

Kinetics of reverse water gas shift (RWGS) reaction on metal disulfide catalysts

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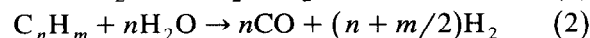
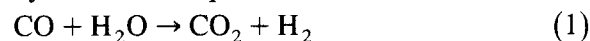
Abstract

The hydrogenation of CO₂ was studied on disulfides of molybdenum and tungsten by comparison with that on the group VIII metals of Fe, Co, and Ni supported on Al₂O₃. The hydrogenation activity was lower on the disulfides on a per active site of catalyst basis than on the transition metals, however, the selective reverse water gas shift (RWGS) reaction (CO₂ + H₂ → CO + H₂O) was observed on the disulfides. The selectivity was close to ca. 100% in the reaction conditions examined. The rate was expressed by the equation: $r = kP_{\text{CO}_2}^{0.61-0.73}P_{\text{H}_2}^{0.36}$ on the disulfides, and the activation energy was ca. 18.0–19.1 kcal mol⁻¹. The disulfides exhibited little activities for the hydrogenation of CO (viz. CO + 3H₂ → CH₄ + H₂O) and also for the disproportionation of CO (viz. 2CO → C + CO₂). These results were in contrast to those for the transition metals where high activities were observed for both reactions, suggesting that the retardation of C–O bond cleavage in the CO molecule produced by the CO₂ hydrogenation must be the cause for the selective hydrogenation of CO₂ to CO on the disulfides. The effect of supports on the hydrogenation of CO₂ was also investigated for MoS₂. The reaction rate on a per active site of catalyst basis was not influenced by the supports, suggesting that the CO₂–H₂ reaction is insensitive to the morphology of MoS₂ supported on metal oxides. © 1997 Elsevier Science B.V.

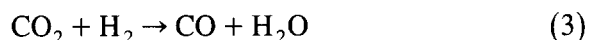
Keywords: Hydrogenation of CO₂; Reverse water gas shift; MoS₂; WS₂; Structure-insensitive

1. Introduction

The water gas shift (WGS) Eq. (1), the reaction of carbon monoxide and water to produce carbon dioxide and hydrogen, is frequently used in industries in conjunction with the production of pure hydrogen via the steam reforming of hydrocarbons Eq. (2):



On the other hand, the reverse water gas shift (RWGS) Eq. (3), the reaction of carbon dioxide and hydrogen to produce carbon monoxide and water, is also a reaction of considerable industrial importance:



The RWGS reaction technology is recently expected in industries in the production of valuable CO from cheap CO₂ using hydrogen. Carbon monoxide is valuable and necessary in many

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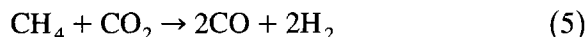
chemical companies. In the partial oxidation of asphalt, coal, and heavy oil, hydrogen is also produced with CO, however, it is not always utilized commercially.

The hydrogenation of CO₂ usually reaches the production of CH₄ on transition metal catalysts at atmospheric pressure [1–4]. It is considered that the methanation of CO₂ is the conversion of CO₂ to CO via the RWGS reaction, followed by the methanation of CO, viz.



Methane is less valuable than CO because methane is a stable molecule and its reactivity is very low, while CO is an important raw material for many chemicals such as formaldehyde, methanol, and acetic acid. The RWGS reaction may open a route for the production of valuable CO from CO₂ using hydrogen produced as a by-product. For such purpose, it is necessary to develop a high-performance catalyst for producing CO in the CO₂ hydrogenation.

Aside from the industrial requirement, our interest in the RWGS reaction grew out of the study of CO₂ reforming of methane to produce CO and H₂ Eq. (5):



The RWGS reaction can occur whenever CO₂ and H₂ are present in a reacting mixture. In the CO₂ reforming of methane, the H₂ product easily reacts with CO₂ feed via the RWGS reaction and as a result, the H₂/CO ratio often becomes less than unity due to a contribution of the RWGS reaction [5].

