The solids were first dried in N_2 at 200°C to eliminate the remaining water. They were cooled to 25°C, at which temperature N_2 was replaced by the sulfiding mixture. The temperature was then raised from 25 to 300°C at 4°C min^{-1} and the sulfidation was maintained at 300°C for 3h. Last the samples were cooled to 25°C in the sulfiding mixture.

33DMB1 Isomerization

The reaction was carried out in a dynamic reactor at 200°C. The reactant (20 kPa 33DMB1 in H_2) was supplied by a saturator maintained at 0°C. For the oxided catalysts, the samples (0.1 g) were pretreated under a nitrogen flow at 300°C for 2 h, then cooled to 200°C. For the sulfided catalysts, the samples were heated at 200°C in pure H_2. Dimethyl disulfide (DMDS, 1000 ppm) was added to the reactant in the saturator to maintain the sulfidation state of the catalysts. The products (33DMB1, 23DMB1, 23DMB2, and eventually DMDS) were analyzed on line by gas chromatography (CP Wax 57 CB, 50 m, 0.32 mm i.d., 25°C). In every case the principal product was 23DMB2.

Oxygen Chemisorption

Certain sulfided catalysts were characterized by O_2 chemisorption (O_C) carried out at 0°C in a pulse chromatographic apparatus

TABLE I

Chemical Composition and BET Surface Area of the Oxided Catalysts Supported on Al_2O_3

Catalysts	wt% Co	wt% Mo	Co − Mo (mmol g^{-1})	r%	A_{BET} (m^2g^{-1})
CoMo-0	0	8.34	0.869	0	215
CoMo-10	0.46	7.32	0.841	9.3	175
CoMo-20	0.95	6.48	0.836	19.3	184
CoMo-30	1.45	5.74	0.846	29.3	195
CoMo-40	2.11	5.13	0.893	40.1	179
CoMo-60	2.87	3.31	0.835	58.6	167
CoMo-70	3.49	2.65	0.868	68.2	182
CoMo-100	4.91	0	0.835	100	187

described elsewhere (*18*). This chemisorption temperature was chosen because it gave the best correlation between O_C and the HDS activity of the same catalysts (*19*).

Ammonia Thermodesorption

The acidity of the oxided catalysts was evaluated by NH_3 thermodesorption. The catalyst samples were pretreated at 500°C under a helium flow and then saturated with NH_3 at 50°C. After having eliminated the nonchemisorbed gas, ammonia was thermodesorbed up to 500°C by stages of 50°C. The desorption was monitored by catharometry and calibrated by acid–base titration. The total acidity was divided into three classes: weak, medium, and strong acid sites, which desorbed ammonia at 50–150, 150–300, and 300–500°C, respectively.

RESULTS AND DISCUSSION

Oxided-Supported Catalysts

The chemical composition and BET area of the oxided precursors are given in Table 1. The actual contents in cobalt and molybdenum are close to 0.85 mmol g^{-1} and can be considered constant through the series. Values of r are very close to the nominal values, which justifies a posteriori the nomenclature adopted for these catalysts. Impregnation of molybdenum does not change the specific area of the solid. However, additional impregnation of cobalt decreases slightly this area.

The changes in the acidity with the atomic percentage of cobalt are shown in Fig. 1. For the weak acid centers, acidity is a linear function of the molybdenum content. For the medium and strong acid centers, an optimum of acidity can be observed for CoMo 30. In every case, CoMo-100 is found to be less acid than the support itself.

The activity of the oxided catalysts in 33DMB1 isomerization is shown in Fig. 2. After a decrease which was particularly marked for the molybdenum-rich catalysts, the activity becomes stable after about 1 h on stream. In Fig. 2 are given the curves corresponding to the initial and the steady-state activities. CoMo-0 (Mo/Al_2O_3) is by far the most active catalyst and a sharp decrease of activity is observed as soon as a small amount of cobalt is substituted by molybdenum. The exceptional activity of MoO_3/Al_2O_3 is probably linked to the great number of Brønsted sites contained in this catalyst (*19, 20*). This is in agreement with Boorman *et al.* (*10*) who showed that the Brønsted acidity of the oxided catalysts decreases in the order: Mo > CoMo > Co. For the pure molybdenum catalyst, the ratio A_L/A_B between the number of Lewis and Brønsted sites (as determined by IR study of pyridine absorption) would be 3.4 (*19*). This figure was used to determine the change of A_L/A_B with r, based on the following assumptions: the activity in 33DMB1 isomerization is proportional to A_B while ammonia TPD gives the total number of acid

