

Activity and Stability of Molybdenum Carbide as a Catalyst for CO₂ Reforming

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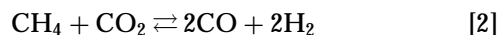
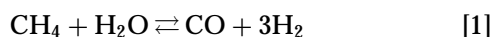
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The activity for CO₂ reforming of methane over a Mo₂C catalyst was studied at 8 and 1.6 bar total pressure using a plug flow reactor and a differential plug flow reactor with external recycle operated as a continuously stirred tank reactor (CSTR), respectively. In the plug flow reactor, the catalyst deactivation started from the top of the reactor and proceeded downward, while it was stable in the CSTR at high conversions. Comparison of the activity of the Mo₂C with that of a 1.8% Ru/MgAl₂O₄ catalyst demonstrates that this noble metal catalyst is more than two orders of magnitude more active than the Mo₂C catalyst on the basis of weight. Thermodynamic calculations of the stability of Mo₂C catalysts during CO₂ reforming conditions show that Mo₂C is only stable at high product concentrations. Finally, the carbon resistance of Mo₂C is calculated to be higher than that of nickel-based catalysts. Carbon formation on a Mo₂C catalyst at 700°C requires an extra Gibbs-free energy of 4.5 kJ/mole compared to a nickel catalyst with nickel particles up to 2500 Å. © 2001 Academic Press

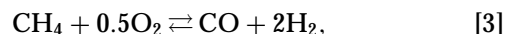
Key Words: molybdenum carbide; ruthenium; CO₂ reforming; stability; carbon resistance.

INTRODUCTION

Since Levy and Boudart (1) reported that tungsten carbide exhibits catalytic properties resembling those of platinum, there has been a growing interest in exploring carbide and nitride catalysts. Molybdenum carbide and tungsten carbide catalysts have received special attention because they are easily prepared with high surface areas using the temperature programmed reaction method described by Volpe *et al.* (2). Molybdenum carbide catalysts have been claimed to have comparable or even higher activities than noble metal catalysts in cyclohexene hydrogenation (3), carbon monoxide hydrogenation (4), isomerization of hydrocarbons (5), and heteroatom removal in petroleum upgrading (6, 7). It has recently been reported that molybdenum carbide catalysts are also active for methane activation in steam reforming and CO₂ reforming



and partial oxidation of methane



and that the activity of molybdenum carbide catalysts is comparable to that of noble metal catalysts (8–10). This is a remarkable observation since these metals are known to be the most active materials for steam reforming (11). It is also worth noting that for these reactions this seems to be the first report of an active catalyst, which is not truly metallic, even though it is known that zeolite-supported molybdenum carbide catalysts are active for methane activation in the dehydrocyclization of methane to benzene (12) and that the nature of the carbide phase influences the activity (13).

Steam reforming is widely used within the chemical industry to provide hydrogen for, e.g., ammonia and methanol production. Steam reforming is usually achieved industrially with a nickel catalyst (11). However, in special circumstances, noble metal catalysts are used to prevent carbon deactivation of the catalyst that might result from the Boudouard reaction



or directly from methane decomposition



Industrially, the lifetime of a steam-reforming catalyst is often determined by the amount of sulfur left in the feed after purification since the nickel catalyst is poisoned by sulfur (11). Therefore, the feed stream must be cleaned for sulfur components to ppb levels. It would in many cases be desirable to use a catalyst that is less susceptible to carbon formation or to sulfur poisoning than the traditional nickel catalysts. It has been reported that molybdenum carbide catalysts are less prone to form carbon than metallic catalysts (9) and that molybdenum carbide might be expected to tolerate sulfur impurities.

The combination of high resistance to deactivation and an activity similar to that of ruthenium catalysts appears to make molybdenum carbide an interesting candidate for a commercial steam-reforming catalyst. Therefore, we decided to study the stability and activity of molybdenum carbide catalysts in CO₂ reforming of methane. CO₂ reforming was chosen as it is apparently easier to stabilize the molybdenum carbide catalyst in the absence of water. Claridge *et al.* (9) reported that molybdenum carbide catalysts are only stable at elevated pressures (ca. 8 bar) and they transform into MoO₂ at ambient pressure. Since steam reforming is conducted at ca. 30 bar industrially this might not be a problem. However, it was decided to further explore the stability of the molybdenum carbide catalysts and to compare the activity of a molybdenum carbide catalyst with a supported ruthenium catalyst for CO₂ reforming of methane. Furthermore, we show how simple thermodynamic calculations can be used to assess the stability of molybdenum carbide catalysts in CO₂ reforming and steam reforming, and we show how molybdenum carbide catalysts can be stabilized at low pressures using a continuously stirred tank reactor.