The WGS and/or RWGS reactions are readily catalyzed by both metals and metal oxides. Prichard and Hinshelwood studied the kinetics of the RWGS reaction over platinum in 1925 [6]. For both WGS and RWGS reactions, Amenomiya investigated the kinetics of the reactions by using infrared spectroscopy, and was able to identify the presence of formate ion in both reactions [7,8]. He concluded that the formate ion was an intermediate in the reaction, viz. depending on the direction of the WGS

reaction, formate ion is decomposed into either CO₂ and H₂ or CO and H₂O. Thus, many studies on the kinetics of WGS and/or RWGS reactions on metals or metal oxides were reported [9–13], however, only a few studies were focused on the WGS and/or RWGS reactions over metal sulfide catalysts [14]. The metal sulfides would be durable against sulfur atom involved in coal, heavy oil, and asphalt. In the present paper, a detailed study of specific activity, selectivity, and dependence of reaction rate on partial pressures of both reactants for the hydrogenation of CO₂ over MoS₂ and WS₂ was made by comparing with that over Al₂O₃-supported Fe, Co, and Ni catalysts. In addition to this, the effect of supports on the hydrogenation of CO₂ was also studied for MoS₂.

2. Experimental

2.1. Characterization of molybdenum and tungsten disulfides

X-ray diffraction of the disulfides was measured using Rigaku RAD-1VC (CuKα, 30 kV, 30 mA). BET surface area of the disulfides was examined with an N₂ adsorption apparatus (Carlo Erba Sorptomatic 1800). Chemical analysis of the disulfides was carried out by use of a sulfur–carbon analyzer and an oxygen–nitrogen analyzer (LECO).

2.2. Catalyst preparation and reagents

The disulfides of molybdenum and tungsten were respectively prepared from (NH₄)₂MoS₄ and (NH₄)₂WS₄ (both from Aldrich, the purity; 99.97% and 99.9%, respectively) by decomposing them in a stream of hydrogen (20 ml min⁻¹) at 773 K for 2 h. Supported metal catalysts were prepared by impregnating an Al₂O₃ with an aqueous solution of Fe(NO₃)₂ · 6H₂O, Co(NO₃)₂ · 6H₂O, and Ni(NO₃)₂ · 6H₂O (Wako chemicals, the purity 99.0%, 97%, and 98%,

respectively). The alumina support, a reference catalyst (JRC-ALO-4; the purity, Fe_2O_3 : 0.01%, SiO_2 : 0.01%, and Na_2O : 0.01%; the surface area, $177 \text{ m}^2 \text{ g}^{-1}$) supplied by The Catalyst Society of Japan, was used by crashing it to 300–500 nm fragments prior to impregnation. The impregnated samples were dried at 383 K for 24 h followed by being calcined at 773 K for 3 h. Before use, the catalysts were reduced in a hydrogen stream (20 ml min^{-1}) at 773 K for 2 h. The metal loading was 20 wt%.

Supported MoS_2 catalysts were prepared as follows: the metal oxides (Al_2O_3 , TiO_2 , SiO_2 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, MgO , HY-zeorite, and H-mordenite; supplied by The Catalyst Society of Japan) were impregnated with an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, followed by being dried and subsequently being calcined at 773 K for 3 h. The MoO_3 loading on a metal oxide was 20 wt%. Then, a mixture of H_2S and H_2 diluted by N_2 ($\text{H}_2\text{S}:\text{H}_2:\text{N}_2 = 2.5:50:47.5$, 40 ml min^{-1}) was flowed over the supported molybdenum trioxides at 673 K for 3 h.

Hydrogen (99.999%) was purified by passage through a silica gel column after converting a very small amount of oxygen present (less than 1 ppm) to water. Helium (99.995%) was also purified by passing through a gas-purifier (Japan Pure Hydrogen, MCN-005) to remove oxygen, and then through a molecular sieve trap to remove water. CO_2 (ca. 99.9%) was used without further purification.

2.3. Steady state $\text{H}_2\text{-CO}_2$ reaction

The hydrogenation of CO_2 was investigated in a conventional flow apparatus operating at atmospheric pressure. The reactor, made of a 4 mm i.d. quartz tube, contained a packed bed consisting of a catalyst and quartz glass wool. Before admitting $\text{H}_2\text{-CO}_2$ gases, the catalyst was reduced with hydrogen under the conditions described above. After the reduction, a mixture of CO_2 and H_2 was introduced to the catalyst at a constant flow rate. The reactions were carried out under the conditions of a differential reac-

tor. After steady state, the products were analyzed by a gaschromatography (Shimadzu GC 8A) with a thermal conductivity detector using active carbon as the separation column.

