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Low-Temperature Selective Oxidation of Methane to Methanol over a Platinum Oxide

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The low-temperature activation of methane is highly important as a reaction that can dissociate the strongest C-H bond and convert it into useful compounds. This study demonstrated that supported platinum oxide was found to activate methane near room temperature and selectively afford methanol in the presence of oxygen.

Activation of methane, which has the strongest C-H bond, at low temperatures is of great academic and industrial significance. Liang et al. demonstrated theoretically as well as experimentally that IrO₂, which has a rutile crystal structure, dissociates the C-H bonds of methane below room temperature.¹ When methane was adsorbed on the IrO₂(110) surface at 88 K and then the temperature was increased, most of the adsorbed methane was oxidized and resulting CO, CO₂ and water were desorbed at 400-600 K. Pairs of coordinatively unsaturated metal and oxygen atoms on the surface are important active sites for adsorption of methane and cleavage of C-H bonds. The oxygen-precovered IrO₂(110) surfaces were active for low-temperature methane complete oxidation,² and the IrO₂(110) films proceeded the catalytic oxidation of methane in a CH₄-O₂ mixture which was revealed using

ambient-pressure X-ray photoelectron spectroscopy (XPS).³ The titania-supported IrO₂ catalyst exhibited an exceptional activity for methane complete oxidation, indicating the best combustion catalyst.⁴

Tsuji and Yoshizawa theoretically reported that β-PtO₂, which has an orthorhombic CaCl₂ crystal structure⁵ closely related to the rutile structure like IrO₂, can activate the C-H bond of methane more efficiently than IrO₂ at lower temperatures.⁶ The high activity of β-PtO₂ is assigned to the exposure of the pair of coordinatively unsaturated metal and oxygen atoms on the surface like IrO₂. Furthermore, the energy of the d₂₂ orbital of Pt is lower than that of Ir, suggesting that an effective charge transfer interaction is formed with the σ_{C-H} orbital of methane, promoting activation of the C-H bond and allowing dissociation of the C-H bond at a lower temperature. However, experimentally, β-PtO₂ is difficult to prepare because it is stable only at very high oxygen pressures of several hundred atmospheres and at high temperatures above 873 K.⁷ Calculations of the free energies of formation of the platinum oxide phases indicate that α-PtO₂ with a hexagonal CdI₂ structure is a thermodynamically stable phase at low temperatures up to 870 K and at low oxygen pressure such as 0.1 MPa.⁸ Contrary to β-PtO₂, α-PtO₂ is also known as Adams catalyst⁹ and can be easily synthesized. The crystal structure of α-PtO₂ indicates that the coordinatively unsaturated platinum metals are not exposed on the surface and are all covered by oxygen, thus activation of methane is expected to be difficult. However, actual heterogeneous catalysts, particularly highly dispersed ones, often have oxygen defects and exposed metals on the surface, unlike the model. In these regards, we synthesized supported platinum oxide and explored the possibility of their reactivity with methane at low temperatures close to room temperature. In addition, a theoretical study with density functional theory (DFT) calculations was performed on the reactivity of α-PtO₂ with an oxygen defect towards methane.

The platinum oxide samples in this study were synthesized by oxidation treatment after impregnation of Pt(NH₃)₄(NO₃)₂ on

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an amorphous silica. Silica was used as support because of its weak interaction with metals. X-ray diffraction (XRD) patterns of prepared samples showed no specific peaks, suggesting that supported Pt species were highly dispersed (Fig. S1). Fig. 1 shows Pt L₃-edge X-ray absorption fine structure (XAFS) spectra of 1wt%PtO₂/SiO₂ samples calcined at various temperatures. The spectra of Pt foil, α-PtO₂ and Pt(NH₃)₄(NO₃)₂ are also added as references. The Pt L₃-edge X-ray absorption near edge structure (XANES) spectra show a characteristic white line, the intensity of which corresponds to the oxidation state of platinum (Fig.1(a)). The spectrum of the sample treated at 373 K was mostly the same as that of Pt(NH₃)₄(NO₃)₂, indicating that the impregnated platinum precursor was still intact. The XANES spectrum of the sample treated at 473 K showed some change, and the Fourier transform of EXAFS signal exhibited a shift of the first shell signal (Fig.1(b)). XPS measurements showed a clear decrease of nitrogen species, although some remained (Fig. S2), indicating that some of the precursors were decomposed and slightly oxidized. The treatment at 573 K significantly changed the spectra and the structure was found to be close to that of bulk PtO₂ (Fig.1(a)). A linear combination fitting of the intensity of the white line with Pt foil (Pt⁰) and PtO₂ (Pt⁴⁺) as references gives the approximate average oxidation state of the material.^{10,11} Using the fitting, the sample treated at 573 K was found to have an average oxidation state of +3.3, which is lower than that of bulk PtO₂, suggesting that it contains oxygen defects. This result is supported by the results of charge analysis based on DFT calculations (Fig. S6). In the radial distribution function, the Pt-O signal was observed for the sample treated at 573 K as in the bulk PtO₂, while the Pt-Pt signal was not observed clearly, indicating that the particle size of the supported Pt oxide was small (Fig.1(c)). The average particle size determined from transmission electron microscopy (TEM) image was 3.1 nm (Fig. S3). XPS measurement confirmed the absence of nitrogen species in the sample treated at 573 K. (Fig. S2).