EXPERIMENTAL

A molybdenum carbide catalyst was prepared according to the procedure by Volpe and Boudart (14) through the method described below. The catalyst was shown by X-ray powder diffraction to be pure Mo₂C with an average crystal size of 10 nm estimated by the Debye–Scherrer method. The surface area of the catalyst was 40 m²/g determined by the BET method.

Ruthenium nitrosulfate was impregnated onto a support of magnesium aluminum spinel preshaped as cylindrical pellets. After drying for 2 h, the catalyst was heated to 525°C at 1.5°C/min in a flow of hydrogen at ambient pressure. After 2 h at 525°C and after cooling to room temperature, the catalyst was passivated by treatment with 1000 ppm dioxygen in argon. The activity and the stability of molybdenum carbide for CO₂ reforming were studied using two different experimental systems. The first setup was a high-pressure plug flow reactor operated at 8 bar total pressure. The second setup was a continuously stirred tank reactor (CSTR) operated at 1.6 bar total pressure. The two experimental setups are briefly described in the following: The high-pressure reactor system had electronic flow controllers for controlling the inlet flows, a reactor with an inner diameter of 18 mm and a length of 600 mm, a five zone oven, a water condenser, and a back pressure valve to control the total pressure in the reactor. All parts of the system, where high partial pressures of water were present, were heated. The total flow of dry gas was measured and a GC was used to determine the product distribution. The temperature of the gas at the top of the catalyst bed was con-

trolled by a thermocouple on the outside wall of a steel reactor and the actual temperature in the bed was measured by a movable thermocouple in a small tube (outer diameter = 3.2 mm) through the center of the reactor. Only the molybdenum carbide catalyst was tested in this setup using 40 g of MoO₃ as 4.5 mm × 4.5 mm tablets loaded to a bed height of 10 cm. The big size of the tablets were chosen to avoid a high pressure drop over the reactor. It means, however, that the reaction in this reactor is subject to significant mass and heat transfer restrictions. Hence, comparison of catalyst activities remains semiquantitative.

The second setup was mounted with a reactor loop and a powerful recirculation pump delivering 6 l/min (NTP), which ensured a homogeneous gas phase composition over the catalyst. Electronic flow controllers were used to control the H₂, CH₄, and CO₂ flows into the reactor. The reactor loop consisted of four parts: (i) glass-lined stainless steel tubes; (ii) a bellow recirculation pump; (iii) a pressure controller for controlling the total pressure in the reactor loop; and (iv) a U-shaped quartz reactor in which the catalyst was fitted between wads of quartz wool. The reactor had an inner diameter of 4 mm. MoO₃, 0.4 g, or 0.051 g Ru/MgAl₂O₄ and 0.152 g MgAl₂O₄ (size fractions 0.3–0.5 mm) was loaded in the reactor to a bed height of 20 and 17 mm, respectively. With the exception of the recirculation pump, the system was heated—the reaction zone had its own oven and a box heated to 200°C covered the tubing. The connections were all heated with heating tape. The surface of the recirculation pump reached a temperature of approximately 75°C during operation and this was enough to avoid condensation of water in the pump. The reaction products were detected by a mass spectrometer, BINOS infrared CO and CO₂ detectors, and a flow detector.

RESULTS AND DISCUSSION

This section is divided into four parts: the first part describes CO₂ reforming over Mo₂C at 8 bar total pressure using a plug flow reactor performed at conditions comparable to those used by Claridge *et al.* (9); the second and the third subsections deal with the CO₂ reforming activity of Mo₂C and Ru/MgAl₂O₄ using a CSTR reactor operated at 1.6 bar; and finally, in the fourth subsection, we discuss the stability and the resistance toward carbon formation of the Mo₂C catalyst.