2.4. CO and NO chemisorption

Chemisorption behavior of CO onto the disulfides prepared from the ammonium compounds and also onto the transition metals was investigated by a pulse technique using helium as a carrier gas. After reducing the catalyst in a stream of hydrogen followed by purging with helium, a constant volume of CO (0.54 ml) was pulsed onto the catalyst in helium carrier gas (30 ml min^{-1}) at 298 K for several times.

Chemisorption behavior of NO onto the supported MoS_2 catalysts was also examined by a pulse method using helium as a carrier gas. After preparing the supported MoS_2 catalysts according to the method described above, a constant volume of NO (1.22 ml) was pulsed onto the catalysts in helium carrier gas (40 ml min^{-1}) at 298 K for several times.

2.5. CO hydrogenation and CO disproportionation

Hydrogenation of CO was investigated by a pulse method. After reducing the catalyst with hydrogen, a constant volume of CO (0.54 ml) was pulsed onto the catalyst in hydrogen carrier gas (30 ml min^{-1}). The reaction was carried out in the temperature range 523–673 K, and the effluent gases were analyzed by a gaschromatography (Shimadzu, GC-3BT) with a thermal conductivity detector. Active carbon was used for the separation column.

Disproportionation of CO was investigated in helium carrier gas. After the reduction of a catalyst, helium was admitted into the reactor at a constant flow rate (30 ml min^{-1}). After the steady state, a constant volume of CO (0.54 ml) was pulsed onto the catalyst via the helium carrier gas, and the effluent gases containing CO and CO_2 were analyzed by a gaschromatog-

raphy (Shimadzu, GC-3BT). Active carbon was used for the separation column.

3. Results

3.1. Characterization of metal disulfides

The metal sulfide catalysts prepared from their ammonium precursors showed broad diffraction peaks, and their diffraction patterns could be assigned to those for MoS_2 and WS_2 , respectively. Chemical analysis also showed that the ratio, S/M (M = Mo or W), of the sulfides was 1.94 and 1.96 for MoS_2 and WS_2 , respectively. The BET surface area was 27.9 and 41.1 $\text{m}^2 \text{g}^{-1}$ for MoS_2 and WS_2 , respectively.

3.2. Activity and selectivity for H_2 - CO_2

The information about CO adsorption on the catalysts is shown in Table 1. As for the supported metal catalysts, the dispersion of the metals, the particle size of the metals calculated from the dispersion, and the crystallite size of the metals calculated from XRD peak-width are also shown for comparison. As appropriate for the metal catalysts, one chemisorbed CO molecular is assumed to be presented on one surface metal atom. In the same way, although precise active sites for the disulfides are not clearly identified, it is also assumed that one chemisorbed CO is presented on one surface active site of the disulfides.

Fig. 1 shows activities of the catalysts for H_2 - CO_2 reaction. The rates of CO_2 conversion,

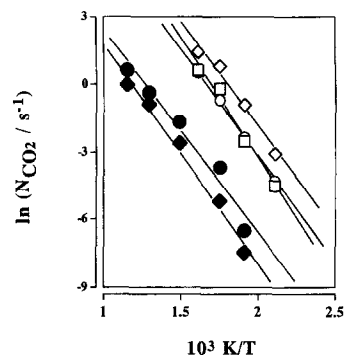


Fig. 1. Arrhenius plots of specific activities for the continuous flow reaction of CO_2 - H_2 ; ●: MoS_2 (100 mg), ◆: WS_2 (100 mg), □: $\text{Ni}/\text{Al}_2\text{O}_3$ (19.8 mg), ◇: $\text{Co}/\text{Al}_2\text{O}_3$ (19.9 mg) and ○: $\text{Fe}/\text{Al}_2\text{O}_3$ (19.7 mg); feed ratio: $\text{H}_2/\text{CO}_2 = 1$, total flow rate: 60 ml min^{-1} .

expressed as turnover frequency: $N_{\text{CO}_2}/\text{s}^{-1}$, are plotted in an Arrhenius fashion. As shown, (1) the disulfide catalysts exhibited lower activities than the metal catalysts, (2) among the metal catalysts, the activity order was $\text{Co}/\text{Al}_2\text{O}_3 > \text{Ni}/\text{Al}_2\text{O}_3 = \text{Fe}/\text{Al}_2\text{O}_3$, while (3) between the disulfides, the activity was a little higher for MoS_2 than for WS_2 . From the slopes of the straight lines, activation energies are calculated and are presented in Table 1. The activation energies on the disulfides are almost the same as those observed on the transition metals.

