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# Heterogeneous Pt and $MoO_x$ Co-Loaded TiO<sub>2</sub> Catalysts for Low-Temperature CO<sub>2</sub> Hydrogenation to Form CH<sub>3</sub>OH

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# ABSTRACT

Efficient conversion of CO<sub>2</sub> into useful chemicals, exemplified by the development of methods for low-temperature hydrogenation of CO<sub>2</sub> to form methanol (CH<sub>3</sub>OH), is a highly attractive research target. Herein, we report that Pt nanoparticles, loaded on MoO<sub>x</sub>/TiO<sub>2</sub> as a support (Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub>; Pt = 3 wt%, MoO<sub>3</sub> = 30 wt%), promote selective hydrogenation of CO<sub>2</sub> to produce CH<sub>3</sub>OH in a 73% yield under mild conditions (*T* = 150 °C; *t* = 48 h;  $p_{CO2}$  = 1 MPa;  $p_{H2}$  = 5 MPa). It is significant that the observed yield is almost the equilibrium yield of CH<sub>3</sub>OH expected under the current reaction condition. In terms of both the yield and selectivity for CH<sub>3</sub>OH production, the performance of Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> is better than that of other metal catalysts supported on MoO<sub>x</sub>(30)/TiO<sub>2</sub> and Pt catalysts on other supports. Moreover, the results of an investigation of the reaction mechanism using *in situ* X-ray absorption fine structure (XAFS) suggest that reduced MoO<sub>x</sub> species are responsible for progress of this efficient reaction.

**KEYWORDS:** Hydrogenation of  $CO_2$ ,  $CH_3OH$  synthesis, platinum,  $MoO_x$ ,  $TiO_2$ , *in situ* spectroscopy

## **1. INTRODUCTION**

Energy generation and chemical production from renewable carbon sources has gathered much attention recently because of the increasing concern about the fossil fuels depletion and climate change.<sup>1,2</sup> Carbon dioxide (CO<sub>2</sub>), which is one of the major components of green-house gases, is a promising substance for potential use as an abundant and inexpensive carbon source in the production of useful chemicals.<sup>3,4,13,5–12</sup> Among various chemicals that can be synthesized from CO<sub>2</sub>, preparation of methanol (CH<sub>3</sub>OH) by CO<sub>2</sub> hydrogenation reactions has been of great interest in the industrial and scientific communities.<sup>14–20</sup> The reason for this interest lies in the fact that CH<sub>3</sub>OH can be a precursor for various chemicals.<sup>21</sup> In addition, CH<sub>3</sub>OH can be utilized as a fuel and a liquid energy carrier.<sup>22,23</sup>

In the 1920's, it was observed that  $CH_3OH$  can be produced from syngas ( $CO/H_2$ ) mixtures) by using a ZnO catalyst.<sup>24</sup> However, this process is highly inefficient, and it requires extremely high pressures and temperatures (p = 20 MPa; T = 400 °C). Although addition of Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub> improved the stability of the catalyst and its activity, it had only a minor impact on the requirement for harsh reaction conditions. Also, addition of Cu was found to significantly improve the activity, but the catalytic activity of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> was short lived due to poisoning or sintering. In the 1960's, workers at Imperial Chemical Industries (ICI) discovered a new co-precipitation method for the preparation of a highly active and stable Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst for CH<sub>3</sub>OH synthesis. Since then, much effort has been devoted to this problem and, consequently, CH<sub>3</sub>OH is mainly manufactured from fossil-derived synthesis gas, which is composed of H<sub>2</sub> and CO in addition to a little amounts of CO<sub>2</sub>, by using the Cu-based catalysts operated under harsh reaction conditions (p = 5-10 MPa; T > 200 °C).<sup>25</sup> Recently, direct production of CH<sub>3</sub>OH through CO<sub>2</sub> hydrogenation has been realized industrially by employing similar Cu catalysts.<sup>26,27</sup> Although seminal and impactful, this method suffers from a low equilibrium conversion of CO<sub>2</sub>. Because the hydrogenation process is an exothermic reaction,<sup>28,29</sup> use of a lower reaction temperature would be preferred for CH<sub>3</sub>OH formation.

Low-temperature hydrogenation reaction of  $CO_2$  ( $T \le 150$  °C) to afford  $CH_3OH$  using homogeneous catalysts has been investigated recently.<sup>30–42</sup> The homogeneous catalysts generally exhibit good catalytic performance and operate under mild conditions.

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However, these processes normally require additives in order to accomplish high catalytic activity and they suffer from problems associated with product separation. Methods employing solid catalysts have also been examined but most of the catalytic systems developed to date suffer from low catalytic activity.<sup>43–48</sup> Yet some systems based on solid catalysts for low-temperature CO<sub>2</sub> hydrogenation display high catalytic performance.<sup>49–53</sup> These catalytic systems include Pt<sub>3</sub>Co octapods,<sup>49</sup> Rh<sub>75</sub>W<sub>25</sub> nanosheets,<sup>50</sup> Pt/MoS<sub>2</sub>,<sup>51</sup> carbon-supported Pt<sub>4</sub>Co nanowires,<sup>52</sup> and RhCo catalysts.<sup>53</sup> Although being important progress for realizing the low-temperature synthesis of CH<sub>3</sub>OH, the methods utilize catalysts still needs to be improved. Hence, the design and development of easily prepared heterogeneous catalysts that operate to selectively and efficiently form CH<sub>3</sub>OH under mild conditions typically temperature below 150 °C is highly important. In addition, the previous reports describing these catalysts do not discuss the by-products formation such as CH<sub>4</sub> and CO, which is problematic with CO<sub>2</sub> hydrogenation as we normally observe these by-products even when employing homogeneous catalytic systems.<sup>54</sup>

