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The Activity of Several Molybdenum Compounds for the Methanation of CO

M. SAITO[1] AND R. B. ANDERSON

Department of Chemical Engineering and Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada

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Several molybdenum compounds—oxides, sulfide, metal, carbide, and nitride—were prepared, and their catalytic properties in the methanation of CO at 350°C were investigated and compared with those of nickel and iron. The initial specific activities, i.e., rates per unit surface area of catalyst, decreased in the following sequence: Ni > Mo carbide > Mo metal > Mo nitride > MoO_2 > MoS_2 > MoO_3. The rate of aging, loss in activity for methanation, decreased in the following way: Fe > Mo carbide > Mo metal > Ni > $MoS_2 \simeq$ Mo nitride > MoO_2. The zero-valent molybdenum compounds produced much larger amounts of C_2 and C_3 hydrocarbons than MoO_2 and MoS_2, and about the same amount as iron. Nickel produced the smallest amount of higher hydrocarbons. The molybdenum compounds except MoS_2 and MoO_3 had higher activities for the water-gas-shift reaction than nickel and iron. Molybdenum compounds were as active in $1H_2 + 1CO$ gas as in $3H_2 + 1CO$ feed; nickel and iron were substantially less active in the CO-rich gas.

1. INTRODUCTION

Methanation of oxides of carbon with hydrogen is an important step in the preparation of a substitute natural gas (SNG) from hydrogen-deficient materials such as coal, residual oil, oil shale, etc. Although extensive research and development has been done on methanation catalyzed by the Group VIII metals especially nickel, the catalytic behavior of other metals has not been as extensively investigated. Workers at the U.S. Bureau of Mines (*1*) reported that molybdenum catalysts had the highest activity in methanation except for iron group metals and ruthenium. Interesting features of these catalysts were that they operated well in $1H_2 + 1CO$, produced small amounts of higher hydrocarbons, and had a modest activity in a sulfur-containing feed. Further basic research on molybdenum catalysts seems warranted. In the present study, a number of unsupported molybdenum compounds—oxides, sulfide, metal, carbide, and nitride—were prepared, and their catalytic properties in the methanation of CO were investigated and compared with those of nickel and iron.

2. EXPERIMENTAL

2.1 Apparatus and Procedures

The glass flow system shown in Fig. 1 was used for preparation of catalyst samples and also for the methanation studies. The furnace was equipped for linear temperature programming and the system contained a thermal conductivity detector (TCD) for determining rates of reduction and the time required for complete reduction. Methanation was studied at 350°C and 1 atm, and the product gases were analyzed with two gas chromatographs equipped with TCD.

Pretreatment and synthesis experiments were performed at 1 atm in a 0.8-cm-diameter quartz reactor. An amount of molybdenum catalysts from 1.0 to 1.7 g, 0.5 to 1.0 cm^3, was used; space velocities in methanation tests varied from 4000 to 6500 h^{-1} and in pretreatment steps from 4500 to 12,000 h^{-1}. For Ni and Fe, respectively, 0.1 and

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[1] Present address: National Research Institute for Pollution and Resources, Tsukuba, Ibaraki, Japan.

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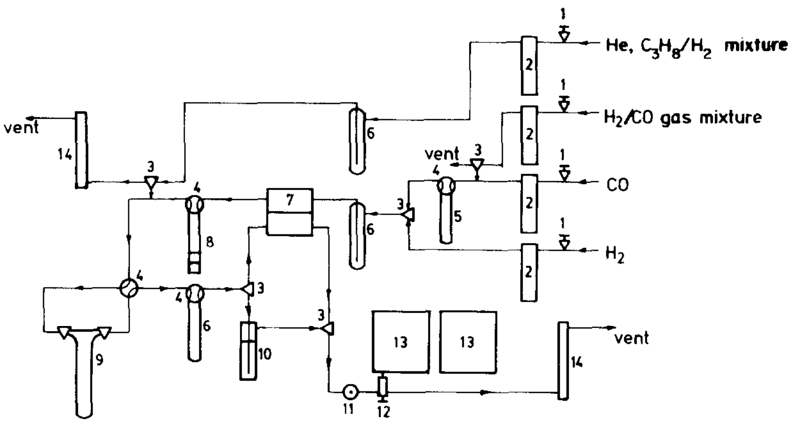