Catalytic Testing of Mo₂C at 8 Bar Total Pressure

Molybdenum carbide was prepared *in situ* by heating the reactor in a flow of 20% CH₄/H₂ with a space velocity of 11,300 h⁻¹ from room temperature to 750°C at a heating rate of 1°C/min. At this temperature, the inlet gas mixture was changed to feed gas (50% CH₄ and 50% CO₂) and the space velocity was decreased to 2830 h⁻¹ (Total inlet flow/bed volume). Finally, the catalyst bed was heated to

TABLE 1

Results Obtained from an Experiment with an Inlet Pressure of 8 Bar, CO₂ and CH₄ as the Reactants, T_{in} = 830°C, and T_{exit} = 810–822°C (See Text for Details)

O/C	Inlet flow (Nl/h)	Pressure drop (bar)	Conversion (CH ₄)	ΔT(approach) ^a (°C)
1	72	4	50%	-49
1.33	72	10	59%	-96
1.7	73	10	85%	-140

$$^a \Delta T(\text{approach}) = T(Q_R) - T(\text{Exit}) \text{ and } Q_R = \frac{p_{\text{CO}} p_{\text{H}_2}^3}{p_{\text{CH}_4} p_{\text{H}_2\text{O}}}.$$

830°C at the inlet of the reactor. Three observations were made at these experimental conditions: (i) high conversion of the reactants into products. A measurement of the conversion was done after 22 h on steam and the result is given in Table 1. (ii) The movable thermocouple inside the reactor was used to determine the temperature profile down through the reactor. A temperature dip was observed 3 cm from the top of the catalyst bed with a minimum temperature of 751°C. The temperature at the outlet of the reactor was 810°C; (iii) After 12 h in feed gas, the pressure drop over the reactor began to increase from 14 mbar to 4 bar, indicating that carbon had formed in the reactor. Below a temperature of 1200°C, there is a thermodynamic potential for making graphite from the gas equilibrated over the catalyst. However, a decrease in the catalyst temperature increases the affinity for carbon formation. Claridge *et al.* (9) demonstrated that carbon is not formed in the reactor at a reactor temperature of 850°C. The reason for the carbon formation in our experiment is probably related to the lower inlet temperature and the temperature drop in the reactor. Inspection of the catalyst bed after the experiment showed that carbon was not formed at the inlet of the reactor but only at the bottom 75% of the reactor. This is in agreement with the fact that the affinity for carbon formation increases with decreasing temperature.

To limit the carbon formation in the reactor, the O/C ratio was increased by increasing the flow of CO₂ and decreasing the flow of CH₄ but at the same time keeping the space velocity constant. First, the atomic ratio, O/C, was increased from O/C = 1 to 1.33 for 3 h, but this did not stop the carbon formation (thermodynamic calculations show that there is affinity for graphite formation below 824°C at these conditions). Measurements of the conversion and pressure drop were performed after 3 h at these experimental conditions and the results are given in Table 1. Finally, the O/C was increased to 1.7 for 3 h and no further increase in the pressure drop was observed at these conditions. The conversion and pressure drop at O/C = 1.7 are also reported in Table 1. Thermodynamic calculations demonstrate that at O/C = 1.7 and H/C = 0.75, graphite cannot form above 726°C, which is well below the lowest temperature in the reactor.

Thermodynamic calculations also show that Mo₂C is the stable form of molybdenum in the equilibrated gas at O/C = 1.7. After the test, the catalyst was cooled in N₂, passivated and analyzed by X-ray powder diffraction. The phases observed in the top layer of the catalyst were MoO₂ and Mo²C indicating that the catalyst was partly oxidised. Mo₂C was the only phase observed, at 3 cm from the top of the catalyst bed.

The conclusion from these observations is that in a plug flow reactor, the catalyst deactivates from the top by oxidation of the catalyst because the catalyst is not stable in the inlet gas. However, Claridge *et al.* (9) observed that Mo₂C is stable at 8.3 bar total pressure but unstable at the same space velocity at 1 bar total pressure. To understand the reason for this, one should calculate the axial dispersion in the reactor at these two pressures. This is not possible, since Claridge *et al.* do not give the particle size of the catalyst used in their reactor, but it is interesting to note that the relative “back mixing” at the two pressures are about equal. However, a decrease in the “by pass” or/and an increase in the intrinsic activity of the catalyst when the total pressure is increased from 1 to 8 bar may explain the increased stability observed by Claridge *et al.* The stability of the Mo₂C catalysts will be discussed further below.