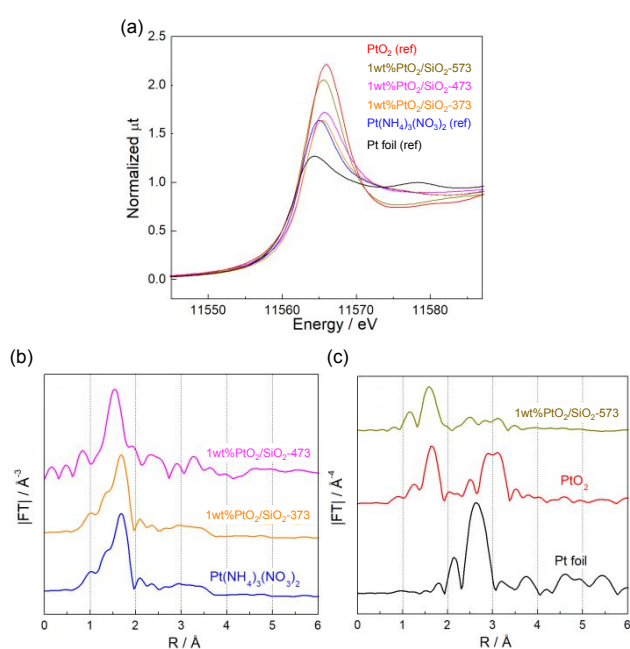


Fig. 1 Pt L₃-edge XAFS spectra of 1wt%PtO₂/SiO₂ samples. (a) XANES, (b) and (c) EXAFS.

The reactivity of the platinum oxide to methane was first evaluated by temperature-programmed reaction of methane (CH₄-TPR). After pretreatment of the catalyst under oxygen flow, only methane was introduced at 313 K and the temperature was increased under the methane flow. This measurement can be used to evaluate the reactivity with methane, and if CO or CO₂ was produced by raising the temperature, it indicates that the catalyst has activated methane and reacted with oxygen contained in the catalyst or oxygen chemisorbed on the catalyst during the pretreatment. Note that the reaction is irreversible because no oxidant is supplied while methane is flowing. Fig. 2 shows the results of CH₄-TPR using 1wt%PtO₂/SiO₂-X (X = 373, 473 and 573 K; calcined temperature during the preparation). In the sample treated at 373 K, CO₂ was produced from around 473 K and peaked at around 523 K (Fig.2(a)). Desorption of CO and water was also observed in the same temperature range. The XAFS spectra of the sample treated at 373 K were almost identical to those of the platinum precursor, suggesting that methane was activated and reacted with divalent platinum and the oxygen chemisorbed on it. The sample treated at 473 K also gave CO₂ desorption peak centred around 523 K (Fig.2(b)). The sample treated at 573 K, which has oxygen-deficient PtO₂ structure, was found to produce CO₂ at even lower temperatures (Fig.2(c)). CO₂ was produced around 373 K, and a peak was observed around 423 K. As a comparison, the result for 1wt%IrO₂/SiO₂ is also shown (Fig.2(d)), in which XRD pattern indicated the formation of IrO₂ crystal phase (Fig. S4). For the IrO₂/SiO₂, CO₂ started to be formed around 423 K with a peak after 573 K. These results demonstrate that PtO₂ can activate methane at much lower temperatures than IrO₂.