FIG. 1. Diagram of reaction system. 1, needle valve; 2, capillary flow meter; 3, three-way stopcock, 4, four-way stopcock; 5, charcoal trap, 6, cold trap; 7, thermal conductivity cell; 8, water vapor saturator; 9, quartz reactor; 10, liquid trap; 11, sampling port; 12, sample injection valve; 13, gas chromatograph; 14, soap-film flow meter.

0.5 g of catalysts were used. In methanation and reduction large space velocities were used, in excess of 70,000 h^{-1} for Ni and 17,000 for Fe. All of the catalysts were fine powders.

The surface area of each sample was measured by physical adsorption of nitrogen at −195°C, using a sorptometer.

Measurements of the chemisorption of CO and H_2 were made at room temperature in a volumetric adsorption system capable of a dynamic vacuum $\leq 10^{-5}$ Torr. Adsorption isotherms for CO and H_2 were measured in a pressure range of 20 to 250 Torr. Strongly adsorbed CO was obtained from an original isotherm, evacuating to remove the reversibly held CO, and determining a second isotherm in the same manner as the first; the difference between the isotherms is strongly adsorbed CO. H_2 uptake was determined by extrapolating the linear portion of the isotherm to zero H_2 pressure.

Phases present in the samples were identified by powder X-ray diffraction using Cu$K\alpha$ radiation. Carbon and sulfur in samples were determined by Leco analyzers; nitrogen was determined by the Kjeldahl method.

2.2 Materials

The catalyst samples prepared in this study are given in Table 1. The molybdenum trioxide (MoO_3) was prepared by thermal decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, ammonium molybdate, in air at 500°C for 5 h. Oxygen content of this sample was determined from weight decrease after complete reduction to Mo; the O/Mo atomic ratio was 3.0.

When MoO_3 was reduced with hydrogen at 400°C, small peaks of Mo metal were found in the diffraction pattern. MoO_2 was produced from MoO_3 at 350°C during methanation with H_2 + CO; the O/Mo ratio from weight decrease was 1.92. X-Ray diffraction on this sample indicated MoO_2 to be the principal phase; however, three other broad peaks were found at 2θ angles of 38.2, 44.3, and 64.5°. The d spacings calculated by Bragg's equation for those peaks were 2.36, 2.04, and 1.44 Å. This X-ray diffraction pattern is similar to those for NiO and TiO which have face centered cubic lattices. Possibly fcc MoO with a lattice a = 4.09 Å was formed along with MoO_2 during the reduction of MoO_3. The formation of MoO may account for the O/Mo ratio being less than 2.0. It was reported that a black material of a composition near MoO was formed in the reaction of $K_{0.66}MoO_2$ and $K_{1.5}MoO_3$ with alcohol or water (2). However, its lattice parameter (a

TABLE 1

Composition and Properties of Catalysts Prepared in This Study

Catalyst	Composition (atom/atom)	Phases detected by X-ray diffraction	Surface area (m^2/g)	Gas uptake at 25°C (μmol/g)	
				CO	H_2
MoO_3	O/Mo = 3.0	MoO_3	1.6	0.3	0.0
MoO_2	O/Mo = 1.92	MoO_2, MoO (?)	70.7	180	10.7
MoS_2	S/Mo = 2.0	MoS_2 (broad)	23.0	67.0	5.4
Mo	—	Mo	7.5	26.0	9.9
Mo-C-1	C/Mo = 0.63	Mo_2C	6.6	[a]	[a]
Mo-C-2	C/Mo = 0.38	Mo_2C, Mo	7.3	0.8	0.0
Mo-C-3	C/Mo = 0.54	Mo_2C	6.8	[a]	[a]
Mo-C-4	C/Mo = 0.44	Mo_2C, Mo (trace)	7.3	36.4	13.5
Mo-N	N/Mo = 0.63	γ-Mo_2N, Mo (trace)	7.3	47.3	14.3
Ni	—	Ni	0.97	[a]	11.4
Fe	—	α-Fe	8.5	47.5[b]	30.7

[a] Not determined.

