

博士論文（要約）

**Methane partial oxidation on Pt based catalysts using an NO/NO<sub>2</sub> oxygen atom  
shuttle**

(NO/NO<sub>2</sub> 酸素原子シャトルを用いた白金系触媒によるメタン部分酸化)

ヴァルギース ヴィビン

## **Introduction**

### **Partial oxidation of methane**

The availability of natural gas has increased over the last decade due to the discovery of new geological fields and the development of methods to extract the gas from shale deposits. Natural gas contains 70-90% methane and is a much cleaner fuel to burn than petroleum or coal, because of its high H/C ratio. However, some of the natural gas is found in remote locations, and it is costly to transport it. Cryogenic liquefaction is uneconomical because of the low boiling point of methane (-162 °C) and pipeline transport is expensive because of high compression and infrastructure costs. The direct conversion of methane to high-density, high-value, liquid products such as methanol, dimethyl ether, or formaldehyde is a means of solving these problems. This thesis deals with the selective oxidation of methane to dimethyl ether with supported platinum catalysts using NO/NO<sub>2</sub> as an oxygen transfer agent with molecular oxygen as the terminal oxidant. Methane is difficult to activate because of its symmetrical tetrahedral structure with strong C-H bonds (440 kJ/mol)[1], high ionization potential, low electron affinity, and low proton affinity (544 kJ/mol). In the present study a catalyst screening was conducted for the direct partial oxidation of CH<sub>4</sub> with NO and O<sub>2</sub> as the oxidant with Pt on different supports. It was found that Pt/Y<sub>2</sub>O<sub>3</sub> was the best catalyst for DME synthesis and it was selected for further studies. A contact time study with Pt/Y<sub>2</sub>O<sub>3</sub> showed that the selectivity to DME reached close to 100 % at very low conversions, suggesting that DME was a primary product. A study of the adsorbed species on the catalyst surface by in situ FTIR analysis on Pt/Y<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> with NO+O<sub>2</sub> showed the formation of a surface bridging nitrate species which was likely involved in the methane selective oxidation reaction. The results of the studies allow a picture to be developed of the likely reaction steps that lead to the transformation of methane to dimethylether.

### **Synthesis of bimetallic catalysts**

Supported bimetallic alloys are important materials because of their many uses as catalysts for a variety of reactions at reducing and oxidizing conditions, and their applications as electrodes in electrochemical devices. The present study reports a new synthesis method, redox deposition (RD) method for the synthesis of bimetallic catalyst at room temperature. In the RD method, the precursor salt of the non-noble metal is initially deposited on the support, negating the use of protecting polymers, and the subsequent treatment to decompose the polymer. The RD method also uses NaBH<sub>4</sub> instead of ethanol or ethylene glycol as the reducing agent. Results presented in this work for NiPt, CuPt, FePt, and CoPt systems highlight key variables and provide relevant guidance for the controlled synthesis of bimetallic alloys via redox mechanism. In this study, the one-pot synthesis of NiPt, CuPt, FePt, and CoPt bimetallic alloys by redox deposition is presented. Initially, silica-supported Ni, Cu, Fe, or

Co seed metals are formed by the reduction of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{+3}$ , and  $\text{Co}^{+2}$  with  $\text{NaBH}_4$  at room temperature, followed by the reduction of Pt ions by Ni, Cu, Fe, or Co metal.

### Partial oxidation of methane

The direct partial oxidation of  $\text{CH}_4$  on a Pt/ $\text{Y}_2\text{O}_3$  catalyst was studied using a mixture of NO and  $\text{O}_2$  as the oxidant. The reactions were carried out in a fixed bed reactor at 0.1 MPa and 275-400 °C using 20 %  $\text{CH}_4$ , 1% NO, and 1%  $\text{O}_2$  in inert gas. The activity results showed the formation of dimethyl ether (DME) and a contact time study demonstrated

that DME was a primary product. The presence of Pt and the NO+ $\text{O}_2$  gas mixture was necessary for DME formation as without NO only  $\text{CO}_2$  was produced. During the methane partial oxidation reaction, NO and  $\text{NO}_2$  were not reduced to  $\text{N}_2$ , indicating that they worked as a shuttle to transfer oxygen from  $\text{O}_2$  to  $\text{CH}_4$ . In situ FTIR showed the formation of a bridged nitrate species on the Pt/ $\text{Y}_2\text{O}_3$  catalyst which was associated with the reaction of  $\text{CH}_4$  at different temperatures. A comprehensive study of this bridged nitrate species indicated they were formed on yttria sites close to Pt and were likely responsible for the formation of DME (Fig. 1).