In this study described below, we employed Pt nanoparticles loaded on a  $MoO_x/TiO_2$  support (Pt(3)/MoO\_x(30)/TiO\_2; Pt = 3 wt%, MoO\_3 = 30 wt%) as a catalyst for  $CO_2$  hydrogenation to form CH<sub>3</sub>OH at low reaction temperature (150 °C). We observed that the catalyst is highly active, selective for CH<sub>3</sub>OH production, and can be readily prepared and handled. A comparison of the performance of several catalysts, including the Cu-based CH<sub>3</sub>OH synthesis catalyst (Cu/Zn/Al<sub>2</sub>O<sub>3</sub>) which is industrially used, revealed that the performance of Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> surpasses those of all others tested in terms of both the yield and selectivity for production of CH<sub>3</sub>OH. Finally, the results of this effort demonstrate that a combination of Pt and Mo is crucial to achieve the observed high activities.

#### 2. EXPERIMENTAL

#### Chemicals and Preparation of the Catalysts

Chemicals and materials were purchased from commercial suppliers and used without further purification. TiO<sub>2</sub> (P25) was obtained from Degussa. The carbon support and MoO<sub>3</sub> were commercially obtained from Kishida Chemical. Al<sub>2</sub>O<sub>3</sub> was prepared by calcination of boehmite (Catapal B, Sasol) for 3 h at T = 900 °C. ZrO<sub>2</sub> (JRC-ZRO-2) was supplied by the Catalysis Society of Japan. HZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio = 22:1 was purchased from TOSOH Co., Ltd. SiO<sub>2</sub> (CariACT Q-10) was purchased from Fuji Silysia Chemical Company Ltd. Nb<sub>2</sub>O<sub>5</sub> was prepared by calcination of niobic acid (Nb<sub>2</sub>O<sub>5</sub>·*n*H<sub>2</sub>O, HY-340) supplied from CBMM (Companhia Brasileira de Metalurgia e Mineração), at 500 °C for 3 h. CeO<sub>2</sub> was prepared by calcination (600 °C, 3 h, in air) of CeO<sub>2</sub> (Type A) obtained from Daiichi Kigenso Kagaku Kogyo Co., Ltd. An industrial Cu/Zn/Al<sub>2</sub>O<sub>3</sub> catalyst (MDC-7; Cu = 34 wt%) was obtained from Clariant.

Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> (3 wt% Pt, 30 wt% MoO<sub>3</sub>) was prepared by using the sequential impregnation method. First, MoO<sub>3</sub>-loaded TiO<sub>2</sub> (MoO<sub>3</sub>(30)/TiO<sub>2</sub>) was prepared by using impregnation of TiO<sub>2</sub>. In the process, a mixture of 1.4 g of TiO<sub>2</sub> and 0.74 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O in a 500 mL glass vessel containing 100 mL of deionized water was stirred for 15 min with 200 rpm agitation at room temperature. The mixture was evaporated to dryness at 50 °C, dried at 110 °C for 12 h and calcinated in air at 500 °C for 3 h to give MoO<sub>3</sub>(30)/TiO<sub>2</sub>. The formed MoO<sub>3</sub>(30)/TiO<sub>2</sub> was then added to an aqueous HNO<sub>3</sub> solution containing Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>. The mixture was evaporated to dryness at 50 °C and further dried in air at 110 °C for 12 h to give PtO<sub>2</sub>(3)/MoO<sub>3</sub>(30)/TiO<sub>2</sub> (Unreduced sample). The catalyst used in the hydrogenation process was prepared by reduction of Pt(3)/MoO<sub>3</sub>(30)/TiO<sub>2</sub> in a quartz tube under a flow of H<sub>2</sub> (20 cm<sup>3</sup> min<sup>-1</sup>) at 300 °C for 0.5 h to give Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub>. The Pt/MoO<sub>x</sub>/TiO<sub>2</sub> catalysts having different Pt and MoO<sub>3</sub> contents were prepared in the same manner using different amounts of MoO<sub>3</sub>(30)/TiO<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.

Other supported catalysts were prepared in the manner described above by using  $MoO_3(30)/TiO_2$  and other metal sources including aqueous solutions of  $NH_4ReO_4$ ,  $RuCl_3$ ,  $IrCl_3 \cdot nH_2O$ ,  $AgNO_3$ ,  $Cu(NO_3)_2 \cdot 3H_2O$ ,  $Ni(NO_3)_2 \cdot 6H_2O$ , and  $Co(NO_3)_2 \cdot 6H_2O$  and aqueous  $HNO_3$  solutions of  $Rh(NO_3)_3$  and  $Pd(NH_3)_2(NO_3)_2$ . For the preparation of  $Pt(3)/MO_x(30)/TiO_2$  (M = V and W),  $NH_4VO_3$  and  $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$  were independently used as respective precursors,

and the procedure is the same manner as described above.  $TiO_2$ -supported Re catalysts (Re/TiO<sub>2</sub>) were prepared with TiO<sub>2</sub> (ST-01; Ishihara Sangyo Co., Ltd.) and NH<sub>4</sub>ReO<sub>4</sub> (SigmaAldrich) as precursors according to the literature.<sup>55</sup>