[b] The difference between an original isotherm at −195°C and a second isotherm at −195°C following evacuation at −78°C.

= 5.019) was very different from the value obtained in this study.

Molybdenum disulfide was prepared by reduction of molybdenum trisulfide with H_2 at 370°C for 3 h. The molybdenum trisulfide with S/Mo of 2.8 was made by adding an aqueous ammonium sulfide solution to an ammonium molybdate solution and subsequently acidifying with sulfuric acid (*3*). Since broad diffraction peaks were found for MoS_2, this material seemed to be of a low crystallinity.

Mo metal was obtained by the reduction of MoO_3 with hydrogen at 600°C for 3 h. Four samples of molybdenum carbide were prepared. Mo-C-1 was made by carburizing the Mo metal with CO at 600°C for 3 h. The phase detected in this sample by X-ray diffraction was Mo_2C, one of the interstitial compounds of Mo metal. Carbon atoms occupy interstitial sites in a hexagonal close-packed arrangement of Mo metal atoms (*4*). The C/Mo ratio was 0.63, the sample containing elemental as well as interstitial carbon. Mo-C-2 was prepared by carburizing the metal with CO at 500°C for 5 h. The diffraction pattern showed Mo_2C and Mo metal to be present. Since Mo-C-1 and Mo-C-2 showed no activity for methanation, Mo-C-3 was prepared by carburizing the metal with H_2 + CO(H_2/CO = 16) at 580°C for 3 h. For the last molybdenum carbided sample, Mo-C-4, the metal was carburized with C_3H_8 + H_2(H_2/C_3H_8 = 40) at 580°C for 3 h. This preparation is similar to that employed by Sinfelt and Yates (*5*). The molybdenum nitride was prepared by treating Mo metal with NH_3 at 450°C for 9 h. Relatively broad peaks assigned to γ-Mo_2N and a small peak for Mo metal were found in the X-ray diffraction pattern. γ-Mo_2N is also one of the interstitial compounds of Mo metal. Interstitial nitrogen atoms are located in interstitial sites in a cubic close-packed arrangement of Mo metal atoms (*4*). The N/Mo ratio in the sample was 0.63.

The nickel metal was prepared by reduction of nickel oxide with hydrogen at 450°C for 3 h. The nickel oxide was obtained by calcining at 450°C for 5 h nickel hydroxide, which was precipitated from an aqueous solution of nickel nitrate with aqueous ammonia.

The iron metal was prepared by reducing ferric oxide with hydrogen at 550°C for 4 h.

The ferric oxide was obtained by calcining at 450°C for 5 h ferric hydroxide, made by adding an aqueous ammonia to an aqueous solution of ferric nitrate.

The hydrogen (Matheson, 99.99% purity) was further purified by passage through a Deoxo unit followed by a dry ice trap. The carbon monoxide (Matheson, 99.9% purity) and the gas mixtures of CO and H_2 were passed over activated charcoal to remove metal carbonyls. The other gases were used as received from Matheson of Canada.

3. RESULTS AND DISCUSSION

3.1 Surface Areas of Catalysts and the Chemisorption of CO and H_2

Surface areas of the catalysts used and CO and H_2 uptakes by the catalysts are summarized in Table 1. The surface area of MoO_2 was the largest and MoO_3 the smallest. The zero-valent molybdenum compounds, Mo metal, molybdenum carbides, and nitride had about the same surface area.

Chemisorption of CO by MoO_2 and MoS_2 was more than 10 times the H_2 uptakes, but the zero-valent molybdenum samples adsorbed about 3 times as much CO as H_2. The amount of oxygen chemisorbed on MoO_2 was also determined by the method of Parekh and Weller (*6*). A first and second O_2 adsorption isotherm at −195°C, with intermediate pumping at −78°C, were determined; chemisorbed O_2 was the difference between the two isotherms. The ratio of BET surface area to oxygen chemisorption was 14.7 (m^2/ml), close to the value of 14.1 that Parekh and Weller (*6*) obtained for the prereduced unsupported molybdenum sample with a surface area of 15.5 m^2/g.