Catalytic Testing of Mo₂C at 1.6 Bar Total Pressure Using a CSTR Reactor

To avoid the problem with deactivation of the top layer of the catalyst bed and to demonstrate that the molybdenum carbide catalyst can be stable at low pressures, an experiment was performed at 1.6 bar total pressure.

The catalyst was heated to 600°C at a heating rate of 1°C/min in a flow of 100 ml/min (SV ≈ 60,000 h⁻¹) of 20% CH₄ in H₂. The catalyst was left at this temperature for 10 h. After this treatment, the catalyst was heated in 2% CH₄ in H₂ at a total flow of 100 ml/min to 900°C. The reason for choosing this ratio between CH₄ and H₂ was to avoid a thermodynamic potential for carbon formation over the catalyst. Molybdenum carbide is thermodynamically stable at these experimental conditions. The CH₄/H₂ mixture was replaced by nitrogen. After 10 min, a reaction mixture consisting of 46% CH₄ and 54% CO₂ was allowed into the reactor. The total flow into the reactor was 16.7 ml/min. The product concentrations as a function of time on feed gas are given in Fig. 1. The initial conversion of methane was 83%, ΔT(approach) = -168°C, where ΔT(approach) = T(Q_R) - T(Exit) (11) and

$$Q_R = \frac{p_{\text{CO}} p_{\text{H}_2}^3}{p_{\text{CH}_4} p_{\text{H}_2\text{O}}}.$$

At equilibrium, 99% of the methane is converted into CO and CO₂. After 3600 min on stream, the conversion had dropped to 67%, ΔT(approach) = -233°C. Deactivation of

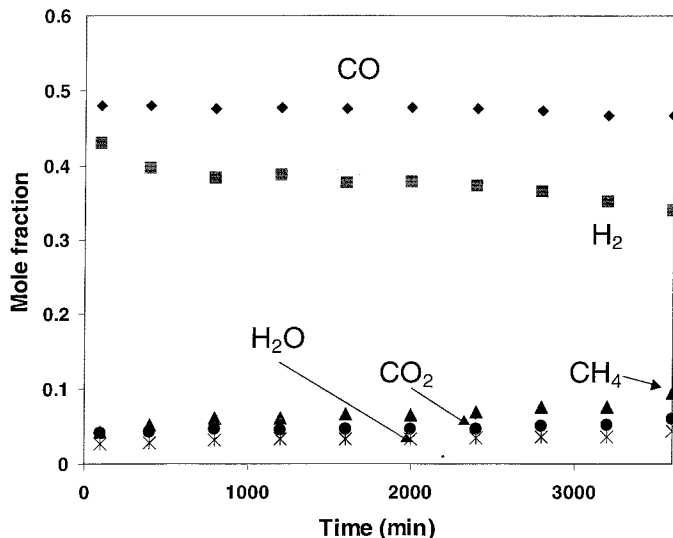
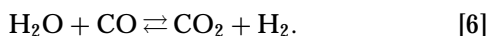


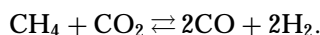
FIG. 1. The product concentrations as a function of time for an experiment with an inlet flow of 16.7 ml/min, $\text{CH}_4:\text{CO}_2 = 0.46:0.54$, 1.6 bar total pressure, 0.4 g MoO_3 precursor, and a temperature of 900°C .

the Mo_2C was also observed by Claridge *et al.* (9) at low pressures (1 bar). In their experiment, however, the deactivation was apparent after 360 min in synthesis gas. The deactivation was very severe and could be attributed to oxidation of the catalyst. The loss in activity observed here is explained by a loss of surface area of the molybdenum carbide. After the test, the BET area was determined to be $7\text{ m}^2\text{ g}^{-1}$, while the BET area of a fresh sample of Mo_2C prepared in the reactor and passivated was ca. $40\text{ m}^2\text{ g}^{-1}$. X-ray powder diffraction showed that both samples consisted of pure Mo_2C .

