Journal of Catalysis **195,** 31–37 (2000)
doi:10.1006/jcat.2000.2968, available online at http://www.idealibrary.com on IDEAL®

Origin of Cracking Functionality of Sulfided (Ni) CoMo/SiO_2–ZrO_2 Catalysts

M. S. Rana, B. N. Srinivas, S. K. Maity, G. Murali Dhar,[1] and T. S. R. Prasada Rao

Catalysis Division, Indian Institute of Petroleum, Dehradun 248 005, India

Received February 1, 2000; revised May 2, 2000; accepted June 17, 2000

DEDICATED TO PROFESSOR F. E. MASSOTH ON THE OCCASION OF HIS 75TH BIRTHDAY

A systematic investigation of the hydrocracking activity of Mo, CoMo, and NiMo catalysts as a function of support composition, Mo content, and Co or Ni content on supported ZrO_2–SiO_2 catalysts of varying composition ($Zr/Zr + Si = 0.0, 0.15, 0.30, 0.45, 0.70, 1.0$) carried out in a microcatalytic reactor at 400°C and atmospheric pressure is presented. Varying the composition of the support, the Mo content, and the Co or Ni content was studied. Cumene cracking in the presence of hydrogen on the sulfided catalysts indicated that the supported molybdenum phase and the promoted counterparts contribute significantly to the cracking functionality of the catalysts. From the studies based on SiO_2 and carbon supported catalysts it appears that it is unlikely that the observed high activities of supported MoS_2 and its promoted analogues are due to increased activity as a result of reduction in coke formation on the support surface. The creation of sulfhydryl groups and their role in generating the acid function are discussed. © 2000 Academic Press

Key Words: **CoMo catalysts; ZrO_2–SiO_2 support; oxygen chemisorption; catalytic cracking functionality; hydroprocessing catalysts.**

1. INTRODUCTION

Sulfided Co–Mo and Ni–Mo hydroprocessing catalysts supported on various oxide supports were studied in relation to hydrotreating and hydrocracking (1–4). These catalysts present hydrogenolysis, hydrogenation, and hydrocracking functionalities (5, 6). While extensive studies have been carried out on the hydrogenolysis and hydrogenation functionalities of supported MoS_2 and WS_2, there is only a small number of studies on the hydrocracking functionality of these active components because it was generally believed that the hydrocracking functionality is related to the support only. The cracking functionality of the support or the active component is generated by the acid sites present on the support or on the active component. Therefore, the question is whether the active component contains Brønsted acid sites that are strong enough to generate significant acidity compared to the supports. There have been a number of studies on the acidity of (Ni) CoMo/γ-Al_2O_3 systems, the earliest of which focused on the acidity in the oxidic state. These studies revealed that pure γ-Al_2O_3 has Lewis acid sites only, while Mo/γ-Al_2O_3 contains both Lewis and Brønsted acid sites (7, 8). Sulfidation or reduction of these catalysts resulted in the disappearance of these Brønsted sites. However, Topsøe and Topsøe reported the presence of Brønsted acid sites in sulfided Mo/γ-Al_2O_3 when pyridine was used at high temperatures (9). The absence of Brønsted sites in other studies was attributed to the activated nature of the adsorption of the probe molecule pyridine. Using dimethylpyridine as the probe molecule, Petit *et al.* (10) recently showed that Brønsted acid sites are indeed present on Mo, CoMo, and NiMo supported on γ-Al_2O_3 and that the number of these sites increased due to the presence of H_2S. There is always a significant concentration of H_2S in industrial reactors; therefore, it is likely that the sulfided molybdenum phase has significant cracking functionality under actual reaction conditions.

Catalytic reactions can be used not only to test the cracking functionality but also to test the acidity of the catalysts. Boorman *et al.* (11–13) studied acidity and cumene cracking activity on fluorinated CoMo/γ-Al_2O_3 catalysts in oxide, reduced, and sulfided forms and concluded that sulfided catalysts are less active than the oxide forms. Massoth and co-workers (5, 6) studied the cracking of isooctene on various supported Mo catalysts and found significant activity for the cracking of isooctene to isobutene (14). Small amounts of cracking products were also observed during hexene hydrogenation on CoMo catalysts (15). Appreciable dealkylation of *m*-diisopropylbenzene to cumene was also reported (5). Dealkylation of 1-methylnaphthalene has been reported (16) to take place over Co- and Ni-promoted molybdenum catalysts. Significant cracking of isooctene was observed on silica-supported CoMo catalysts, which indicates that the sulfided CoMo active phase is the seat of hydrocracking activity; it is well known that SiO_2 surfaces

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[1] To whom correspondence should be addressed. Fax: 091-135-671986. E-mail: gmurli@iip.res.in.