Carbon monoxide molecules and hydrogen atoms adsorbed per surface metal atom (CO/M_s and H/M_s) were calculated for Mo, Fe, and Ni metal from the BET surface areas of those metals (*7*). The values of CO/Mo_s and H/Mo_s were 0.15 and 0.12, respectively, suggesting that all of the surface metal atoms are not active sites for chemisorption. Similarly, H/Fe_s was 0.27. Sinfelt and Yates (*8*) reported a similar result for an unsupported iron which was reduced with H_2 at 550 to 600°C. The ratio H/Ni_s was 0.92, indicating most of the surface nickel atoms are active sites for the chemisorption, as shown by Pannell *et al.* (*9*).

3.2. Catalytic Properties

Figure 2 shows the activities of MoO_3 and MoO_2 for methanation at 350°C, expressed as rate of formation of C_1–C_3 hydrocarbons. The starting material was MoO_3; its activity was negligible. the activity and surface area increased with time on stream and reached a constant value in about 20 h, while the O/Mo ratio decreased with time to a constant value. Both the activity and the surface area increased linearly with the extent of reduction of MoO_3, defined as 1 − (O/Mo)/3. The WGS value, defined as $P_{CO_2} \times P_{H_2}/(P_{CO} \times P_{H_2O})$, measures the progress of the water-gas-shift reaction during methanation. The WGS value approached the equilibrium constant

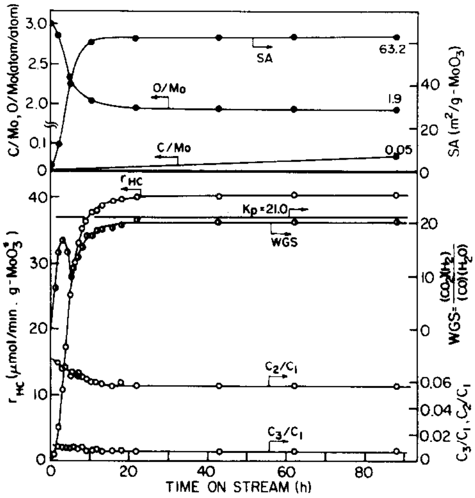

FIG. 2. Methanation on MoO_2 at 1 atm and 350°C. Feed gas was $3.1H_2 + 1CO$. r_{HC} is rate of production of hydrocarbons. Surface area, SA, and atomic ratios of oxygen and carbon to molybdenum are given in the top portion. WGS is a measure of the approach to equilibrium of the water-gas shift calculated from the exit gas; the equilibrium value of WGS is 21. C_2/C_1 and C_3/C_1 are the ratios of moles of ethane and propane to moles of methane, respectively, in the exit gas.

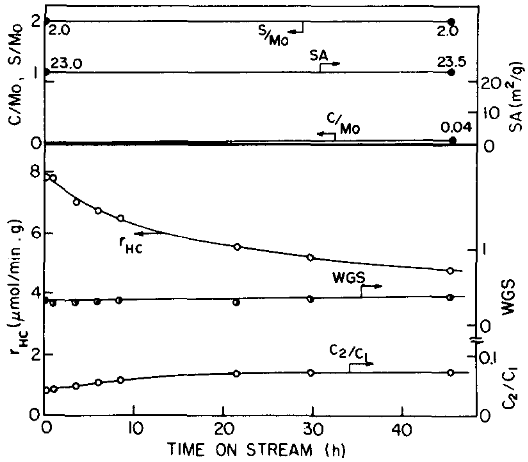

FIG. 3. Methanation on MoS_2 at 1 atm and 350°C. See legend of Fig. 2.

of the water-gas-shift reaction ($K_p = 21.0$) in 22 h; the MoO_2 had a higher activity for water-gas-shift reaction than for methanation. The peak in the WGS curve in the first 5 h resulted from more CO than H_2 being used in the reduction of MoO_3. The ratios of C_2 to C_1 and C_3 to C_1 in the product gas remained constant after the activity leveled out. Although MoO_2 formed during reaction seemed to contain a small amount of MoO, as previously described, the present study could not decide which had a higher activity, MoO_2 or MoO.