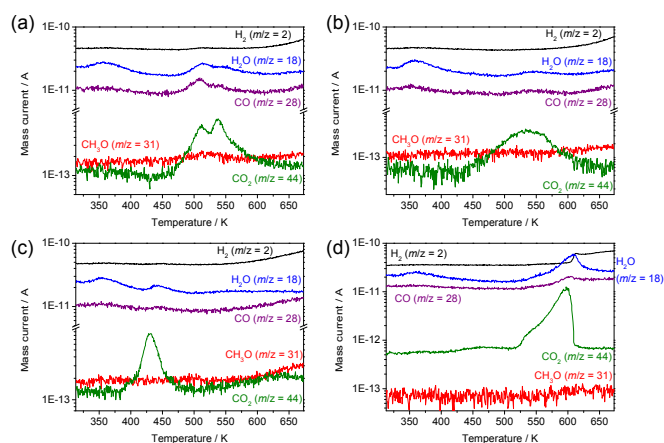


Fig. 2 Results of CH₄-TPR using 1wt%PtO₂/SiO₂ and 1wt%IrO₂/SiO₂ samples. (a) 1wt%PtO₂/SiO₂-373 (b) 1wt%PtO₂/SiO₂-473 (c) 1wt%PtO₂/SiO₂-573, and (d) 1wt%IrO₂/SiO₂.

From CH₄-TPR measurements, silica-supported PtO₂ was found to activate methane and produce CO₂ from ca. 373 K, much lower temperature than IrO₂. As next experiment, we carried out the reactivity test of methane with oxygen over 1wt%PtO₂/SiO₂-573 using a fixed-bed flow reactor (for detailed

reaction setup, see ESI). Methanol and CO₂ were formed, albeit in a very small quantity. Table 1 lists the formation rate of products at 323, 348 and 373 K. The production rates of methanol and CO₂ at 348 K were 0.047 and 0.22 μmol g⁻¹ h⁻¹, respectively, and the selectivity to methanol was 18%. However, no formation of methanol was observed at 373 K probably due to overoxidation. The CO₂ signals seen in the CH₄-TPR were at higher reaction temperatures than those seen when using the fixed-bed flow reactor, at which temperatures only large amounts of CO₂ were produced. Thus, while the CH₄-TPR measurements do not directly provide information on methanol production, these are important experiments showing the prepared platinum oxide could activate methane, i.e. cleave the C-H bond, at low temperatures.

Table 1 Formation rate of products from the reaction of methane over 1wt%PtO₂/SiO₂-573 in the presence of oxygen.

Reaction temp. /K	Formation rate of products / μmol g ⁻¹ h ⁻¹		Product selectivity /%	
	CH ₃ OH	CO ₂	CH ₃ OH	CO ₂
323	0.028	0.14	16	84
348	0.047	0.22	18	82
373	0.00	0.47	0	100

Reaction conditions: 100 mg of 1 wt%PtO₂/SiO₂-573, CH₄/O₂/He = 1.0/1.0/18, Total flow rate: 20 mL min⁻¹.

The reaction mechanism was investigated with DFT calculations. Since α-PtO₂ is a layered compound with a van der Waals gap perpendicular to the c axis,¹² the (001) surface of α-PtO₂ with an oxygen defect was employed as a model for the PtO₂ catalyst so that a coordinatively unsaturated Pt/O pair can be exposed on the surface. For comparison, the α-PtO₂ surface without oxygen defects was also examined. The conditions of the calculations and the details of the model are described in ESI. Fig. 3 shows the activation barriers along with the structures of the intermediate and transition states in the sequence starting from adsorption of CH₄ and ending with desorption of CH₃OH. Methane transitions from the stable adsorption state to the pre-activation state with a small energy cost of 13.6 kcal/mol, and then the C-H bond is cleaved with a moderate activation barrier of 24.2 kcal/mol to form a methyl group and a hydroxy group on the surface. In contrast, the energy cost required for C-H bond cleavage on the oxygen-defect-free α-PtO₂ surface was calculated to be very high at 48.1 kcal/mol (Fig. S7). The methyl group generated on the defective surface then jumps to the O atom of the neighbouring hydroxy group with an activation barrier of 28.3 kcal/mol, yielding methanol. Although a CH₃ radical species appears to be formed in the transition state, the H-C-H bond angle is smaller than 120°, suggesting that it is not an isolated radical. It is also confirmed that this transition state has only one imaginary mode of 81.6i cm⁻¹. This step is considered to be the rate-limiting step of the whole reaction. Such a Mars-van Krevelen-type reaction mechanism for methanol formation was also studied for the β-PtO₂ and IrO₂ surfaces:¹³ the activation barriers of the methyl group transfer on the β-PtO₂ and IrO₂ surfaces were calculated

to be 47.9 and 60.6 kcal/mol, respectively, which are much higher than that on the α-PtO₂ surface.

On the α-PtO₂ surface, the coordination environment around the Pt atom adsorbing CH₃ is characterized as a distorted C-PtO₅ octahedron. Such a structural feature results in the weakening of the overlap between the 2p_z orbital of the C atom and the 5d_{z²} orbital of the Pt atom. Similarly, the orbital overlap between the O atom in CH₃OH and the Pt atom is expected to be reduced, leading to a small methanol desorption barrier of 13.7 kcal/mol. Note that the same process on the β-PtO₂ surface requires a larger desorption barrier of 26.1 kcal/mol.¹³ With such a small methanol desorption barrier, methanol production is competitive with over-oxidation (Fig. S8).

