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Catalysis over Molybdenum Carbides and Nitrides

II. Studies of CO Hydrogenation and C_2H_6 Hydrogenolysis

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The hydrogenation of CO and the hydrogenolysis of C_2H_6 were studied over the hcp and fcc phases of Mo_2C, and the fcc phase of Mo_2N. The CO hydrogenation activity and selectivity of the fcc phases of Mo_2C and Mo_2N are identical. The activity of the hcp phase of Mo_2C is half that of the other two catalysts but the olefin selectivity is higher. Elemental analysis reveals that the catalysts contain a substantial amount of oxygen following extended use for CO hydrogenation. The hydrogenolysis activity of both Mo_2C phases increases markedly with decreasing content of oxygen in the catalyst. Consistent with the known structure sensitivity of C_2H_6 hydrogenolysis, the activity of the hcp phase of Mo_2C is 200-fold higher than that of the fcc phase. This difference in activity is attributed to differences in the structure of the principal planes exposed by each phase of the carbide.

INTRODUCTION

Molybdenum carbides were first reported to have catalytically interesting properties by Sinfelt and Yates (*1*). They discovered that the ethane hydrogenolysis activity over unsupported Mo increased 60-fold over the course of 5 h. Subsequent examination of the catalyst indicated that a Mo_2C phase had formed and extended appreciably into the bulk. Later experiments by Kojima *et al.* (*2*) and Boudart *et al.* (*3*) showed that the carbide layers served as the active catalyst. These results have stimulated other researchers to investigate the properties molybdenum carbide, and also nitride, for CO hydrogenation (*4–12*), olefin hydrogenation (*13*), hydrocarbon reforming (*14–16*), NH_3 synthesis (*3, 17*), CO oxidation (*18*), and NO reduction (*19, 20*). This paper reports the results of an investigation of CO hydrogenation over the hcp and fcc phases of Mo_2C and the fcc phases of Mo_2N, and the C_2H_6 hydrogenolysis over both carbide phases. A detailed study of the physical and chemical characteristics of all three catalysts is given in a companion paper (*21*).

EXPERIMENTAL

The methods of preparing the hcp and fcc phases of Mo_2C and the fcc phase of Mo_2N have been described previously (*21*). The starting material in all cases is MoO_3 (Mallinkrodt, 99.5% pure). Mo_2C(hcp) was produced by H_2 reduction of the oxide to the metallic Mo and subsequent carburization in a CH_4/H_2 mixture, using a modification of the procedure described by Boudart *et al.* (*5*). The preparation of Mo_2N(fcc) was carried out by reducing MoO_3 in NH_3 (*22*). The Mo_2N(fcc) was then converted to Mo_2C(fcc) by heating the nitride in a CH_4/H_2 mixture. This results in a topotactic substitution of carbon for nitrogen.

The freshly synthesized carbides were passivated in oxygen and then air exposed. Prior to use in reaction studies, these catalysts were pretreated in a 3/1 : CH_4/H_2 mixture at 623 K for 1 h and then evacuated for 1 h. The purpose of this pretreatment was

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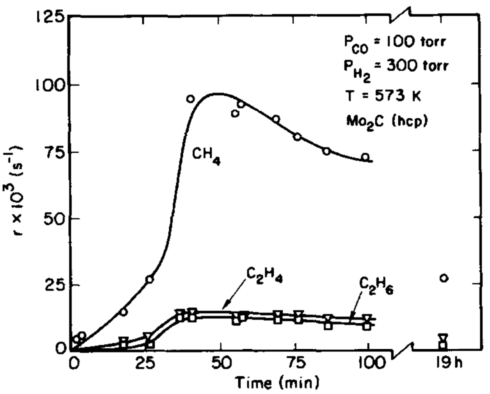

FIG. 1. Approach to steady-state activity for CO hydrogenation over Mo_2C(hcp).

to assure carburization of any metallic Mo present on the surface and to remove as much oxygen from the catalyst as possible. Mo_2N (fcc) was not air exposed and was used for CO hydrogenation without pretreatment.

Each of the three catalysts was characterized after synthesis, pretreatment, and exposure to reaction conditions. The characterization techniques used were elemental analysis, X-ray diffraction, transmission electron microscopy, BET surface area measurement, and CO chemisorption. Details concerning the application of these techniques and the results obtained are given in Ref. (*21*).