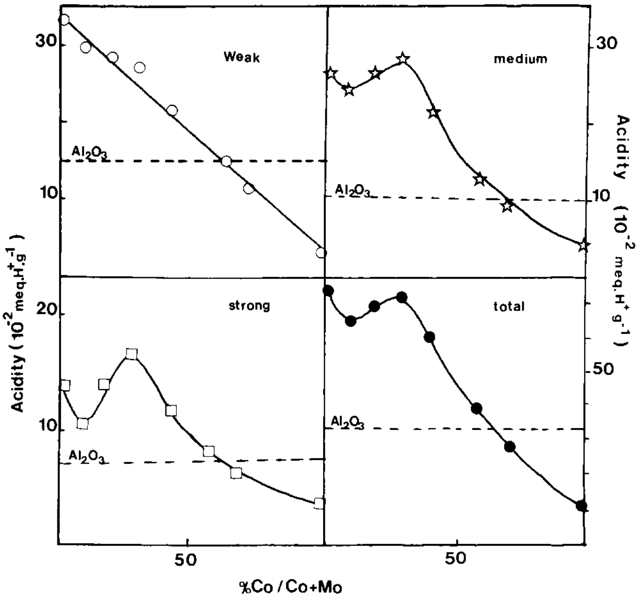

FIG. 1. Acidity of the oxided CoMo/Al$_2$O$_3$ catalysts, determined by NH$_3$ temperature-programmed desorption. Weak, medium, and strong refer to acid sites desorbing ammonia at 50–150, 150–300, and 300–500°C, respectively.

sites (A_B + A_L). The results, given in Table 2, show that the value of A_L/A_B is maximum for r = 30–40%: this is due essentially to the decrease of A_B, A_L remaining practically constant between 0 and 40% Co. Above 40% Co, A_B and A_L decrease simultaneously but A_L faster than A_B.

The fact that alumina presents a significant activity in 33DMB1 may appear surprising because it is generally assumed that oxidic alumina possesses no Brønsted acidity. In fact, this statement based essentially on IR results is a subject of controversy: certain authors claim that oxidic alumina may have a weak protonic acidity (21–24). The study of the isomerization of 2-butenes selectively deuterated in the allylic and vinylic positions led Perot *et al.* (*25, 26*) to the same conclusion. This weak protonic acidity cannot be detected by IR measurements of chemisorbed pyridine and it is a fact that the band at 1545 cm^{-1} characteristic of the pyridinium ions has never been observed on transition alumina (*27, 28*). Nevertheless it should be noted that the isomerization of 33DMB1 occurred on acid sites slightly poisoned by pyridine when this base was desorbed below 220°C (*13*). This is very close to the reaction temperature, which confirms that pyridine interacts little with the acid sites involved in 33DMB1 isomerization.

Supported Sulfided Catalysts

The changes, with the cobalt content, in the activities of the sulfided catalysts are

TABLE 2

Acidity of the Oxided CoMo/Al$_2$O$_3$ Catalysts

Catalysts	Number of acid sites (10^{-2} meq g^{-1})			A_L/A_B
	Total	A_B	A_L	
CoMo-0	75	17	58	3.4
CoMo-10	63	11	52	4.7
CoMo-20	71	8	63	7.8
CoMo-30	73	5	68	13.6
CoMo-40	59	4	55	13.7
CoMo-60	34	4	30	7.5
CoMo-70	32	4	28	7
CoMo-100	11	2	9	4.5

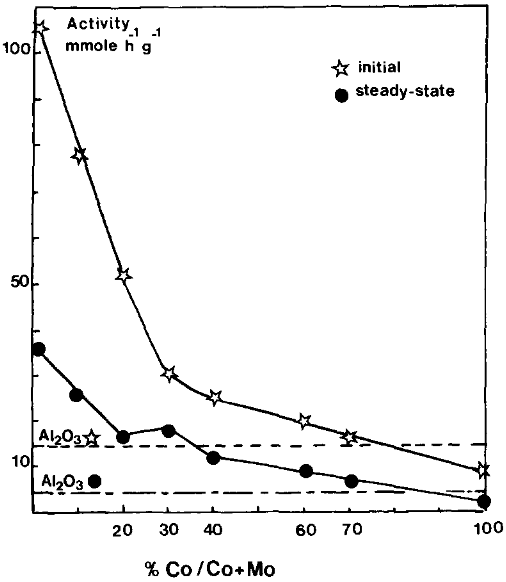

FIG. 2. Activity of the oxided CoMo/Al_2O_3 catalysts in 33DMB1 isomerization at 200°C.