#### **Catalysts Characterization**

X-ray diffraction (XRD) measurements were carried out using Miniflex (Rigaku) with CuK $\alpha$  radiation. Scanning transmission electron microscopy (STEM) observations were performed using a JEM-ARM200F microscope equipped with a JED-2300 EDX spectrometer (JEOL). Samples were prepared by dropping an ethanol solution containing the catalyst on carbon-supported Cu grids. Temperature programmed reduction with H<sub>2</sub> (H<sub>2</sub>-TPR) was performed by using BELCAT II (MicrotracBEL) with a cryo apparatus. A sample was mounted in a cell and then heated at a ramping rate of 10 °C min<sup>-1</sup> under a flow of 5% H<sub>2</sub>/Ar (20 cm<sup>3</sup> min<sup>-1</sup>). The effluent gas was passed through a trap system that contains MS4A to remove the produced water and then through a thermal conductivity detector (TCD) to determine the consumed amount of H<sub>2</sub> in the process. Due to the experimental setup, separate experiments were carried out using temperature range of -100-50 °C and 100-900 °C.

Pt L<sub>3</sub>-edge and Mo K-edge X-ray absorption fine structure (XAFS) spectra were collected at the BL01B1 of SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI) (proposal 2018B1126). A Si(311) double crystal monochromator was used for the measurements. For pseudo *in situ* analysis, Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub>, pre-reduced under a flow of H<sub>2</sub> (20 cm<sup>3</sup> min<sup>-1</sup>) for 0.5 h at 300 °C, was cooled down to room temperature under the H<sub>2</sub> flow and sealed in a cell made of polyethylene under N<sub>2</sub> atmosphere. The XAFS spectrum was then recorded at room temperature. Fourier transformation of the k<sup>3</sup>-weighted extended XAFS (EXAFS) was conducted over a k range 3.0-12.0 Å<sup>-1</sup>. Curve-fitting EXAFS analysis was performed using the REX ver. 2.5 program provided by RIGAKU and parameters for the Pt–Pt and Pt–O shells simulated with FEFF6. For *in situ* analysis, samples in pellet forms ( $\phi$ 10 mm) were introduced into a cell equipped with Kapton film windows and gas lines. Pretreatment of the samples involved heating under a flow of 5% H<sub>2</sub>/He (100 cm<sup>3</sup> min<sup>-1</sup>) at 300 °C. Spectra were recorded on samples under a flow of 5% H<sub>2</sub>/He (100 cm<sup>3</sup> min<sup>-1</sup>) and under subsequent exposure to 10% CO<sub>2</sub>/He (100 cm<sup>3</sup> min<sup>-1</sup>) at 150 °C.

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IR measurements were carried out using JASCO FT/IR-4200 equipped with a MCT detector. Self-supporting pellets were prepared using 40 mg samples ( $\phi$  = 2 cm), and placed in a quartz cell having CaF<sub>2</sub> windows. Prior to measurements, the pellets were subjected to pretreatment (300 °C, 0.5 h) using 30% H<sub>2</sub>/He flow (70 cm<sup>3</sup> min<sup>-1</sup>). This was followed by lowering temperature to 150 °C under He (100 cm<sup>3</sup> min<sup>-1</sup>). Subsequently, the mixed gas that contains CO<sub>2</sub> (10 cm<sup>3</sup> min<sup>-1</sup>), H<sub>2</sub> (30 cm<sup>3</sup> min<sup>-1</sup>), and He (50 cm<sup>3</sup> min<sup>-1</sup>) was fed into the *in situ* IR cell, and the IR observations were performed. A spectrum for a reference collected at 150 °C under the 30% H<sub>2</sub>/He flow was subtracted from each measured spectrum.

#### Catalytic CO<sub>2</sub> Hydrogenation Reactions

The following representative procedure was used for the CO<sub>2</sub> hydrogenation reactions. After being reduced with H<sub>2</sub> at 300 °C (*cf.* preparation of the catalyst), the catalyst (300 mg) and 1,4dioxane (1 mL) were added to an autoclave (10 mL). The reaction mixture was magnetically stirred at 150 °C under a pressurized condition ( $p_{CO2}$  = 1 MPa and  $p_{H2}$  = 5 MPa). CH<sub>3</sub>OH was analyzed employing a GC-FID (Shimadzu GC-2014 equipped with a capillary column PoraBond Q; Agilent Technologies) using *n*-decane (0.3 mmol) as an internal standard while other products analysis was accomplished by employing a GC-FID (Shimadzu GC-2014 having a Porapak Q column) equipped with a Shimadzu MTN-1 methanizer.

## **3. RESULTS AND DISCUSSION**

## Characterization of the Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> Catalyst

Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> was prepared employing a sequential impregnation method using Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and TiO<sub>2</sub> followed by H<sub>2</sub> reduction (T = 300 °C). XRD was used to characterize the prepared materials (**Figure 1**). The XRD pattern of pristine TiO<sub>2</sub> (P25) contains peaks associated with both the anatase and rutile phase. Analysis of the peaks formed after loading the Mo species shows that the introduced Mo species in MoO<sub>3</sub>(30)/TiO<sub>2</sub> exist as MoO<sub>3</sub>. These MoO<sub>3</sub> peaks were also seen in the pattern of PtO<sub>2</sub>(3)/MoO<sub>3</sub>(30)/TiO<sub>2</sub> (Unreduced sample). After H<sub>2</sub> reduction at 300 °C, peaks corresponding to MoO<sub>3</sub> were minimal and only those corresponding to TiO<sub>2</sub> are present, indicating the absence of the crystalline Mo oxides which can be detectable by XRD. It should be noted that peaks assignable to Pt species are not present in the XRD patterns.