The sample of MoS_2, Fig. 3, had lower activities for both methanation and water-gas shift than MoO_2. Methanation activity decreased slowly, and WGS remained constant. The ratio C_2/C_1 was smaller than that for MoO_2. The activity of Mo metal for methanation, Fig. 4, decreased with time, while the amount of carbon in the sample increased. X-Ray diffraction from the sample taken after 128 h indicated a trace amount of Mo_2C. Because molybdenum carbide Mo_2C has a larger activity than the metal, we may infer that the carbon deposited was not in this form. The C_2/C_1 and C_3/C_1 ratios as well as WGS also decreased with time. Metallic Mo reduced at 600°C for 24 h had 40% of the surface area and a half of the activity of the Mo metal reduced for 3 h. The WGS value for this sample was 15.4,

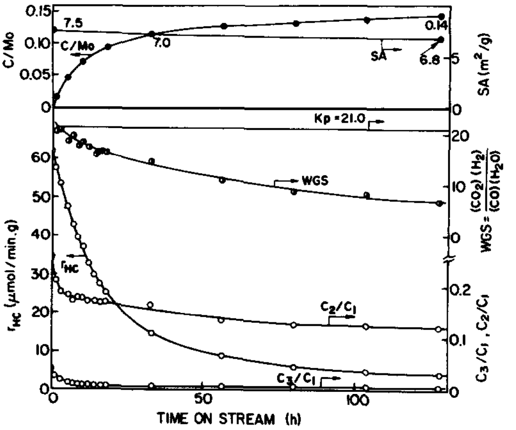

FIG. 4. Methanation on metallic Mo at 1 atm and 350°C. See legend of Fig. 2.

and the C_2/C_1 and C_3/C_1 ratios were 0.25 and 0.02, respectively. Mo-C-1 and Mo-C-2, prepared by carburization with pure CO, had no activity. Mo-C-3, carburized with a mixture of CO and H_2, had a higher activity than the Mo metal, but a smaller activity than Mo-C-4 which was carburized with a mixture of C_3H_8 and H_2. Mo-C-4 had the highest activity of all the molybdenum catalysts in this study. Thus, catalysts treated with pure CO or CO + H_2 were less active than those carburized with H_2 + propane. The initial activity of Mo-C-4 was about three times that of the Mo metal, but its activity decreased more sharply than that of the metal as shown in Fig. 5. The C_2/C_1

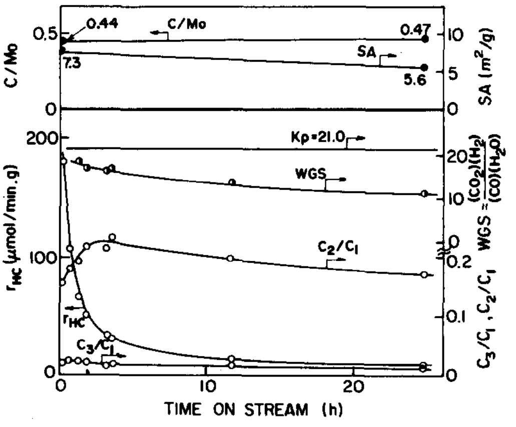

FIG. 5. Methanation on molybdenum carbide, Mo-C-4, at 1 atm and 350°C. See lengend for Fig. 2.

and C_3/C_1 ratios increased during the first 3 h and then decreased with time. The activity of Mo-C-4 for water-gas-shift reaction was higher than for methanation, but decreased as its methanation activity decreased.

The decarburization of Mo-C-4 by H_2 was conducted in the flow system and in the closed system used for chemisorption measurements. Table 2 shows the amount of carbon remaining in Mo-C-4 after sequential treatments at different temperatures in flowing H_2 determined from the weight decrease of the sample.

