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Reactions of Carbon Monoxide with Hydrogen over Molybdenum/Charcoal Catalysts

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Molybdenum-on-charcoal catalysts have been prepared and characterised and their activities and selectivities determined for the reaction of carbon monoxide with hydrogen at temperatures in the range 573 to 673 K, and at pressures from 0.16 to 1.6 MPa. The catalysts have been activated either by calcination under nitrogen at 773 K followed by heating in hydrogen at 773 K, or by reduction in hydrogen at 1073 K. The former procedure led to the formation of MoO_2 as the major phase, whereas the latter resulted in the formation of Mo_2C. The influence of potassium, either present as an impurity in the charcoal or added during preparation of the catalysts, was investigated. The results show that the activities and selectivities of the MoO_2/C and Mo_2C/C catalysts are comparable, which may indicate that the active sites in both catalysts are similar. Potassium was found to seriously poison both types of catalyst, a result which is in contrast to previous published observations. Comparison of the catalytic results with literature data shows that the catalysts have quite high activity and stability, but are very susceptible to impurities such as potassium. This emphasises the importance of the type of charcoal chosen as the support for molybdenum catalysts.

INTRODUCTION

The catalytic properties of molybdenum and the early transition metals in their metallic states are not as well known as those of the Group VIII metals. Previously we investigated *n*-hexane isomerisation over catalysts prepared by reduction of high-surface-area MoO_3 in hydrogen (*1*). The catalysts consisted of Mo dispersed on MoO_2, the amount of Mo depending on the time and temperature of reduction. The catalysts combined a metallic function provided by Mo and an acidic function provided by Mo oxide.

The original object of the work described in the present paper was to study the catalytic properties of well-dispersed Mo metal which, we hoped, would be obtained by hydrogen reduction of MoO_3 dispersed on charcoal. In an earlier publication (*2*) we described the properties of such catalysts in hydrocarbon reforming. In this paper we describe characterisation of the catalysts and their properties in hydrogenation of carbon monoxide. The conversion of CO/H_2 mixtures (synthesis gas) into hydrocarbons is technically of great interest. Whereas much research has been published on metals as catalysts (*3–5*), much less is known about the catalytic properties of compounds. Schultz *et al.* (*6*) compared the activities of molybdenum and tungsten with the Group VIII metals and concluded that only Mo had sufficient activity to justify further investigation. Molybdenum oxide, sulphide, carbide, and nitride were moderately active and also relatively resistant to sulphur poisoning (a difficult problem with metallic catalysts). Moreover, all could catalyse the water gas shift reaction simultaneously with the synthesis gas reaction thus allowing CO-rich gas mixtures to be used.

Leclercq *et al.* (*7*), and Saito and Anderson (*8*) have also investigated unsupported Mo compounds, including the oxide, car-

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bide, oxycarbide, sulphide, and nitride, and concluded that the specific activity of these catalysts (expressed as the number of CO molecules reacted/active site/s) was comparable to that of the best metallic catalysts. The objective of our work has been to investigate catalysts consisting of Mo compounds supported on charcoal in an attempt to obtain more highly dispersed, and more active catalysts.

EXPERIMENTAL

Catalyst Preparation

A coconut charcoal, Girdler G32, was used as the support, and was ground to 35–60 mesh (425–250 μm) before use [BET surface area, 700 m^2g^{-1}; pore volume, 0.646 cm^3g^{-1}; impurities (wt%): Fe, 0.4; K, 0.7; SiO_2, 0.5; total ash, 2.5%]. Previous work (*2*) had demonstrated that the potassium impurity affected the properties of catalysts prepared with this support. Potassium and other soluble impurities were removed by extracting the charcoal with boiling acetic acid, and washing several times with distilled water (*9*). After washing, the concentrations of metal impurities (wt%) were Fe 0.09 and K 0.08.

Catalysts containing 10 wt% Mo were prepared from ammonium heptamolybdate solution by the pore-filling method as before (*2*), using as support either the untreated charcoal (designated K–C) or the washed charcoal (designated C). Immediately after impregnation the catalysts were dried in air at 400 K for 1.5 h. To confirm the importance of potassium as an impurity a catalyst was prepared from washed charcoal impregnated as follows with potassium. To 10 cm^3 of a solution of potassium carbonate (6.2 g dm^{-3}) was added 4.96 g of acid-washed charcoal. This support (designated K/C) was dried at 400 K for 16 h and then used to prepare a catalyst in the usual way.

