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Activity of carbided molybdena–alumina for CO_2 hydrogenation

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Abstract

The relationship between the catalytic activity of carbided molybdena–alumina and the methane desorption from carbidic carbon through temperature-programmed surface reaction (TPSR) were studied. The effects of passivation and hydrogen treatment on the catalytic activities of molybdenum carbides for CO_2 hydrogenation were determined. When the 973 K-carbided catalyst was reduced at 773 K with hydrogen, the catalyst exhibited the highest activity for the reaction, the activity decreasing with increasing H_2 pretreatment temperature. Passivation of this catalyst decreased the reaction rate by 20%. TPSR results were correlated with the activity to reveal that molybdenum carbide with slightly deficient carbidic carbon ($Mo_2C_{0.96}$<$Mo_2C_{1.0}$) serves as an active site for CO_2 hydrogenation.

Keywords: Carbon dioxide; Hydrogenation; Molybdenum carbide; Temperature-programmed surface reaction

1. Introduction

Molybdenum carbide is an active catalyst for a variety of reactions that emulate the catalytic properties of noble metals. Although much research has been done on unsupported catalysts, little attention has been paid on supported catalysts. Most of the catalytic studies of molybdenum carbides have focused on determining the activity of the unsupported molybdenum carbides toward such reactions as hydrogenolysis of methylcyclopentane [1], isomerization of *n*-hexane [2], and hydrogenation of CO [3,4]. The molybdenum carbides exhibiting VIII metal catalyst activity encounter such problems as low surface area, accumulation of polymeric carbons, and poisoning by chemisorbed oxygen for most of the reactions. Although a high surface area carbided Mo has been prepared by temperature-programmed reaction (TPR) of MoO_3 with a CH_4/H_2 stream [5], the latter two problems are still debatable. Lee et al. [6] reported that the addition of a small amount of oxygen to polymeric carbon inhibited chemisorption of hydrogen. Ledoux et al. [2] also reported that molybdenum carbide was unreactive for reforming reaction when polluted by uncontrolled oxygen. Furthermore, the hydrogenolysis of hydrocarbons on molybdenum carbide markedly increased with decreasing oxygen content in the catalyst after hydrogen reduction [5,7]. This paper deals with (1) the effects of H_2 treatment before and after the passivation on the catalytic activity, and (2) the relationship between (carbidic) carbon and the catalytic activity of the molybdenum carbide catalyst.

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2. Experimental

12.5% MoO_3/Al_2O_3 (Nikki Chemicals), prepared by mixing ammonium paramolybdate with γ-alumina, was dried at 393 K for 24 h and calcined at 823 K for 3 h. The microreactor was constructed of quartz tubing (10 mm i.d.), having a total volume of 2.4 ml. The 12.5% MoO_3/Al_2O_3 and 100% MoO_3 (more than 150 mesh) were held in place by means of a fretted ceramic disk. The catalyst was oxidized at 773 K in dry air and was then carbided for 3 h at this temperature using 20% CH_4/H_2 (99.99995%) [8]. Alternatively, the oxidized catalyst was raised in a stream of 20% CH_4/H_2 from 573 K to 773 K (973 K or 1173 K) at a rate of 1 K min^{-1} and held at this temperature for 3 h. The catalyst was cooled to room temperature in flowing 20% CH_4/H_2 and either supplied in situ for the reaction or passivated using 1% O_2/He for 24 h.

Hydrogen and He (99.9999%) were dried using super Deoxo units (Supelco Co., Oxysorb) and Linde 13X molecular sieve traps prior to use. For temperature-programmed surface reaction (TPSR), the catalyst was purged in situ in flowing He after carburizing and heated in flowing H_2 (99.9995%) at 11.2 μmol s^{-1} at a rate of 10 K min^{-1} from 313 K to 1213 K. The catalysts were treated in flowing H_2 at a rate of 10 K min^{-1} and held at 773, 923, and 1073 K for 1 h and then cooled to room temperature in flowing H_2. The desorption rate of CO_2 and CH_4 gases, monitored with a quadrupole mass spectrometer, was calculated through calibration curves obtained for each gas. Surface area was measured by the BET method with N_2 physisorption at liquid nitrogen temperature. The reactivity of the catalysts toward hydrogenation of CO_2 using $CO_2 : H_2 = 1 : 3$ (25 : 76 kPa) was measured in situ at 573 K using the reactor unit under atmospheric pressure after the preparation. The products formed during the reaction were identified by GC equipped with TCD. The reaction rate was calculated by conversion of CO_2 and reported as molecules min^{-1} g^{-1}.