Reaction studies were carried out using a quartz microreactor. Products were analyzed with a Varian Model 1200 gas chromatograph containing a 1.8 mm × 2.16 mm i.d. column packed with Poropac Q. An FID was used to detect the eluted products. The flow of reactants to the reactor was controlled with mass flow controllers. CO (Matheson, 99.9%) was passed through ascarite and heated glass beads to remove CO_2 and iron carbonyls, respectively, and through a molecular sieve trap to remove H_2O. H_2 (Matheson, 99.999%) was passed over heated Pd followed by a molecular sieve trap to remove O_2 and H_2O. C_2H_6 (Matheson, 99.9%) was used without further purification.

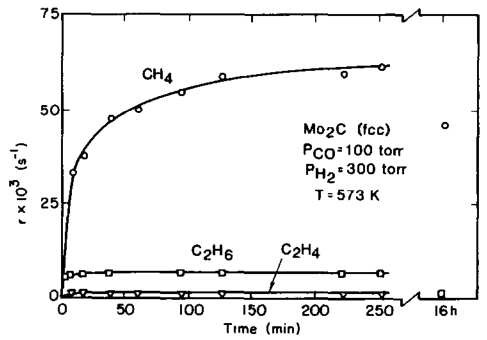

FIG. 2. Approach to steady-state activity for CO hydrogenation over Mo_2C(fcc).

CO Hydrogenation

The behavior of Mo_2C(hcp), Mo_2C(fcc), and Mo_2N(fcc) with time on stream for a fixed set of reaction conditions is illustrated in Figs. 1, 2, and 3, respectively. The overall activity of Mo_2C(hcp) increases rapidly during the first 50 min but then slowly decreases. A steady-state activity was achieved after 16 h and is characterized by the points shown in Fig. 1 for 19 h. Figure 1 also shows that while the selectivity to CH_4 is very high initially, it decreases as the catalyst approaches its steady-state activity. The behavior of Mo_2C(fcc) is similar to that of Mo_2C(hcp). The principal difference

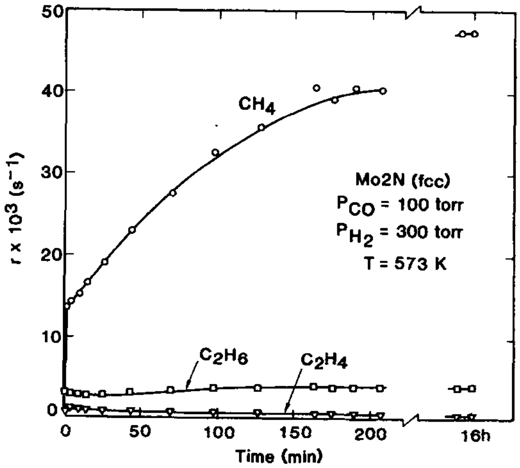

FIG. 3. Approach to steady-state activity for CO hydrogenation over Mo_2N(fcc).

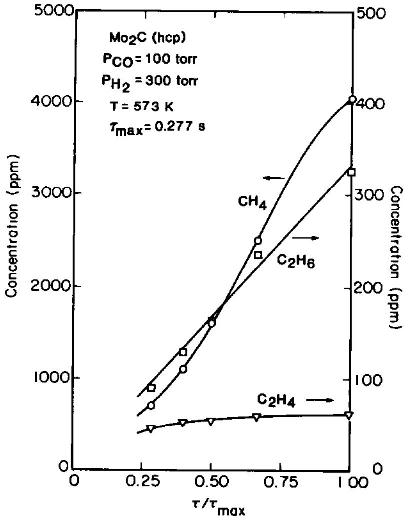

FIG. 4. Variation of conversion with residence time for Mo_2C(hcp).

is that the maximum activity is not reached until the catalyst has been under reaction conditions for more than 250 min. The approach to steady state of Mo_2N(fcc) is different from that of the two Mo_2C modifications in that the total activity does not go through a maximum. Another difference is that the CH_4 selectivity steadily increases with time under reaction conditions.

The distribution of reaction products over Mo_2C(hcp) observed under steady-state conditions was found to vary with reactant residence time, as shown in Fig. 4. The formation of CH_4 exhibits an upward curvature with increasing residence time (i.e., lower gas flow rate). Ethylene, on the other hand, shows a downward curvature. The curvature in the plots of CH_4 and C_2H_4 are indicative of secondary reactions. One possibility is the readsorption and subsequent hydrogenation of C_2H_4. This interpretation is consistent with the observation that C_2H_6 is produced in preference to C_2H_4 as the residence time increases. The upward curvature of the plot for CH_4 may result from a partial hydrogenolysis of the C_2H_4 formed by CO hydrogenation. Such a reaction has been observed to occur over Group VIII metals (*23*). The variations in product distribution with residence time observed for Mo_2C(fcc) and Mo_2N(fcc) were virtually identical to that shown in Fig. 4 for Mo_2C(hcp).