In addition to the study of the stability of Mo_2C at low pressure, the activation energy was estimated by measurements of the conversion of methane in the $700\text{--}800^\circ\text{C}$ temperature range. The inlet flow was kept constant at 16.7 ml/min. The conversion of methane was relatively high, between 14 and 35% to avoid deactivation of the catalyst. The data are plotted in Fig. 2 as a function of $1000/T$. The activation energy was estimated from these data to be 80 kJ/mole, which is in reasonable agreement with that reported by Claridge *et al.* (9) of 100 kJ/mole. Finally, it is interesting to note that in all the product mixtures studied, equilibrium was established for the water-gas-shift reaction:



This demonstrates that the shift reaction at these experimental conditions is much faster than the CO_2 reforming reaction:



This observation is in line with the data in a recently published paper (15), where it is shown that Mo_2C is an efficient

catalyst for reaction (6) at temperatures as low as $220\text{--}295^\circ\text{C}$. The fact that Mo_2C is an effective catalyst for the water-gas-shift reaction has important consequences for the thermodynamic calculations below.

Comparison of the Activity of the Mo_2C Catalyst with a $\text{Ru}/\text{MgAl}_2\text{O}_4$ Catalyst

Claridge *et al.* (9) compare the activity of Mo_2C with that of three noble metal catalysts and conclude that the activity for CO_2 reforming of Mo_2C is comparable with that of rhodium and iridium and somewhat smaller than that of ruthenium on the basis of the turnover frequency. Here, we have chosen to compare the activity for CO_2 reforming of Mo_2C with that of a ruthenium catalyst. The activities of the catalysts are compared on a weight basis because the method used for the measurement of the number of active sites on Mo_2C is not well established. Claridge *et al.* (9) determined the number of active sites of Mo_2C by hydrogen chemisorption and obtained a very low number of active sites ($2.2 \times 10^{18}\text{ g}^{-1}$) compared with the surface area of Mo_2C ($91\text{ m}^2\text{ g}^{-1}$) and thus, a high turnover frequency. The activity for CO_2 reforming of Mo_2C is compared with that of a 1.8% $\text{Ru}/\text{MgAl}_2\text{O}_4$ with a metal surface area of about $1.0\text{ m}^2\text{ Ru/g}$ catalyst determined by chemisorption of hydrogen. The ruthenium catalyst showed a much higher activity than Mo_2C . In order to measure the intrinsic activity of this catalyst, it was necessary to decrease the reactor temperature to $350\text{--}500^\circ\text{C}$ and increase the space velocity to 10^5 h^{-1} . The same feed was used for the $\text{Ru}/\text{MgAl}_2\text{O}_4$ and the Mo_2C catalyst. The activities of $\text{Ru}/\text{MgAl}_2\text{O}_4$ obtained in this work are plotted in Fig. 2 together with the activity obtained for the Mo_2C catalyst at 900°C after 3600 min on stream and the activities of Mo_2C in the $700\text{--}800^\circ\text{C}$ temperature range. The activities at 700°C obtained by Claridge

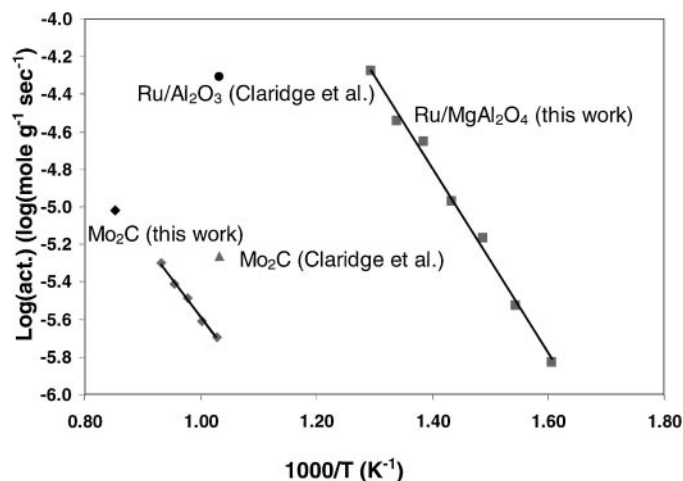


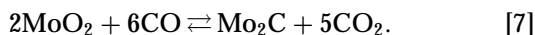
FIG. 2. The logarithm of the CO_2 reforming activity in mole $(\text{g catalyst})^{-1}\text{ s}^{-1}$ obtained in this work and the work of Claridge *et al.* (9) plotted as a function of $1000/T$.