In order to investigate the morphologies and particle sizes of the introduced Mo and Pt species, high-angle annular dark-field STEM observations were made. **Figure 2** displays HAADF-STEM images of pristine TiO<sub>2</sub> (P25), MoO<sub>3</sub>(30)/TiO<sub>2</sub> and Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> (see also **Fig. S1-3** in Supporting Information). Analysis of the image of MoO<sub>3</sub>(30)/TiO<sub>2</sub> shows that the Mo oxide species is highly dispersed over the TiO<sub>2</sub> surface. In addition, Pt nanoparticles, which can be seen in the image of Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub>, were found to be highly dispersed. The average Pt particle diameter was determined to be 2.7 nm. In addition, energy dispersive x-ray spectroscopy (EDX) mapping of Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> was also performed (**Figure 3**). The results of EDX analysis show that Mo species are present and highly dispersed over the TiO<sub>2</sub> particles, and that the bright nanoparticles are Pt.



**Figure 1.** XRD patterns of pristine  $TiO_2$ ,  $MoO_3(30)/TiO_2$ ,  $PtO_2(3)/MoO_3(30)/TiO_2$ , and  $Pt(3)/MoO_x(30)/TiO_2$ .



**Figure 2.** HAADF-STEM images for pristine  $TiO_2$  (P25),  $MoO_3(30)/TiO_2$ , and  $Pt(3)/MoO_x(30)/TiO_2$  together with the particle size distribution of Pt.





**Figure 3.** A HAADF-STEM image and EDX mapping for  $Pt(3)/MoO_x(30)/TiO_2$ . The Pt, Mo, Ti, and O signals are related to the catalyst composition. The C and Cu signals arise from the grid used for the measurement.

XAFS measurements were performed in order to determine the states in which Pt and Mo species exist in the catalyst. **Figure 4(A,B)** show the results of the Pt L<sub>3</sub>-edge X-ray absorption near-edge structure (XANES) and EXAFS measurements for unreduced PtO<sub>2</sub>(3)/MoO<sub>3</sub>(30)/TiO<sub>2</sub>, reduced Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub>, and the reference compounds (PtO<sub>2</sub> and Pt foil). The atomic distances and coordination numbers (CNs) for the Pt–O and Pt–Pt shells were obtained by a curve-fitting analysis of the EXAFS, as given in **Table 1**. The XANES spectrum of PtO<sub>2</sub>(3)/MoO<sub>3</sub>(30)/TiO<sub>2</sub> contains a prominent white-line peak which is similar to that in the spectrum of PtO<sub>2</sub>. The EXAFS of PtO<sub>2</sub>(3)/MoO<sub>3</sub>(30)/TiO<sub>2</sub> is composed of only a Pt–O contribution at 1.99 Å with a CN of 5.4. These results show that the Pt species in PtO<sub>2</sub>(3)/MoO<sub>3</sub>(30)/TiO<sub>2</sub> are PtO<sub>2</sub>. The XANES spectrum of the reduced Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> is identical to that of Pt foil used as a reference. The EXAFS analysis of Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> shows the presence of Pt–Pt bonds with CN of 3.5 at 2.77 Å. The observed distance is slightly longer

than the distance of Pt–Pt seen in bulk Pt metal (2.76 Å) although it is known that the distance becomes shorter if nanoparticles are formed,<sup>56</sup> as we observed to exist by using STEM measurements. The elongation of the Pt–Pt bond in reduced  $Pt(3)/MoO_x(30)/TiO_2$  might be a result of formation of Pt–Mo bimetals for some Pt species.<sup>57</sup>

The results of Mo K-edge XAFS measurements are shown in **Fig. 4(C)**. The XANES spectra demonstrate that the edge position and shape of  $PtO_2(3)/MoO_3(30)/TiO_2$  are almost the same as those observed for MoO<sub>3</sub> as a reference. This result is in agreement with observations made using XRD measurements. On the other hand, the absorption edge of reduced  $Pt(3)/MoO_x(30)/TiO_2$  is shifted to lower energy, indicating that the Mo oxide species is reduced in the H<sub>2</sub> pretreatment. These results were confirmed by performing H<sub>2</sub>-TPR using a cryo apparatus (**Fig. 4(D**)). A peak corresponding to the reduction of Pt species appeared below temperature of 0 °C. The fact that XANES spectrum of  $PtO_2(3)/MoO_3(30)/TiO_2$  after H<sub>2</sub> reduction at room temperature is essentially the same as that of Pt foil confirms this conclusion (**Figure S4**). Also, a small peak can be found at around 250 °C. Considering the fact that the reduced Mo species was identified by XAFS analysis for Pt(3)/MoO\_x(30)/TiO<sub>2</sub> which is reduced at 300 °C, this small peak is assignable to the reduction of Mo oxide species. A broad peak around 500 °C and another peak at around 850 °C were also observed. On the other hand,  $MoO_3(30)/TiO_2$  exhibits only two peaks at around 500 °C and 850 °C. These observations indicate that Pt promotes reduction of Mo oxide species.