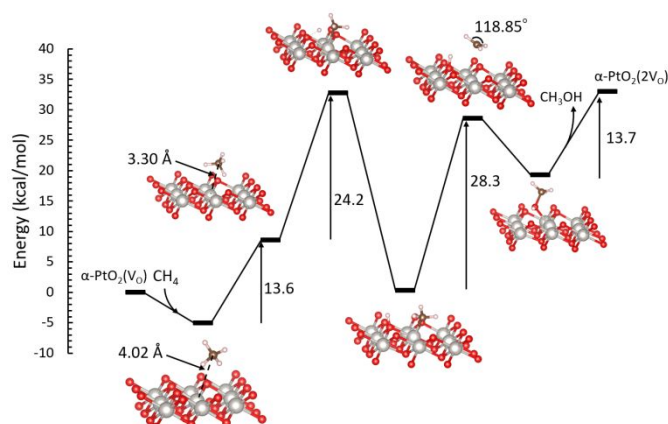


Fig. 3 Calculated energy diagram for methanol formation from methane on the (001) surface of α-PtO₂ with an oxygen defect. The structures of the intermediate and transition states are drawn with VESTA;¹⁴ only the O-Pt-O top surface layer is shown. Colour scheme: grey-platinum, red-oxygen, brown-carbon, white-hydrogen.

We further examined methane activation using a commercial 1wt%Pt/Al₂O₃ which is purchased from Aldrich. The average particle size obtained from TEM measurement was 5.2 nm (Fig. S3). Prior to the reaction, the supported Pt sample was pretreated with 5%O₂/He at 573 K for 1h. As a comparison, the same 1wt%Pt/Al₂O₃ pretreated with 50%H₂/He at 673 K for 1 h was used. The results are shown in Fig. 4. There was a clear difference in activity between the oxygen oxidation pretreatment and the hydrogen reduction pretreatment samples. The oxidized platinum sample produced methanol at temperatures lower than 373 K, and the amount of methanol produced was higher than that of CO₂. In contrast, reduced platinum exhibited no formation of methanol and produced smaller amount of CO₂ than oxidized sample below 373 K. This low-temperature activation of methane over oxidized Pt was unique whereas other precious metals including Pd, Ru, and Rh could not produce methanol by oxidation pretreatment (Table S1). These oxidized metals only gave CO₂ near room temperature.

Table S2 lists the representative examples of low-temperature selective oxidation of methane to methanol. Previous reports of direct methanol production have required

temperatures of 423 K or higher, except when hydrogen peroxide as an oxidant was used in liquid-phase. Although the amount of methanol reported in this study was small, it is significant that methanol was formed at temperatures as low as around room temperature to 373 K.

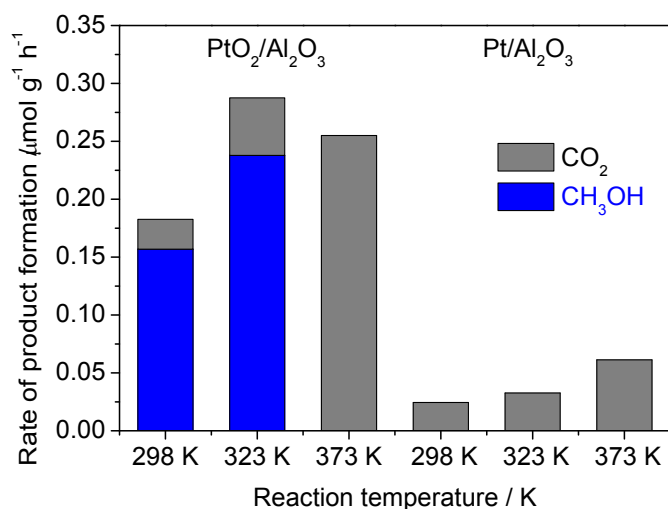


Fig. 4. Methane oxidation over PtO₂/Al₂O₃ and Pt/Al₂O₃ at low temperatures. Reaction conditions: 100 mg of 1wt%Pt samples. CH₄:O₂:He = 8:0.2:16.8. Total flow rate 25 mL min⁻¹.

In summary, the oxidized platinum was found to activate methane and produce methanol at temperatures as low as 323 K, close to room temperature. Theoretical investigations suggest that oxygen-deficient α -PtO₂ has coordinatively unsaturated metal sites that can activate the C-H bond of methane effectively.

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Conflicts of interest

There are no conflicts to declare.

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