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Low-Temperature Hydrogenation of CO₂ to Methanol over Heterogeneous TiO₂-Supported Re Catalysts

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ABSTRACT

Hydrogenation of carbon dioxide (CO₂) to methanol (MeOH) is an effective strategy for CO₂ utilization. Due to a low equilibrium conversion of CO₂ to MeOH at high temperature, development of efficient catalytic CO₂ hydrogenation processes that operate under low reaction temperature is of extreme importance. Herein, we report that TiO₂-supported Re (Re(1)/TiO₂; Re = 1 wt%) promotes the selective hydrogenation of CO₂ to MeOH (total TON based on Re = 44, MeOH selectivity = 82%) under mild conditions ($p_{CO2} = 1$ MPa; $p_{H2} = 5$ MPa; T = 150 °C). Both in terms of TON and methanol selectivity, the performance of Re(1)/TiO₂ is superior to that of TiO₂ catalysts loaded with other metals and to Re catalysts on other support materials. In addition, our investigations include the reaction mechanism and structure-activity relationship for the catalytic system used in this study, suggesting that relatively reduced Re species (oxidation state: 0-4) of sub-nanometer size serve as the catalytically active site for the formation of MeOH.

KEYWORDS: CO₂ hydrogenation, methanol synthesis, rhenium, TiO₂, in situ XAFS, in situ FT-

IR

1. INTRODUCTION

The growing concern about climate change and the depletion of fossil fuels have prompted the search for alternative carbon sources for the generation of energy and the production of chemicals.^{1–10} Carbon dioxide (CO₂), which is regarded to be by far the largest contributor to global warming, is a promising prospective for potential applications as a raw material for the production of fine chemicals.^{11–19} The direct synthesis of methanol (MeOH) from the hydrogenation of CO_2 has thus attracted significant interest in the scientific community.²⁰⁻²⁸ MeOH is used as a precursor for a vast variety of chemical products, which makes it arguably one of the most important commodity chemicals.²⁹ Additionally, MeOH can be used as a fuel.³⁰ Traditionally, MeOH is almost exclusively produced from fossil-derived syngas, which primarily consists of CO and H₂ in addition to small amounts of CO₂, by employing Cu-based catalysts, typically under relatively extreme conditions (T > 200 °C; p = 5-10 MPa).³¹ Industrially, the direct production of MeOH from the hydrogenation of CO₂ has recently been achieved by using similar Cu-based catalysts and reaction conditions.³² However, this process suffers from a low equilibrium conversion of CO₂ since the hydrogenation reaction is exothermic.^{33,34} Consequently, a lower reaction temperature is more favorable for the formation of MeOH.

Several methods for the low-temperature ($T \le 150$ °C) hydrogenation of CO₂ to afford MeOH over homogeneous catalysts under mild conditions have recently emerged (**Table S1**).^{34–46} Although homogeneous catalysts normally exhibit high activity and operate under mild conditions, they typically suffer from product-separation issues and usually require additives in order to achieve high catalytic performance. Methods based on heterogeneous catalysts have also been actively explored recently. However, most methods hitherto reported suffer from low activity.^{47–52} Yet some reports on heterogeneous catalytic systems for the low-temperature hydrogenation of CO₂ to MeOH show high activity.^{53–57} For instance, Zen and co-workers reported Pt₃Co octapods,⁵³ Rh₇₅W₂₅ nanosheets,⁵⁴ and Pt/MoS₂⁵⁵ catalysts that produce MeOH with TON > 2000 (**Table S1**). Carbon-supported Pt₄Co nanowires (Pt₄Co NWs/C)⁵⁶ and RhCo porous nanospheres⁵⁷ have also been reported recently as active catalysts for the hydrogenation of CO₂. These processes represent important contributions to the synthesis of MEOH under mild conditions. However, in all cases platinum-group metals (PGMs) are ACS Catalysis

employed and the preparation of these catalysts is complicated. Yet, catalysts employed for such selective hydrogenation reactions should be easily accessible. Hence, the development of versatile heterogeneous catalysts that can be operated under mild conditions ($T \le 150$ °C) is of extreme importance. Moreover, it should be emphasized that the previous reported studies usually do not mention the formation of byproducts such as CO and CH₄. This is especially problematic for dealing with the hydrogenation of CO₂, which usually generates such byproducts to some extent even over homogeneous catalysts.²²

