JOURNAL OF CATALYSIS 67, 296–302 (1981)

The Activity of Several Molybdenum Compounds for the Methanation of CO_2

MASAHIRO SAITO[1] AND ROBERT B. ANDERSON

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

Received March 10, 1980; revised August 27, 1980

Several molybdenum compounds–oxides, sulfide, metal, carbide, and nitride—were prepared, and their catalytic properties in the hydrogenation of CO_2 at 350°C were investigated and compared with those of nickel and iron. The initial specific activities, rates per unit surface area of catalyst, decreased in the sequence Ni > Mo carbide > Mo metal > Mo nitride > MoO_2 > MoS_2 > MoO_3. Iron deactivated so rapidly that its initial activity could not be determined. The molybdenum compounds produced very much smaller amounts of C_2 and C_3 hydrocarbons in the hydrogenation of CO_2 than in that of CO. Iron produced the largest amount of higher hydrocarbons from CO_2, and Ni only CH_4. The molybdenum compounds, except MoS_2 and MoO_3, had high activities for water–gas-shift reaction.

INTRODUCTION

The previous paper (*1*) described the preparation of a number of molybdenum compounds—oxides, sulfide, metal, carbide, and nitride—and their catalytic properties in the hydrogenation of CO at 350°C and 1 atm, and compared them with nickel and iron. In the present study, the same molybdenum preparations and nickel and iron were used in the hydrogenation of CO_2. The results for the reactions of CO and CO_2 are compared.

EXPERIMENTAL

The flow system of the previous study (*1*) was used for the pretreatment of catalyst samples and also for the methanation studies. The hydrogenation of CO_2 was studied at 350°C and 1 atm. The surface area of each sample was measured by the physical adsorption of nitrogen at −195°C using a sorptometer. Phases present in the samples were identified by powder X-ray diffraction. Carbon and sulfur in the samples were determined by Leco analyzers and nitrogen by the Kjeldahl method.

Catalyst samples were prepared by the methods given in our previous paper (*1*). A new set of catalysts was prepared for the present work; however, powder X-ray diffraction indicated the same phases as those reported in Table 1 of the previous paper (*1*) and the surface areas and chemisorptions of H_2 and CO were about the same as those reported previously, as shown in Table 1. The $3.7H_2 + 1CO_2$ synthesis gas was furnished premixed in a cylinder by Matheson of Canada.

RESULTS AND DISCUSSION

The activity of MoO_3 was negligible. Figure 1 shows the activity of MoO_2 for methanation of CO_2. The activity is expressed as the conversion of CO_2 to C_1–C_3 hydrocarbons, X_{HC}, and as the rate of formation of hydrocarbons, r_{HC}, which was calculated by $r_{HC} = X_{HC}F/W$, where F is the feed rate of CO_2 (moles per minute) and W is the weight of the catalyst (grams). The activity decreased slightly with time on stream, while the concentration of oxygen and carbon and the surface area changed very little. The initial activity for CO_2 methanation was about one-fifth of that for CO methanation. The ratio of C_2/C_1 in the CO_2

---

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

0021-9517/81/020296-07$02.00/0

TABLE 1

Compositions 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 = 1.91	MoO_2, MoO(?)	75.0	192.	11.5
MoS_2	S/Mo = 2.0	MoS_2(broad)	20.4	58.4	4.9
Mo	—	Mo	7.2	24.6	9.3
Mo-C-4	C/Mo = 0.44	Mo_2C, Mo(trace)	7.0	35.0	12.9
Mo-N	N/Mo = 0.60	γ-Mo_2N, Mo(trace)	6.8	43.2	13.2
Ni	—	Ni	1.2	—	14.1
Fe	—	α-Fe	8.0	44.7[a]	28.9

