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CO_2 Hydrogenation over Carbide Catalysts

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Carbides such as Mo_2C, Fe_3C, and WC have proved to be effective catalysts for hydrogenation of CO_2. Mo_2C and Fe_3C showed high CO_2 conversion and good methanol selectivity at 220 °C. A considerable amount of dimethylether was produced over WC. TaC and SiC were almost inactive. Copper promoted carbide catalysts were also tested for CO_2 hydrogenation.

Catalytic hydrogenation of CO_2 into valuable chemicals and fuels such as methanol and gasoline has been recently recognized as one of the promising recycling technologies for emitted CO_2. Generally metallic and oxide catalysts have been studied for hydrogenation of CO_2 so far. For example, supported transition metal catalysts such as Ni,[1,2] Rh,[3] Ru[3] are effective for methane formation. Furthermore, Fe[4] and Co[5] catalysts are effective for C_2^+ hydrocarbon formation. On the other hand, promoted copper catalysts[6,7] are effective for methanol formation. However, carbides have not been studied as CO_2 hydrogenation catalysts though carbides such as WC and Mo_2C were tested as hydrogenation catalysts for olefin[8] and.CO[9,10]

In this letter, we wish to report CO_2 hydrogenation over carbides such as Mo_2C, Fe_3C, WC, TaC, and SiC. It was found that Mo_2C and Fe_3C have high activities for CO_2 conversion and produce a fairly good amount of methanol.

All carbides used in this study are commercially available materials (SiC: Wako Pure Chemical Ind. Ltd., WC and TaC: Soekawa Chemicals Co., Fe_3C and Mo_2C: Mitsuwa Chemicals Co.). Silicagel (Davison#57) was used for comparison with carbide catalysts. The powdered carbide was compressed and crushed. Then it was sieved to obtain a fraction of particles of 0.5 mm - 1.0 mm in diameter. Copper promoted carbide catalysts were prepared by the incipient wetness method using an aqueous solution of $Cu(NO_3)_2$ $3H_2O$. After impregnation, catalysts were dried up to 120 °C and then reduced with H_2 flow at 350 °C for 4 h. Surface areas of the carbides were measured by the BET method using N_2. The volumetric adsorption of CO on catalyst was measured by a conventional glass vacuum apparatus. High pressure CO_2 hydrogenation reaction was conducted with a flow type fixed bed microreactor at a temperature between 220 °C and 280 °C, a pressure of 6 MPa and a flow rate of 50 ml/min of a reaction mixture of $Ar/H_2/CO_2$=10.1/22.7/67.2. Before reaction, 1 g of packed catalyst was pretreated *in situ* with hydrogen at 350 °C for 30 min. The effluent gas was analyzed by on-line gas chromatography using PEG-1500 column (3 m), 2wt%-squarane/Activated Carbon column (3 m) and VZ-10 column (3 m).

Table 1 shows the reaction behavior of CO_2 hydrogenation over carbide catalysts. Carbides, except SiC (13.3 m^2/g), have very low surface area, between 1.0 m^2/g and 3.7 m^2/g. Carbide catalysts used in this study are classified into three groups. The first group consists of Mo_2C and Fe_3C, which have high activities for CO_2 conversion. Main products were hydrocarbons, however, methanol and dimethylether were also produced with relatively high selectivity, between 20.2% and 24.5%, at the reaction temperature of 220 °C. The second group consists of WC. This activity is somewhat lower than those of Mo_2C and Fe_3C, however, selectivity of dimethylether is fairly higher than those of other carbides. It is known that dimethylether formation from methanol proceeds over acidic catalyst. From this point, dimethylether formation over WC and Mo_2C has to be attributed to the acidic property of these carbides though it is not clear that WC and Mo_2C have such enough acidic property. Another explanation is also possible. That is, dimethylether formation might be attributed to the acidic and surface WO_3 and MO_3, which are produced during reaction. Because a considerable amount of steam is produced during reaction and this steam may reacts with WC and Mo_2C to form surface WO_3 and Mo_2C at the condition of 6 MPa and 220 °C. Altough this possibility seems to be probable, further investigation is requested to clarify the reason for dimethylether formation over WC and Mo_2C. The third group consists of TaC and SiC which have almost no activity like SiO_2. Over these carbides, CO and CH_4 were the main products and some amount of methanol was produced at 220 °C. It is noted that methanol is produced over carbide catalysts but not over SiO_2 at 220 °C. As mentioned above, catalytic hydrogenation of CO_2 over carbide catalysts were much influenced by the nature of carbides. It is not apparent why Mo_2C, Fe_3C, and WC are so active compared with TaC and SiC at this moment. However, Mo_2C catalyst on CO hydrogenation10) and WC catalyst on both isomerization of 2,2-dimethylpropane11) and CO hydrogenation9) are known to behave like noble metal catalyst such as Ru and Pt. L. H. Bennet et al. found that the electronic structure of WC was similar to that of Pt by XPS measurement and they suggested this was the reason why WC behave like Pt catalyst.12) In CO_2 hydrogenation of the present study, a similar speculation might be applied. It is noted that methanol is produced over noble metal catalysts such as Pt13) and Pd14) by the hydrogenation of CO_2.