In this study, a Re/TiO₂ catalyst, which exhibits high activity and product selectivity for i) the hydrogenation of carboxylic acid derivatives, ii) the *N*-methylation of amines using CO₂ and H₂, and iii) the *N*-alkylation of amines with carboxylic acids or esters in the presence of H₂,^{58,59} was employed for the hydrogenation of CO₂ to MeOH at low temperature (T = 150 °C). A series of Re/TiO₂ catalysts with different Re loadings, which ensured a wide range of Re dispersion, were prepared and evaluated with respect to their performance in the hydrogenation of CO₂. Whereas a Re loading of 5 wt% (Re(5)/TiO₂) furnished the best performance in previous studies,^{58,59} the best performance under the conditions applied in this study (*vide infra*) was achieved using a catalyst containing 1 wt% of Re (Re(1)/TiO₂). A comparison of the performance of the Re(1)/TiO₂ catalyst to that of various other catalysts, including the industrially used methanol synthesis catalyst Cu/Zn/Al₂O₃, revealed that Re(1)/TiO₂ surpassed the performance of all the other catalysts tested.

2. EXPERIMENTAL

Materials and Catalyst Preparation

Inorganic and organic chemicals were obtained from common commercial suppliers. The obtained reagents were used as received. TiO₂ (ST-01) was purchased from Ishihara Sangyo Co., Ltd. Its BET (Brunauer-Emmett-Teller) specific surface area is 188 m² g⁻¹ and its CO₂-TPD profile is given in **Fig. S1**. ZrO₂ (JRC-ZRO-2), MgO (JRC-MGO-3), and SiO₂-Al₂O₃ (JRC-SAL-2, Al₂O₃ = 13.75 wt%) were obtained from the Catalysis Society of Japan. Conversely, γ -Al₂O₃ was prepared by calcination of γ -AlOOH (Catapal B Alumina) obtained from Sasol (*T* = 900 °C; *t* = 3 h). CeO₂ was prepared by calcination (*T* = 600 °C, *t* = 3 h, in air) of CeO₂ supplied by Daiichi Kigenso Kagaku Kogyo Co., Ltd (Type A). SiO₂ (Q-10) was supplied by Fuji Silysia Chemical Ltd. The carbon support (Kishida Chemical) was commercially obtained. SnO₂ was prepared by calcination (*T* = 500 °C, *t* = 3 h) of H₂SnO₃ (Kojundo Chemical Laboratory Co., Ltd.). HZSM-5:SiO₂/Al₂O₃ = 22:1 and HY:SiO₂/Al₂O₃ = 5.5:1 were obtained from TOSOH Co., Ltd. Re₂O₇ and ReO₂ were purchased from Strem Chemicals Inc. and Hydrus Chemical Inc., respectively. [NH₄]ReO₄ and metallic Re were purchased from SigmaAldrich. Cu/Zn/Al₂O₃ (MDC-7; 34 wt% Cu) was supplied by Clariant Catalysts (Japan).