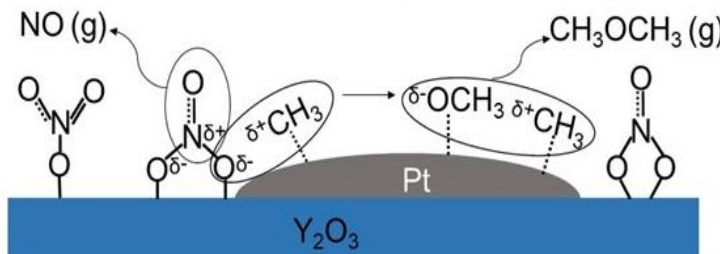


Fig. 1. A possible mechanism for the formation of DME during  $\text{CH}_4$  partial oxidation by  $\text{NO} + \text{O}_2$

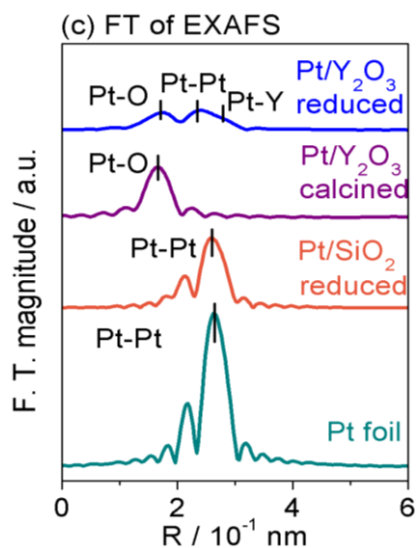


Fig. 2. Fourier transform of EXAFS ( $k^3\chi(k)$ ) spectra for Pt/ $\text{Y}_2\text{O}_3$  and Pt/ $\text{SiO}_2$ , Conditions: from the top, Pt/ $\text{Y}_2\text{O}_3$  after pretreatment at 400 °C in  $\text{H}_2$ , Pt/ $\text{Y}_2\text{O}_3$  after calcination at 400 °C, Pt/ $\text{SiO}_2$  after pretreatment at 400 °C in  $\text{H}_2$ , and Pt foil.

The characterization of catalysts using X-ray diffraction and CO uptake showed that the Pt was highly dispersed and had a particle size of ~ 3 nm. Analysis by XAFS and XANES measurements showed the formation of Pt in a +2 oxidation state with Pt-O, Pt-Y, and Pt-Pt bonds. For the calcined Pt/ $\text{Y}_2\text{O}_3$  a first-shell curve fitting analysis of the Pt  $L_{III}$ -edge over an R range of 1.0-2.5 Å shows a scattering peak for Pt-O at 0.202 nm (Fig. 2). This Pt-O distance is in agreement with the findings from other studies. The presence of only Pt-O scattering in the calcined Pt/ $\text{Y}_2\text{O}_3$  suggests that Pt is in an oxide form, consistent with the observations from the XANES analysis. The presence of Pt-O bonds is expected as the catalyst was calcined at 400 °C in air, and the absence of Pt-Pt bonds suggests a high dispersion of Pt on the  $\text{Y}_2\text{O}_3$  support. For the reduced Pt/ $\text{Y}_2\text{O}_3$  a three-shell curve fitting analysis of the Pt  $L_{III}$ -edge over an R range of 1.1-3.6 Å shows scattering peaks of Pt-O at 0.201 nm, Pt-Pt at 0.269

nm, and Pt-Y at 0.301 nm. This is in agreement with the observation from the XANES analysis which shows a high oxidation state of Pt which indicates a high density of unoccupied 5d orbitals in Pt, due to electron transfer from Pt to its neighboring O atoms. The presence of Pt-O, Pt-Pt, and Pt-Y bond is evidence for the strong interaction between Pt and the  $Y_2O_3$ .