Fig. 2(a)–(e) show the effect of time factor (W/F) on the hydrogenation of CO_2 . As shown in Fig. 2(c)–(e), (i) the selectivity to CH_4 increased with increasing the W/F on the metal catalysts, while the selectivity to CO monotonically decreased with increasing the W/F , (ii)

Table 1
Characterization of catalysts and kinetic data for the hydrogenation of CO_2

Catalyst	BET surface area ($\text{m}^2 \text{g}^{-1}$)	CO adsorption ($\mu\text{mol g}^{-1}$)	Dispersion (%)	Particle size (dispersion) (nm)	Crystallite size (XRD) (nm)	Activation energy (kcal mol^{-1})	Reaction order	
							<i>a</i>	<i>b</i>
$\text{Ni}/\text{Al}_2\text{O}_3$	177 ^a	124.7	3.7	11.8	14.1	20.8	0.50	0.81
$\text{Co}/\text{Al}_2\text{O}_3$	177 ^a	55.1	1.67	24.2	17.1	18.4	0.51	0.59
$\text{Fe}/\text{Al}_2\text{O}_3$	177 ^a	24.9	0.71	61.5	21.1	18.7	1.10	0.37
MoS_2	27.9	15.0				18.0	0.73	0.36
WS_2	41.1	38.6				19.1	0.61	0.36

^a Surface area of supported metal catalysts was substitute for that of Al_2O_3 support.

the selectivity to CH_4 was the highest on $\text{Ni}/\text{Al}_2\text{O}_3$ while it was the lowest on $\text{Fe}/\text{Al}_2\text{O}_3$, on the contrary, the selectivity to CO was the highest on $\text{Fe}/\text{Al}_2\text{O}_3$ while it was

the lowest on $\text{Ni}/\text{Al}_2\text{O}_3$. (iii) On the disulfide catalysts, the selectivity to CO was more than 99.5% in all the W/F examined, and it was scarcely decreased by increasing the W/F as