Precursors for M(1)/TiO₂ (M = 1 wt% Re, Pt, Pd, Rh, Ir, Ru, Ni, Co, Ag, or Cu) and Re(1)/Support (1 wt% Re; Support = metal oxides, carbon, or zeolites) were prepared by mixing the support material with the metal sources, i.e., an aqueous solution of [NH₄]ReO₄, nitrates of Ni, Co, Ag, Cu, RuCl₃ or IrCl₃·nH₂O, or aqueous HNO₃ solutions of Pt(NH₃)₂(NO₃)₂, Pd(NH₃)₂(NO₃)₂, or Rh(NO₃)₃. For the preparation of Re/TiO₂, typically 0.072 g of [NH₄]ReO₄ were added to a glass vessel (500 mL) containing 100 mL of deionized water ([Re] = 0.0027 M). After sonication (1 min) to completely dissolve the NH₄ReO₄, TiO₂ (4.95 g) was added to the solution. The mixed solution was then stirred at 200 rpm for 30 min at room temperature. Subsequently, the solvent of the mixture was evaporated at *T* = 50 °C, followed by drying in air (*T* = 110 °C; *t* = 12 h). The thus obtained material was calcined (*T* = 500 °C, *t* = 3 h, in air). The individual catalysts were prepared by reducing the individual materials in a quartz vessel (*T* = 500 °C, *t* = 0.5 h) under a flow of H₂ (20 cm³min⁻¹) prior to each experiment. All other M(1)/TiO₂ catalysts were prepared as described above.

Characterization of the Catalysts

X-ray diffraction (XRD; Rigaku Miniflex) measurements were conducted using CuK α radiation. Re L₃-edge X-ray absorption fine structure (XAFS) measurements were performed at the BL14B2 line (SPring-8) using a Si(111) double crystal monochromator operated at 8 GeV (proposal 2018A1757). Scanning transmission electron microscopy (STEM) images were recorded on a JEM-ARM200F microscope (JEOL) at an acceleration voltage of 200 kV. The Cs-corrector CESCOR (CEOS GmbH, Germany) was used in the STEM mode.

FT-IR spectra were measured on a JASCO FT/IR-4200 with a Mercury-Cadmium-Telluride (MCT) detector. Samples (40 mg) were pressed into self-supporting pellets (ϕ = 2 cm), which were fitted in the quartz FT-IR cell with CaF₂ windows connected to a gas-flow set up. Prior to the measurements, the samples were pre-treated (*T* = 500 °C; *t* = 0.5 h) under a flow of H₂ (30 mL min⁻¹) and He (50 mL min⁻¹), followed by cooling to *T* = 150 °C under He. Subsequently, the gas stream containing CO₂ (10 mL min⁻¹) and H₂ (30 mL min⁻¹) with He (50 mL min⁻¹) was introduced to the cell, and the FT-IR measurements were carried out. Spectra were measured by accumulating 15 scans (resolution: 4 cm⁻¹). A reference spectrum (*T* = 150 °C; H₂ and He flow) was subtracted from each spectrum.

Catalytic Reactions

The following procedure for the hydrogenation reactions can be considered representative: after the reduction with H₂ at T = 500 °C (*cf.* catalyst preparation), the catalyst (0.0054 mmol relative to the Re loading), and a mixture of 1,4-dioxane (1 mL) and *n*-decane (0.15 mmol) as an internal standard were added to an autoclave (30 cm³). The reaction mixture was stirred magnetically (T= 150 °C; $p_{CO2} = 1$ MPa; $p_{H2} = 5$ MPa). MeOH was analyzed using a gas chromatograph with a flame-ionization detector (GC-FID; Shimadzu GC-14B; Ultra ALLOY capillary column UA⁺-1; Frontier Laboratories Ltd.); while the other products were analyzed using a GC-FID (Shimadzu GC-2014; Porapak Q column) with a methanizer (Shimadzu MTN-1).

3. RESULTS AND DISCUSSION **Catalyst Characterization**

 $Re(1)/TiO_2$ was synthesized using a facile impregnation method employing NH₄ReO₄ and TiO₂. followed by H₂ reduction at 500 °C. Powder X-ray diffraction (XRD) and scanning transmission electron microscopy (STEM) measurements were carried out in order to characterize Re(1)/TiO₂. As given in **Fig. 1**, a XRD pattern of the reduced Re(1)/TiO₂ catalyst was essentially identical to that of pristine TiO₂, while peaks arising from the Re species were not observed. It should be noted that its structure was confirmed to be anatase. Figure 2 shows the annular bright field STEM (ABF-STEM) image and high-angle annular dark-field STEM (HAADF-STEM) images of Re(1)/TiO₂. These images show that the Re loaded on the TiO₂ support forms highly dispersed sub-nanometer clusters. It is also observed that some Re species exist as single atoms in the matrix of TiO₂.60-62



Figure 1. XRD patterns of a) TiO₂; b) NH₄ReO₄-impregnated TiO₂ calcined at 500 °C in air; c) after reduction of (b) at 500 °C under H₂ flow (Re(1)/TiO₂).





