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RESEARCH NOTE

Acidity and Hydrogenation Properties of Mo-P-Alumina Catalysts Prepared by a Sol–Gel Method

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The decrease of the S, N, and metal compounds (Ni, V) in petroleum fractions is an important task to solve recent environmental problems. For this purpose, improvements of Mo-alumina based catalysts by addition of promotors (Co, Ni) (1–3) and also by incorporation of P (4–8) have deserved a considerable interest. However, the role of P in the catalysts formulations is still a matter of controversy (4–23). Several studies (9–18) using IR spectroscopy, temperature-programmed desorption of basic molecules, and surface reactions have tried to show the influence of P on the acid–basic properties of the catalysts. P has an effective influence, but the debate still exists as different techniques are used to probe the catalysts and also because they are prepared according to different methods with various amounts of P. Relevant studies (12, 19–23) also pointed out the influence of P in catalytic reactions, namely in hydrogenation reactions, in terms of changes of the activity and selectivity as well. Once again, the P loading, the way to introduce it in the catalyst, and the nature of the reactant lead to different conclusions.

In a previous paper (24), we have shown that catalysts prepared by a sol–gel method exhibit higher hydrodesulphurization (HDS) activity than conventional catalysts as it was possible to obtain high Mo loadings up to 30 wt% (in Mo) as well dispersed Mo oxo-species. Recently (25), we extended this preparation procedure to investigate Mo-P-alumina catalysts. Textural and structural characteristics were extensively discussed with data on HDS of thiophene. In the present note, we wished to elucidate the role of P on the acidity and hydrogenation property of those Mo-P-alumina catalysts containing ~26 wt% of Mo and up to 11 wt% of P. Cyclohexene (CHE) hydrogenation and cyclopropane (CP) were the selected reactions to test the hydrogenation and acidity changes induced by P.

The procedures for the catalysts preparation and their textural and structural characteristics are extensively described in Ref. (25). The alumina precursor is the aluminium sec-butylate. Mo as ammonium heptamolybdate and P as P_2O_5 or H_3PO_4 are incorporated during the gel formation. Among the two series prepared with ~17 wt% Mo and ~26 wt% Mo, only the second one has been considered in this work as it shows higher HDS activity, despite a decrease of the specific surface area for the highest P loading. Nomenclature of the catalysts is the same as previously (25).

Hydrogenation of cyclohexene (CHE) was carried out at atmospheric pressure in a flow-type reactor with 0.2 g of catalyst presulphided at 400°C for 2 h with a H_2/H_2S (90/10) gas mixture (50 $\text{ml} \cdot \text{min}^{-1}$). Then, CHE was introduced in the reactor at 350°C at constant partial pressure (100 Torr) with dry H_2 at a total gas flow rate of 10 $\text{ml} \cdot \text{min}^{-1}$. The reaction products were analyzed by gas chromatography, at the steady state, 2 h after introduction of CHE. Cracking of cyclopropane (CP) was carried out at atmospheric pressure in a flow-type reactor with 0.2 g of catalyst. Two reaction conditions were used. In the first case, activity was measured at 350°C in the absence of H_2 on the oxidic catalysts with a CP/He (5/95) gas mixture at a flow rate of 5 $\text{ml} \cdot \text{min}^{-1}$. For the second condition, activity was measured at 350°C in the presence of H_2 on the presulphided catalysts (same conditions as above). A $CP/He/H_2$ (2.5/47.5/50) gas mixture at a total flow rate of 10 $\text{ml} \cdot \text{min}^{-1}$ was used. Conversion of CP was determined by gas chromatography, at the steady state, 1 h after introduction of CP.

The results on CHE hydrogenation obtained with the Mo-P-alumina catalysts prepared with H_3PO_4 as the P precursor are reported on Table 1. Whatever the P content, the CHE conversion remains constant at about 26%. The main products are isomerized molecules like methylcyclopentane (MCPA) and methylcyclopentenes (MCPE), a totally hydrogenated molecule as cyclohexane (CHA) and the corresponding dehydrogenated benzene (BZ). Less than 1% of converted CHE is distributed in lighter fragments. The product distribution shows (Table 1) that the amount of BZ is quite independent on the P content while the amount of

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TABLE 1

Results of Cyclohexene (CHE) Hydrogenation at 350°C over Sulphided Mo-P-Alumina Sol–Gel Catalysts

					Product distribution (%)[b]			
Catalysts[a]	Mo (wt%)	P (wt%)	S.S.A. (m^2/g)	CHE conv. (%)	MCPA	MCPE	CHA	BZ
MPC(30-0)	26.0	0	523	27.2	3	10	63	24
MPC(30-2)H	26.5	2.2	443	24.7	4	14	66	16
MPC(30-5)H	25.3	4.6	411	27.4	5	20	55	20
MPC(30-7)H	25.8	6.8	405	26.3	6	27	48	19
MPC(30-11)H	25.3	11.1	263	26.2	7	39	38	16