0021-9517/00 $35.00

are not acidic (5). With the aim of increasing our understanding of the origin of the cracking functionality with reference to the supported phase and promoters, a systematic study of the roles of support, the active component, and the promoters in generating cracking functionality on Mo and CoMo supported on various SiO_2–ZrO_2 compositions is presented. We have been investigating support effects in hydrotreating reactions on a variety of mixed oxide supports and this study using SiO_2–ZrO_2 forms a part of such investigation (3). In addition, some of the patent literature reported (17, 18) beneficial effects in hydrocracking when ZrO_2–SiO_2-containing supports are used. The ZrO_2–SiO_2 support presents only moderately strong acid sites and such a support, we thought, is better suited to differentiate the contribution of the active component. This investigation was carried out with the aid of the cumene hydrocracking (HCR) reaction, which is known to be a conventional test for protonic acid catalysis.

2. EXPERIMENTAL

A series of ZrO_2–SiO_2 supports was prepared according to the homogeneous precipitation method using aqueous silicic acid, zirconium oxychloride, and sufficient amounts of urea. The solution was kept at 90°C for 4 h to allow complete precipitation. After washing, to completely remove chloride ions, the precipitate was dried overnight at 110°C and calcined at 550°C for 5 h. Samples with varying ZrO_2/SiO_2 ratios were prepared by adjusting the amounts of the reagents accordingly. These samples are referred to as ZS-A (15wt% ZrO_2–85wt% SiO_2), ZS-B (30wt% ZrO_2–70wt% SiO_2), ZS-C (45wt% ZrO_2–55wt% SiO_2), and ZS-D (70wt% ZrO_2–30wt% SiO_2). Pure ZrO_2 and SiO_2 were also prepared according to a similar procedure.

The molybdenum-supported catalysts were prepared by the incipient wetness impregnation method using appropriate concentrations of ammonium heptamolybdate. The Co- and Ni-promoted catalysts were prepared by impregnating the promoter on an oven-dried Mo-supported catalyst. The impregnated catalysts were dried in air at 100°C overnight, and all the catalysts were calcined at 500°C for 5 h.

Oxygen chemisorption was measured at −78°C in a conventional high-vacuum system on a catalyst sulfided at 400°C for 2 h using a CS_2/H_2 mixture at a flow rate of 40 ml/min, according to the double-isotherm procedure of Parekh and Weller (19) for reduced molybdenum catalysts. The same system was also used for BET surface area measurements.

The cumene cracking reaction was carried out at 400°C on a catalyst sulfided at 400°C for 2 h in a flow of a CS_2/H_2 mixture in a fixed-bed reactor operating at atmospheric pressure and interfaced with a six-way sampling valve for product analysis (20). First-order rates were calculated according to the equation $x = r(W/F)$, where r is the rate in mol h^{-1} g^{-1}, x is the fractional conversion, W is the weight of the catalyst in g, and F is the flow rate of the reactant in mol h^{-1} (21). The particle size of these catalysts were 20–40 mesh and the conversions were kept below 15% to avoid diffusional limitations.

3. RESULTS

3.1. *Catalyst Characterization*

All the ZrO_2–SiO_2 supports, pure ZrO_2 and SiO_2, and supported Mo and CoMo or NiMo catalysts were characterized by BET surface area and mercury pressure porosimetry measurements. The surface area and pore volume data are shown in Fig. 1. It can be seen that all the ZrO_2–SiO_2 supports have a very high surface area in the range 525 to 373 m^2/g. Pure ZrO_2 has a surface area of 73 m^2/g. The mean pore radius is 33 Å. The pore volumes of all the mixed oxide supports are in the vicinity of 0.2 ml/g. X-ray diffraction results indicate that all the ZrO_2–SiO_2 supports are X-ray amorphous except for a broad hump due to SiO_2 in the 20 to 30 2θ region, indicating that there is a homogeneous mixing of both components of the mixed oxides. In the case of molybdenum-supported catalysts, no peaks due to molybdenum were detected up to about 6 wt% Mo. However, at higher loadings we found evidence for the presence of crystalline MoO_3 in the oxide precursors, indicating that molybdenum is well dispersed in these catalysts up to 6 wt% Mo. A detailed account of characterization results will be discussed in a separate communication. Only a summary of relevant characterization results is presented to aid in appreciation of the following discussion.

3.2. *Oxygen Chemisorption*

The oxygen uptake was evaluated for all four catalysts using ZrO_2–SiO_2 as a support as a function of the molybdenum content at −78°C on sulfided catalysts. The corresponding data without substracting support contribution are plotted in Fig. 2. The oxygen chemisorption increases up to 6 wt% Mo and then decreases at higher loading on the four ZrO_2–SiO_2 catalysts. Since it is generally accepted

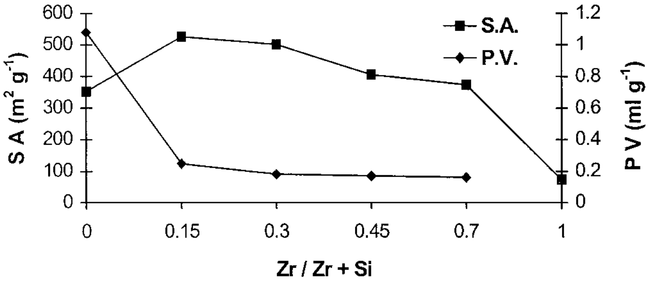


FIG. 1. Variation in the surface area and pore volume as a function of Zr/Zr + Si ratio.