Figure 2. ABF- and HAADF-STEM images for Re(1)/TiO2.

Low-Temperature Hydrogenation of CO₂

Hydrogenations of CO₂ were performed in order to screen the catalytic performances of various catalysts. These reactions were carried out using a catalyst (0.0054 mmol of catalytically active metal) in a stainless autoclave (V = 30 cm³; p_{CO2} = 1 MPa; p_{H2} = 5 MPa; T = 150 °C; t = 24 h) after pre-treatment of the catalyst under a flow of H₂ (T = 500 °C). Table 1 summarizes the obtained results. Re(1)/TiO₂ afforded a total turnover number (TON) of 44 with 82% MeOH selectivity (entry 1). As minor byproducts, CO and CH₄ were obtained. In contrast, using TiO₂ or various other TiO₂-supported metal catalysts (entries 2-10) did not afford significant amounts of MeOH. CO and/or CH₄ were produced as the main products over these catalysts. No reaction occurred when pristine TiO₂ was employed as the catalyst (entry 11). Various supported Re catalysts were also tested for the direct hydrogenation of CO₂ (entries 12-21). The obtained total TONs were lower than that for Re(1)/TiO₂, while the formation of MeOH was not observed. The industrial Cu-based catalyst Cu/Zn/Al₂O₃ supplied by Clariant Catalysts (MDC-7; 34 wt% Cu) was also tested and found to be ineffective under the reaction conditions tested in this study (entry 22). Moreover, unsupported Re catalysts including metallic Re, NH₄ReO₄, ReO₂, ReO₃, and Re₂O₇ did not efficiently catalyze the hydrogenation of CO₂ (entries 23-27). It should be noted here that the catalytic tests were also carried out after a H₂ reduction at 300 °C (**Table S2**), given that a H₂ reduction at 500 °C may not be appropriate for some of the catalysts.¹⁹ Still, it was confirmed that $Re(1)/TiO_2$ is the most effective catalyst for the direct hydrogenation of CO_2 to afford MeOH. These results demonstrate that the combination of Re and TiO₂ is particularly effective for the synthesis of MeOH from the hydrogenation of CO₂.