These results indicate that MoC-4 is stable in a H_2 atmosphere up to 400°C. The amount of CH_4 formed at 350°C was measured in the closed system as a function of reaction time. The rate of carbon removal from the initial slope of the curve was taken as 8 μmol/min · g. This value was one-twentieth of the initial activity of Mo-C-4 for methanation. The molybdenum carbide was therefore considered to act as a catalyst and not as an intermediate of methanation.

Figure 6 shows the increase in activity with increasing amount of carbon incorporated into the metal with the mixture of C_3H_8 and H_2. The C/Mo ratio required to obtain the highest activity was about 0.35, supporting Sinfelt and Yates' suggestion that the properties of the surface may depend on the nature of the underlying structure (*5*).

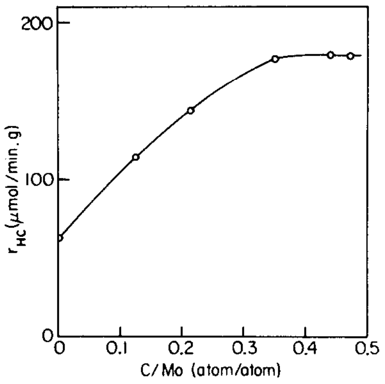

FIG. 6. Initial activity of carbided molybdenum as a function of carbon content.

The activity for methanation of the nitride, shown in Fig. 7, gradually increased during the first 5 h and then slowly decreased. The amount of carbon in the sample increased slowly with time, and the nitrogen content decreased slowly. X-Ray diffraction pattern for the sample showed no change before and after the reaction.

The C_2/C_1 and C_3/C_1 ratios were slightly smaller than those for Mo metal, and these ratios decreased with time. The activity of Mo-N for water-gas-shift reaction was higher than that for methanation.

The removal of nitrogen from Mo-N by H_2 was studied in the flow system. The amount of N removed from Mo-N was

TABLE 2

Stability of Molybdenum Carbide and Nitride at 1 atm

Mo-C-4				Mo-N			
Temperature (°C)	Time (h)	C/Mo (atom/atom)	Surface area (m^2/g)	Temperature (°C)	Time (h)	N/Mo (atom/atom)	Surface area (m^2/g)
—	—	0.45	7.0	—	—	0.61	7.0
350	5	0.45	7.0	300	5	0.59	7.3
350	17	0.45	7.0	350	5	0.56	7.4
400	5	0.45	7.0	350	17	0.55	7.5
500	5	0.44	7.0	400	5	0.51	7.7
600	5	0.43	6.7	500	5	0.42	8.0
650	5	0.41	6.4	600	5	0.27	8.3

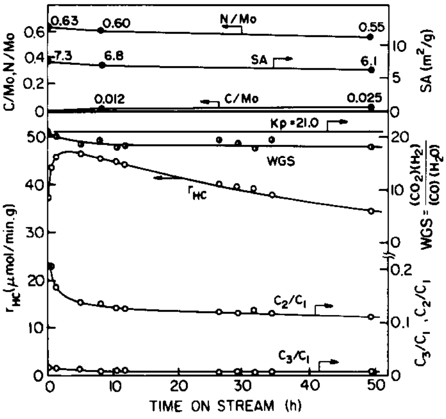

FIG. 7. Methanation on molybdenum nitride at 1 atm and 350°C. See legend of Fig. 2.

determined from the weight decrease of the sample as shown in Table 2. The molybdenum nitride was less stable in H_2 than the carbide; however, compared with carbides and nitrides of iron, the molybdenum compounds are very stable.

The activities of unsupported iron and nickel were examined at 350°C for comparison with the activities of the molybdenum compounds. The activity of the iron for methanation, Fig. 8, decreased so sharply during the first hour that its initial activity could not be determined. The activity dropped to a minimum at 1 to 2 h and then increased slightly to a constant value. The carbon content (C/Fe) of the sample after 38 h was 0.81, and X-ray diffraction for this sample indicated the presence of χ-Fe_2C (Hägg carbide) and α-Fe. The stable activity might have resulted from χ-Fe_2C. The total surface area of the sample more than doubled during the methanation, probably due to the area of elemental carbon deposited on the catalyst. The C/Fe ratio of 0.81 exceeds that of Hägg carbide substantially. The C_2/C_1 and C_3/C_1 ratios and the WGS value also decreased as sharply as the activity for methanation.