In light of the preceding results it was decided to compare catalyst activities at a fixed CO conversion, rather than at a fixed residence time. The results are presented in Table 1 for a CO conversion of 1.5%. It is evident that the steady-state activity of Mo_2C(hcp) is roughly half that of Mo_2C(fcc) or Mo_2N(fcc). The selectivity of the two carbide catalysts are very similar, with metane being the major product. The C_2 and C_3 hydrocarbons are predominantly paraffinic even though the overall conversion of CO is small. For the reaction conditions indicated in Table 1, the activity and selectivity of Mo_2N(fcc) are identical to those of Mo_2C(fcc).

The physical and chemical characteristics of each catalyst were determined before and after 24 h of exposure to synthesis gas. The results are given in Table 2 (*21*). The elemental analysis of both phases of molybdenum carbide, following pretreatment, indicate that in addition to a near-stoichiometric amount of carbon there is a substantial amount of oxygen present. X-ray diffraction patterns of these catalysts show no evidence for oxide phases of molybdenum. This together with evidence from TPR studies (*13, 21*) has led to the conclusion that the oxygen is contained in

TABLE 1

Comparison of Activities and Selectivities of Mo_2C (hcp), Mo_2C (fcc), and Mo_2N (fcc) for CO Hydrogenation[a]

	Mo_2C (hcp)	Mo_2C (fcc)	Mo_2N (fcc)
$N_{CH_4} \times 10^3$ (s^{-1})	27.4	46.0	50.1
S_{CH_4} (%)	76.9	83.7	83.5
$S_{C_2H_4}$ (%)	5.2	1.2	1.5
$S_{C_2H_6}$ (%)	15.6	14.3	14.0
$S_{C_3H_6}$ (%)	1.1	0.0	0.0
$S_{C_3H_8}$ (%)	1.3	0.9	1.0

[a] Reaction conditions: $T = 573$ K, $P_{CO} = 100$ Torr, $P_{H_2} = 300$ Torr.

TABLE 2

Characteristics of Mo_2C and Mo_2N Catalysts Before and After Use for CO Hydrogenation

Catalyst	State[a]	Composition	BET surface area (m^2/g)	CO capacity ($\times 10^{-14}$ mol/cm^2)
Mo_2C (hcp)	A	$Mo_2C_{1.04}O_{0.88}$	28.1	0.24
	B	$Mo_2C_{0.94}O_{0.66}$	14.9	0.40
Mo_2C (fcc)	A	$Mo_2C_{1.13}O_{3.03}$	139.3	0.27
	B	$Mo_2C_{0.99}O_{0.73}$	122.0	0.54
Mo_2N (fcc)	A	$Mo_2N_{1.08}O_{0.19}$	185.3	1.18
	B	$Mo_2N_{1.00}C_{0.51}O_{0.34}$	178.0	0.65

[a] State A for Mo_2C(hcp) and Mo_2C(fcc)—following synthesis, air exposure, and pretreatment in a 3/1 : CH_4/H_2 mixture at 623 K for 1 h and evacuation for 1 h. State A for Mo_2N(fcc)—following synthesis. State B for all catalysts—following reaction for 24 h at $T = 573$ K, $P_{CO} = 100$ Torr, $P_{H_2} = 300$ Torr.

the vacant octahedral voids of the Mo_2C lattice. Following exposure to synthesis gas, there is a small decline in the carbon content of both carbide phases, and a more significant decrease in the oxygen content, particularly in the case of Mo_2C(fcc). The freshly prepared Mo_2N(fcc) shows a near-stoichiometric amount of nitrogen and a small content of oxygen. As in the case of the carbide phases, XRD shows no evidence for molybdenum oxide phases. Elemental analysis of the molybdenum nitride shows no loss of nitrogen after exposure of the catalyst to synthesis gas. There is clear evidence, though, of both carbon and oxygen accumulation. The X-ray diffraction pattern of the nitride shows that the bulk structure continues to be Mo_2N, and that no new phases are formed.

TABLE 3

Rate Parameters for CO Hydrogenation over Mo_2C and Mo_2N Catalysts[a]

Product	$k_0[s^{-1}\ Torr^{-(n+m)}]$	E_a(kcal/mol)	m	n
		Mo_2C (hcp)		
CH_4	5.26×10^2	19.1	0.30	0.97
C_2H_4	4.23×10^4	31.3	1.38	0.61
C_2H_6	2.49×10^1	17.1	0.52	0.61
		Mo_2C (fcc)		
CH_4	3.65×10^1	15.0	0.23	0.96
C_2H_4	3.68×10^2	25.6	1.13	0.59
C_2H_6	6.28	15.7	0.86	0.43
		Mo_2N (fcc)		
CH_4	4.54×10^1	19.5	1.20	0.84
C_2H_4	5.00×10^{-2}	21.3	2.39	0.52
C_2H_6	4.00×10^{-2}	15.6	1.80	0.54

[a] $N = k_0 e^{-E_a/RT} P_{H_2}^{m} P_{CO}^{n}$.