Catalyst Pretreatment

MoO_2/C and MoO_2/K–C. Catalyst samples (0.5 g) were dried in air and then decomposed by heating in a Pyrex reactor under nitrogen at 773 K for 16 h. Separate experiments (see later) had shown that during this decomposition the Mo was reduced from Mo(VI) to Mo(IV), the charcoal acting as the reducing agent. The catalysts, after decomposition/reduction, were cooled, diluted with 2 g of alumina powder (previously shown to be inert), and loaded into a stainless-steel reactor (vide infra). The samples were finally heated in hydrogen (1.8 dm^3 h^{-1}) at 723 K for 16 h. These catalysts are designated MoO_2/C and MoO_2/K–C to indicate the presence of oxides.

Mo_2C/C and Mo_2C–K/C. Mo carbide (Mo_2C) can be formed by heating mixtures of MoO_3 and carbon in a reducing atmosphere (*10*). Samples of our catalysts in the oxidic form were heated in a silica glass reactor under hydrogen at 1073 K for 16 h. The carbides thereby produced were cooled, removed from the reactor, diluted with 2 g of alumina, and loaded into the stainless-steel reactor.

Catalyst Testing

Catalysts were tested to determine their activity and selectivity[2] in the conversion of synthesis gas (H_2 : CO ratio = 3 : 1) into hydrocarbons, using a high-pressure stainless-steel reactor constructed from 10-mm-i.d. steel tubing and fitted with Hoke stainless-steel valves. The gas flow (hourly space velocity = 4000 cm^3/g catalyst/h) was adjusted by a needle valve and the pressure (0.16 to 1.6 MPa) was controlled by a Fisher controller which operated a Platon diaphragm valve at the outlet of the reactor. The reactor was heated by an electric furnace and the temperature maintained to ±1 K by a Eurotherm controller. Axial thermocouples were used to measure the temperature of

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[2] The activity (x) is the fraction of the carbon monoxide converted into products either including CO_2 (x_t, total activity) or excluding CO_2 (x_{hc}, activity to hydrocarbons). The selectivity (S) is the ratio of the amount of a product (B) actually formed to the amount of B that could theoretically be formed if all the CO was converted to B.

the catalyst bed. (The catalyst was supported on a stainless-steel sinter in the centre of the reactor.) The reaction products were collected in a gas sampling valve, and analysed by gas chromatography using a 2-m Poropak N column at 333 K with a Perkin–Elmer F11 thermal conductivity detector linked to an Infotronics CRS 308 integrator. Water, CO, CO_2, CH_4, and C_2H_6 could all be separated and determined. Pure gases were used to determine the sensitivity of the detector for each of the products. A Perkin–Elmer F33 F.I.D. chromatograph, fitted with a silicone fluid column, was used to confirm the absence of significant amounts of higher hydrocarbons.

The activity and selectivity of the catalysts were determined in the range 573 to 673 K (mainly at 623 K) and at pressures from 0.16 to 1.6 MPa (mainly at 1.6 MPa).

Catalyst Characterisation

Nitrogen adsorption isotherms were determined at 77 K using a glass volumetric apparatus fitted with a "flow-through" reactor which allowed samples to be calcined and reduced *in situ*. Pressures were measured using Bell and Howell pressure transducers (1 to 10^5 Pa).

The bulk phases present in the catalysts were characterised by X-ray diffraction using either a Debye–Scherrer camera, in which case the powered samples could be mounted in sealed Lindemann tubes, or a Philips horizontal diffractometer, in which case the samples were mounted in a special holder sealed with "cling film." Comparison of the two techniques, and repeat scans on the same samples before and after exposure to air, showed that no detectable oxidation occurred during handling of the sample.