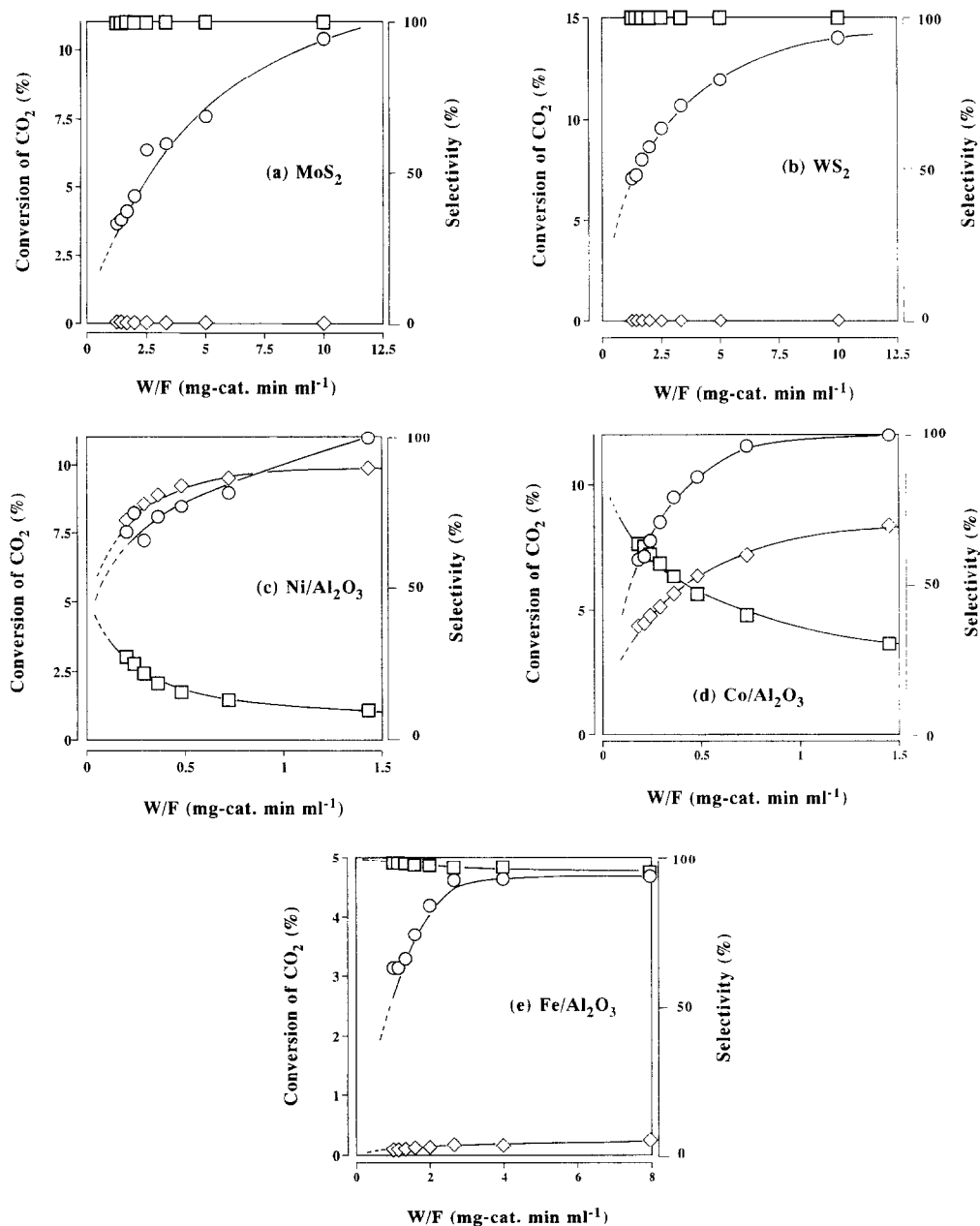


Fig. 2. Influence of W/F upon conversion of CO_2 (\circ) and selectivity to CO (\square) and CH_4 (\diamond); reaction temperature: 773 K for MoS_2 and WS_2 , 573 K for $\text{Ni}/\text{Al}_2\text{O}_3$, $\text{Co}/\text{Al}_2\text{O}_3$ and $\text{Fe}/\text{Al}_2\text{O}_3$; feed ratio: $\text{H}_2/\text{CO}_2 = 1$, total flow rate: $10\text{--}80\text{ ml min}^{-1}$; (a): MoS_2 (100 mg), (b): WS_2 (100 mg), (c): $\text{Ni}/\text{Al}_2\text{O}_3$ (14.3 mg), (d): $\text{Co}/\text{Al}_2\text{O}_3$ (14.5 mg) and (e): $\text{Fe}/\text{Al}_2\text{O}_3$ (79.6 mg).

shown in Fig. 2 (a)–(b). (iv) As a by-product, a small amount of CH_4 was detected for the disulfides.

Influence of CO_2/H_2 molar feed ratio upon the selectivity to CO was also investigated over the disulfides. Fig. 3(a), (b) illustrate both the conversion of CO_2 and the selectivity to CO and CH_4 as a function of $F[\text{CO}_2]/(F[\text{CO}_2] + F[\text{H}_2])$, where F (ml min^{-1}) is a feed rate for CO_2 and H_2 . The conversion of CO_2 increased with a decrease in the molar ratio of CO_2 , however, the selectivity to CO was not influenced by the feed ratio; viz. the selectivity was more than 99.2% in the molar ratio examined.

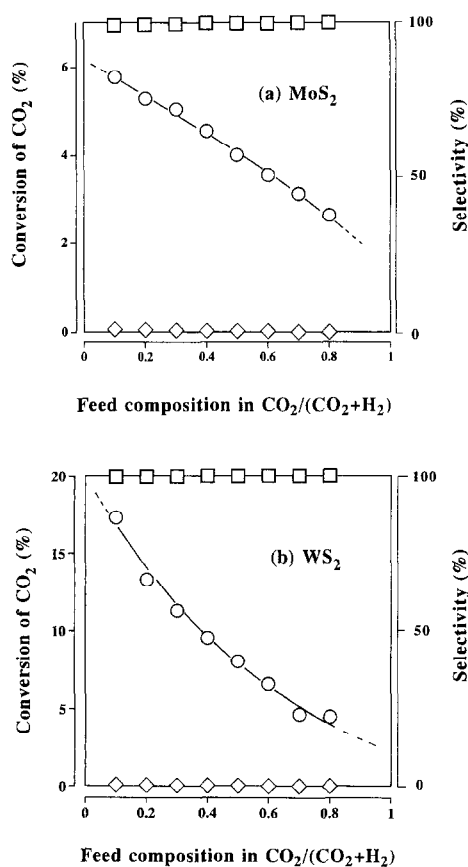


Fig. 3. Influence of feed composition upon CO_2 conversion (\circ) and selectivity to CO (\square) and CH_4 (\diamond) over MoS_2 (a) and WS_2 (b); reaction temperature: 773 K; catalyst weight: 100 mg; total flow rate of reactant mixture ($\text{CO}_2 + \text{H}_2$): 50 ml min^{-1} .