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**Figure 4.** Pt L<sub>3</sub>-edge (A) XANES, (B) EXAFS Fourier transforms, and (C) Mo K-edge XANES of  $PtO_2(3)/MoO_3(30)/TiO_2$ ,  $Pt(3)/MoO_x(30)/TiO_2$ , and the reference compounds. The spectra were recorded at room temperature. The spectra of  $Pt(3)/MoO_x(30)/TiO_2$  were recorded on samples that were not exposed to air after the reduction pretreatment and contained in sealed vessels under N<sub>2</sub>. (D) H<sub>2</sub>-TPR profile of  $MoO_3(30)/TiO_2$ , and  $Pt(3)/MoO_x(30)/TiO_2$ . The sample was heated using a temperature ramp-rate of 10 °C min<sup>-1</sup> in a flow of 5% H<sub>2</sub>/Ar (20 cm<sup>3</sup> min<sup>-1</sup>).

Table 1. Curve-fitting analysis of the Pt L <sub>3</sub> -edge EXAFS of the PtO <sub>2</sub> (3)/MoO <sub>3</sub> (30)/TiO <sub>2</sub> ar	nd
Pt(3)/MoOx(30)/TiO <sub>2</sub> catalysts.	

$PtO_{a}(3)/MOO_{a}(30)$	$1)/TiO_{2}$ Pt_O	54	1 99	0.055	36
$Pt(3)/M_0O_(30)/T$	iΩ <sub>2</sub> Pt–Pt	3.5	2 77	0.050	29

## Low-Temperature (T = 150 °C) Hydrogenation of CO<sub>2</sub>

CO<sub>2</sub> hydrogenation reactions were carried out to assess the catalytic properties of catalysts. Reactions were performed employing a catalyst (300 mg) that is pretreated with H<sub>2</sub> at 300 °C in a stainless autoclave (V = 10 mL; T = 150 °C;  $p_{CO2} = 1$  MPa;  $p_{H2} = 5$  MPa; t = 24 h). Analysis of the results displayed in **Table 2** shows that a process catalyzed by Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> generates CH<sub>3</sub>OH in 66% yield (entry 1) and that CH<sub>4</sub> is produced as a minor by-product. In contrast, reactions promoted by other metal catalysts supported on MoO<sub>x</sub>(30)/TiO<sub>2</sub> do not form significant amounts of CH<sub>3</sub>OH (entries 2-10) and no reaction occurs when MoO<sub>3</sub>(30)/TiO<sub>2</sub> is used (entry 11). In reactions promoted by the other supported Pt catalysts (entries 12-20), formation of CH<sub>3</sub>OH along with by-products such as CO and CH<sub>4</sub>. This observation indicates that catalysts comprised of bulk MoO<sub>3</sub> as a support are ineffective in this reaction.

It is well known that combining more than two active components is highly effective in creating catalysts for various hydrogenation reactions. Also, it is known that catalysts which combine group 5–7 metals with group 8–10 metals efficiently promote these processes.<sup>58–64</sup> Therefore, we explored the use of a combination of Pt and other metals such as W and V (entries 21-22). However, these catalyst combinations were found to be ineffective. We also explored other supports that utilize a combination of Pt and Mo species (entries 23-26). The results show that these catalysts promote generation of  $CH_3OH$  relatively efficiently, indicating the importance of combination of Pt and Mo as active components. However, the yields of these processes are still lower than that using Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub>, suggesting that TiO<sub>2</sub> as a catalyst support plays roles for efficient progression of the reaction. Furthermore, the industrially-used Cu-based catalyst Cu/Zn/Al<sub>2</sub>O<sub>3</sub> (MDC-7; Cu = 34 wt%) was employed and found to be ineffective under our low-temperature reactions conditions (entry 27). We have also tried Re/TiO<sub>2</sub> which were reported to be active for the low-temperature hydrogenation of CO<sub>2</sub> to form CH<sub>3</sub>OH (entries 28-**29**).<sup>55</sup> While a catalyst with Re loading amount of 1 wt% (Re(1)/TiO<sub>2</sub>) showed the best catalytic performance based on CH<sub>3</sub>OH formation rate per Re in the previous study, we also employed a catalyst with Re loading amount of 3 wt% (Re(3)/TiO<sub>2</sub>) that has the same loading amount of the supported metal for Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub>. The result shows that Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> exhibits better CH<sub>3</sub>OH yield. Thus, Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> is the best catalyst for low-temperature CO<sub>2</sub> hydrogenation to form  $CH_3OH$ .