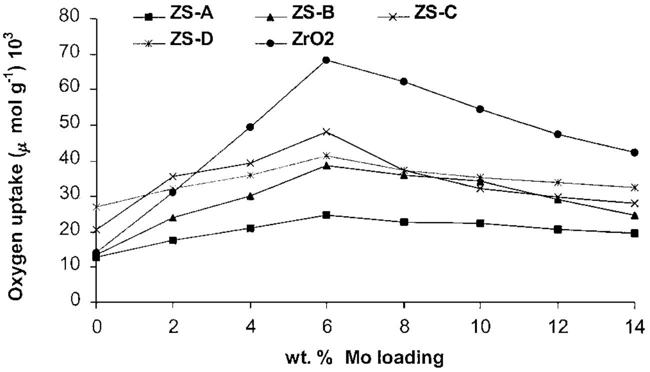


FIG. 2. Variation in the oxygen uptake with Mo loading.

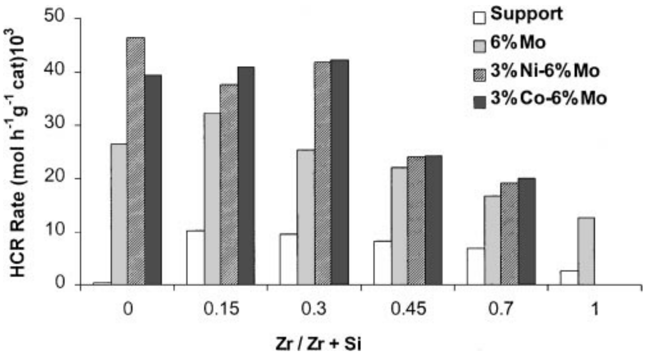


FIG. 3. Comparison of HCR activity as a function of support composition.

that oxygen chemisorption is related to anion vacancies and the general state of dispersion of Mo (22), the trend in the variation of oxygen chemisorption as a function of Mo loading suggests that the dispersion of molybdenum increases with Mo loading, attaining a maximum at 6 wt% Mo. These observations agree with the XRD results discussed earlier. Several investigators studied X-ray diffractograms as a function of Mo or W loading in the oxide state on a number of supports (23–25). Some of these investigations studied oxygen chemisorption in the sulfided state as a function of Mo or W loading. In all these investigations, oxygen chemisorption as a function of Mo or W loading increased linearly up to a certain loading, depending on the nature and the surface area of the support, and start to decrease or level off with further increasing of the loading. The appearance of MoO_3 or WO_3 peaks are generally noted at the Mo loading immediately following the maximum in the oxygen chemisorption. Our results are in general agreement with the results reported on other supports.

3.3. Cumene Cracking Reaction Studies

A systematic study of the cracking function was carried out using the cumene cracking model reaction at 400°C on sulfided catalysts, on pure supports, on supports containing various amounts of molybdenum, and on Co- and Ni-promoted catalysts. Similar measurements under identical conditions were carried out on SiO_2 and ZrO_2 supports and on Mo, CoMo, and NiMo catalysts prepared using these supports.

3.3.1. Comparison of cumene HCR activity of various catalysts. The cumene cracking activity on pure supports (6 wt% Mo, 3% Ni, 6% Mo, 3% Co and 6% Mo catalysts) supported on various ZrO_2–SiO_2 catalysts is presented in Fig. 3. In the case of all the Mo, CoMo, and NiMo catalysts supported on various supports, the support contribution is not subtracted while the data are presented. The activity for cumene cracking on the pure supports shows a maximum at a Zr/Zr + Si ratio of 0.15. As expected, pure SiO_2 has negligible activity, and all the ZrO_2–SiO_2 mixed oxide supports have a higher activity than their parent oxides. For the 6 wt% Mo-supported catalysts, the HCR activity is higher than that of the pure supports, indicating that the molybdenum phase indeed has significant cracking functionality. It is interesting that, on SiO_2-rich catalysts, the contribution of molybdenum appears to be higher. In Co- and Ni-promoted catalysts, the cracking function is significantly promoted on pure SiO_2 and SiO_2-rich catalysts and is not as well promoted in ZrO_2-rich catalysts. Since SiO_2 has insignificant HCR activity, the results indicate that the MoS_2 phase and the promoted phase have significant activity, although the extent of the increase in activity depends on the support.