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

methanation was about one-sixth of that in CO methanation. The reverse water-gas-shift reaction occurred simultaneously with methanation. The WGS value, defined as

$$p_{CO_2} \times p_{H_2} / (p_{CO} \times p_{H_2O}),$$

was used as a measure of the approach to equilibrium. The activity for water-gas shift was expressed by the conversion of CO_2 to CO, X_W, and by the rate of formation of CO, r_W, obtained from $r_W = X_W F/W$. However, r_W may give incorrect values when X_W is greater than 20% of the equilibrium conversion of the water-gas shift. When no methanation takes place, the equilibrium conversion of CO_2 to CO by the reverse shift is 33% for the present reaction conditions. The WGS value and X_W were near the equilibrium value, indicating that MoO_2 had a much higher activity for water-gas shift than for methanation of CO_2.

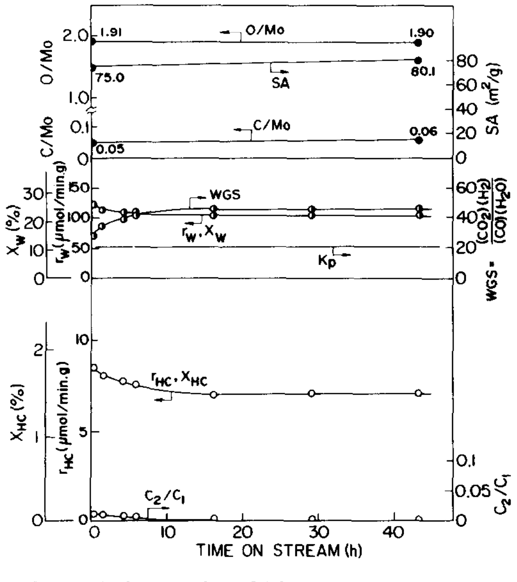

FIG. 1. Hydrogenation of CO_2 on MoO_2 at 350°C and 1 atm, using 3.7 H_2 + 1 CO_2 feed. W/F = 2110 g·min/mol.

MoS_2 had a lower activity than MoO_2 for hydrogenation of CO_2. Its activity changed slightly during the reaction, as shown inFig. 2, but the sulfur content and surface area remained constant. The activity of MoS_2 for CO_2 methanation was one-seventh of that for CO methanation, and no higher hydrocarbons were produced in CO_2 methanation. The activity of MoS_2 for the water-gas shift was also very much smaller than that of MoO_2.

Figure 3 shows that the activity of Mo metal for CO_2 methanation increased with time and reached a constant value in 30 hr at about twice its initial value. Although the carbon content increased substantially during methanation, the X-ray diffraction pattern did not change. The initial activity of Mo metal for CO_2 methanation was 1/16th

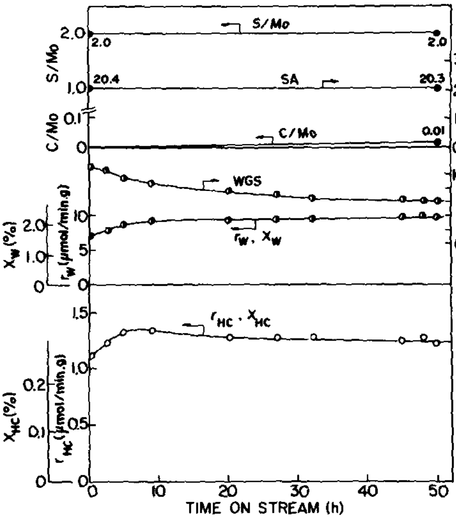

FIG. 2. Hydrogenation of CO_2 on MoS_2 at 350°C and 1 atm, using $3.7 H_2 + 1 CO_2$ feed. $W/F = 2310 g \cdot min/mol$.

of that for CO methanation. The C_2/C_1 ratio increased slightly with time, but was about 1/20th of that for CO methanation. The activity for water–gas shift also increased with time, and was very much higher than that for CH_4 production. The molybdenum carbide Mo–C-4, prepared by carburization of the metal with a mixture of C_3H_8 and H_2 (Fig. 4), had the highest initial activity of all the molybdenum compounds in this study. The initial activity for CO_2 methanation was about one-fourth of that for CO methanation. The activity of Mo–C-4 decreased sharply with time, but the deactivation rate in CO_2 methanation was around one-tenth of that in CO methanation. The carbon content changed very little during methanation but the surface area decreased about 15%. The C_2/C_1 ratio in CO_2 methanation was about half of that in CO methanation, whereas the C_3/C_1 ratio in CO_2 methanation was about the same as that in CO methanation. The WGS value and X_W were near the equilibrium values.