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Entry	Catalvet	Yield / %		
	Catalyst	CH₃OH	CO	CH <sub>4</sub>
1	Pt(3)/MoO <sub>x</sub> (30)/TiO <sub>2</sub>	66	<1	4
2	Re(3)/MoO <sub>x</sub> (30)/TiO <sub>2</sub>	6	<1	1
3	Ru(3)/MoO <sub>x</sub> (30)/TiO <sub>2</sub>	<1	<1	4
4	$Ir(3)/MoO_x(30)/TiO_2$	3	1	19
5	Rh(3)/MoO <sub>x</sub> (30)/TiO <sub>2</sub>	14	1	5
6	Pd(3)/MoO <sub>x</sub> (30)/TiO <sub>2</sub>	<1	<1	4
7	Ag(3)/MoO <sub>x</sub> (30)/TiO <sub>2</sub>	<1	<1	<1
8	Cu(3)/MoO <sub>x</sub> (30)/TiO <sub>2</sub>	<1	<1	<1
9	Ni(3)/MoO <sub>x</sub> (30)/TiO <sub>2</sub>	<1	<1	4
10	Co(3)/MoO <sub>x</sub> (30)/TiO <sub>2</sub>	<1	<1	<1
11	MoO <sub>x</sub> (30)/TiO <sub>2</sub>	<1	<1	<1
12	Pt(3)/Carbon	<1	<1	<1
13	$Pt(3)/Al_2O_3$	<1	1	<1
14	Pt(3)/ZrO <sub>2</sub>	<1	2	<1
15	Pt(3)/HZSM-5(22)	<1	<1	<1
16	Pt(3)/SiO <sub>2</sub>	<1	1	<1
17	Pt(3)/Nb <sub>2</sub> O <sub>5</sub>	<1	3	<1
18	Pt(3)/CeO <sub>2</sub>	<1	2	<1
19	Pt(3)/TiO <sub>2</sub>	<1	6	1
20	Pt(3)/MoO <sub>3</sub>	5	4	2
21	Pt(3)/WO <sub>x</sub> (30)/TiO <sub>2</sub>	9	3	3
22	Pt(3)/VO <sub>x</sub> (30)/TiO <sub>2</sub>	<1	7	<1
23	Pt(3)/MoO <sub>x</sub> (30)/Al <sub>2</sub> O <sub>3</sub>	33	1	5
24	Pt(3)/MoO <sub>x</sub> (30)/SiO <sub>2</sub>	4	4	1
25	Pt(3)/MoO <sub>x</sub> (30)/Carbon	8	2	8
26	Pt(3)/MoO <sub>x</sub> (30)/ZrO <sub>2</sub>	42	<1	5
27	Cu/Zn/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	20	2	<1
28 <sup>c</sup>	Re(1)/TiO <sub>2</sub>	5	1	<1
29 <sup>c</sup>	Re(3)/TiO <sub>2</sub>	19	1	4

## Table 2. Hydrogenation of CO<sub>2</sub> promoted by various catalysts.<sup>a</sup>

<sup>a</sup>Pretreatment: H<sub>2</sub> (20 cm<sup>3</sup> min<sup>-1</sup>), 300 °C, 0.5 h; catalytic reaction conditions: Catalyst (300 mg), CO<sub>2</sub> (1 MPa), H<sub>2</sub> (5 MPa), 1,4-dioxane (1 mL), 150 °C, 24 h. <sup>b</sup> 34 wt% of Cu. <sup>c</sup> H<sub>2</sub> reduction as a pretreatment was performed at 300 °C.

To further optimize the Pt/MoO<sub>x</sub>/TiO<sub>2</sub> catalysts, the effects varying loading amount of Pt and Mo were investigated (Figure 5). The highest yield and selectivity for CH<sub>3</sub>OH formation was achieved using  $Pt(3)/MoO_x(30)/TiO_2$  with a Pt loading of 3 wt% and a  $MoO_3$  loading of 30 wt%. Although the CH<sub>3</sub>OH yield increases with increasing Pt loading, the selectivity for formation of CH<sub>3</sub>OH decreases and a large amount of CH<sub>4</sub> is produced when a catalyst containing 10 wt% Pt is employed. This finding suggests that larger Pt nanoparticles favor the production of CH<sub>4</sub>,

which is in good agreement with previous reports on  $CO_2$  hydrogenation over Rh/TiO<sub>2</sub> and Re/TiO<sub>2</sub>.<sup>55,65</sup> Moreover, the results show that addition of Mo has a huge impact on the efficiency of CH<sub>3</sub>OH generation and that a 30 wt% loading is optimal for the process. As a consequence, we conclude that among the catalysts explored in this study Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> is the best for low-temperature (150 °C) CO<sub>2</sub> hydrogenation of to form CH<sub>3</sub>OH.

Using this optimized catalyst, the time course of the  $CO_2$  hydrogenation reaction was observed. Inspection of the time-course plot shown in Fig. 6 demonstrates that the concentrations of CH<sub>3</sub>OH and CH<sub>4</sub> increase with increasing reaction time. It is significant that the CH<sub>3</sub>OH yield after a reaction time of 48 h is 73%, which is almost the equilibrium yield expected under the reaction conditions used. Note that other possible by-products such as formaldehyde (HCOH) and formic acid (HCOOH) are not formed in this process. In addition, recycling tests of Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> were carried out to investigate the recyclability of our heterogeneous catalyst system, as shown in Fig. S5. Following the reaction,  $Pt(3)/MoO_x(30)/TiO_2$  was separated from the reaction solution, washed with 1,4-dioxane, dried in an oven (110 °C) under air atmosphere, and subsequently reused for an ensuing reaction. Note that the recycling reaction was carried out with and without H<sub>2</sub> reduction at T = 300 °C as a pretreatment for every catalytic run. The obtained results show that the catalyst can be reused but the CH<sub>3</sub>OH yield and selectivity gradually decreased for both recycling tests. It was also found that the activity loss was more significant when the H<sub>2</sub> reduction was performed for each recycling run. This finding indicates that the catalyst does not need to be reduced for recycling. The total turnover number on the basis of CO adsorption amount performed at 30 °C for the fresh sample was determined to be 3588 (Fig. S5(A)). In order to assess reasons of the catalyst deactivations, HAADF-STEM observations were made for samples after the 4th recycling experiments (Figs. S6 and S7). Both spent catalysts show larger average Pt particle diameters than that of the fresh  $Pt(3)/MoO_x(30)/TiO_2$  catalyst. The average Pt particle diameter for the used catalyst recycled with the H<sub>2</sub> reduction pretreatment for each recycling run (3.7 nm) was larger than that for the one that a pretreatment was only performed before the first run (3.2 nm). These results suggest that aggregation of Pt particles would be a reason for the observed activity loss. It should also be noted that formation of Pt–Mo bimetals can also be a possible reason for the deactivation.57