EDITY	Catalvet	Total TON	Selectivit	Selectivity (%)		
	Oddalyst		MeOH	CO	CH4	
1	Re(1)/TiO ₂	44	82	16	2	
2	Pt(1)/TiO ₂	64	<1	87	13	
3	Pd(1)/TiO ₂	21	<1	88	12	
4	Rh(1)/TiO ₂	41	<1	100	<1	
5	Ir(1)/TiO ₂	5	<1	89	11	
6	Ru(1)/TiO ₂	3	<1	100	<1	
7	Ni(1)/TiO ₂	4	<1	100	<1	
8	Co(1)/TiO ₂	2	<1	100	<1	
9	Ag(1)/TiO ₂	<1	-	-	-	
10	Cu(1)/TiO ₂	<1	-	-	-	
11	TiO ₂	<1	-	-	-	
12	Re(1)/ZrO ₂	8	<1	65	35	
13	Re(1)/Al ₂ O ₃	2	<1	9	91	
14	Re(1)/SiO ₂	1	<1	65	35	
15	Re(1)/Carbon	1	<1	36	64	
16		<1	-	-	-	
17	Re(1)/MaO	<1	-	-	-	
18	$Re(1)/SiO_2-Al_2O_3$	<1	_	_	-	
19	$Re(1)/SnO_2$	<1	_	_	-	
20	Re(1)/HZSM-5(22)	1	<1	92	8	
20 21	Re(1)/HY(5.5)	-1	-	-	-	
27	$Cu/Zn/Al_2O_2^b$	~1	_	_	_	
22 ⁰	Metallic Re	~1	_	_	_	
20 2/C		2	-1	2	98	
27		1	<1	2	96	
25 ^C	ReO ₂	ן ר	<1	4 ~1	100	
25 ^c	RoCoc				100	
25 ^c 26 ^c	ReO₃ ^c	2	-1	-1	100	
25° 26° 27° ^a Pre-treatme	ReO ₃ ° <u>Re2O7</u> ° nt: H ₂ (30 mL min ⁻¹), 500 °	2 10 °C, 0.5 h; reactio	<1 on conditions: (<1 0.0054 mm	100 ol of cat	
25° 26° 27° ^a Pre-treatme active metal, based on the without pre-ti	ReO ₃ ^c Re ₂ O ₇ ^c nt: H ₂ (30 mL min ⁻¹), 500 ^c 1,4-dioxane (1 mL), CO ₂ e total amount of metal at reatment.	2 10 C, 0.5 h; reaction (1 MPa), H ₂ (5 N froms used. ^b 34	<1 on conditions: (∕IPa), 150 °C, 2 wt% of Cu. °	<1 0.0054 mm 24 h; TONs Reactions	100 ol of cat were ca were ca	
25° 26° 27° ^a Pre-treatme active metal, based on the without pre-tr	ReO ₃ ^c Re ₂ O ₇ ^c ent: H ₂ (30 mL min ⁻¹), 500 ^c 1,4-dioxane (1 mL), CO ₂ total amount of metal at reatment.	² 10 C, 0.5 h; reactio (1 MPa), H ₂ (5 M roms used. ^b 34	<1 on conditions: (/IPa), 150 °C, 2 wt% of Cu. °	<1 0.0054 mm 24 h; TONs Reactions	100 ol of cat were ca were ca	
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Mechanistic Study

The time-course plot of the CO₂ hydrogenation reaction shows that the concentration of all the products (MeOH, CO, and CH₄) increases with increasing the reaction time, as given in Fig. 3. It should also be noted that other possible byproducts such as formic acid (HCOOH) and formaldehyde (HCOH) were not observed when using a GC-FID apparatus equipped with a methanizer. In order to get further insight into the specifics of the reaction, hydrogenation reactions employing CO or HCOOH as a starting substrate were carried out (Scheme 1). The hydrogenation of CO, carried out at lower pressure (0.5 MPa) for safety reasons, hardly proceeded, whereas that of CO₂ (0.5 MPa) afforded MeOH at a formation rate of 0.8 mmol mmol_{Re⁻¹} h⁻¹ based on the Re used. This result indicates that the potentially produced CO is not an intermediate for the formation of MeOH. On the other hand, the reaction of HCOOH afforded MeOH, suggesting that the derivatives of HCOOH (e.g. HCOO⁻) adsorbed on the catalyst surface could serve as intermediates for the formation of MeOH. This hypothesis was corroborated by in-situ FT-IR measurements (Fig. 4). Specifically, the formation of surface species was investigated at 150 °C under a gas stream containing CO₂ (10 mL min⁻¹), H₂ (30 mL min⁻¹), and He (50 mL min⁻¹). Note that the measurements were carried out at ambient pressure. Prior to each measurement, the samples were pre-treated under a flow of H₂ for 0.5 h at 500 °C. Bands that were clearly observed at 1360 and 1560 cm⁻¹ over Re(1)/TiO₂ indicate the formation of HCOO^{-,21,63} In addition, a band observed at 1130 cm⁻¹ proves the formation of methoxy species.²⁸ The evolution of several bands in the v_{CH} region (2800-2950 cm⁻¹) also supports the formation of these species.^{21,28,63} The same features can be seen over pristine TiO₂, although their intensities are not as high as those for $Re(1)/TiO_2$. In contrast, these bands were negligible for $Re(1)/SiO_2$, demonstrating the importance of TiO_2 as a support. We have also examined the adsorption and activation features of CO₂, MeOH and HCOOH separately on the $Re(1)/TiO_2$ catalyst (Fig. S2). The results are consistent with the discussion described above. It should be noted that that a CO adsorption experiment was also carried out, albeit that CO did not adsorb on the Re(1)/TiO₂ catalyst surface. The results obtained from several control reactions and *in-situ* FT-IR studies suggest that the hydrogenation of CO₂ over Re(1)/TiO₂ proceeds through the formation of HCOO⁻ and methoxy species on the surface to give MeOH.