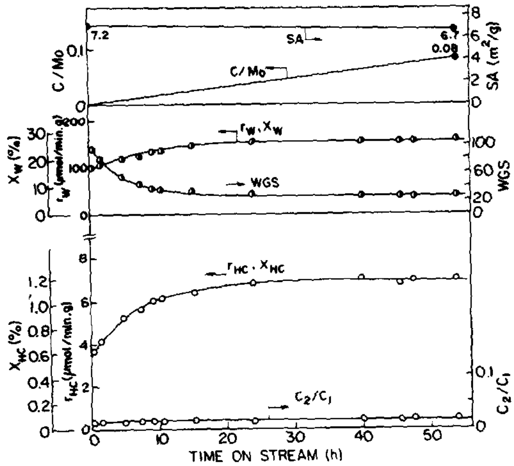

FIG. 3. Hydrogenation of CO_2 on Mo metal at 350°C and 1 atm, using $3.7 H_2 + 1 CO_2$ feed. $W/F = 1710 g \cdot min/mol$.

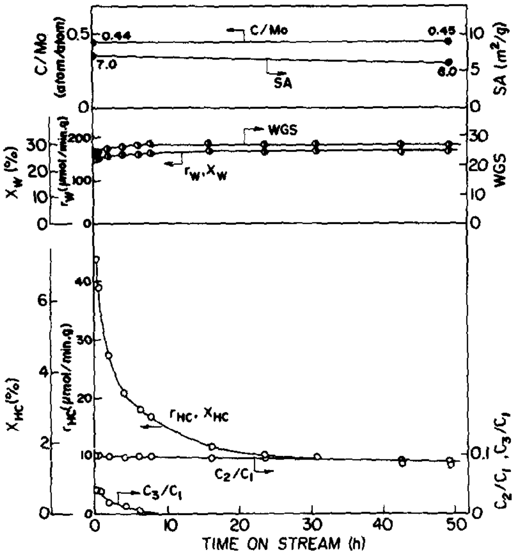

FIG. 4. Hydrogenation of CO_2 on molybdenum carbide, Mo–C-4, at 350°C and 1 atm, using $3.7 H_2 + 1 CO_2$ feed. $W/F = 1640 g \cdot min/mol$.

The activity of Mo–N in Fig. 5 increased with time to a constant value at 25 hr; this pattern was similar to that for Mo metal. The surface area remained constant, but the nitrogen content decreased about 10% during methanation. The initial activity of Mo–N for CO_2 methanation was about 1/30th of that for CO methanation. No higher hydrocarbons were formed in CO_2 methanation, whereas both C_2 and C_3 hydrocarbons were formed in CO methanation. The WGS value for Mo–N and X_W remained nearly constant at 68 and 19%, respectively; the activity of Mo–N for water–gas-shift reaction was very much higher

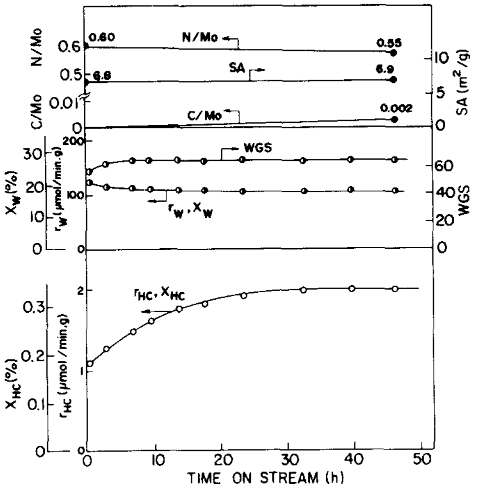

FIG. 5. Hydrogenation of CO_2 on molybdenum nitride at 350°C and 1 atm, using $3.7 H_2 + 1 CO_2$ feed. $W/F = 1690$ g·min/mol.