The great affinity of the charcoal support for adsorbate molecules precluded the use of chemisorption methods to determine the number of active sites, and hence the specific activities of the various catalysts (activities are reported on a unit weight of Mo basis). Similarly, slow conversion of carbon to methane under reducing conditions (773 K) made it impossible to estimate accurately the degree of reduction of the Mo either by gravimetric or by hydrogen consumption measurements. Note, however, that the formation of methane by reduction of the support is not a problem at the temperatures used to test the catalysts. In the absence of CO, no hydrocarbon products were detected when the catalysts were heated in hydrogen at 673 K.

RESULTS

The State of the Catalysts

Adsorption isotherms. Figure 1 shows the nitrogen adsorption isotherms for the charcoal before and after acid washing, and for the catalyst in the dried, calcined, or reduced form. All the isotherms are Type I and are typical of solids having a very large number of micropores (*11*). The flatness of the isotherms at high relative pressures indicates the near absence of mesopores, except possibly in the fresh charcoal. The surface areas determined from the isotherms using the BET calculation cannot be relied upon for microporous materials and so are not reported. However, some indication of changes in *relative* surface areas can be given since the higher-pressure regions of the isotherms are approximately parallel. Acid washing had little effect on the physical structure of the support (compare curves a and b); its effect was the removal of impurities. A washed catalyst sample

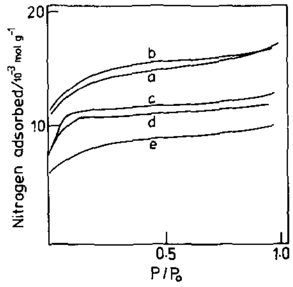

FIG. 1. Nitrogen adsorption isotherms for charcoal and Mo/C catalysts. (a) As-received charcoal; (b) acid-washed charcoal; (c) dried catalyst; (d) calcined catalyst MoO_2/C; (e) reduced catalyst MoO_2/C.

which had been dried (400 K, 1.5 h) but not calcined (curve c) contained fewer micropores than the unwashed charcoal, and had an apparent surface area about 17% less. Preparation of the catalyst by the pore-filling method probably leads to deposition of ammonium molybdate crystals in the narrow micropores, which may consequently become blocked. Since in our preparations 1 g of catalyst of total pore volume 640 μl would contain about 40 μl of molybdate solution, the amount of molybdate solution was not sufficient to fill about one-fifth of the micropores (as required to account for the apparent decrease of surface area through micropore filling). The molybdate solution does not selectively enter micropores, otherwise the shape of the isotherm would be less flat rather than more flat. Therefore blocking of the mouths of micropores is indicated. After calcination (400 K, 16 h) (curve d) there was a small, further, loss of surface area. After reduction there was a 40% decrease in surface area and microporosity. This decrease is attributed to the loss of carbon as methane (which was detected during reduction). There is a small change in the shape of the isotherm; it is less steep at low relative pressures, and curves up at higher relative pressures. We would expect that hydrogenation of the support would occur preferentially next to Mo oxide particles where hydrogen spillover could catalyse the reduction. Therefore, the difference in the shape of isotherms (e) and (d) may indicate that micropores adjacent to Mo oxide particles are being widened into mesopores. We do not have data for the samples reduced at 1073 K, but we would expect the trend towards larger pores to be continued.

X-Ray data. Table 1 summarises the X-ray data on catalyst MoO_2/C, and the data for catalysts Mo_2C/C and Mo_2C–K/C. The results for the *oxide* catalysts show that whether the samples were heated in hydrogen or only in nitrogen MoO_2 was the major phase present. Two very weak lines which might correspond to Mo_2C (1–2%) were present but no lines of metallic Mo were observed. We could not determine through weight losses or hydrogen consumption whether further reduction occurred when samples were heated in hydrogen since

TABLE 1

d Spacings (nm) for Mo-on-Charcoal Catalysts

Calcined MoO_2/C[a]	Reduced MoO_2/C[b]	Reduced Mo_2C/C[b]	Reduced Mo_2C–K/C[b]	Assignment	
				MoO_2	Mo_2C
0.340	0.340			0.341	
		0.260	0.260		0.260
0.241	0.242			0.242	
		0.237	0.237		0.237
		0.228	0.228		0.228
		0.175	0.175		0.175
0.172	0.172			0.172	
0.171	0.171			0.170	
0.169	0.169			0.169	
		0.1502	0.1502		0.1503
0.140	0.140			0.140	
		0.1349			0.1349
		0.1270			0.1269
		0.1255			0.1255

[a] Calcined under nitrogen for 16 h at 773 K.