Figure 3. Time-course plot of the hydrogenation of CO₂ catalyzed by Re(1)/TiO₂. Pre-treatment: H₂ (30 mL min⁻¹), 500 °C, 0.5 h; reaction conditions: 0.0054 mmol Re, 1,4-dioxane (1 mL), CO₂ (1 MPa), H₂ (5 MPa), 150 °C.

(a) $CO_2 + O_2$ 0.5 MPa = 5 MPa $150 ^{\circ}\text{C}, 24 \text{ h}$ 0.8 = 0.1	
0.8 0.1	
Re(1)/TiO ₂	0.3
(b) $CO + H_2 \xrightarrow{(7)} 2 \xrightarrow{(7)} CH_3OH + CH_4$ 0.5 MPa 5 MPa 150 °C, 24 h No formation	
(c) HCOOH + H ₂ $\xrightarrow{\text{Re}(1)/\text{TiO}_2}$ $\xrightarrow{\text{CH}_3\text{OH} + \text{CH}_4}$ - 10.7 mmol 5 MPa $\xrightarrow{\text{150 °C}, 24 \text{ h}}$ Formation rate =	- CO
14.0 0.7 Unit = mmol mmol _F	3.8 _e -1 h-1

Scheme 1. Hydrogenation of model substrates over $Re(1)/TiO_2$. (a) CO_2 , (b) CO, and (c) HCOOH. Pre-treatment: H₂ (30 mL min⁻¹), 500 °C, 0.5 h; reaction conditions: 0.0054 mmol Re, 1,4-dioxane (1 mL).



Figure 4. *In-situ* FT-IR spectra collected at 150 °C under a gas stream that contains CO₂ (10 mL min⁻¹), H₂ (30 mL min⁻¹), and He (50 mL min⁻¹). Pre-treatment conditions: H₂ (30 mL min⁻¹), He (50 mL min⁻¹), 500 °C, 0.5 h.

Structure-Activity Relationship

Subsequently, the hydrogenation of CO₂ was carried out using Re(x)/TiO₂ (x = 0.2, 1.0, 5.0, 10, and 20 wt%) in order to i) determine the optimal Re loading and ii) investigate the effect of the size of the Re species on the hydrogenation reaction. The corresponding HAADF-STEM images for Re(x)/TiO₂ (x = 0.2, 1, 5, 10, and 20 wt%) are shown in **Fig. 5** and **Figs. S3-S7**. The highest formation rate and selectivity for MeOH was achieved using Re(1)/TiO₂ (**Fig. 6**). With increasing Re loading, the MeOH selectivity is gradually shifting toward CH₄. This could be attributed to the fact that larger clusters of Re nanoparticles favor the formation of CH₄, while isolated atoms (single atoms) of Re mainly seen for Re(x)/TiO₂ with low Re loadings favor the formation of CO₂ over Rh/TiO₂.⁶⁴ Moreover, our results indicate that the formation of MeOH should be favored over Re/TiO₂ given the sub-nanometer size of the Re species. These considerations could explain why Re(1)/TiO₂ serves as the most effective catalyst for the formation of MeOH in this study.