et al. (9) for a 5% Ru/Al₂O₃ and a Mo₂C (91 m² g⁻¹) catalyst are plotted in the figure for comparison. It is evident from the Fig. 2 that Mo₂C is much less active for CO₂ reforming than ruthenium. The Mo₂C tested by Claridge *et al.* is more active than the Mo₂C used here. Probably the reason is that the surface area of the Mo₂C catalyst used by Claridge *et al.* was 91 m² g⁻¹, while the surface area of the Mo₂C used here was only 7 m² g⁻¹ after 3600 min in synthesis gas at 900°C. The Mo₂C used to study the temperature dependence of CO₂ reforming was ca. 40 m² g⁻¹. It is also seen from Fig. 2 that the 1.8% ruthenium catalyst tested here is much more active than the 5% ruthenium catalyst tested by Claridge *et al.* (9). The reason for this difference in activity is mainly the difference in metal surface area of a factor of 5–10. However, this cannot explain the observed difference in activation energy. The activation energy obtained by Claridge *et al.* is 48 kJ/mole, while 94 kJ/mole is measured in this work and ca. 115 kJ/mole is obtained from the work by Rostrup-Nielsen and Hansen (16) for a Ru/MgO catalyst. Therefore, the low activation energy obtained by Claridge *et al.* is probably due to diffusion limitations, which will result in a lower apparent activation energy.

A comparison of the activity of a high surface area Mo₂C (91 m²/g) presented by Claridge *et al.* (9) with an activity determined from a temperature extrapolation from 500 to 700°C of the activity of the 1.8% Ru/MgAl₂O₄ shows that the ruthenium catalyst is more than 2 orders of magnitude more active for CO₂ reforming per gram of catalyst than Mo₂C. Examination of the data in Table 2 in Claridge *et al.* (9) shows that on a catalyst weight basis, 5% Ru/Al₂O₃ is an order of magnitude more active than Mo₂C. In addition, Claridge *et al.* compare the activity of a very low surface area ruthenium catalyst with that of a very high surface area Mo₂C catalyst. Using the activity for ruthenium obtained in this work, the difference in activity between noble metal catalysts and Mo₂C is higher than presented by Claridge *et al.* It should be added here that the turnover frequencies for CO₂ reforming of Ru catalysts are 40% higher than that of Ni catalysts at 500°C (16).

Stability and Carbon Resistance of Molybdenum Carbide

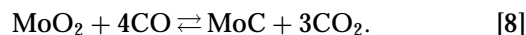
Thermodynamic calculations were performed to evaluate the stability of molybdenum carbide. To make these calculations, we must identify the reaction that determines the stability of molybdenum carbide. It is assumed in the following that Reaction (7) determines the stability of Mo₂C:



This assumption is justified by the following observations: First, the work of Patt *et al.* (15) shows that Mo₂C is a very active catalyst for the water-gas-shift reaction even at temperatures as low as 220–295°C. The stability of Mo₂C

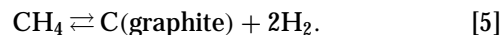
at these temperatures, when the gasses over the catalyst is in equilibrium with regard to the water-gas-shift reaction, must be determined by the concentrations of H₂O, CO, CO₂, and H₂ but not CH₄ since Mo₂C does not form methane at the conditions used by Patt *et al.* (15). The interaction of CH₄ with Mo₂C is therefore too slow to influence the stability of this catalyst at low temperatures. Therefore, we only need to consider Reaction [7], to evaluate the stability of molybdenum carbide and not other reactions involving H₂, and H₂O and CO_x (CO and CO₂), since if these reactions show potential for oxidation of Mo₂C, Reaction [7] will also do so. It was noted above that Mo₂C deactivates by oxidation at the inlet of the reactor. Consequently, the reaction of CO₂ with Mo₂C to give MoO₂ is faster than the reaction of CH₄ with MoO₂ to give Mo₂C. If methane determined the stability of Mo₂C through equilibrium, the stability of Mo₂C would have an optimum at the inlet of the reactor. This is in conflict with the observed deactivation and oxidation from the top of the reactor. For these reasons it seems reasonable to assume that Reaction [7] determines the stability of molybdenum carbide.