[b] Calcined under nitrogen for 16 h at 773 K, followed by heating in hydrogen for 16 h at 773 K.

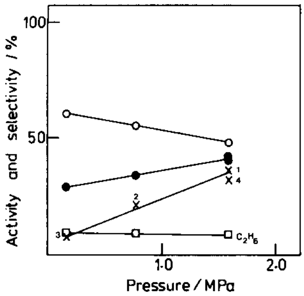

FIG. 2. Variation with pressure of the activity and selectivity of the MoO_2/C catalyst. Activity, ×; selectivity to methane (●), ethane (□), and carbon dioxide (O).

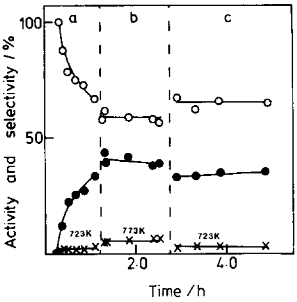

FIG. 3. Activity and selectivity of catalyst $MoO_2/$K–C at various temperatures. (a) 723 K; (b) 773 K; (c) 723 K. Activity, ×; selectivity to methane (●), and carbon dioxide (O).

changes could be due to methanation of the support. According to the X-ray data, there is no significant reduction below Mo(IV). Evidence will be presented elsewhere (*12*) that both the calcined and the reduced materials had similar activities, and selectivities in hydrocarbon reforming reactions, which suggests similar types of active site in both cases.

The X-ray data in Table 1 for catalysts Mo_2C/C and Mo_2C–K/C clearly identify Mo_2C as the major phase present. Potassium apparently has no effect on the formation of the Mo_2C phase (*13*).

Activity Measurements

Oxide catalysts. Many published data on the synthesis gas reaction refer to a pressure of 10^5 N m^{-2}, so to make comparisons we determined the pressure dependence of the activity of our catalysts. Figure 2 shows typical data for catalyst MoO_2/C at 623 K. There is a linear increase in activity and selectivity towards methane as the pressure is increased. A tenfold increase in pressure results in a sevenfold activity increase (for hydrocarbon formation).

Figure 3 shows the activity and selectivity of catalyst MoO_2/K–C (Mo oxide on the K-containing support) as a function of time first at 723 K, then at 773 K, and finally at 723 K again. The catalyst is almost inactive initially, but activity develops and increases during the first hour on stream. The amount of products formed changes in parallel with the increase in activity with methane increasing and CO_2 decreasing. Probably these changes reflect a conditioning of the catalyst by the synthesis gas mixture resulting in a partial carbiding of the surface, a process known to occur with other synthesis gas catalysts (*14*). Increasing the temperature by 50 K approximately doubles the activity of the catalyst and increases the selectivity for hydrocarbon formation.

Figure 4 shows the activity and selectivity of catalyst MoO_2/C (K-free support) versus time at 623 K. As previously, activity increases during the first 0.5 h, although in this case the selectivity for hydrocarbon formation decreases. After 0.5 h the activity (39%) and the selectivity to CH_4 (42%) and C_2H_6 (8%) are stable. By comparing Figs. 3 and 4 we see the dramatic effect of potassium: the potassium-containing catalyst, MoO_2/C–K, has an activity (0.2%) less by a factor of 200 than that of the potassium-free catalyst, MoO_2/C. Later results

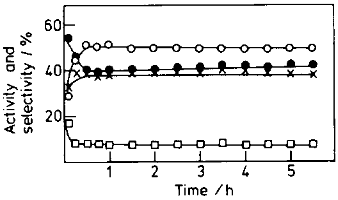

FIG. 4. Activity and selectivity of catalyst MoO_2/C at 623 K. Activity, ×; selectivity to methane (●), ethane (□), and carbon dioxide (O).

will confirm that it is the presence of potassium which is responsible for this 200-fold decrease in activity, although it is not clear why potassium should have such a dramatic effect.