shown in Fig. 3. In the same figure are drawn the curves corresponding to the initial activities and to the steady-state activities. The results show clearly that sulfided CoMo/Al_2O_3 catalysts have a Brønsted acidity. Moreover, the protonic acidity of the sulfided catalyst is just slightly less than that of the oxided catalysts (Fig. 2). Compared to CoMo-0 (Mo/Al_2O_3), the promoted catalysts appear to be very stable. Nevertheless, their activity depends little on the cobalt content and is relatively close to the initial activity of the support itself. It should also be noted that the sulfided alumina is not able to maintain, alone, its initial activity.

The presence of Brønsted acid sites on sulfided CoMo/Al_2O_3 catalysts is still a matter of controversy. It seems that the sulfidation increases the total acidity of MoO_3/Al_2O_3 catalyst but essentially the Lewis acidity (*29, 30*). This was confirmed by Boorman *et al.* (*11*) for promoted and unpromoted Mo/Al_2O_3 catalysts. However, it should be noted that sulfided CoMo/Al_2O_3 catalysts containing fluoride were found to be very active in cumene cracking which is a reaction typically controlled by Brønsted acidity (*11*). Yet, even on these fluorided catalysts, Boorman *et al.* could not detect any Brønsted-pyridine bands. On the contrary, quite recently, Topsøe *et al.* (*31*) were able to detect the characteristic IR bands of the pyridinium ions after the chemisorption of pyridine on sulfided CoMo/Al_2O_3 catalysts. It therefore seems that the IR band at 1545 cm^{-1} characteristic of the Brønsted acidity is not easy to observe on sulfided catalysts and that the absence of this band is not a definitive proof of the absence of Brønsted acidity.

Distribution of Acid Sites on Sulfided CoMo/Al_2O_3 Catalysts

An important question concerns the distribution of the acid sites responsible for the isomerization of 33DMB1. Except for CoMo-0 (Mo/Al_2O_3), which has a great activity, it seems that the protons necessary for the isomerization of 33DMB1 are mainly found on the support itself since there was

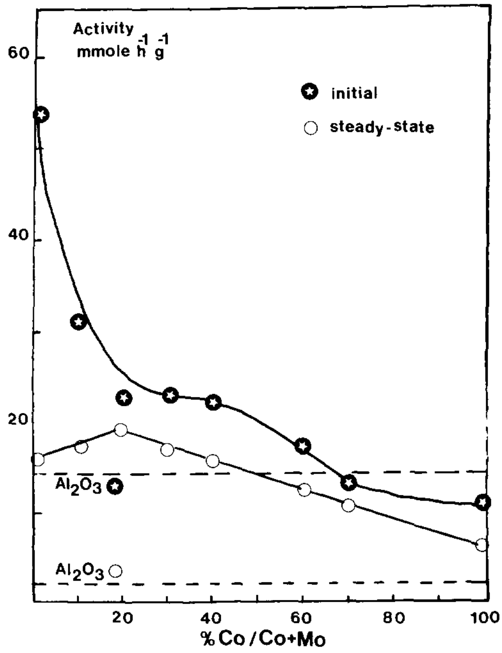

FIG. 3. Activity of the sulfided CoMo/Al_2O_3 catalysts in 33DMB1 isomerization at 200°C.

TABLE 3

Activities of Supported and Unsupported CoMo Catalysts in 33DMB1 Isomerization at 200°C (Sulfided Catalysts)

Catalysts	Oxygen chem. (O_C) μmol at.O g^{-1}	33DMB1 isomerization (200°C)		
		Weight of catalyst (g)	Activity (mmol $h^{-1}g^{-1}$)	
			Initial	Steady state
CoMo-30	500	0.1	23.3	17.9
Al_2O_3	184	0.1	14.2	1.4
CoMo-30ns	227	0.2	1.8	1.7
CoMo-30ns + Al_2O_3	—	0.2 + 0.1	21.3	6.4