The stability of Mo₂C can now be calculated at all conversions of methane using the thermodynamic data for the species involved in Reaction [7] and assuming that the water-gas-shift reaction is equilibrated. Thermodynamic data were taken from Barin (17). Figure 3 shows the stable phases of molybdenum at different temperatures as a function of the methane conversion. The figure also shows the conversion of methane at equilibrium and the intervals of conversion and temperature where MoC is the stable phase. The thermodynamic stability of MoC is calculated through



The calculations support the observations from the previous sections, i.e., that molybdenum carbides are only stable in a plug flow reactor at high conversion and in the case of significant axial dispersion. Figure 3 shows that MoC is the stable phase at very high conversions. However, only Mo₂C has been observed when analyzing the spent catalyst by X-ray powder diffraction. This may either be due to a too low conversion over the catalyst or to the fact that MoC is only formed very slowly from Mo₂C.

The carbon resistance of Mo₂C was studied by Clair *et al.* (18) and Claridge *et al.* (9). Clair *et al.* found that carbon is formed on Mo₂C when exposed to 20% CH₄ in H₂ at 708°C at 1 bar total pressure while carbon was not formed when the temperature was 688°C. Carbon in this system is formed via



The resistance toward carbon formation can be calculated from $\Delta G_c = -RT \ln(K_{p,\text{observed}}) + RT \ln(K_{p,\text{graphite}})$ (19), where $K_{p,\text{graphite}}$ is the equilibrium constant for Reaction [5] calculated by thermodynamics and $K_{p,\text{observed}}$ is