Figure 5. HAADF-STEM images of $Re(x)/TiO_2$ (x = 0.2, 5, 10, and 20 wt%).



Figure 6. Effect of the Re loading on the hydrogenation of CO₂ catalyzed by Re(x)/TiO₂ (x = 0.2, 1, 5, 10, and 20 wt%). Pre-treatment: H₂ (30 mL min⁻¹), 500 °C, 0.5 h; reaction conditions: 0.0054 mmol of Re, 1,4-dioxane (1 mL), CO₂ (1 MPa), H₂ (5 MPa), 150 °C, 24 h.

Finally, we tested Re(1)/TiO₂ for the hydrogenation of CO₂ after a reduction with H₂ at different temperatures (200, 300, 500, 700, and 900 °C), as shown in **Fig. 7**. The results show that the best performance is observed for Re(1)/TiO₂ pre-treated at 500 °C. X-ray absorption near edge structure (XANES) measurements were measured in order to determine the oxidation states of Re species, as given in **Fig. 8**. Note that the XANES spectra were collected at room temperature without exposure to air after the H₂ reduction by sealing the samples in a glove bag filled with N₂. Chemical shifts of the binding energy as a function of the reduction temperature are also plotted.⁶⁵ The shifts for reference samples ReO₃, ReO₂, and Re metallic powder are shown with dotted lines. The obtained results suggest that the valence of the Re species decreases with increasing reduction temperature, which implies that the average oxidation state of the Re species responsible for the catalytic formation of MeOH should be higher than 0 and below +4. It is well-known that Re often shows high dispersion on supports, that it is difficult to be reduced, and exhibits a variety of oxidation states.⁶⁶⁻⁶⁸ These features render research on

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catalytically active Re components highly challenging, and consequently, little is known about the chemical identity of such catalytically active Re species.⁶⁹ The precise nature of the catalytically active Re species remains unknown and the catalyst may contain a variety of Re species in different oxidation states. At present, we cannot exclude the possibility that these mixtures of Re species in different oxidation states and the interfaces between them are necessary for the efficient progression of the reaction. HAADF-STEM measurements suggest that reduction temperatures beyond 500 °C should lead to sintering of the Re species, which

would prevent the formation of MeOH (Figs. 9 and 10).



Figure 7. Effect of the pre-treatment reduction temperature on the CO₂ hydrogenation catalyzed by Re(1)/TiO₂ catalysts. Pre-treatment: H₂ (30 mL min⁻¹), 0.5 h; reaction conditions: 0.0054 mmol of Re, 1,4-dioxane (1 mL), CO₂ (1 MPa), H₂ (5 MPa), 150 °C, 24 h.



Figure 8. Re L₃-edge XANES spectra of Re(1)/TiO₂ after temperature-dependent reductions (left) and the chemical shift of the binding energy as a function of the reduction temperature (right). The samples were treated at 200, 500, or 900 °C under a flow of H₂. The XANES spectra were taken at room temperature without exposure to air after the reduction treatment by sealing the samples under N₂.



Figure 9. HAADF-STEM images of Re(1)/TiO₂ after the reduction at 200 °C under a flow of H₂.



Figure 10. HAADF-STEM images of Re(1)/TiO₂ after the reduction at 900 °C under a flow of H₂.

CONCLUSIONS

The hydrogenation of CO₂ was carried out under mild conditions (T < 150 °C; $p_{CO2} = 1$ MPa; $p_{H2} = 5$ MPa) using various heterogeneous Re/TiO₂ catalysts and a series of other catalysts that includes TiO₂-supported catalysts, oxide-supported, and unsupported Re catalysts. The highest TON and selectivity for the formation of MeOH was observed for Re(1)/TiO₂, i.e., a TiO₂-supported Re catalyst with a Re loading of 1 wt%. Studies on structure-activity relationship indicates that Re species responsible for the catalytic formation of MeOH should be sub-nanometer size and have oxidation states higher than 0 and below +4.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org. CO₂-TPD, FT-IR, and STEM images.

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