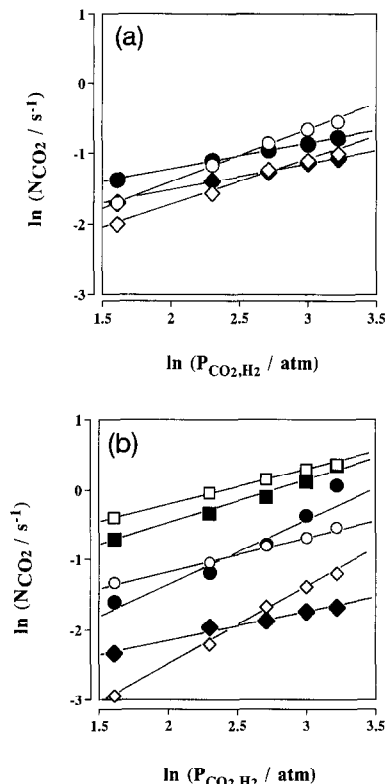


Fig. 4. (a) Dependence of reaction rate on partial pressures of CO_2 and H_2 on MoS_2 ($\bullet\circ$, 100 mg) and on WS_2 ($\blacklozenge\lozenge$, 100 mg); reaction temperature: 773 K; total flow rate: 40 ml min^{-1} ; partial pressure of both reactants, P_{CO_2} (or P_{H_2}), investigated was in the range 0.125–0.625 atm; closed symbols indicate $\ln N_{\text{CO}_2}/\text{s}^{-1}$ vs. $\ln P_{\text{H}_2}$, while open symbols indicate $\ln N_{\text{CO}_2}/\text{s}^{-1}$ vs. $\ln P_{\text{CO}_2}$. (b) Dependence of reaction rate on partial pressures of CO_2 and H_2 on $\text{Ni}/\text{Al}_2\text{O}_3$ ($\bullet\circ$, 19.4 mg), on $\text{Co}/\text{Al}_2\text{O}_3$ ($\blacksquare\square$, 19.5 mg) and on $\text{Fe}/\text{Al}_2\text{O}_3$ ($\blacklozenge\lozenge$, 79.3 mg); reaction temperature: 573 K; total flow rate: 40 ml min^{-1} ; partial pressure of both reactants, P_{CO_2} (or P_{H_2}), investigated was in the range 0.125–0.625 atm; closed symbols indicate $\ln N_{\text{CO}_2}/\text{s}^{-1}$ vs. $\ln P_{\text{H}_2}$, while open symbols indicate $\ln N_{\text{CO}_2}/\text{s}^{-1}$ vs. $\ln P_{\text{CO}_2}$.

3.3. Kinetics for $\text{CO}_2\text{--H}_2$ reaction

The dependence of reaction rate on the partial pressures of both reactants was investigated. Fig. 4 shows the rates of CO_2 conversion as a function of partial pressures of both CO_2 and H_2 . The rate for $\text{CO}_2\text{--H}_2$, $N_{\text{CO}_2}/\text{s}^{-1}$, is expressed by the following equation:

$$N_{\text{CO}_2}/\text{s}^{-1} = kP_{\text{CO}_2}^a P_{\text{H}_2}^b \quad (6)$$

where P_{CO_2} and P_{H_2} are the partial pressures of

CO₂ and H₂, respectively, and *a* and *b* are the reaction orders with respect to the partial pressures of CO₂ and H₂, respectively. From the slopes of the straight lines shown in Fig. 4, the reaction orders are calculated and are presented in Table 1. On all the catalysts, the orders are positive with respect to both reactants. The order is larger for the partial pressure of H₂ than for that of CO₂ on Ni/Al₂O₃ and Co/Al₂O₃. On the other hand, the order is larger for the partial pressure of CO₂ than for that of H₂ on Fe/Al₂O₃, MoS₂, and WS₂. On Fe/Al₂O₃ catalyst, the order with respect to CO₂ partial pressure is significantly large compared with that on other catalysts.