3. Results and discussion

3.1. CO_2 hydrogenation

Carbon monoxide and water are produced in the CO_2 reaction on 973 K-carbided 12.5% Mo/Al_2O_3 catalyst. For the unsupported catalyst, the reaction product was CH_4 as well as CO. In Fig. 1, the ratio of CH_4/CO is 0.5 for the unsupported catalyst, although no formation of methane was observed for the supported catalyst. The CH_4 selectivity is 33%. The activities of the unsupported and 12.5% Mo/Al_2O_3 carbided at 973 K were 150 and 50 μmol min^{-1} g^{-1}, respectively. The O_2 adsorption amounts for the unsupported and supported are 1763 and 62.3 μmol g^{-1}, respectively, based on the desorption of CO and CO_2 in the O_2–TPD profile. The TOF of the supported catalyst was 9.4 times greater than that of the unsupported catalyst, indicating that the supported catalyst was more active than the unsupported catalyst, although CH_4 selectivity is lower.

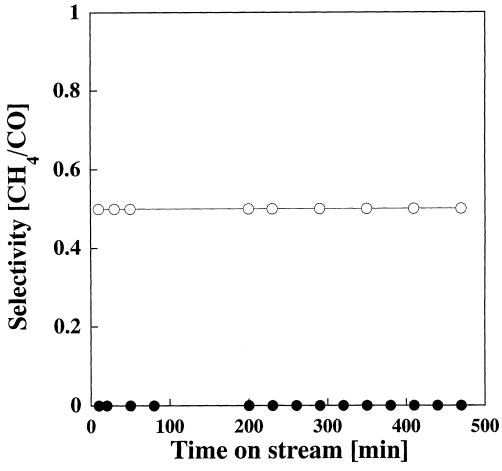

Fig. 1. Variation of selectivity at 573 K with the time on stream for (○) unsupported and (●) 12.5% Mo/Al_2O_3 catalysts carbided at 973 K.

3.2. Effect of passivation and H_2 pretreatment on CO_2 hydrogenation

It was found from this experiment that the activity of the unsupported catalyst in H_2 treatment depended on carburizing temperature and reduction temperature. The effect of H_2 reduction on the activity of the unsupported molybdenum carbide is shown in Fig. 2. The activities of the 973 K and 1173 K-carbided catalysts are either constant, or nearly so at the reaction temperature of 573 K. The activity of the 973 K-carbided catalyst decreased with increasing reduction temperature but that of the 1173 K-carbided catalyst

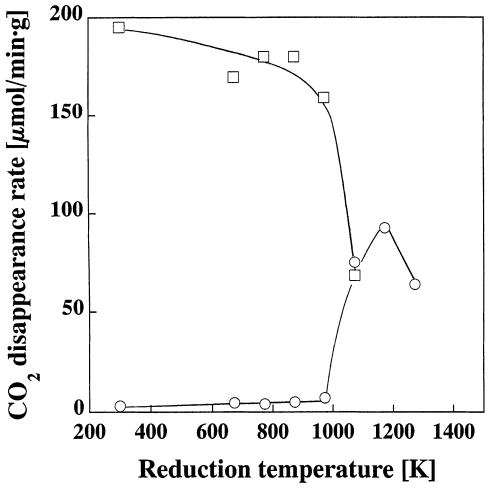

Fig. 2. The effect of reduction temperature on activities of unsupported catalysts carbided at (□) 973 K and (○) 1173 K for CO_2 hydrogenation reaction at 573 K.

increased with increasing H_2 reduction, reaching a maximum at 1120 K and then decreasing. The decreased activity of the 1173 K-carbided catalyst is due to the removal of carbidic carbon whereas the volcanic curve type activity of the 973 K-carbided catalyst is due to the removal of accumulated carbon and carbidic carbon. The activity of the 1173 K-carbided catalyst shifted 200 K higher than that of the 973 K-carbided catalyst. Thus, H_2 reduction is not effective for the 973 K-carbided catalyst but may be utilized for catalysts carburized at higher temperatures such as the 1173 K-carbided catalyst.