3.3.2. Effect of varying the Mo content on HCR activity. The molybdenum content was varied from 2 to 14 wt% on each of the ZrO_2–SiO_2 compositions. The catalytic activity data (Fig. 4) show that the cumene cracking activity increases up to 6 wt% Mo and then decreases with higher molybdenum loading on all four ZrO_2–SiO_2-based catalysts. This indicates that the 6 wt% catalyst is the one composition on which the best activity for the cracking functionality is obtained in these systems. The oxygen uptakes on one of the Mo/ZrO_2–SiO_2 catalysts, measured at −78°C,

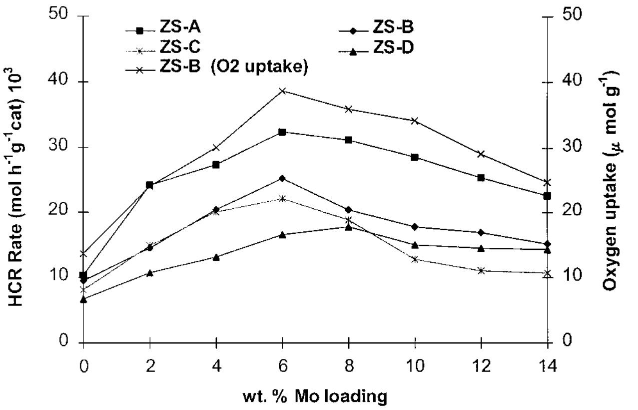


FIG. 4. Variation in the oxygen uptake and HCR rates with Mo loading.

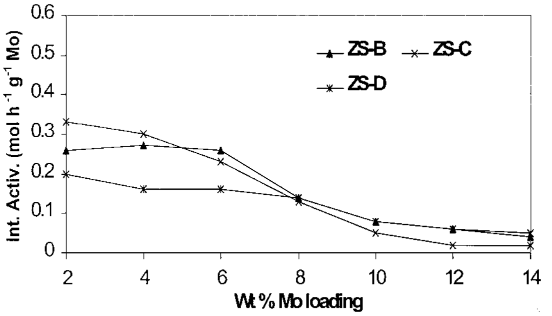


FIG. 5. Variation in the intrinsic activity with Mo loading.

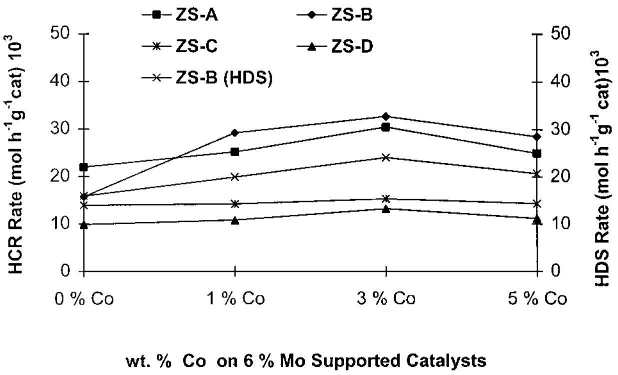


FIG. 6. Variation in the rate of HCR and HDS as a function of promoter content.

is also shown in Fig. 4. Furthermore, oxygen chemisorption increases up to 6 wt% molybdenum loading and then decreases. The supports take up small amounts of O_2, as can be noted from the raw data presented. It is interesting that the oxygen chemisorption, which measures the general state of dispersion of molybdenum (22) and population of anion vacancies, varies in a way similar to the cumene cracking activity. This suggests that the cracking functionality is a property of the supported molybdenum sulfide phase and that sulfide anion vacancies are somehow related to the cracking sites. In addition, the hydrodesulfurization of thiophene followed similar trends. Since it is well known that HDS activity is characteristic of MoS_2 phase, such similarity suggests that the supported MoS_2 phase has significant cracking functionality.

To better understand the activity with respect to the variation in the molybdenum composition of the catalyst, the intrinsic activity (rate divided by molybdenum) as a function of molybdenum loading, of the three ZrO_2–SiO_2 catalysts, is presented in Fig. 5. It can be seen that the intrinsic activity is more or less constant up to 6 wt% Mo and then decreases at higher loading for all three ZrO_2–SiO_2 catalysts The variation was similar to that observed for HDS, which is well known to originate from the supported phase (1, 2). The above-mentioned similarity further supports the view that a significant part of the cracking function originates from the supported molybdenum sulfide component.

3.3.3. Effect of promoter content on HCR activity. To understand the promotional effect of Ni and Co on cumene cracking in Mo/ZrO_2–SiO_2 systems, the concentration of the promoter was varied from 1 to 5 wt%, and the catalysts were tested under exactly the same conditions as those for cumene cracking reaction. The activity data as a function of the concentration of the promoter are shown in Fig. 6 and Table 1. It can be seen that there is a significant promotional effect on the high silica supports and a low promotional effect on ZrO_2-rich supports. To compare the behavior of cracking functionality with that of HDS, the variation in the HDS activity with the amount of promoter is also shown in Fig. 6 for the ZS-B catalyst. The HCR activity was similar to the activity of HDS. Moreover, the cumene cracking activity increases up to 3 wt% of Co with the content of the promoter and then decreases.