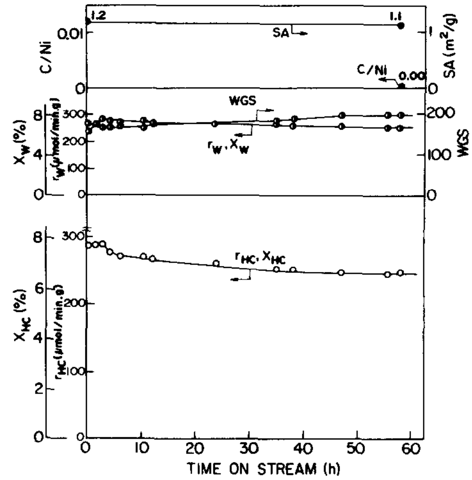

FIG. 7. Hydrogenation of CO_2 on Ni at 350°C and 1 atm, using $3.7 H_2 + 1 CO_2$ feed. $W/F = 269$ g · min/mol.

than that for CO_2 methanation.

The activities of unsupported iron and nickel for CO_2 methanation were examined for comparison with the activities of the molybdenum compounds, and also with the activities of the iron and the nickel for CO methanation. The results for iron are shown in Fig. 6, and data for nickel in Fig. 7.

For iron the patterns of changes in the activities for methanation and for the water–gas shift and in the C_2/C_1 and C_3/C_1 ratios in CO_2 methanation were very similar to those in CO methanation; however, the initial values could not be determined because of the rapid deactivation of the iron. The steady-state activity for CO_2 methanation was 80% of that for CO methanation, and the initial C_2/C_1 and C_3/C_1 ratios in CO_2 methanation were about the same as those in CO methanation. The carbon content (C/Fe) of the sample after 48 hr was 0.76, 90% of that in CO methanation, and χ-Fe_2C (Hägg carbide) and α-Fe were detected in the sample by X-ray diffraction. The total surface area of the sample increased as much as in CO methanation, probably due to the area of elemental carbon deposited on the catalyst.

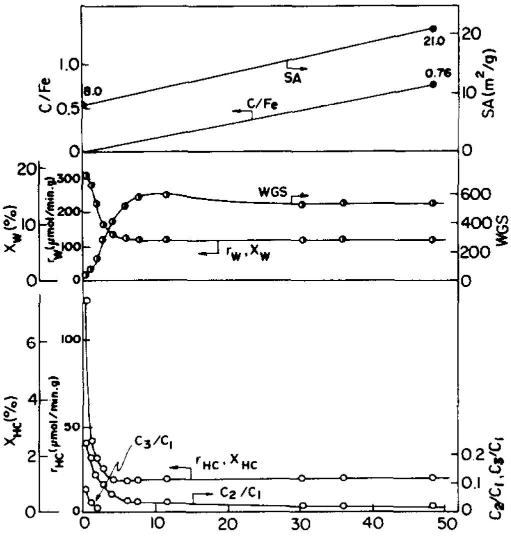

FIG. 6. Hydrogenation of CO_2 on Fe at 350°C and 1 atm, using $3.7 H_2 + 1 CO_2$ feed. $W/F = 608$ g·min/mol.