The rate of CO_2 hydrogenation for the unpassivated and passivated 12.5% Mo/Al_2O_3 catalysts carbided at 973 K are shown in Table 1. The passivated molybdenum carbide catalysts were less active than the unpassivated catalysts for CO_2 hydrogenation. The H_2 pretreatment of the passivated 973 K-carbided catalyst at 773 K did not affect the activity for CO_2 hydrogenation but a change was visible for the activity of the unpassivated catalyst (Table 1). The 2% and 12.5% 773 K-carbided catalysts reduced at 773 K in H_2 showed the highest rate, while increasing H_2 pretreatment temperature caused a decline. The activity did not increase during the reaction. The pretreatment of the unsupported catalysts in a stream of hydrogen removed carbon on the catalyst to expose active sites, but higher temperature treatment removed much of the carbidic carbon. Furthermore, Table 2 shows that the catalyst passivated with 1% O_2/He after the H_2 treatment at 773 K was less active than passivated catalyst without treatment. Thus, H_2 treatment at 773 K before passivation exposed active sites but covered the catalyst surface with O_2, resulting in lowered catalytic activity for CO_2 hydrogenation. Leary et al. [9] reported that O_2 strongly covered the vacancy sites more so than the sites of the carbided catalyst. In light of the fact that a large amount of oxygen enters the crystal structure of the bulk [3,9,10] and the interatomic distance within the Mo_2C structure, 0.3 nm, is smaller than the diameter of O_2 (0.6 nm), it is most likely than the O_2 dissociates on the catalyst surface, diffusing into the crystal structure as atomic oxygen. In turn, the oxygen atoms

Table 1
Catalytic activity of alumina-supported molybdenum carbides at 573 K

Catalyst carbided at 973 K	Surface area[a] ($m^2\ g^{-1}$)	Rate ($\mu mol\ min^{-1}$ g-catalyst^{-1})			
		Unpassivated		Passivated	
		Without pretreatment	H_2 pretreatment at 773 K	Without pretreatment	H_2 pretreatment at 773 K
2 wt%	155	32.0	47.5	27.4[b]	27.6[c]
12.5 wt%	213	50.0	54.4	38.8[b]	39.0[c] (27.9)[d]

[a]Passivated fresh catalyst.
[b]After carburization at 973 K, the catalyst was passivated in flowing 1% O_2/He at room temperature and subsequently used for the activity measurement.
[c]The catalyst was passivated at room temperature with 1% O_2/He after carburization and then reduced at 773 K in flowing 11.2 $\mu mol\ min^{-1}$ H_2.
[d]The catalyst was first reduced at 773 K in flowing 11.2 $\mu mol\ min^{-1}$ H_2 and subsequently passivated with 1% O_2/He at room temperature.

Table 2
Surface area and TPSR data of the 973 K-carbided catalyst in H_2 pretreatment

Catalyst[a]	H_2 treatment (K)			
	None	773	923	1073
Catalytic activity (μmol min^{-1} g^{-1})	50.0	54.4	39.3	32.4
CH_4 desorption in TPSR (a.u.)	0	43.9 (15.2[b], 28.7[c])	98.0 (20.6[b], 77.4[c])	98.7 (15.0[b], 83.7[c])
Surface area[d] (m^2 g^{-1})	213	218	215	182

[a]12.5% Mo/Al_2O_3 carbided at 973 K.
[b,c]Area in the regions A, B, respectively.
[d]The catalyst was measured in treatment of passivation with 1% O_2/He.

bond to the carbidic carbon, desorbing as CO. The formation of CO_2 can be explained by the spontaneous reaction of CO with the dissociative oxygen on the catalyst surface. A decrease in molybdenum carbide lowers the activity. Thus, the presence of excess oxygen may be a factor controlling the direction of the reaction, that is, lowering the activity. Furthermore, the H_2 treatment of the unsupported molybdenum carbide at 873 K for 15 min removed 14.5% of carbon and significantly reduced the C/Mo ratio. In this study, the H_2 treatment of supported catalyst at 773 K removed the carbon of molybdenum carbide to expose active sites on the surface. However, the H_2 treatment of the supported catalyst above 923 K and even at 1073 K lowered the activity because of severe decomposition of carbidic carbon to expose Mo metal. Moreover, Ledoux et al. [11] reported that the TPR peaks for air-exposed molybdenum carbide showed the temperatures of 500 K and 847 K, for the reduction of a superficial layer of oxycarbide and the bulk oxycarbide, respectively. It was concluded that the passivation lowered the activity of carbided molybdenum–alumina for CO_2 hydrogenation, even though the catalyst was reduced with hydrogen at 773 K before reaction.