3.4. C–O bond breaking in CO molecule

Hydrogenation of CO was carried out on all the catalysts so that the activity for the subsequent hydrogenation of CO produced by the CO₂ hydrogenation could be revealed. The results are shown in Table 2. The activity for the CO hydrogenation was markedly lower on the disulfides than on the transition metals. The activity order on a per gram of catalyst basis was in the following: Co/Al₂O₃ > Ni/Al₂O₃ > Fe/Al₂O₃ >> WS₂ > MoS₂. The sequence of which seemed to be much related with the selectivity to CO in the CO₂ hydrogenation.

For comparing the ease of C–O bond breaking in CO molecular between on the transition metals and on the disulfides, the disproportiona-

Table 2
Hydrogenation and disproportionation of CO

Catalyst (catalyst weight)	Hydrogenation of CO (%)		Disproportionation of CO (%)
	573 K	623 K	
Ni/Al ₂ O ₃ (29.7 mg)	28.8	61.1	9.0 ^b
Co/Al ₂ O ₃ (29.9 mg)	42.8	95.0	
Fe/Al ₂ O ₃ (29.1 mg)	14.3	32.4	
MoS ₂ (100 mg)	0.06	0.11 ^a	
WS ₂ (100 mg)	0.11	0.54	0.36

^a At 673 K.

^b 50 mg.

Table 3
NO chemisorption behavior on supported MoS₂ catalysts

Supports ^a	Surface area (m ² g ⁻¹)	NO chemisorption number (μmol g ⁻¹)
Al ₂ O ₃ (JRC-ALO-4)	177	107.1
SiO ₂ (JRC-SIO-4)	347	55.2
TiO ₂ (JRC-TIO-3)	40	28.7
MgO (JRC-MGO-1)	55	59.7
SiO ₂ -Al ₂ O ₃ (JRC-SAL-2)	560	31.8
H-mordenite (JRC-Z-HM 10)	187	159.2
HY-zeorite (JRC-Z-HY 4.8)	663	14.7

^a JRC supports were supplied by The Catalyst Society of Japan.

tion of CO Eq. (7) was also investigated in helium carrier gas.



The disproportionation of CO (%) on Ni/Al₂O₃ and on WS₂ is shown in Table 2. The CO disproportionation is less marked on the disulfide than on the Ni/Al₂O₃. This is consistent with the results of the CO hydrogenation, for which the disulfides exhibited lower activities than the transition metals.

3.5. Effect of support on the CO₂ hydrogenation

The number of NO chemisorbed on the supported MoS₂ catalysts is presented in Table 3.

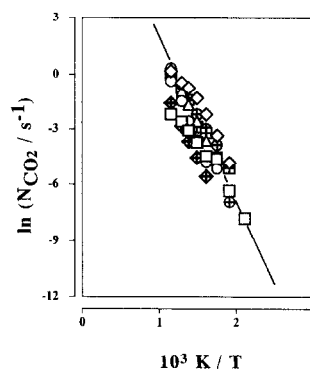


Fig. 5. Effect of support on the hydrogenation of CO₂ over MoS₂ catalysts; □: MoS₂/Al₂O₃, ◇: MoS₂/TiO₂, ○: MoS₂/SiO₂, △: MoS₂/SiO₂-Al₂O₃, ⬡: MoS₂/MgO, diamond with plus: MoS₂/H-mordenite, ⊕: MoS₂/HY-zeorite.

As shown, the number was in the range ca. 15–160 $\mu\text{mol g}^{-1}$ for the supported MoS_2 catalysts examined. Fig. 5 shows the effect of supports on the hydrogenation of CO_2 over the supported MoS_2 catalysts. The rates are shown on a per active site of catalyst basis. As shown, the rate for H_2 – CO_2 was not influenced by the supports. The activation energy was ca. 18.2 kcal mol^{-1} for all the supported MoS_2 catalysts examined.