Carbide catalysts. Figure 5 shows the activity and selectivity of the Mo_2C/C catalyst versus time. At 623 K this catalyst has an activity and selectivity very similar to those of catalyst MoO_2/C (see Fig. 4). On raising the temperature to 673 K the activity is increased from 38 to 64%, but there is a slow deactivation at the higher temperature (rate of deactivation 2.5% h^{-1}). There is a shift in selectivity at the higher temperature to give more methane. On returning the temperature to 623 K, the original activity (38%) and selectivity (CH_4, 41%; C_2H_6, 9.4%; CO_2, 49.3%) are recovered, so although there has been some deactivation at the higher temperature this has not altered the activity or selectivity at the lower temperature. A further slow decline in activity at 623 K is observed but the selectivity remains constant.

Figure 6 shows the activity and selectivity for catalyst Mo_2C–K/C. At 623 K the activity is 2.5%, rising to 6.3% at 673 K and to 11.4% at 723 K. (At low conversions overlap of CO and CH_4 peaks in the gas chromatogram makes CH_4 analysis difficult so the selectivity at 623 K may not be reliable.) As the temperature is raised we find, as before, that the formation of CH_4 is favoured at the expense of CO_2, but that the activity for ethane formation is essentially unaltered.

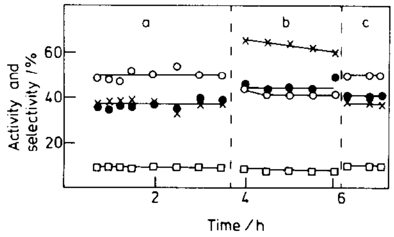

FIG. 5. Variation with temperature of the activity and selectivity of catalyst Mo_2C/C. (a) 623 K; (b) 673 K; (c) 623 K. Activity, ×; selectivity to methane (●), ethane (□), and carbon dioxide (○).

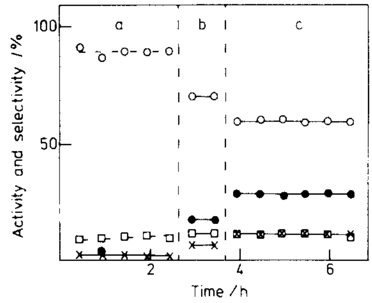

FIG. 6. Activity and selectivity of catalyst Mo_2C–K/C at various temperatures. (a) 623 K; (b) 673 K; (c) 723 K. Activity, ×; selectivity to methane (●), ethane (□), and carbon dioxide (○).

A comparison of the four catalysts is made in Table 2. The large deactivating effect of potassium is clear. For the oxide catalysts the presence of a potassium compound reduces the activity by two orders of magnitude and for the carbide catalysts by an order of magnitude. This difference probably indicates a different sensitivity of the oxide and carbide towards the potassium compound, because although the method of incorporating the potassium compound is different in the two cases, we expect that during impregnation the potassium compound in both cases will redissolve and subsequently recrystallise in contact with the ammonium molybdate. There is only a small difference in the product distributions between the oxides and the carbides in the absence of potassium; addition of potassium reduces the relative amount of methane compared with ethane, and increases the amount of CO_2 compared with hydrocarbons.

DISCUSSION

Composition and Structures of the Catalysts and the Active Sites

The bulk phases in our catalysts according to the X-ray analyses are Mo_2C and MoO_2, the carbide being formed at the higher reduction temperature. The catalytic properties (CO conversions and product distributions) are the same for both the car-

TABLE 2

Comparison of the Activities and Selectivities of Mo/Charcoal Catalysts[a]

Catalyst	Test temperature (K)	Total activity	Activity to hydrocarbons	Product selectivity (%)			$\frac{C_2}{C_1}$
				CH_4	C_2H_6	CO_2	
MoO_2/K–C	723	3.0	1.1	35	—	65	—
MoO_2/K–C	623	<0.2	—	—	—	—	—
MoO_2/C	623	39.2	19.6	41.8	7.8	49.9	0.19
Mo_2C/C	623	37.3	17.9	38.6	9.6	51.8	0.25
Mo_2C/C	673	63.7	36.7	47.0	8.0	44.5	0.17
Mo_2C–K/C	673	6.3	1.9	17.7	11.8	70.3	0.67

[a] $P = 1.6$ MPa; $H_2/CO = 3/1$.