[a] Nomenclature of catalysts is defined in Ref. (25). H means a preparation with H_3PO_4 as a P precursor.
[b] MCPA = methylcyclopentane, MCPE = methylcyclopentenes, CHA = cyclohexane, BZ = benzene.

isomerized molecules (MCPA + MCPE) increases with the P loading. Conversely, the proportion of CHA decreases with the P loading. Thermodynamic data indicate that the dehydrogenation reaction is favored at the working condition used. This can explain the presence of BZ in similar amount on all the sudied catalysts. Clearly, in the sulphided state, introduction of P in the catalyst formulation enhances acidity as CHE isomerization is promoted, whereas the hydrogenation potentiality decreases. This last result is similar to some observations reported by Walendziewski (12), Muralidhar *et al.* (22), and Poulet *et al.* (23) who found that hydrogenation of benzene, hexene, or isoprene respectively decreases with the addition of P in sulphided Co–Mo or Mo-alumina catalysts. However, inverse effects can also be found; for example, toluene hydrogenation increases in the presence of P in a Mo-alumina catalyst (23). The nature of the molecule to hydrogenate, the preparation method of the catalyst, and the amount of P have a strong influence on the hydrogenation ability of the catalysts. The isomerization results shown in Table 1 seem to indicate that P is directly participating in the structure of the active phase and/or influences the strength of the acid sites as C–C bond hydrogenolysis is noticeably enhanced. In the oxidic Mo-P-alumina catalysts, we have already shown, mainly by IR and NMR spectroscopies, that P may interact with Mo to form P–Mo heteropoly species and also with the alumina framework. After sulphidation, the catalysts may have a memory effect of these interactions.

Cracking of CP will be considered first on the oxidic catalysts in the absence of H_2 in the reacting mixture. In the experimental conditions used, pure alumina does not show any evidence of cracking activity, whereas the catalysts containing Mo and/or P are active. The products obtained by CP cracking are mainly propane and propene. In some cases, small amounts of CH_4, C_2H_4, C_4H_6, and C_4H_8 are also obtained. Figure 1 shows the influence of the P content and of the nature of the P precursor (P_2O_5 or H_3PO_4) used to prepare the Mo-P-alumina catalysts on the CP conversion. The catalyst without P (catalyst MPC(30-0)) has already a high acidic potentiality as conversion of CP is 90.8% with a yield in ethylene of only 0.1%. This result has to be compared with the conversion obtained on a catalyst containing only P. For example, the MPC(0-11)H catalyst (10.6 wt% P, 474 $m^2 \cdot g^{-1}$) shows a CP conversion of 88% with no production of ethylene. It seems therefore that introduction of P or Mo in the alumina catalyst develops similar acidity with respect to CP conversion. The combination P–Mo is more efficient for CP cracking when H_3PO_4 is used as the P precursor. The activity increases quite linearly with the P content to reach 98.1% with a C_2H_4 yield of 1.4% for the MPC(30-11)H catalyst. Since the presence of both Mo and P increases the CP conversion and also increases the relative yield of ethylene, it is suggested therefore that the acid sites are probably stronger on the mixed Mo–P oxidic catalysts than on the oxomolybdate species or on the aluminium phosphate. On the other hand, CP conversion for the series prepared from P_2O_5 as a P precursor decreases with P loading, the effect being already noticeable at low

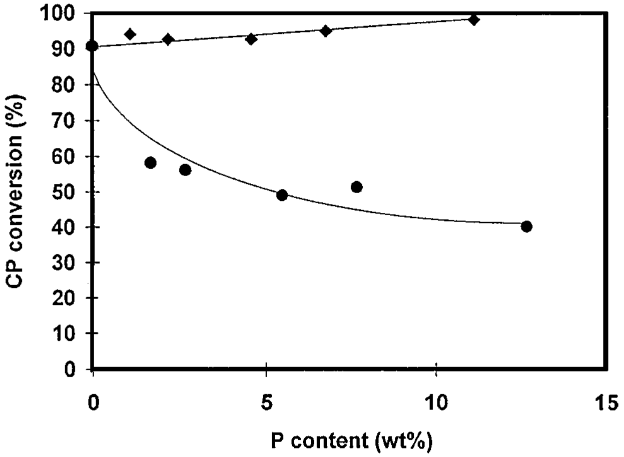

FIG. 1. The effect of the phosphorus precursor on the cyclopropane conversion. The catalysts were not sulphided prior to the tests and the reaction was carried out at 350°C in the absence of H_2: ◆, H_3PO_4 as a P precursor; ●, P_2O_5 as a P precursor.

P loading, where the decrease of the specific surface area is not yet dramatic (25). Clearly, the way of introducing P in the catalyst formulation has a strong influence on their acidic behavior; this can in part explain the discrepancies noted in the literature about the role of P. The decrease of the CP conversion in the series prepared with P_2O_5 might be mainly attributed to fewer interactions between the P oxo-species and the alumina support.