The kinetics of CH_4, C_2H_4, and C_2H_6 formation were investigated by varying the temperature and reactant partial pressures. For these studies, the flow rate of synthesis gas was adjusted so as to maintain the CO conversion at approximately 1.5%. The rate parameters for all three catalysts are presented in Table 3. The partial pressure dependences on H_2 and CO are comparable for Mo_2C(hcp) and Mo_2C(fcc). For Mo_2N(fcc), the H_2 partial pressure dependence is similar to that for the carbide catalysts but the CO partial pressure dependence is about a power of one higher. All three catalysts exhibit positive orders in both H_2 and CO. The latter stands in contrast to Group VIII metal catalysts which characteristically show an inverse order dependence on CO partial pressure. The activation energies for the three catalysts also exhibit similarity and the differences for a given product are never larger than about 6 kcal/mol.

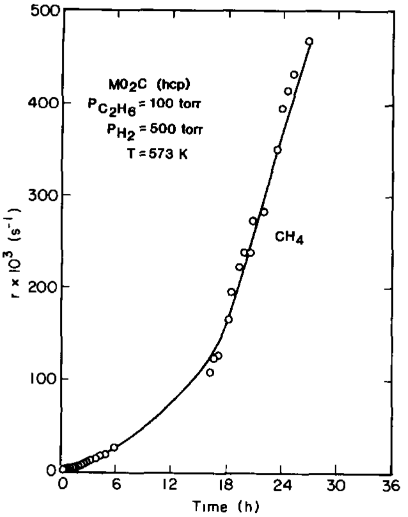

FIG. 5. Variation of ethane hydrogenolysis activity with time for Mo_2C(hcp).

C_2H_6 Hydrogenolysis

The hydrogenolysis of C_2H_6 was examined over both phases of Mo_2C. The reaction conditions were $T = 573$ K, $P_{C_2H_6} = 100$ Torr, and $P_{H_2} = 500$ Torr. Figures 5 and 6 show the rate of CH_4 formation versus time under reaction conditions for Mo_2C(hcp) and Mo_2C(fcc), respectively. For both carbide phases, the initial activity is negligible but steadily increases with time. After 48 h, Mo_2C(hcp) showed no sign of approaching a steady state, whereas the activity of Mo_2C(fcc) reached a steady state after approximately 40 h. It is also significant that for times of up to 30 h, the specific activity of Mo_2C(hcp) is more than 200 times that of Mo_2C(fcc).

Table 4 shows that two major changes in each catalyst can be detected after its use for C_2H_6 hydrogenolysis. The first is a significant reduction in the oxygen content. For Mo_2C(hcp) all of the oxygen present in the pretreated catalyst has been removed, whereas in the case of Mo_2C(fcc) some oxygen is still retained. The second change is a roughly twofold increase in the CO adsorption capacity. It should be noted that the CO adsorption capacities for both carbide phases are virtually identical, both after pretreatment catalysts and use for C_2H_6 hydrogenolysis.

TABLE 4

Characteristics of Mo_2C and Mo_2N Catalysts Following Use for C_2H_6 Hydrogenolysis[a]

Catalyst	Composition	BET surface area (m^2/g)	CO capacity ($\times 10^{-14}$ mol/cm^2)
Mo_2C (hcp)	$Mo_2C_{0.83}$	18.0	0.56
Mo_2C (fcc)	$Mo_2C_{0.89}O_{0.69}$	161.0	0.52

[a] Reaction conditions: $T = 573$ K, $P_{C_2H_6} = 100$ Torr, $P_{H_2} = 500$ Torr.