The activity of the nickel did not decrease as sharply as in CO methanation; the activity at 50 hr was 10% higher than that in CO methanation. The amount of carbon deposited during 58 hr was negligible. These results may support Anderson's suggestion that methanation of CO_2 may have advantages such as longer catalyst life, because many deleterious processes affecting catalyst performance seem attributable to the presence of CO, such as formation of

TABLE 2

Catalytic Properties of Various Mo Compounds, Ni and Fe

Catalyst	Surface area (m^2/g)	Initial rate ($\mu mol/min \cdot g$)	Specific rate[a] ($\mu mol/min \cdot m^2$)	Turnover number ($sec^{-1} \times 10^3$)		Distribution of hydrocarbons produced		Conversion of CO_2 to CO (X_W)[d] (%)	Rate of CO formation (r_W) ($\mu mol/min \cdot g$)	WGS[e]
				I[b]	II[c]	C_2/C_1	C_3/C_1			
MoO_3	1.6	0.0	0.0	0.0	0.0	—	—	0.0	0.0	—
MoO_2	75.0	8.5	0.11	0.74	6.2	0.01	0.00	26.0	123.	28.2
MoS_2	20.4	1.1	0.05	0.31	1.9	0.00	0.00	1.6	7.0	10,800.
Mo	7.2	3.6	0.50	2.4	3.2	0.01	0.00	17.0	99.4	96.5
Mo–C-4	7.0	43.8	6.26	20.9	28.3	0.10	0.04	23.8	145.	24.3
Mo–N	6.8	1.1	0.16	0.42	0.69	0.00	0.00	20.6	122.	57.2
Ni	1.2	285.	238.	—	168.	0.00	0.00	6.3	235.	180.
Fe	8.0	>143.	>17.9	>53.3	>41.2	>0.24	>0.08	>18.7	>308.	>51.4

[a] The initial rate of hydrocarbon formation per unit surface area of catalyst at 350°C, 1 atm, and $H_2/CO_2 = 3.74$.

[b] Based on CO chemisorption.

[c] Based on H_2 chemisorption.

[d] When no hydrocarbon formation takes place, the equilibrium conversion of CO_2 to CO by the water–gas-shift reaction at 350°C is 33.03%.

[e] $WGS = (CO_2)(H_2)/(CO)(H_2O)$. At equilibrium at 350°C, WGS = 21.0.

elemental carbon, nickel carbide, and nickel carbonyl (*2*). No higher hydrocarbons were produced in CO_2 methanation on Ni. r_{HC} and r_W were about equal.

The data obtained in this study are summarized in Table 2. The MoO_2 and the MoS_2 had larger surface areas than the other molybdenum compounds, but their specific rates and turnover numbers were less than those of the Mo metal. The specific activities of the catalysts used, except for iron, decreased in the sequence,

$$\text{Ni} > \text{Mo–C-4} > \text{Mo} > \text{Mo–N} > MoO_2 > MoS_2 > MoO_3.$$

Iron probably should be placed between Ni and Mo–C-4 in the order of activity. The molybdenum compounds produced much smaller amounts of C_2 and C_3 hydrocarbons in CO_2 methanation than in CO methanation. Only methane was formed from CO_2 on the nickel catalyst. Iron produced the largest amounts of C_2 and C_3 hydrocarbons of all the catalysts used. The molybdenum compounds, except for MoS_2 and MoO_3, were very active for the water–gas shift. In CO_2 methanation iron and nickel were as active as molybdenum compounds in the water–gas shift; however, in CO methanation Fe and Ni were less active in the water–gas shift.

The data on the hydrogenations of CO_2 and CO (*1*) are compared in Table 3; the main observations are:

(a) All of the catalysts hydrogenated CO_2 less rapidly than CO and they produced smaller amounts of higher hydrocarbons from CO_2 than from CO. Apparently a moderate concentration of CO in the gas phase is a requisite for production of substantial amounts of higher hydrocarbons. Iron had the largest tendency for producing higher hydrocarbons and nickel the least.

(b) Molybdenum carbide had the largest initial activity of the molybdenum catalysts studied and produced the largest yields of higher hydrocarbons. MoO_3 had the lowest activity. The carbide lost activity rapidly in the first few hours of synthesis.