bide and oxide catalysts. Both types of catalyst were poisoned by potassium ions (atomic ratio K/Mo, 0.17). These observations may imply that the active sites are the same on both types of catalyst and are therefore not specific to the *bulk* oxide or carbide. It is possible that the active sites on the oxide, as well as the carbide, are carbidic, e.g., exposed Mo atoms at the surface partly ligated by carbide. The tendency of molybdenum oxides to become carbided during reduction in the presence of carbon or carbon compounds is well known and at the higher reduction temperatures (1073 K in our work) carbide is formed (*15*). An important conclusion is that even if we were able to prepare well-dispersed Mo metal, the metal would become carbided on exposure to CO or hydrocarbons and the effective catalyst would then be a surface carbide and not molybdenum metal.

Our suggestion that the active species is a surface carbide which may or may not be associated with a bulk carbide is consistent with observations on the effect of the method of preparation on the activity (*7*, *8*). The activities of molybdenum carbide catalysts prepared by carburisation of molybdenum metal increase as the carburisation gas was CO $\ll$ CO/H_2 < hydrocarbon/H_2. Oxycarbides are apparently less active (*7*).

CO Conversions and Product Distributions and Comparisons with Other Catalysts

Our activities are expressed per unit weight of active component. This provides a more realistic comparison of the useful activity of different *types* of catalyst than turnover numbers (number of reactant molecules converted/active site/s). For metals, many of the surface atoms will be active; for compounds, only a small fraction of the surface atoms will be active and so comparisons of turnover numbers can give a misleading impression of relative activities. For carbides the fraction of the total surface which can adsorb CO varies from 0.05 (*7*) to 0.2 (*8*) and so a comparison of turnover numbers makes carbides appear to be quite active.

In Table 3 we compare our potassium-free catalysts, various molybdenum compounds, and a Ni/SiO_2 catalyst. For the molybdenum carbides there is a fivefold difference in the reported activities. The carbide of Leclercq *et al.* (*7*) has five times the surface area of Saito and Anderson's (*8*) carbide but adsorbs the same amount of CO and so has a five times greater turnover number. Since we used a high-surface-area charcoal it is unlikely that our molybdenum carbide catalyst had a low surface area. More probably the specific activity is low because only a small fraction of the surface is active.

Our MoO_2 catalyst (Table 3) is about four times more active than Saito and Anderson's unsupported oxide. Their oxide had a high surface area (70.7 $m^2\,g^{-1}$) so it is likely that the difference is due to a different type of active surface rather than surface area. This is supported by the C_2/C_1 product ratios (Table 2) which are similar for our oxide and carbide catalysts (0.19 and 0.25) and Saito and Anderson's carbides (0.16–0.24) but quite different from their oxide value (0.04). Although a carbidic surface apparently favours the formation of higher hydrocarbons, we should point out that, according to Leclercq *et al.* (*7*) carburisation shifts the selectivity from higher hydrocarbons to methane. Also, Kojima *et al.* (*16*) report a C_2/C_1 ratio of 0.91 for a bulk Mo_2C catalyst prepared by pretreatment at high temperature. The selectivity of these carbide catalysts seems to be dependent on the method of preparation, oxygen content, and other factors.

The activity of our catalysts increased with increasing temperature and pressure and, at the same time, the selectivity to methane increased, while ethane was not affected (Figs. 2, 5, and 6). There is therefore an inverse relation between methane and CO_2 formation. This indicates that the increased activity reflects an increased activity for hydrogenation rather than for chain growth, and would support the contention of Saito and Anderson that the kinetics of the synthesis gas reaction over compounds are different from that over metals.

The Water Gas Shift Reaction

The ability of Mo compounds to catalyse the water gas shift reaction simultaneously with the synthesis gas reaction is an important advantage of these catalysts as compared with metallic catalysts.