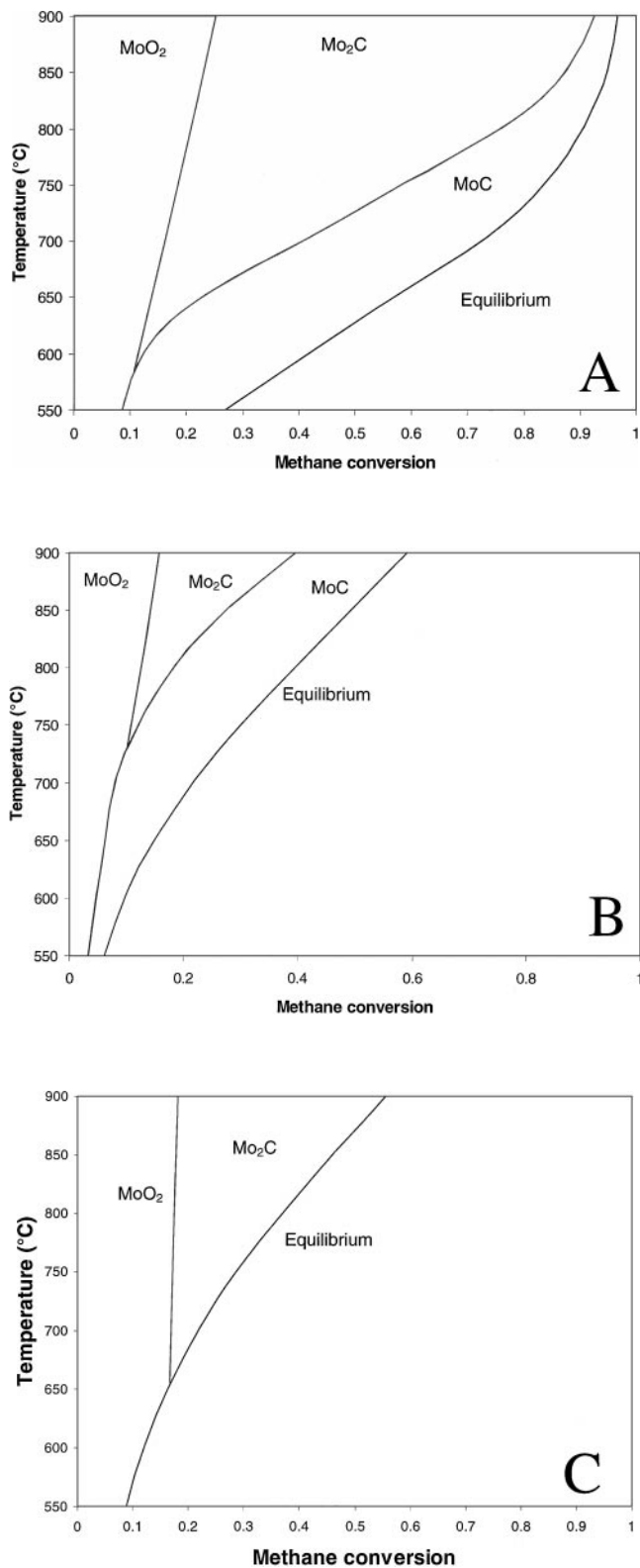


FIG. 3. Stability of Mo_2C , MoC , and MoO_2 as a function of methane conversion and temperature using a feed of $\text{CH}_4:\text{CO}_2 = 1:1$ at (A) 1 and (B) 30 bar total pressure and a feed of (C) $\text{H}_2\text{O}:\text{H}_2 = 1:1$ at 30 bar total pressure. The equilibrium curves for the reforming reaction are plotted for comparison. See text for details.

the observed equilibrium constant calculated from the actual concentrations of CH_4 and H_2 at the conditions where carbon starts to form. Using this equation and assuming that the limiting temperature for carbon formation on Mo_2C is 698°C when exposed to 0.2 bar CH_4 and 0.8 bar H_2 (18), we find that $\Delta G_c(698^\circ\text{C}) = 7.0$ kJ/mol. This should be compared to that of a nickel catalyst with nickel particles up to 2500 \AA for which $\Delta G_c(700^\circ\text{C}) = 2.5$ kJ/mol (19). This means that carbon formation on a Mo_2C catalyst at 700°C requires an extra Gibbs-free energy of 4.5 kJ/mole compared to a nickel catalyst with nickel particles up to 2500 \AA . The temperature dependence of the resistance of Mo_2C toward carbon formation is unknown.

Claridge *et al.* (9) exposed a Mo_2C catalyst, an Al_2O_3 -supported noble metal catalyst, and $\text{Ni}/\text{Al}_2\text{O}_3$ to $\text{CH}_4:\text{CO}_2 = 1:1$ with the catalyst temperature in the 900–970 K temperature range and found that the nickel catalyst formed carbon whiskers, while Mo_2C and the noble metal catalysts did not form carbon. Based on this observation, they concluded that Mo_2C is much more resistant to carbon formation than the nickel catalysts. However, from this experiment it can only be concluded that Mo_2C is more carbon resistant than nickel on alumina but not how resistant it is.

CONCLUSIONS

This work shows that Mo_2C is unstable toward oxidation at the inlet of a plug flow reactor unless axial dispersion is important. Therefore, the space velocity is important for the stability of Mo_2C as indicated by Claridge *et al.* (9). From experiments at 1.6 bar total pressure using a CSTR reactor, we conclude that the catalyst can be stabilized at lower pressures. Comparison of the activity of the Mo_2C with that of a 1.8% $\text{Ru}/\text{MgAl}_2\text{O}_4$ catalyst demonstrates that the activity of this noble metal catalyst is more than two orders of magnitude more active than a Mo_2C with $91 \text{ m}^2 \text{ g}^{-1}$ on the basis of one gram of catalyst. Thermodynamic calculations show that Mo_2C is only stable at high conversion, i.e., in the last part of a plug flow reactor. However, in a primary reformer the catalyst could be stable for CO_2 reforming after introduction of an active top layer of another catalyst. Mo_2C is not stable at steam reforming conditions under 650°C at 30 bar total pressure and $\text{H}_2\text{O}:\text{CH}_4 = 1:1$ and Mo_2C is only stable at high product concentrations. The carbon resistance of Mo_2C is calculated to be higher than that of a nickel catalyst with nickel particles up to 2500 \AA . At 700°C an extra Gibbs-free energy of 4.5 kJ/mol is needed to form carbon over Mo_2C than over this nickel-based catalyst. The temperature dependence of the resistance toward carbon formation is unknown.

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