The similarity between the HDS activity and the cracking activity indicates that the promoter atoms are involved in generating the cracking functionality of these catalysts. Similar variation with the amount of the promoter is also observed in the case of Ni-promoted catalysts. Both Co and Ni behave in a similar manner, and the conclusions reached in the case of Co also apply for nickel. There are only slight differences between Co and Ni in the catalysts prepared using various support compositions. It is, therefore, clear that both MoS_2 and Co or Ni promoted phases supported on ZrO_2–SiO_2 supports make a significant contribution to the cracking activity.

The ZS-B ($30ZrO_2$–$70SiO_2$) catalyst shows the highest cracking activity for Ni-and Co-promoted catalysts, even though ZS-A ($15ZrO_2$–$85SiO_2$) shows the highest activity for Mo catalysts. The ZS-C ($45ZrO_2$–$55SiO_2$) catalyst shows a higher promotional effect in the case of Ni but only a marginal promotional effect in the case of cobalt. These results indicate that there are subtle differences between

TABLE 1

Cumene Cracking Activity of Promoted (Ni, Co) Mo/ZrO_2–SiO_2 Mixed Oxide Catalysts

	HCR rate (mol h^{-1} g^{-1} cat.) 10^3			
Promoted catalysts	**ZS-A**	**ZS-B**	**ZS-C**	**ZS-D**
6% Mo	22.0	15.7	13.9	9.8
1%Co–6%Mo	25.2	29.2	14.2	10.8
3%Co–6%Mo	30.5	32.7	15.3	13.2
5%Co–6%Mo	25.0	28.5	14.3	11.2
1%Ni–6%Mo	24.6	31.6	14.0	10.2
3%Ni–6%Mo	27.3	32.3	16.1	12.2
5%Ni–6%Mo	25.2	29.1	15.0	09.9

Note. ZS-A = (15wt% ZrO_2–85wt% SiO_2); ZS-B = (30wt% ZrO_2–70wt% SiO_2); ZS-C = (45wt% ZrO_2–55wt% SiO_2); ZS-D = (70wt% ZrO_2–30wt% SiO_2).

cobalt and nickel in the promotion of HCR activity, although these catalysts tend to behave similarly in other respects.

4. DISCUSSION

This investigation is focused on the cumene hydrocracking activity of the CoMo, and NiMo catalysts on a series of ZrO_2–SiO_2 supports at 400°C, on catalysts sulfided at 400°C. The supports contain various amounts of molybdenum or 6 wt% Mo and various amounts of Co and Ni on four ZrO_2–SiO_2 catalysts. The results were compared with oxygen uptake and hydrodesulfurization activity. There are significant differences in the cracking activities of Mo, CoMo, and NiMo catalysts as a function of support composition. On SiO_2-rich catalysts, the cracking activity and promotional effects are higher compared to those of ZrO_2-rich supports. The oxygen uptake and cracking activity on all four ZrO_2–SiO_2 catalysts increased up to 6 wt% as a function of Mo loading and then decreased. The variation of cracking activity as a function of promoter content, in the case of Co and Ni, increased up to 3 wt% of the promoter and then decreased. All these variations in activity as a function of support composition, Mo loading on each support, and promoter content are similar to the variation of thiophene hydrodesulfurization activity. It is well known that hydrodesulfurization of the thiophene is an intrinsic property of the supported Mo phase and its promoted analogues. Similarly, oxygen chemisorption is known to measure an important property related to the MoS_2 phase (26). Therefore, the similarity between cracking activity, and oxygen uptakes and HDS activity, suggests that the observed cracking activity has significant contribution from the supported and promoted MoS_2 phases. However, there can be differences in steady state activity of the support in pure form and in the presence of the sulfided phase. The hydrogenation function of the active phase may reduce the coke deposition on the support. In the cumene cracking reaction, the propene produced during reaction may lead to coke deposition due to polymerization. In the presence of a metal sulfide with significant hydrogenation activity, the propene is converted to propane, resulting in much less coke deposition on the support, leading to higher support contribution to the cracking reaction. Olorunyolemi and Kydd reported reduction of coke on a sulfided NiMo/Ga_2O_3–Al_2O_3 catalyst compared to a pure support while studying cumene cracking reaction on these catalysts (27).

To further understand and resolve the problem, we have undertaken additional experiments on a MoS_2/SiO_2 supported system, MoS_2/carbon, and unsupported MoS_2. The results of the experiments, carried out exactly under conditions similar to those mentioned in the Experimental section, are presented in Figs. 7 and 8. It can be seen that SiO_2 has negligible activity, and MoS_2/SiO_2 is 40 times more active and promoted catalysts are 80 times more active than the SiO_2 support. Since it is well known that silica has negligible acidity, the activity is unlikely to be increased to such high levels merely by reduction in coke deposition. Therefore, it appears that MoS_2 and its promoted analogues supported on SiO_2 contributes toward cracking activity in a major way. To substantiate this view point further, we have conducted experiments on activated carbon and MoS_2/carbon. These results, presented in Fig. 8, clearly show that activated carbon has some activity and may be due to oxide impurities present and that MoS_2/carbon is 6 times more active than the pure support. It is evident that supported MoS_2 is a major contributor to the cracking activity. To verify if unsupported MoS_2 has significant cumene cracking activity, experiments on MoS_2 were carried out under exactly the same conditions. The results shown in Fig. 8 clearly indicate that pure MoS_2 has significant ability to crack cumene molecules.