DISCUSSION

CO Hydrogenation

The chemisorption of CO and H_2 on Mo is known to be affected by the presence of surface carbon and oxygen. Ko and Madix (*25, 26*) have reported that on a clean Mo(100) surface CO adsorbs both dissociatively and associatively (molecularly) at room temperature. Carburization or oxidation of the surface inhibits the dissociative component of adsorption and increases the associative component in such a way that

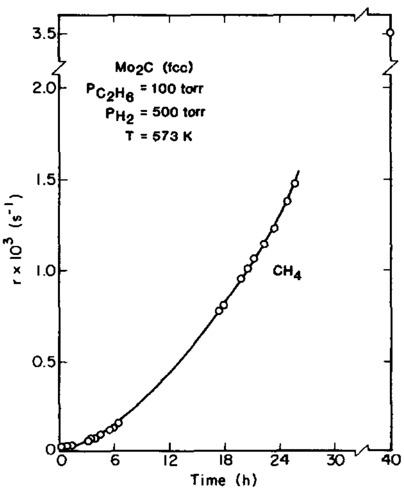

FIG. 6. Variation of ethane hydrogenolysis activity with time for Mo_2C(fcc).

the total amount of CO adsorbed remains constant. LEED studies indicated that the pretreated surface contains carbon or oxygen atoms in the fourfold hollow positions. Once these positions are fully occupied, CO dissociation is suppressed, but molecular chemisorption can still occur at exposed on-top sites of Mo. Similar studies of H_2 chemisorption revealed that the dissociative chemisorption of H_2 is suppressed when carbon or oxygen atoms occupy the fourfold sites of a Mo(100) surface. While the effects of nitriding a Mo(100) surface on the chemisorption of CO and H_2 have not been established, work by Ko and Madix (*27*) has shown nitrogen atoms will occupy the same sites as carbon or oxygen atoms. Since the electronegativity of nitrogen lies halfway between that for carbon and oxygen, we can infer that nitridation of a Mo(100) surface should influence the chemisorption of CO and H_2 in a manner identical to carburization or oxidation.

Work reported in the recent literature indicates that on Group VIII metals and compounds such as Mo_2S, the hydrogenation of CO is initiated by the dissociation of adsorbed CO (*28*). Since Mo_2C and Mo_2N exhibit bulk and surface properties similar to those of metals, we would expect the hydrogenation of CO to proceed via a mechanism similar to that for metals. Hence, CO dissociation should again be a critical first step.

Inferences about the effects of oxygen on the activity of Mo_2C and Mo_2N can be drawn from the studies of Ko and Madix (*25–27*) since the fully carburized or nitrided Mo(100) surface is equivalent to the (200) surface of the fcc phases of Mo_2C and Mo_2N. It seems likely that during CO hydrogenation the surface of the carbide or nitride is partially reduced, so that not all of the fourfold hollow sites are occupied. If oxygen atoms were present in some of these sites, the reduction process might proceed more slowly since the higher electronegativity of oxygen relative to carbon or nitrogen would make it more strongly bound to the Mo. Based on this line of reasoning, we would expect oxygen on the surface of Mo_2C or Mo_2N to inhibit the activity of these catalysts for CO hydrogenation. Leclerq *et al.* (*5*) have observed such an effect. Their studies showed that molybdenum oxide is much less active than molybdenum oxycarbide, and that the activity of the latter catalyst increased upon reduction of its oxygen content. Dun *et al.* (*10*) have also observed that the activity of a charcoal-supported MoO_2 catalyst increased with time under reaction conditions. This change was ascribed to carbiding of the MoO_2 surface.

Based on the preceding discussion, we attribute the rise in CO hydrogenation activity of Mo_2C(hcp), Mo_2N(fcc), and Mo_2C(fcc) seen in Figs. 1, 2, and 3, respectively, to a progressive loss of oxygen from the catalyst surface. Consistent with this, Table 2 shows that the bulk oxygen content of Mo_2C(hcp) and Mo_2C(fcc) decreases after catalyst use. It is significant to note at this point that while changes in bulk oxygen content are suggestive of changes in surface oxygen content they do not tell the whole story. This point is well illustrated by our work on the characterization of Mo_2C(fcc) by temperature-programmed reduction (*21*). These studies show that following CO hydrogenation, the catalyst surface is devoid of oxygen even though there is still oxygen in the catalyst bulk. The importance of surface versus bulk oxygen is also suggested by the behavior of Mo_2N. Figure 2 shows that the activity of this catalyst rises steadily with reaction time. On the other hand, Table 2 shows that the bulk oxygen content is higher after reaction than before. These observations might be explained by suggesting that the rise in bulk oxygen content is due to the exposure of the catalyst to H_2O produced during CO hydrogenation, while the rise in activity with time is due to the progressive reduction in oxygen content of the catalyst surface.