no significant difference between the promoted catalysts and the bare support. To confirm this, some demonstrative experiments were carried out with the unsupported CoMo catalyst (CoMo-30ns). The results, given in Table 3, show that the unsupported catalyst is significantly less active than the supported catalyst. It should be noted that CoMo-30 and CoMo-30ns have similar capacities for O_2 chemisorption and probably have similar sulfide surface areas. It can thus be concluded that CoMoS phases are intrinsically less active than the sulfided support. This is confirmed by the experiment with the physical mixture of CoMo-30ns and Al_2O_3 showing that this catalyst mixture has practically the same initial activity as the supported catalyst: a clear synergy effect is observed between the CoMoS phase and the support, particularly at the steady state. Nevertheless this synergy effect is not so marked as in the supported catalyst since the deactivation of the acid sites remains significant. During sulfidation, the hydroxyl groups of alumina are probably transformed into sulfhydroxyl groups by H_2S. These SH groups would be sufficiently acid to catalyze the isomerization of 33DMB1. Nevertheless, the sulfidation state of alumina is very unstable: SH groups can recombine to give H_2S and Lewis centers which will be inactive in catalysis. The results can be interpreted as follows:

(i) except for CoMo-0 (Mo/Al_2O_3), the reaction occurs on the support via a Brønsted-like mechanism,

(ii) supported CoMo catalysts are very stable since they allow permanent sulfidation of alumina,

(iii) the source of H_2S results mainly from the HDS activity of the CoMoS phase with respect to the DMDS added to 33DMB1 but could also result from a certain *lability* of the sulfur included in MoS_2 crystallites, especially in the presence of cobalt,

(iv) alumina alone is incapable of maintaining its initial sulfidation state since it is not sufficiently active for DMDS hydrogenolysis. The determining role of H_2S in the isomerization activity was confirmed by carrying out the reaction in the presence of 1.4% H_2S. The activity of Al_2O_3 was shown to be remarkably constant (Fig. 4) and close to the activity observed for the CoMo-30 catalyst.

This principal way of transformation of 33DMB1 does not exclude the reaction on the sulfides themselves. This is clear for unpromoted MoS_2 which could have a significant number of Brønsted sites, similar to those described by Topsøe *et al.* (*31*): protons would be produced by heterolytic dissociation of H_2S on the anion vacancy of molybdenum. Nevertheless these acid sites are still more fragile than those of the support: they require a high partial pressure of H_2S to be stabilized. They disappear when molybdenum is promoted by cobalt.

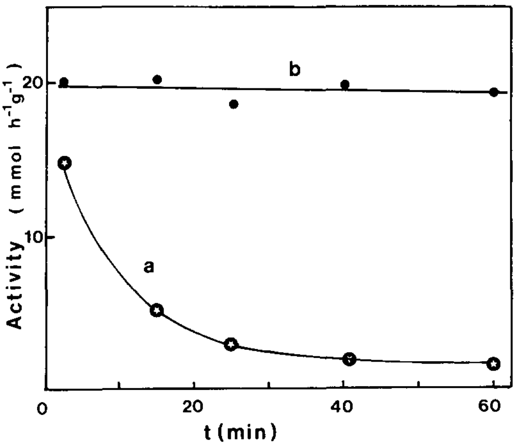

FIG. 4. Changes with time on stream in the isomerization activity of sulfided alumina: (a) 33DMB1 + DMDS (1000 ppm) + H_2, (b) 33DMB1 + H_2S (1.4%) + N_2.

CONCLUSION

On oxided $CoMo/Al_2O_3$, the skeletal isomerization of 3,3-dimethyl-1-butene most likely occurs on Brønsted sites via a mechanism involving carbenium ions. The number of protonic centers necessary for the reaction to occur decreases strongly as soon as cobalt substitutes for a part of the molybdenum, so that the MoO_3/Al_2O_3 catalyst is much more active than the promoted catalysts. The total acidity, and subsequently the Lewis acidity, is less sensitive to the presence of the cobalt: a maximum number of Lewis sites is even recorded for 30% cobalt.

On sulfidation, there is little change in the isomerization activity and alumina has practically the same activity as the promoted catalysts. The reaction occurs essentially on the support whose sulfidation state (and the Brønsted acidity) is maintained by the continuous flow of H_2S produced during hydrogenolysis of DMDS (added to 33DMB1). Therefore the support is rapidly deactivated unless H_2S (instead of DMDS) is added to the reactant mixture. The reaction on the CoMo sulfide phase is not excluded but it is rather limited except on pure MoS_2. These special Brønsted sites existing on the unpromoted sulfide are very unstable and are rapidly deactivated.

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