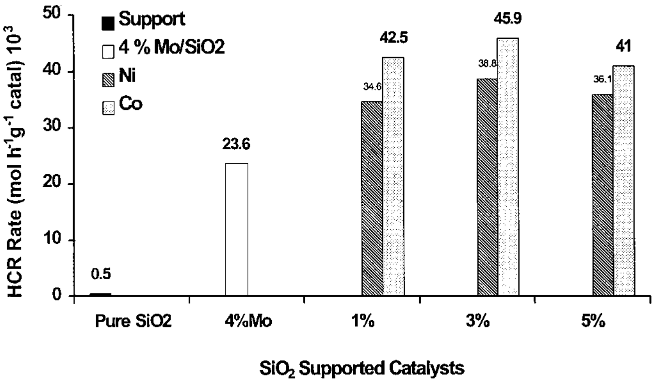


FIG. 7. Comparison of cumene cracking activity of SiO_2 and SiO_2-supported MoS_2 catalysts.

From the above-discussed results, it is clear that supported MoS_2 and promoted analogues contribute significantly to cracking activity. From the studies based on SiO_2 and carbon-supported catalysts it appears that it is unlikely

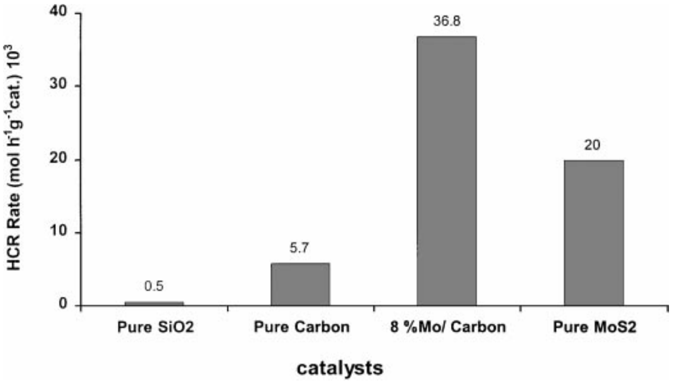


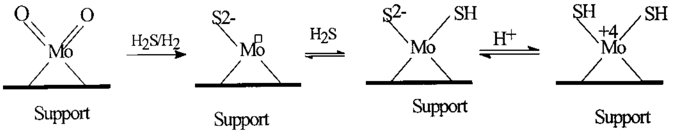
FIG. 8. Comparison of cumene cracking activities of carbon-supported MoS_2 catalysts and unsupported MoS_2.

that the observed high activities in the supported MoS_2 and promoted analogues are due to increased activity as a result of reduction in coke formation on the support surface. It is clear that, in the systems studied, the active phase and its promoted analogues contribute significantly to the cracking activity of these catalysts.

The significance of the above results can be best appreciated by comparing them with the published literature. The cracking function of γ-Al_2O_3-supported hydrotreating catalysts and the Brønsted acid sites that generate the acid function are subjects of much debate (28–30). γ-Al_2O_3 has insufficient Brønsted acidity to contribute to cracking reactions. Sulfided Co-Mo/γ-Al_2O_3 was found to be relatively unreactive for the cumene cracking or isomerization of *n*-butane or *n*-hexane. However, there were some cracking products of hexene, considerable dealkylation of *m*-diisopropylbenzene, and significant cracking of isooctene to isobutene (5). Earlier studies on Mo and CoMo catalysts supported on SiO_2–Al_2O_3 of different SiO_2/Al_2O_3 ratios show the activity for isooctene cracking of supported catalysts resembled that of the support, thereby indicating that the support is the major contributor to the cracking functionality (5, 6). This may be due to the fact that strong acid sites of SiO_2–Al_2O_3 dominated the cracking activity and that the molybdenum dispersion on these catalysts is too low to compete with the strong acid sites of SiO_2–Al_2O_3. It was also reported that CoMo and NiMo catalysts can dealkylate 1-ethylnaphthalene as well as biphenyl moieties (16). However, it is not clear from these investigations whether this is due mainly to the support or to the active component and promoters. Significant cracking activity was reported for sulfided Mo and CoMo supported on SiO_2, which indicates that the active phase has some cracking functionality (5). In a recent study, Topsøe *et al.* produced evidence of isomerization and cracking of *n*-dodecane on CoMo/γ-Al_2O_3 catalysts and correlated the activity with the concentration of the SH group (31). Recent literature reports indicate that the active component does possess cracking functionality. If there is agreement that the active component and promoters contribute to the generation of acidic function, then the question that remains to be addressed is that of the nature of the protonic acid sites that are responsible for such cracking activity.