Table 1. CO_2 hydrogenation over carbide catalysts[a)]

Carbide	Temp	CO_2 conv.	Selectivity in carbon efficiency / %							
(S.A.)[b)]	°C	%	CH_3OH	CH_3OCH_3	C_2H_5OH	CH_4	C_2H_6	C_3H_8	CO	Others[c)]
Mo_2C	220	4.6	17.7	2.5	0.8	30.1	7.9	2.8	36.2	2.0
(1.6m^2/g)	280	16.7	3.3	0.3	0.1	47.5	12.7	4.5	29.4	2.5
Fe_3C	220	2.8	24.3	0.2	1.3	40.7	7.0	3.5	21.2	1.8
(3.7m^2/g)	280	19.5	2.6	1.6	0.8	44.5	17.8	13.3	10.2	9.2
WC	220	1.4	22.4	8.9	0.1	20.4	1.4	0.5	45.4	0.9
(2.2m^2/g)	280	6.9	5.5	2.5	0.1	37.3	2.4	0.5	51.6	0.1
TaC	220	0.1	10.3	0.0	0.0	21.8	0.0	0.0	67.9	0.0
(1.0m^2/g)	280	0.7	6.8	0.4	0.0	9.9	0.4	0.1	82.4	0.0
SiC	220	0.02	12.9	0.0	0.0	38.0	0.0	0.0	49.1	0.0
(13.3m^2/g)	280	0.4	5.2	0.0	0.0	6.8	0.3	0.0	87.0	0.0
SiO_2	220	0.01	0.0	0.0	0.0	56.2	0.0	0.0	43.8	0.0
(295.2m^2/g)	280	0.1	6.5	0.0	0.0	14.2	0.5	0.0	78.7	0.0

a) Conditions: Pressure: 6 MPa, Flow rate: 50 ml/min, Reaction temp: 220 °C and 280 °C, Catalyst weight: 1.0 g.

b) S.A.: Surface area. c) Others: Mainly higher hdrocarbons and alcohols.

Table 2. CO_2 hydrogenation over Cu promoted carbide catalysts[a)]

Carbide	Temp	CO_2 conv.	Selectivity in carbon efficiency / %							
(CO ad.)[b)]	°C	%(TOF)[d)]	CH_3OH	CH_3OCH_3	C_2H_5OH	CH_4	C_2H_6	C_3H_8	CO	Others[c)]
Cu/Mo_2C	220	4.0(79)	31.5	1.4	0.4	13.5	3.0	1.0	48.5	0.7
(14.2 μmol/g)	280	13.4	7.6	2.0	0.4	30.8	7.4	2.4	47.8	1.6
Cu/Fe_3C	220	1.9(407)	37.9	0.0	0.0	32.0	2.3	0.6	27.2	0.0
(1.3 μmol/g)	280	15.5	4.3	0.8	0.8	50.0	15.7	9.3	13.6	5.5
Cu/WC	220	0.6(79)	21.3	27.7	0.0	3.4	0.0	0.0	46.9	0.7
(2.2 μmol/g)	280	1.7	6.3	3.7	0.0	10.9	0.1	0.0	78.8	0.2
Cu/TaC	220	0.2(681)	41.3	1.7	0.0	13.8	0.3	0.0	40.5	2.4
(0.1 μmol/g)	280	1.4	18.2	2.3	0.0	15.2	0.4	0.1	63.6	0.2
Cu/SiC	220	2.0(78)	36.1	0.0	0.0	0.4	0.0	0.0	63.2	0.4
(7.1 μmol/g)	280	6.8	10.2	0.0	0.3	0.3	0.0	0.0	89.4	0.0
Cu/SiO_2	220	5.3(34)	34.2	0.0	0.0	0.2	0.0	0.0	65.4	0.2
(43.8 μmol/g)	280	17.1	23.9	0.0	0.0	0.1	0.0	0.0	76.0	0.0

a) Conditions: Pressure: 6 MPa, Flow rate: 50 ml/min, Reaction temp: 220 °C and 280°C, Catalyst weight: 1.0 g, Cu loading: 5 wt%.

b) CO ad.: CO adsorbed. c) Others: Mainly higher hydocarbons and alcohols.

d) TOF: Turnover frequency based on CO adsorbed / h^{-1}.

Table 2 shows reaction behavior of CO_2 hydrogenation over Cu promoted carbide catalysts. In case of Cu/Mo_2C and Cu/Fe_3C catalysts, CO_2 conversion activity decreased by the addition of Cu onto carbides. However, methanol selectivity increased. Over Cu/WC, the activity also decreased though selectivity of dimethylether increased drastically at 220 °C. On the other hand, over TaC, the activity increased by the factor of two. Furthermore, in case of SiC, the activity increased two orders of magnitude by the addition of Cu like in the case of Cu/SiO_2. Product distribution is also same as that over Cu/SiO_2. As shown in Table 2, turnover frequencies (TOF) of converted CO_2 based on CO chemisorption over Cu promoted carbide catalyts are always larger than that over Cu/SiO_2. And the order is as follows. TOF(Cu/TaC) > TOF(Cu/Fe_3C) > TOF(Cu/Mo_2C) = TOF(Cu/WC) = TOF(Cu/SiC) > TOF(Cu/SiO_2). This shows that support effects of carbides are different from one another and they are better than that of SiO_2.

In conclusion, Mo_2C, Fe_3C, and WC have proved to be effective catalysts for the catalytic hydrogenation of CO_2 to hydrocarbons and oxygenates. The catalytic behavior of Cu promoted carbide catalysts was also shown.

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