TABLE 3

Comparison of Results for Hydrogenations of CO_2 and CO

Catalyst	$3.7\ H_2 + 1\ CO_2$							$3.1\ H_2 + 1\ CO$						
	Initial				After 10 hr			Initial				After 10 hr		
	Rate (μmol/min · g)	Specific rate[a] (μmol/min · m^2)	$\frac{C_2 + C_3}{C_1}$[b]	WGS[c]	Rate (μmol/min · g)	$\frac{C_2 + C_3}{C_1}$[b]	WGS[c]	Rate (μmol/min · g)	Specific rate[a] (μmol/min · m^2)	$\frac{C_2 + C_3}{C_1}$[b]	WGS[c]	Rate (μmol/min · g)	$\frac{C_2 + C_3}{C_1}$[b]	WGS[c]
MoO_2	8.5	0.11	0.01	28.2	7.0	0.00	44	45.9	0.65	0.07	20.0	45.9	0.07	20
MoS_2	1.1	0.05	0.00	10,800.0	1.3	0.00	8500	7.9	0.34	0.04	0.3	6.2	0.06	0.3
Mo	3.6	0.50	0.01	96.5	6.2	0.02	39	61.5	8.20	0.30	21.0	37.0	0.18	18
Mo–C-4	43.8	6.26	0.14	24.3	15.0	0.10	27	181.0	24.8	0.18	18.5	15.0	0.21	13
Mo–N	1.1	0.16	0.00	57.2	1.6	0.00	65	37.4	5.12	0.23	21.3	44.0	0.14	18
Ni	285.0	238.0	0.00	180.0	265.0	0.00	168	504.0	520.0	0.01	0.1	325.0	0.01	0.1
Fe	>143.0	>17.9	>0.32	<51.4	20.0	0.03	600	>93.0	>11.0	>0.30	>3.4	24.0	0.00	0.0

[a] The initial rate of hydrocarbon formation per unit surface area of catalyst at 350°C and 1 atm.

[b] Distribution of hydrocarbons produced.

[c] $WGS = (CO_2)(H_2)/(CO)(H_2O)$. At equilibrium at 350°C, WGS = 21.0.

(c) The oxide, nitride, and metallic molybdenum had modest and relatively constant activity. Iron deactivated rapidly in the methanation reactions of both CO and CO_2. Iron catalysts usually do not perform properly in tests at atmospheric pressure (*3*). The activity of nickel was more stable in the hydrogenation of CO_2 than in that of CO, as has been observed before (*2*).

(d) Molybdenum catalysts, except MoS_2 and MoO_3, were active in the water–gas shift; their activities for the water–gas shift were larger than those for synthesis reactions. Iron and nickel were active for the reverse water–gas shift in CO_2 methanation, but were not very active in the forward-shift reaction in CO methanation.

(e) Molybdenum compounds were as active in $1H_2 + 1CO$ as in $3H_2 + 1CO$ feed, but Ni and Fe were substantially less active in a CO-rich gas.

The present paper shows that molybdenum catalysts have a modest activity in methanation reactions at 350°C and produce small amounts of higher hydrocarbons, confirming the results of an earlier study (*4*).

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of this study by Energy, Mines and Resources, Canada, and thank Dr. D. B. Shah and Mr. C. B. Lee for helpful discussions.

REFERENCES

1. Saito, M., and Anderson, R. B., *J. Catal.* **63**, 438 (1980).
2. Anderson, R. B., Lee, C. B., and Machiels, J. C., *Canad. J. Chem. Eng.* **54**, 590 (1976).
3. Storch, H. H., Golumbic, N., and Anderson, R. B., "The Fischer–Tropsch and Related Syntheses," p. 223, Wiley, New York, 1951.
4. Shultz, J. F., Karn, F. S., and Anderson, R. "U. S. Bureau of Mines Report of Investigation 6974," 1967.