Brønsted acidity and its role in oxide and sulfided catalysts has been a topic of discussion (9, 29–31). Earlier work on the acidity of Mo and CoMo catalysts in their oxidic state was reviewed by Massoth (32). However, there are only a few investigations of these catalysts in their sulfided state. Ratnasamy and co-workers (33, 34) reported on NH_3 adsorption studies on sulfided Mo, CoMo, and NiMo catalysts supported on γ-Al_2O_3, which indicated that Mo and CoMo catalysts are acidic and that the promoted catalysts had stronger acid sites. The Brønsted acid sites on these catalysts are likely to be sulfhydryl groups attached to the sulfided Mo and CoMo moieties. The sulfhydryl groups were estimated and correlated with HDS activity (31, 35). It is difficult to detect SH groups on these catalysts by means of IR spectroscopy. Adsorption of probe molecules that can be protonated by such groups is one way to determining their presence (9, 10). Using pyridine as a probe molecule, it was shown that Brønsted acid sites are present at temperatures that are typical of hydrotreating and hydrocracking reactions (29, 30), suggesting that these groups are responsible for the observed cracking functions. Petit *et al.* recently presented evidence for the presence of Brønsted acid sites on sulfided Mo, CoMo, and NiMo phases as well as on the support, using dimethylpyridine as the probe molecule (10). CoMo/γ-Al_2O_3 was found to have the highest number of Brønsted acid sites, and their number increased with increasing H_2S concentration. Therefore, it seems that Brønsted sites, such as SH groups, are present in the sulfided phase and these sites are responsible for the observed protonic acid catalysis.

This leaves the question of the creation of SH groups on Mo and CoMo catalysts. It is well known that anion vacancies are present on MoS_2 and its promoted analogues (29, 36). In the presence of H_2S and H_2, the anion vacancies are converted to SH groups in the following way (29):



It is assumed that anion vacancies are converted to SH groups and that the reverse is possible depending on the concentration of H_2S. The fact that oxygen chemisorption (which measures the concentration of anion vacancies) shows a relationship that is similar to the cracking activity as a function of molybdenum loading supports the view that anion vacancies are involved in the creation of Brønsted acid sites. Byskov *et al.* proposed that SH groups are located at the edges of MoS_2. They supported this observation by DFT calculations (37). Under fixed conditions, the number of SH groups on similar types of catalysts are likely to be proportional to the edge sites. It is well known that oxygen chemisorption predominantly takes place on vacancies associated with edge sites; the similarity between the variation in oxygen uptake and the cracking activity as observed in this investigation suggests that the SH groups are also probably at or near the edges. The Co, Ni atoms are also located at MoS_2 edges (38), and the variation in the cracking activity as a function of Co, Ni suggests that the acid sites on MoS_2 are connected to these promoter ions. In a recent study, Hensen *et al.* (39) showed that active SH groups are linked to both sulfided Co and Ni in the promoted phase. It is not known whether these promoter ions increase the number of SH groups or the ability of the proton to make donations. The location of the SH groups and Co or Ni atoms near the edge vacancies suggests that these three groups play an important role in the creation of protonic acid sites and their catalysis.

5. CONCLUSIONS

A systematic study of the cracking functionality as a function of the $Zr/Zr + Si$ ratio indicates that Mo, CoMo, and NiMo catalysts supported on ZrO_2–SiO_2 exhibit higher cracking activity in the SiO_2-rich region. The promotional effect of Co and Ni was also higher in SiO_2-rich supports. The variation in the cracking functionality with Mo content and the variation in the Co or Ni content at a fixed Mo content indicated that the MoS_2 phase and its promoted analogues contribute significantly to the cracking functionality. From the studies based on SiO_2 and carbon supported catalysts it appears that it is unlikely that the observed high activities of MoS_2 and promoted analogues are due to increased activity as a result of reduction in coke formation on the support surface. The correlation between the cracking activity and the oxygen uptake indicates that anion vacancies are involved in the creation of acid sites. The results presented also suggest that anion vacancies, SH groups, and edge Co or Ni atoms are associated with the site that generates the cracking functionality on these catalysts.

ACKNOWLEDGMENT

We gratefully acknowledge the encouragement and support that was given to us by the Director of the Indian Institute of Petroleum.