The cause of the decline in activity of

Mo_2C(hcp) and Mo_2C(fcc) for long reaction times cannot be fully explained. The most likely cause of deactivation is the accumulation of free carbon. If activity loss were attributable solely to this cause, then we would expect to see a corresponding loss in CO chemisorption capacity. Table 2 shows that for Mo_2C(hcp), there is a small increase in carbon content after CO hydrogenation but no significant loss in CO adsorption capacity. By contrast, Mo_2C(fcc) shows a small decrease in carbon content and an increase in CO adsorption capacity. It is also significant that after reaction, Mo_2N exhibits a large increase in carbon content, a large decrease in CO adsorption capacity, but no loss of catalytic activity. Taken together, these observations suggest that factors other than carbon accumulation are responsible for the loss of activity for Mo_2C(hcp) and Mo_2C(fcc).

Table 5 compares the rate coefficients obtained in this study with those reported previously for Mo_2C(hcp). It is evident that the H_2 and CO partial pressure dependences of the present work are in good agreement with those of Kojima and Miyazaki (*4*) and Dun *et al.* (*10*) but differ from those of Murchison (*11*). The discrepancy with Murchison's results is most likely a reflection of the high CO conversions (~70%) used in his study. The activation energy for total hydrocarbon formation observed in this work is comparable to that reported by Murchison (*11*) and Dun *et al.* (*10*), but the activation energy for CH_4 formation reported by Leclerq *et al.* (*5*) is smaller by 8 kcal/mol than that found here.

The results presented in Table 3 show that for all three catalysts investigated, the H_2 and CO partial pressure dependences are positive. The occurrence of a positive order CO dependence suggests that CO adsorption does not inhibit H_2 chemisorption. This is consistent with the discussion given earlier which revealed that CO chemisorption will occur preferentially at on-top sites, whereas H_2 chemisorption requires fourfold hollow sites. The cause of the higher CO dependence for Mo_2N (fcc) than for either Mo_2C phase is difficult to understand and at present no satisfactory explanation can be given.

TABLE 5

Comparison of Rate Parameters for CO Hydrogenation over Mo_2C(hcp) Catalysts

Ref.	k_0 molecules/ (cm^2 s Torr^{n+m})	E_a(kcal/mol)	m	n
	Total hydrocarbon formation			
This work	—	19.7	1.0	0.3
Dun *et al.* (*10*)	—	21.0	1.0	0.5
Murchison (*11*)	—	22.8	0.5	1.0
	CH_4 formation			
This work	1.1×10^9	19.1	1.0	0.3
Kojima and Miyazaki (*4*)	1.6×10^9	—	1.0	0.5
Leclerq *et al.* (*5*)	—	11.0	—	—

The data presented in Table 1 indicate that Mo_2C(fcc) is a factor of two more active for CO hydrogenation than Mo_2C(hcp). This activity difference cannot be ascribed to differences in either the partial pressure dependences or the activation energies. We propose, therefore, that the difference in activity is associated with differences in the structure of the predominant crystal faces exposed by the crystallites of each Mo_2C phase. Based on X-ray diffraction studies, Tutiya (*29*) identified the (101) plane to be the predominant surface exposed by Mo_2C(hcp). Using a similar approach Volpe and Boudart (*22*) have concluded that for Mo_2C(fcc) the dominant plane is (200). The structure of these surfaces is illustrated in Figs. 7 and 8. It is evident that the Mo nearest neighbor distance on the (101) surface of Mo_2C(hcp) is 0.06 Å greater than on the (200) surface of Mo_2C(fcc), and that the former surface has a greater fraction of the exposed Mo atoms bonded to carbon. It seems reasonable to expect that both factors might contribute to making the surface of Mo_2C(hcp) less active than the surface of Mo_2C(fcc).

C_2H_6 *Hydrogenolysis*

Figures 5 and 6 show a very significant rise in the hydrogenolysis activity of both

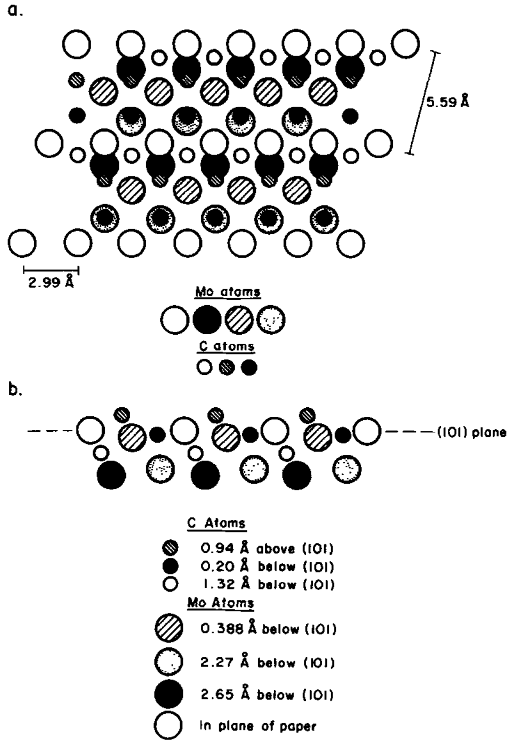

FIG. 7. Mo_2C(hcp) (101) surface. (a) Top view of the (101) plane (unshaded Mo atoms). (b) Side view of the (101) plane (denoted by dashed line).