4. Discussions

4.1. Suppression of C–O bond cleavage in CO produced by CO_2 hydrogenation

MoS_2 and WS_2 showed lower activities for the CO_2 – H_2 than the transition metals on a per active site of catalyst basis. However, the selective hydrogenation of CO_2 to CO was observed on the disulfides. The methanation of CO_2 was almost unobserved on the disulfides even if the contact time, W/F , increased. It is reported that the hydrogenation of both CO and CO_2 gives almost the same reaction rate and also the same activation energy on transition metals [2,15]. This indicates that both reactions proceed through a common intermediate species. The hydrogenation of CO to CH_4 must go through at least two steps; i.e., (i) C–O bond cleavage, and then (ii) hydrogenation of the surface carbon species.

In order to investigate the activity for the C–O bond cleavage in CO molecule, the hydrogenation of CO was carried out on the disulfides and was compared with that on the transition metals. The disulfides showed lower activities for the hydrogenation of CO than the transition metals. This strongly suggests that the subsequent hydrogenation of CO produced by the CO_2 hydrogenation is suppressed on the disulfides. The suppression of C–O bond breaking was also evidenced by the CO disproportionation, for which a significantly low activity was observed on the disulfide in contrast to on the transition metal catalyst.

The apparent activation energy on the transition metals examined in this study was within the range found by other authors [4,10]. The apparent activation energies on the disulfides were very close to those obtained on these transition metals. Although it was reported that a nonlinear relation was observed between $\ln N_{\text{CO}_2}/\text{s}^{-1}$ and $\ln P_{\text{H}_2}$ (or P_{CO_2}) for SiO_2 -supported Ni catalyst [2], the linear relationships were obtained for the transition metals and also for the disulfides under the present experimental conditions. From the dependence of reaction rate on the partial pressures of both reactants, the catalysts were classified for convenience into two groups; (a) Ni/ Al_2O_3 and Co/ Al_2O_3 , (b) Fe/ Al_2O_3 , MoS_2 , and WS_2 . On the former catalysts, the reaction order with respect to the partial pressure of CO_2 was smaller than that of H_2 , while the reaction order with respect to the partial pressure of H_2 was smaller than that of CO_2 on the latter catalysts. The methanation of CO_2 was marked on Ni and Co catalysts, while it was suppressed on Fe, MoS_2 , and WS_2 catalysts. Taking into account these results, it seems that moderately strong adsorption of H_2 rather than CO_2 gives a favorable condition for the hydrogenation of CO_2 to CO. In other words, for designing a catalyst for the selective conversion of CO_2 to CO, the catalyst surface should have a relatively strong affinity for H_2 rather than CO_2 so that the subsequent methanation of CO produced by the CO_2 hydrogenation would be suppressed. Further study is necessary for revealing the relation between the reaction orders and the selectivity to CO.

4.2. Insensitive to MoS_2 structure

The effect of supports on the hydrogenation of CO_2 was also investigated over the supported MoS_2 catalysts on the basis of rate per active site. It is reported for the supported metal catalysts that the turnover frequency (the rate per active site) is often dependent [11,12] or independent [13] on the particle size of the metals. The former is so-called ‘structure-sensitive’,

while the latter is the 'structure-insensitive' proposed by Boudart [14]. The structure-sensitive is caused by an increase of the collective atoms which are present on the top or the edge of the particle upon decreasing the particle size of the metal. The structure-sensitive is also observed on metal oxide or metal sulfide catalysts [15–19]. The striking result of our investigation is that the specific activity of the supported MoS₂ is independent on the nature of the supports as shown in Fig. 5. Since the surface active site of the supported MoS₂ varies by one order of magnitude, in the number range ca. 15–160 μmol g⁻¹ for the supported MoS₂ catalysts, almost the same specific activities observed for the H₂–CO₂ reaction suggest that the reaction is insensitive to the MoS₂ structure.

5. Conclusions

The hydrogenation of CO₂ on the disulfides of molybdenum and tungsten was investigated. The disulfides exhibited lower activities than the transition metals of Fe, Co, and Ni supported on Al₂O₃, however, the selective hydrogenation of CO₂ to CO via the RWGS reaction was observed. A moderately strong affinity for H₂ rather than for CO₂ was observed on MoS₂ and WS₂ catalysts. The cause for the selective hydrogenation of CO₂ to CO was found to be due to the suppression of C–O bond breaking in

CO molecule produced by the CO₂ hydrogenation. The reaction rate on a per active site of catalyst basis was not influenced by the supports for MoS₂.

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