REFERENCES

1. Topsøe, H., Clausen, B. S., and Massoth, F. E., “Hydrotreating Catalysis Science and Technology” (J. R. Anderson and M. Boudart, Eds.), Vol. 11. Springer-Verlag, New York, 1996.
2. Whitehurst, D. D., Isoda, T., and Mochida, I., *Adv. Catal.* **42**, 345 (1998).
3. Murali Dhar, G., Rana, M. S., Maity, S. K., Srinivas, B. N., and Prasada Rao, T. S. R., *in* “Chemistry of Diesel Fuels” (C. Song, S. Hsu, and I. Mochida, Eds.), Chap. 8. Taylor & Francis, London, 2000.
4. Prins, R., de Beer, V. H. J., and Somorjai, G. A., *Catal. Rev.-Sci. Eng.* **31**, 1 (1989).
5. Murali Dhar, G., Massoth, F. E., and Shabtai, J., *J. Catal.* **85**, 44 (1994).
6. Massoth, F. E., Murali Dhar, G., and Shabtai, J., *J. Catal.* **85**, 53 (1994).
7. Ratnasamy, P., and Knözinger, H., *J. Catal.* **54**, 155 (1978).
8. Segawa, K., and Hall, W. K., *J. Catal.* **76**, 133 (1982).
9. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **139**, 641 (1993).
10. Petit, C., Maugé, F., and Lavalley, J.-C., *Stud. Surf. Sci. Catal.* **106**, 157 (1997).
11. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somogyavari, A., *J. Catal.* **96**, 115 (1985).
12. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somogyavari, A., *J. Catal.* **100**, 287 (1986).
13. Boorman, P. M., Kydd, R. A., Sarbak, Z., and Somogyavari, A., *J. Catal.* **106**, 544 (1987).
14. Cable, T. L., Massoth, F. E., and Thomas, M. G., *Fuel Process. Technol.* **4**, 26 (1981).
15. Ramachandran, R., and Massoth, F. E., *J. Catal.* **67**, 248 (1981).
16. Patzer, J. F., Farruato, R. S., and Montagne, A. A., *Ind. Eng. Chem. Process Res. Dev.* **18**, 625 (1979).
17. Hansford, R. C., U.S. Patent 3,159,588, 1964.
18. Jaffe, J., U.S. Patent 3,401,125, 1968.
19. Parekh, B. S., and Weller, S. W., *J. Catal.* **47**, 100 (1977).
20. Rao, K. S. P., and Murali Dhar, G., *J. Catal.* **115**, 277 (1989).
21. Rao, K. S. P., Ramakrishna, H., and Murali Dhar, G., *J. Catal.* **133**, 146 (1992).
22. Zmierczak, W., Murali Dhar, G., and Massoth, F. E., *J. Catal.* **77**, 432 (1982).
23. Reddy, B. M., Chary, K. V. R., and Subrahmanyam, V. S., *J. Chem. Soc. Faraday Trans. 1* **81**, 1655 (1985).
24. Vissers, J. P. R., Groot, C. K., van Oers, E. M., de Beer, V. J. H., and Prince, R., *Bull. Soc. Chim. Belg.* **93**, 813 (1984).
25. Reddy, B. M., Chary, K. V. R., Rama Rao, B., Subrahmanyam, V. S., Sunandana, C. S., and Nag, N. K., *Polyhedron* **5**, 191 (1986).
26. Weller, S. W., *Acc. Chem. Res.* **16**, 101 (1983).
27. Olorunyolemi, T., and Kydd, R. A., *Catal. Lett.* **63**, 173 (1999).
28. Brunn, L. W., Montagna, A. A., and Paraskos, J. A., *Am. Chem. Soc., Div. Petrol. Chem. Prepr.* **21**, 173 (1976).
29. Topsøe, N.-Y., Topsøe, H., and Massoth, F. E., *J. Catal.* **119**, 252 (1989).
30. Rajagopal, S., Marzari, J. A., and Miranda, R., *J. Catal.* **151**, 192 (1995).
31. Topsøe, H., Clausen, B. S., Topsøe, N.-Y., Nørskov, J. K., Ovesen, C. V., and Jacobsen, C. J. H., *Bull. Chem. Soc. Belg.* **104**, 283 (1995).
32. Massoth, F. E., *Adv. Catal.* **27**, 265 (1978).
33. Sivasanker, S., Ramaswamy, A. V., and Ratnasamy, P., “Proceedings, 3rd International Conference on Chemistry & Uses of Molybdenum” (H. F. Barry and P. C. H. Mitchell, Eds.), p. 98. Climax Molybdenum Co., Ann Arbor, MI, 1979.
34. Ratnasamy, P., Ramaswamy, A. V., and Sivasanker, S., *J. Catal.* **61**, 519 (1980).
35. Miciukiewicz, J., Zmierczak, W., and Massoth, F. E., *Bull. Chem. Soc. Belg.* **96**, 915 (1987).
36. Anderson, A. B., Al-Saigh, Z. Y., and Hall, W. K., *J. Phys. Chem.* **92**, 803 (1988).
37. Byskov, S. L., Nørskov, J. K., Clausen, B. S., and Topsøe, H., *J. Catal.* **187**, 109 (1999).
38. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **84**, 386 (1983).
39. Hensen, E. J. M., Lardinois, G. M. H. J., de Beer, V. H. J., van Veen, J. A. R., and van Santen, R. A., *J. Catal.* **187**, 95 (1999).