phases of Mo_2C with time under reaction conditions. This trend agrees very closely with the observations reported by Sinfelt and Yates (*1*). Since the elemental analysis of both catalysts reveals that C_2H_6 hydrogenolysis removes oxygen from the catalyst bulk (see Table 4), the increase in activity is ascribed to this change. Recent studies of hexane and heptane reforming over Mo_2C(fcc) conducted in our laboratory support this interpretation (*30*). As in the case of CO hydrogenation, it is anticipated that the surface concentration of oxygen is more a significant factor than the bulk concentration.

The most significant point of the data is that the specific activity of Mo_2C(hcp) is 200-fold greater than that of Mo_2C(fcc) at any time. Most of this difference in activity is ascribed to differences in the structure of the dominant planes making up the surface of Mo_2C(hcp) and Mo_2C(fcc). It is well known that C_2H_6 hydrogenolysis is a demanding reaction which is sensitive to the catalyst structure (*31*). Studies of the reaction mechanism for Group VIII metals suggest that C_2H_6 dehydrogenates to a C_2H_x species prior to cleavage of the C–C bond (*32*). The hydrogen atoms released from C_2H_6 are believed to be bound to sites different from those to which C_2H_6 or C_2H_x is bound, but both types of sites must occur near each other. Figures 7 and 8 show that the predominant surfaces of Mo_2C(hcp) and Mo_2C(fcc) are quite different. The (101) surface of Mo_2C(hcp) is more open and corrugated than the (200) surface of Mo_2C(fcc). These differences are likely the reason why C_2H_6 hydrogenolysis occurs so much more rapidly on Mo_2C(hcp) than Mo_2C(fcc). While it is possible that the higher bulk oxygen content of Mo_2C(fcc) may contribute to the lower hydrogenolysis

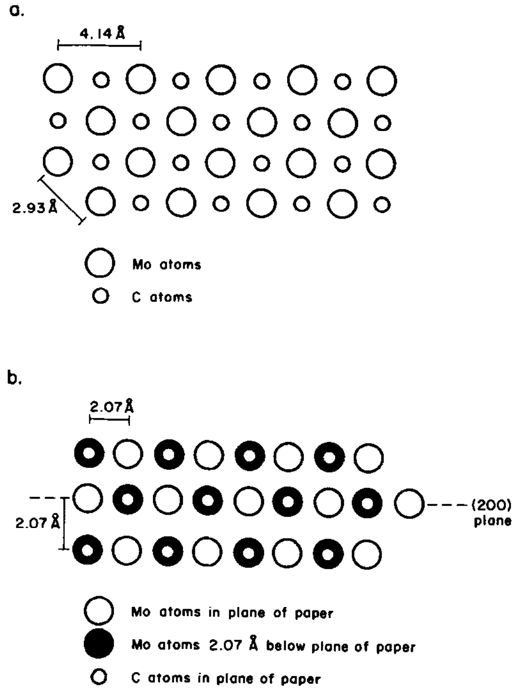

FIG. 8. Mo_2C(fcc) (200) surface. (a) Top view of the (200) plane. (b) Side view of the (200) plane (denoted by dashed line).

activity of Mo_2C(fcc), experiments conducted with hexane and heptane (30) suggest that this factor could account for no more than a 10-fold difference in the activities of Mo_2C(fcc) and Mo_2C(hcp).

CONCLUSIONS

The present studies demonostrate that the activities of Mo_2C(fcc) and Mo_2N(fcc) for CO hydrogenation are equivalent and twofold higher than the activity of Mo_2C(hcp). The carbon number selectivities are comparable for all three catalysts but the olefin selectivity is higher for Mo_2C(hcp) than for either Mo_2(fcc) or Mo_2N(fcc). The rate parameters for the three catalysts are similar in most respects. The activation energy for C_2H_4 synthesis is substantially greater than that for the synthesis of either CH_4 or C_2H_6. Both the H_2 and CO partial pressure dependences are positive order. The H_2 dependence decreases in the order $C_2H_4 > C_2H_6 > CH_4$ and the values are nearly identical for the two carbide catalysts, but a power of one greater for Mo_2N(fcc). The CO dependence is strongest for CH_4, but weaker for both C_2H_4 and C_2H_6. Following reaction, all three catalysts evidence a significant fraction of lattice oxygen.