Let us now consider the CP conversion over sulphided catalysts (only catalysts prepared with H_3PO_4 are considered). Figure 2 shows that the CP conversion, in the presence of H_2 in the feed, increases with the amount of P introduced in the catalysts. In parallel, the relative amount of C_2H_4 increases as well. Clearly, the sulphidation step of the catalysts has not inhibited the synergy between P and Mo for developing acid sites strong enough to crack CP and produce a minor amount of ethylene. However, we have no direct evidence of whether the strong acid sites due to the interaction between Mo and P in the sulphided catalysts are the same as the ones present in the oxidic precursors. But it is possible, as already mentioned in the part concerning the CHE conversion results, that the sulphided state of the catalysts has a memory effect of the P–Mo interaction. To show the effect of H_2 in the reactive mixture, the CP conversion has been measured in the same run with and without the presence of hydrogen over the sulphided MPC(30-7)H catalyst (Fig. 3). The CP conversion decreases drastically from ~95% in presence of H_2 to ~75% in the absence of H_2 while the activity recovers almost the same level when the hydrogen is reintroduced in the reactive feed. Such a positive effect of hydrogen in the reactive feed is a clear indication that CP cracking on Mo-P-alumina catalysts proceeds differently, at least in part, on the sulphided state and on the oxidic form, even if the conversion values are at the same level. On the sulphided catalysts, the effect of H_2 might be to increase the quantity of acid SH groups (Brönsted sites) and/or to create coordinated unsaturated sites (CUS) which then act as Lewis acid sites. Since P has a negative effect on the Mo sulphidation extent (26), the presence of H_2 in the feed may also create acid OH groups associated with the Mo remaining oxo-species. The last possible effect of H_2 could be the modification of the P oxo-species, probably associated with the alumina framework, where the $P{=}O_t$ groups (identified by IR; see Ref. (25)) are giving P–OH surface species. At the present time, it is not possible to exclude one of these possibilities for explaining the positive effect of H_2. Note only that chemical analyses of the sulphided catalysts after tests in CP cracking with H_2 in the feed revealed a S/Mo atomic ratio decreasing from ~2.0 to ~1.7 with the increase of the P content. This result could be associated with a worse sulphidability of the Mo oxo-species in the presence of P or also with the formation of smaller MoS_2 crystallites. In such a case, the relative amount of Mo at the edges of the MoS_2 patches is optimal (see the geometrical model of Kasztelan *et al.* (27, 28)) with, consequently, the presence of an optimal number of CUS created by the effect of H_2 (29). Nevertheless, the other possible effects of H_2, as mentioned before, cannot be ruled out. Anyway, it is considered that the P addition in Mo-alumina-based catalysts does not increase the strength of acid sites enough to enhance hydrogenolysis of C–S as the HDS activity of thiophene at atmospheric pressure bond is not deeply modified (25).

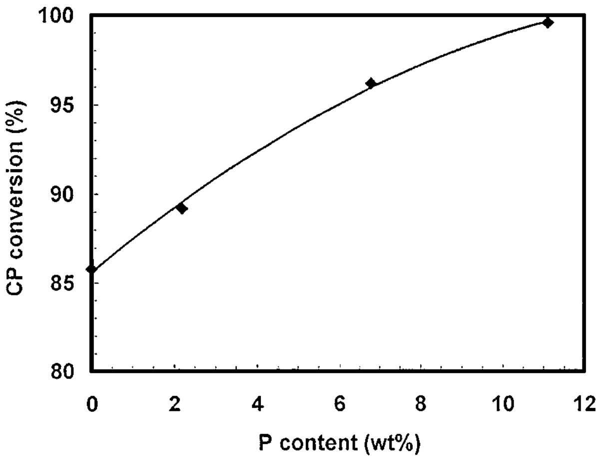

FIG. 2. The cyclopropane conversion over presulphided catalysts prepared from H_3PO_4 as a precursor. The reaction was carried out at 350°C in the presence of H_2.

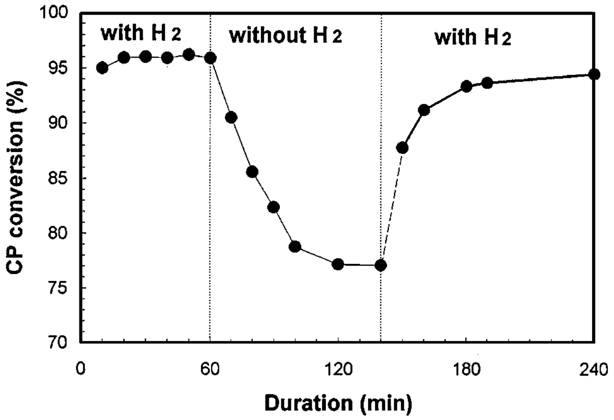

FIG. 3. The effect of hydrogen in the reactive feed on the cyclopropane conversion on the presulphided MPC(30-7)H catalyst.

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