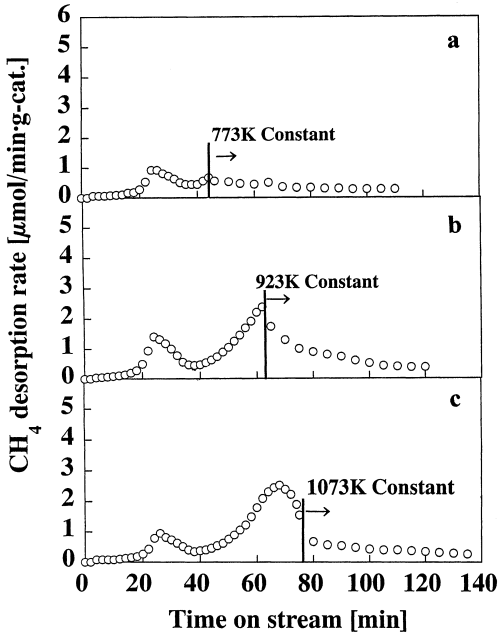

Fig. 3. The desorption rates of CH_4 from the 973 K-carbided catalysts where the temperature is held constant after reaching (a) 773 K, (b) 923 K, and (c) 1023 K, during TPSR.

3.3. CH_4 formation during TPSR

The desorption rates of CH_4 from the 12.5 wt% 973 K-carbided catalysts where the temperature is held constant after reaching 773 K, 923 K, and 1073 K, during TPSR are shown in Fig. 3(a), (b) and (c), respectively. The desorption peaks of CH_4 were observed at about 580 and 1000 K. The desorption peak of CH_4 at about 30 min corresponded to the desorption temperature at about 580 K. The peak area of CH_4 desorption was divided into two regions A and B. These areas of CH_4 desorption are shown in Table 2. The CH_4 desorption in region A starts to desorb at 580 K, suggesting physically adsorbed CH_4 on the catalyst surface which was left in with the CH_4 gas [8]. The A region was up to 40 min, while the B region was above 40 min. The desorption rate of CH_4 for the 973 K-carbided catalyst after pretreatment at 773 K was 0.45 times less than that for the carbided catalysts pretreated at 923 K and 1073 K.

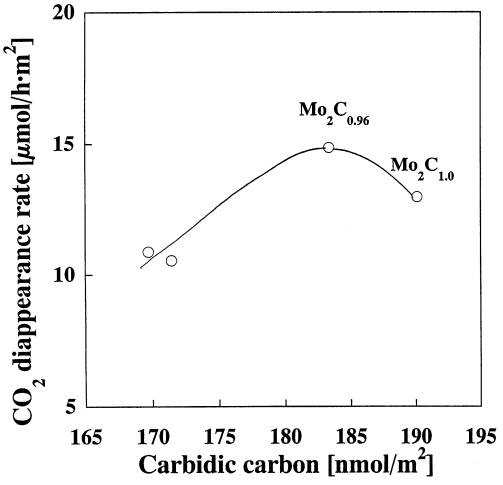

Fig. 4. The activity of molybdenum carbide catalyst for CO_2 hydrogenation as a function of the amount of carbidic carbon.

3.4. Active sites

The relationship between catalytic activity of the 973 K-carbided 12.5% catalyst and the amount of carbon species of the catalyst after CH_4 desorption during TPSR is shown in Fig. 4. The catalytic activity for CO_2 hydrogenation was related with the area of B which was ascribed to carbon of the molybdenum carbide and slightly pyrolytic carbons. Region B was due to CH_4 desorption from the decomposition of molybdenum carbides. This result is in agreement with the result of a rapid decrease in the activity of the unsupported catalyst pretreated at 1000 K with H_2 rather than the catalyst without H_2 pretreatment, as described before. The amount of CH_4 desorption was related with the rate of CO_2 hydrogenation. Since the composition of the 12.5% Mo/Al_2O_3 carbided at 973 K was $Mo_2C_{1.0}$ without H_2 pretreatment, the most active catalyst (773 K-H_2 treatment) was $Mo_2C_{0.96}$. A slightly carbon-vacant Mo carbide ($Mo_2C_{0.96}$< $Mo_2C_{1.0}$) is more active than a fully carbonic Mo carbide ($Mo_2C_{1.0}$) because of the highly electrophilic molybdenum atom.

4. Conclusions

1. The passivated Mo_2C catalyst was less active than the unpassivated catalysts for CO_2 hydrogenation. The catalyst passivated after the H_2 treatment of the carbided catalyst at 773 K was less active than the passivated catalyst without treatment.
2. The H_2 pretreatment at 773 K did not affect the activity of the passivated 973 K-carbided catalysts for CO_2 hydrogenation, but influenced that of the unpassivated catalysts. For the unpassivated catalysts, however, the catalyst reduced at 773 K with H_2 was greater than the catalyst reduced at 923 and 1073 K and the catalyst without H_2 pretreatment.
3. A slight carbon-vacancy of molybdenum carbide ($Mo_2C_{0.96}$<$Mo_2C_{1.0}$) is a more active site than a fully carbidic molybdenum carbide.

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