The activity of the nickel, Fig. 9, decreased with time, but more slowly than that of the iron. Its initial activity expressed in μmole per minute gram was about three times that of Mo-C-4. Both the C_2/C_1 ratio in the product gas and the activity for water-gas-shift reaction were the smallest of all of the catalysts studied.

Table 3 summarizes initial rates and selectivities from this study and values from the literature. Rates are also given after 20 h; metallic Mo and the carbide lost activity rapidly. Recently, the turnover number, defined as molecules formed (or reacted) per active site per second, has been used as a measure of catalyst activity. The number of active sites was determined by chemisorption of CO or H_2. The specific rates, defined as μmole of CO converted to hy-

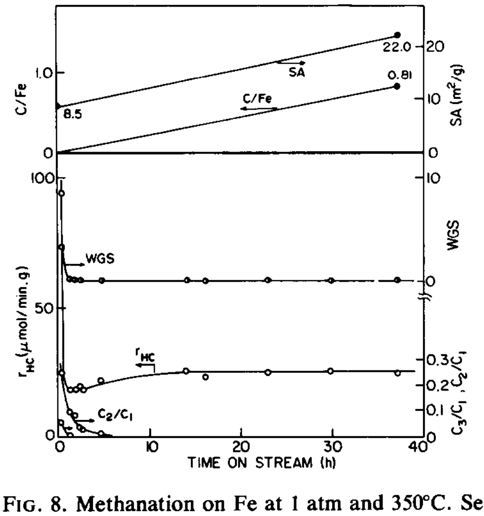

FIG. 8. Methanation on Fe at 1 atm and 350°C. See legend of Fig. 2.

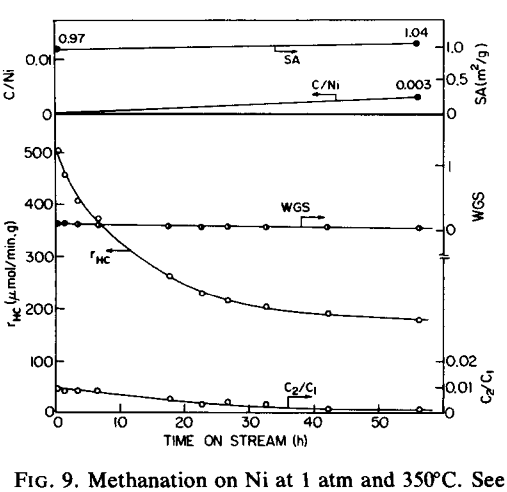

FIG. 9. Methanation on Ni at 1 atm and 350°C. See legend of Fig. 2.

TABLE 3

Catalytic Properties of Various Mo Compounds, Ni, and Fe

Catalyst	Initial surface area (m^2/g)	Rate ($\mu mol/min \cdot g$)		Initial specific rate[a] ($\mu mol/min \cdot m^2$)	Initial turnover number ($s^{-1} \times 10^3$)		Initial distribution of hydrocarbons produced		$WGS = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$[d]	$(r_{HC})_1/(r_{HC})_3$[e]
		Initial	After 20 h		I[b]	II[c]	C_2/C_1	C_3/C_1		
MoO_3	1.6	0	0	0	0	0		—	—	—
MoO_2	70.7	45.9	40	0.65	4.3	35.8	0.06	0.01	20.0	1.23
MoS_2	23.0	7.9	6	0.34	2.0	12.2	0.04	0	0.3	1.11
Mo	7.5	61.5	28	8.20	39.4	51.8	0.26	0.04	21.0	1.08
Mo-C-1	6.6	0	0	0	0	0	—	—	—	—
Mo-C-2	7.3	0	0	0	0	0	—	—	—	—
Mo-C-3	6.8	95.2		14.0	—	—	0.24	0.04	15.8	—
Mo-C-4	7.3	181	10	24.8	82.9	112	0.16	0.02	18.5	0.98
Mo-N	7.3	37.4	42	5.12	13.2	21.8	0.21	0.02	21.3	1.28
Fe	0.97	504	245	520	—	369	0.01	0	0.1	0.70
Fe	8.5	>93.5	24	>11.0	>33	>25	>0.25	>0.05	>3.4	≈0.5
Ni	1.0 or 2.3[f]	970		420 or 970[f]	637[f]	273[f]	0.1[g]	0.0[g]	—	0.63[f]
5%Fe/SiO_2	0.1 or 1.0[f]	2800		2.8×10^3 or 2.8×10^4[f]	17×10^3[f]	1.7×10^3[f]	0.25[h]	0.22[h]	—	0.60[f]