**Figure 5.** Effect of the (A) Pt and (B)  $MoO_3$  loading amount on the hydrogenation reaction of  $CO_2$  over Pt/MoO<sub>x</sub>/TiO<sub>2</sub>. Pretreatment: H<sub>2</sub> (20 cm<sup>3</sup> min<sup>-1</sup>), 300 °C, 0.5 h; catalytic reaction conditions: Catalyst (300 mg), CO<sub>2</sub> (1 MPa), H<sub>2</sub> (5 MPa), 1,4-dioxane (1 mL), 150 °C, 24 h. 30 wt% of MoO<sub>3</sub> loading was employed for investigation on the effect of Pt loading while 3 wt% of Pt loading was employed for investigation on the effect of MoO<sub>3</sub> loading.



**Figure 6.** Time course for the hydrogenation reaction of  $CO_2$  over  $Pt(3)/MoO_x(30)/TiO_2$ . Pretreatment:  $H_2$  (20 cm<sup>3</sup> min<sup>-1</sup>), 300 °C, 0.5 h; catalytic reaction conditions: Catalyst (300 mg),  $CO_2$  (1 MPa),  $H_2$  (5 MPa), 1,4-dioxane (1 mL), 150 °C, 24 h.

# Mechanistic Study

Catalytic hydrogenation reactions using HCOOH or CO as a starting material were performed in order to obtain additional insights into the catalytic reaction promoted by Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> (Scheme 1). Hydrogenation of CO, employing the same pressure used in the CO<sub>2</sub> reduction reaction catalyzed by Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> (1 MPa), proceeds to form CH<sub>3</sub>OH. However, hydrogenation of CO<sub>2</sub> forms CH<sub>3</sub>OH at the higher rate of 0.16 mmol h<sup>-1</sup>. Also, a larger amount of CH<sub>4</sub> is generated as a by-product when CO is employed as starting material. This result suggests that it is possible that CO is an intermediate in the formation of CH<sub>3</sub>OH but direct hydrogenation of CO<sub>2</sub> to form CH<sub>3</sub>OH would be a preferable process. It is worth mentioning here that CO<sub>2</sub> can be formed through the water-gas shift reaction between CO and the produced H<sub>2</sub>O to give CO<sub>2</sub> and H<sub>2</sub>. In contrast, reaction of HCOOH generates CH<sub>3</sub>OH at a higher rate than that for the reaction of CO<sub>2</sub>, implying that derivatives of HCOOH such as HCOO<sup>-</sup> adsorbed on the surface of the catalyst can be intermediates for the CH<sub>3</sub>OH formation. Note that the decomposition of HCOOH to form CO and CO<sub>2</sub> may occur faster although they can be recycled for the CH<sub>3</sub>OH forming process.<sup>66</sup> Decomposition of the CH<sub>3</sub>OH produced in this process is also an important issue. As a result, we explored the decomposition reaction of 5 mmol of CH<sub>3</sub>OH under N<sub>2</sub> atmosphere (0.5 MPa). Note that the amount of CH<sub>3</sub>OH used is almost the same as that of CO<sub>2</sub> used in the hydrogenation process (1 MPa). The result shows that although CH<sub>3</sub>OH does decompose in the presence of the Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> catalyst, the decomposition rate is not as high as that for  $CH_3OH$  formation in the direct hydrogenation of  $CO_2$ .

The hypothesis suggested by observations made in the experiments described above was confirmed by using *in situ* IR analysis (**Fig. 7A**). For this purpose, generation of surface species was investigated for a reaction carried out using Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> at ambient pressure and 150 °C under a gas flow containing CO<sub>2</sub> (10 cm<sup>3</sup> min<sup>-1</sup>), H<sub>2</sub> (30 cm<sup>3</sup> min<sup>-1</sup>) and He (50 cm<sup>3</sup> min<sup>-1</sup>). The samples were subjected to a pretreatment under H<sub>2</sub> flow for 30 min at 300 °C prior to each measurement. Several features in the range of 1300-1600 cm<sup>-1</sup> associated with carbonate and formate species were found to be present in the IR spectrum. For example, the bands at 1340 and 1555 cm<sup>-1</sup> indicate the formation of formate species.<sup>67</sup> In addition, a band occuring at 1430 cm<sup>-1</sup> can be assigned to asymmetric stretching vibration of monodentate carbonates (v<sub>as</sub>(COO)).<sup>68</sup> In contrast, these bands are not prominent in the reaction promoted by MoO<sub>x</sub>(30)/TiO<sub>2</sub>, demonstrating the importance of Pt as a supported metal. Finally, *in situ* Mo