There was no water among our reaction products even though the reaction [Reaction (1)] produces water.

$$(2n + 1)H_2 + nCO = C_nH_{2n+2} + nH_2O. \quad (1)$$

Our failure to obtain water could be because the reaction occurring does not produce water [e.g., Reaction (2)],

$$(n + 1)H_2 + 2nCO = C_nH_{2n+2} + nCO_2, \quad (2)$$

or because water produced according to (1) is consumed in the water gas shift reaction [Reaction (3)] or in a reaction with carbon [Reaction (4)].

$$H_2O + CO = H_2 + CO_2, \quad (3)$$

$$C + 2H_2O = CO_2 + 2H_2. \quad (4)$$

Reactions (3) and (4) are catalysed by potassium carbonate and so it is possible that the presence of potassium could account for the high proportion of CO_2 produced over the potassium-containing catalysts.

TABLE 3

Comparison of the Activity of Mo Catalysts with that of Ni/SiO_2

Catalyst	Initial rate[a]
MoO_2[b]	0.77
MoS_2[b]	0.13
Mo–C[b]	3.0
Mo–N[b]	0.62
Ni/SiO_2[c]	240
Mo_2C/C[d]	3.3
MoO_2/C[d]	3.0
Mo_2C[e]	15.0

[a] Initial rate of hydrocarbon formation expressed in units of micromoles of CO converted per second per gram of active component. Temperature, 623 K; pressure, 0.1 MPa; H_2/CO = 3.0.

[b] Ref. (*8*).

[c] R. Burch, unpublished results.

[d] This work.

[e] From Ref. (*7*), assuming the rate increases by a factor of 2 between 573 and 623 K.

Certainly over these catalysts the amount of CO_2 was much greater (Table 2) than could be accounted for by Reactions (*1*) and (3). In some cases, when the catalysts have low activities, more CO_2 is producted than is possible from the water gas shift reaction alone. It is probable that the Boudouard reaction [Reaction (5)] is proceeding in parallel with Reactions (1)–(4).

$$2CO = CO_2 + C. \qquad (5)$$

However, this latter reaction seems to be associated with different sites on the catalyst, since no appreciable deactivation of our catalysts due to carbon deposition is observed.

The Role of Potassium and the Course of the Reaction

Potassium, whether as an impurity in the charcoal or added as K_2CO_3, had a striking effect on the catalysts (Table 2). The potassium-containing catalysts were hardly active. In our catalysts K is more correctly described as a poison than a promoter. Potassium also affected the product distribution giving much more CO_2 and higher C_2/C_1 ratios, an effect similar to that observed with iron catalysts and with Mo/C catalysts described in patents (*17, 18*) and earlier work (*5*). However, these catalysts, unlike ours, were *not* poisoned by potassium which hardly affected their activities. Potassium is generally regarded as a promoter of CO/H_2 catalysts and analogous ammonia synthesis (N_2/H_2) catalysts. There is an optimum concentration of potassium, and there have been reports of potassium (*19*) (and also sodium (*20*)) poisoning Ni catalysts. It is certainly relevant that potassium concentrates at the surface of ammonia synthesis catalysts (e.g., 1% K as K_2O covers 90% of the surface of a Fe catalyst) (*21*). The poisoning effect of K in our Mo/C catalysts may be due to blocking of the active sites on the surface. This is possible even though potassium *promoted* reforming reactions over these catalysts (*e.g.*, the conversion of *n*-heptane over K-containing catalysts was almost twice the conversion over K-free catalysts), because the CO/H_2 reaction places more stringent requirements on the active site (*22*). The effect of potassium must be specific to the Mo sites involved in the CO/H_2 reaction. We cannot distinguish between a direct poisoning effect, in which the potassium physically blocks active sites, and an electronic effect, in which the potassium modifies the electron density of the surface atoms. What seems likely is that the CO/H_2 reaction involves low-valent Mo sites on oxygen-deficient MoO_2 or on Mo_2C and that, in our catalysts, the concentration of the latter sites is low. In support of this is a report (*23*) that reduced molybdenum catalysts supported on Saran carbon beads, which are active in the CO/H_2 reaction and *not* poisoned by potassium carbonate, contain according to XPS measurements 53% zerovalent molybdenum. On the contrary, we were unable to detect Mo metal in our reduced Mo/C catalysts.

We conclude, in agreement with other workers, that Mo/C catalysts are active in the CO/H_2 reaction. In addition, our work draws attention to the effects on the catalytic properties of quite small amounts of impurities like potassium in the charcoal support and, by implication, the importance of the type of charcoal or carbon used as a support for molybdenum.

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