Both phases of Mo_2C are active for C_2H_6 hydrogenolysis. The activity of these catalysts increases substantially with time on stream due to a progressive removal of oxygen from the carbide lattice. For comparable duration under reaction conditions, the specific activity of Mo_2C(hcp) is 200-fold higher than that of Mo_2C(fcc). The difference in the activities of the two phases is attributed to differences in the structure of the principal surfaces exposed by each phase.

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REFERENCES

1. Sinfelt, J. H., and Yates, D. J. C., *Nature Phys. Sci.* **229,** 27 (1971).
2. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **59,** 472 (1979).
3. Boudart, M., Oyama, S. T., and Leclerq, L., "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 578. Elsevier, Amsterdam, 1981.
4. Kojima, I., and Miyazaki, E., *J. Catal.* **89,** 168 (1984).
5. Leclerc, L., Imura, K., Yoshida, S., Barbee, T., and Boudart, M., "Preparation of Catalysts II" (B. Delmon, Ed.), p. 627. Elsevier, New York, 1978.
6. Saito, M., and Anderson, R. B., *J. Catal.* **63,** 438 (1980).
7. McCandlish, L. E., Wright, F. J., and Kugler, E. L., U.S. Patent 4,345,038, August 17, 1982.
8. Logan, M., Gellman, A., and Somorjai, G. A., *J. Catal.* **94,** 60 (1985).
9. Bridgewater, A. J., Burch, R., and Mitchell, P. C. H., *J. Catal.* **78,** 116 (1982).
10. Dun, J. W., Gulari, E., and Ng, K. Y. S., *Appl. Catal.* **15,** 247 (1985).
11. Murchison, C. B., "Fourth International Conference on Chemistry and Uses of Mo" (H. Barry, Ed.), p. 197. Climax Molybdenum Co., Ann Arbor, MI, 1982.
12. Slaugh, L. H., and Hoxmeier, R. J., U.S. Patent 4,326,992, April 27, 1982.
13. Leary, K. J., Michaels, J. N., and Stacy, A. M., *J. Catal.* **101,** 301 (1986).
14. Levy, R. B., and Boudart, M., *Science* **181,** 547 (1973).
15. Burch, R., and Mitchell, P. C. H., *J. Less-Common Metals* **54,** 363 (1977).
16. Bridgewater, A. J., Burch, R., and Mitchell, P. C. H., *J. Chem. Soc. Faraday I* **76,** 1811 (1980).
17. Mittasch, A., "Advances in Catalysis and Related Subjects," Vol. 2, p. 81 (1950).
18. Yang, R. T., and Wong, C., *J. Catal.* **85,** 154 (1984).
19. Tsuchimoto, K., Suzuki, M., and Yamaki, N., *Nippon Kagaku Kaishi* **10,** 1420 (1979).
20. Sermon, P. A., *et al.*, British Appl. 76/35,202 August 1976.
21. Ranhotra, G. S., Haddix, G. W., Bell, A. T., and Reimer, J. A., *J. Catal.* **108,** 24 (1987).
22. Volpe, L., and Boudart, M., *J. Solid State Chem.* **59,** 332, 348 (1985).
23. Jordan, D. A., and Bell, A. T., *J. Phys. Chem.* **90,** 4797 (1986).
24. Vannice, M. A., *in* "Catalysis: Science and Technology," Vol. 3 (J. R. Anderson and M. Boudart, Eds.). Springer-Verlag, New York, 1982.
25. Ko, E. I., and Madix, R. J., *Surf. Sci.* **100,** L505 (1980).

26. Ko, E. I., and Madix, R. J., *Surf. Sci.* **109,** 221 (1981).

27. Ko, E. I., and Madix, R. J., *Surf. Sci.* **100,** L449 (1980).

28. Happel, J., Cheh, H. Y., Otarod, M., Bajars, L., Hnatow, M. A., and Yin, F., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984." Dechema, Frankfurt-am-Main, 1984.

29. Tutiya, H., *Bull. Inst. Phys. Chem. Res.* (*Tokyo*) **11,** 1150 (1932).

30. Gao, Z., and Bell, A. T., submitted for publication.

31. Djega-Mariadassou, G., and Boudart, M., "Kinetics of Heterogeneous Catalytic Reactions." Princeton Univ. Press, Princeton, NJ, 1984.

32. Sinfelt, J. H., "Bimetallic Catalysts: Discoveries, Concepts, and Applications." Wiley, New York, 1983.