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K-edge XANES analysis was carried out on Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> using CO<sub>2</sub> (**Fig. 7B**). Prior to the XANES measurement, the sample was pretreated by heating at 300 °C under 5% H<sub>2</sub>/He flow (100 cm<sup>3</sup> min<sup>-1</sup>). The spectrum was then recorded under 5% H<sub>2</sub>/He flow (100 cm<sup>3</sup> min<sup>-1</sup>) and under subsequent exposure to 10% CO<sub>2</sub>/He flow (100 cm<sup>3</sup> min<sup>-1</sup>) at 150 °C. XANES analysis shows that the edge position in the spectrum of Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> is positively shifted by introducing CO<sub>2</sub>, demonstrating that CO<sub>2</sub> acts as an oxidant. In other words, the Mo species is oxidized by CO<sub>2</sub>. This result suggests that redox reaction of the Mo species takes place in order to promote the CO<sub>2</sub> hydrogenation reaction, consistent with an oxygen-vacancy driven mechanism (or reverse Mars–van Krevelen mechanism<sup>69</sup>) wherein oxygenates are activated at undercoordinated Mo sites as reported for hydrodeoxygenation reactions.<sup>70</sup> Namely, the surface defect sites, formed during pretreatment by H<sub>2</sub>, play important roles in the hydrogenation of CO<sub>2</sub>. Note that only CO was detected by a thermal conductivity detector GC (490 Micro GC, Agilent Technologies Inc.) upon the introduction of CO<sub>2</sub>. This is probably because the *in situ* Mo K-edge XAFS experiment was performed ambient pressure unlike the catalytic CH<sub>3</sub>OH forming process performed at *p*<sub>CO2</sub> = 1 MPa; *p*<sub>H2</sub> = 5 MPa.

(a) 
$$CO_2 + H_2$$
  
 $1 MPa + 5 MPa$   
 $1 MPa + 5 MPa$   
 $150 °C$   
 $160 °C$   
 $160 °C$   
 $160 °C$   
 $160 0.02 0.01$   
(b)  $CO + H_2$   
 $1 MPa + 5 MPa$   
 $160 °C$   
 $160 0.02 0.01$   
 $160 0.02 0.01$   
 $CH_3OH + CH_4 + CO_2$   
Formation rate = 0.08 0.06 0.05  
 $150 °C$   
 $CH_3OH + CH_4 + CO + CO_2$   
Formation rate = 0.22 0.02 0.40 0.62  
(c)  $HCOOH + H_2$   
 $5 mmol - 5 MPa$   
 $150 °C$   
 $CH_3OH + CH_4 + CO + CO_2$   
Formation rate = 0.22 0.02 0.40 0.62  
 $CH_4 + CO + CO_2$   
Formation rate = 0.19 1.40 2.20  
(e)  $CH_3OH + N_2$   
 $5 mmol - 0.5 MPa$   
 $150 °C$   
 $CH_4 + CO + CO_2$   
Formation rate = 0.19 1.40 2.20  
 $CH_4 + CO + CO_2$   
Formation rate = 0.19 1.40 2.20  
 $CH_4 + CO + CO_2$   
Formation rate = 0.19 1.40 2.20  
 $CH_4 + CO + CO_2$   
Formation rate = 0.19 1.40 2.20  
 $CH_4 + CO + CO_2$   
Formation rate = 0.19 1.40 2.20  
 $CH_4 + CO + CO_2$   
Formation rate = 0.19 1.40 2.20  
 $CH_4 + CO + CO_2$   
Formation rate = 0.19 1.40 2.20  
 $CH_4 + CO + CO_2$   
Formation rate = 0.19 1.40 2.20  
 $CH_4 + CO + CO_2$   
Formation rate = 0.01 0.04 0.03  
Unit = mmol h^{-1}

**Scheme 1.** Hydrogenation and decomposition of model reaction substrates over  $Pt(3)/MoO_x(30)/TiO_2$ . (a)  $CO_2$ , (b) CO, (c,d) HCOOH, (e)  $CH_3OH$ . Pretreatment:  $H_2$  (20 cm<sup>3</sup> min<sup>-1</sup>), 300 °C, 0.5 h; catalytic reaction conditions: Catalyst (300 mg), 1,4-dioxane (1 mL).



**Figure 7.** (A) *In situ* IR spectra measured at 150 °C under a gas flow containing CO<sub>2</sub> (10 cm<sup>3</sup> min<sup>-1</sup>), H<sub>2</sub> (30 cm<sup>3</sup> min<sup>-1</sup>), and He (50 cm<sup>3</sup> min<sup>-1</sup>). Pretreatment: H<sub>2</sub> (20 cm<sup>3</sup> min<sup>-1</sup>), He (50 cm<sup>3</sup> min<sup>-1</sup>), 300 °C, 0.5 h. (B) *In situ* Mo K-edge XANES spectra of Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> collected at 150 °C just after the H<sub>2</sub> reduction at 300 °C (orange line) and after subsequent introduction of 10% CO<sub>2</sub>/He (100 cm<sup>3</sup> min<sup>-1</sup>) (blue line).

# CONCLUSIONS

The catalytic hydrogenation reaction of CO<sub>2</sub> was performed under mild conditions ( $p_{CO2}$  = 1 MPa;  $p_{H2}$  = 5 MPa; T = 150 °C) employing a Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> catalyst and various catalysts including MoO<sub>x</sub>(30)/TiO<sub>2</sub>-supported catalysts, and oxide-supported as well as the industrially-used Cu-based catalyst. Pt(3)/MoO<sub>x</sub>(30)/TiO<sub>2</sub> exhibited the best CH<sub>3</sub>OH yield among the catalysts tested and the CH<sub>3</sub>OH yield after the reaction time of 48 h reached 73%. The obtained findings indicate that the combination of Pt and Mo is highly important to achieve the high activities for CH<sub>3</sub>OH production. More specifically, the reduced MoO<sub>x</sub> species would be a key to success realizing the low-temperature hydrogenation of CO<sub>2</sub> for both academic research and the industrial manufacture of methanol, the presented system would be a highly active and versatile hydrogenation catalyst.

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# ASSOCIATED CONTENT

# Supporting Information

STEM, XAFS, and recycling tests.

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