[a] The rate of hydrocarbon formation per unit surface area of catalyst at 350°C, 1 atm, and $H_2/CO = 3.1$.

[b] Based on CO chemisorption.

[c] Based on H_2 chemisorption.

[d] K_p for water-gas-shift reaction at 350°C is 21.0.

[e] The ratio of the rate of hydrocarbon formation for $1H_2 + 1CO$ gas to the rate for $3H_2 + 1CO$.

[f] Calculated from Vannice's data (*10–12*).

[g] At 229°C.

[h] At 275°C.

drocarbons per unit surface area of the catalyst per minute, are presented along with turnover numbers in Table 3. The MoO and the MoS had larger surface areas than the other molybdenum compounds, but their specific rates and turnover numbers were smaller than those of Mo metal. The specific rates and the turnover numbers based on CO uptakes for the zero-valent molybdenum compounds were greater than those for the other molybdenum compounds with the exception of Mo-C-1 and Mo-C-2 which had zero activity. Although Mo-C-4 had the highest activity of our molybdenum catalysts, its specific rate was one-twentieth and its turnover number was one-third of that of metallic nickel. The turnover number of our nickel was 35% greater than that of the nickel of Vannice (*11*), as calculated from the kinetic equation of Vannice. This agreement seems satisfactory. In the present study, the initial activity of the iron could not be determined because of its rapid deactivation. On the basis of Vannice's data (*12*), the turnover number of 5% Fe/SiO_2 at 350°C was calculated to be 1.7 or 17 s^{-1}.

The specific rates and the turnover numbers based on CO chemisorption for the catalysts used, except for iron, decreased in the following sequence:

$$\text{Ni} > \text{Mo-C-4} > \text{Mo} > \text{Mo-N} > \text{MoO}_2 > \text{MoS}_2 > \text{MoO}_3.$$

The sequence of the turnover numbers based on H_2 chemisorption is different from that based on CO chemisorption because H_2 uptakes by MoO_2 and MoS_2 were much smaller than CO uptakes.

The activities of all the catalysts except MoO_2 decreased with time as previously described. The rate of aging, loss of activity for methanation, decreased in the following order:

$$\text{Fe} > \text{Mo-C-4} > \text{Mo-C-3} > \text{Mo} > \text{Ni} > \text{MoS}_2 \simeq \text{Mo-N} > \text{MoO}_2.$$

The molybdenum catalysts, especially those of zero valence, produced modest amounts of higher hydrocarbons, about the same as the iron catalyst and significantly larger amounts of C_2^+ than nickel. The molybdenum compounds except MoS_2 and MoO_3 had higher activities for the water-gas-shift reaction than nickel and iron.

The last column of Table 3 gives the ratio of the rate of hydrocarbon production from feed gas mixture of $1CO + 1H_2$ to that from the mixture of $1CO + 3.1H_2$. The ratio for the molybdenum compounds ranges from 0.96 to 1.28, whereas the ratios for the nickel and the iron are 0.70 and 0.5, respectively. The ratios for the nickel and the 5% Fe/SiO_2 used by Vannice (*10, 11*) were calculated to be 0.63 and 0.60, respectively. The present results are also consistent with the data of Shultz *et al* (*1*) and suggest that the reaction kinetics for molybdenum catalysts are very different from those for the Group VIII metal catalysts.

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