### Activity test

Reactivity tests were conducted in a packed-bed flow reactor with full gas-chromatographic and infrared spectroscopic analyses of the reactants and products of reactions. Fig. 3 show the methane conversion and DME selectivity on Pt/ $Y_2O_3$  and  $Y_2O_3$  between 275-400 °C at 0.1 MPa as a function of temperature with either  $O_2$  or a mixture of NO and  $O_2$  as the oxidant. The DME product was obtained only with the Pt/ $Y_2O_3$

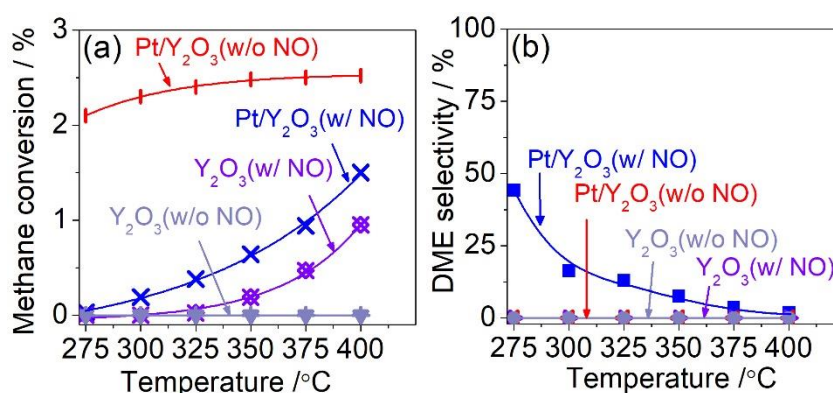


Fig. 3. (a) Methane conversion and (b) DME selectivity. Conditions: Pt/ $Y_2O_3$  and  $Y_2O_3$  with NO/ $O_2$  ( $CH_4:NO:O_2:inert=20:1:1:78$ ) and  $O_2$  ( $CH_4:O_2:inert = 20:1:79$ ) as oxidant at 0.1 MPa.

catalyst using the NO+ $O_2$  mixture as the oxidant and no DME was obtained using  $O_2$  alone as the oxidant. Both the  $Y_2O_3$  support and the Pt/ $SiO_2$  catalyst gave only  $CO_2$  with either oxidant, showing that the presence of both Pt and  $Y_2O_3$  were necessary for the formation of DME. A high DME selectivity of 44 % was obtained on Pt/ $Y_2O_3$  at low methane conversion (0.03 %) and low reaction temperature (275 °C). The DME selectivity decreased with increase in temperature and gave a low DME selectivity of 2 % at high methane conversion (1.5 %) and high reaction temperature (400 °C).

### In situ FTIR study

Fig. 4 (a) shows a series of spectra of  $NO_x$  species on Pt/ $Y_2O_3$  taken at

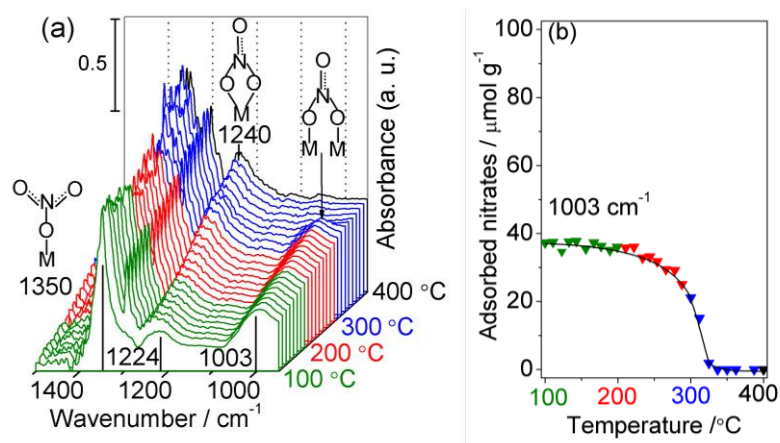


Fig. 4. In situ FTIR spectroscopy results under flow of  $CH_4$  (a) for the treatment of adsorbed  $NO_x$  species on Pt/ $Y_2O_3$  (b) concentration of adsorbed  $NO_x$  species at 1003  $cm^{-1}$  with an increase in temperature. Conditions: 10 %  $CH_4$  in He ( $50 ml min^{-1}$ ) from 100 °C to 400 °C

increasing temperature to probe the reactions of surface nitrate species with CH<sub>4</sub>. After the adsorption of NO<sub>x</sub> species on Pt/Y<sub>2</sub>O<sub>3</sub> at 100 °C, the temperature was raised at 10 °C min<sup>-1</sup> to 400 °C under a flow of 10% CH<sub>4</sub> in He (100 ml min<sup>-1</sup>), the peak at 1300 cm<sup>-1</sup> was due to the gas phase CH<sub>4</sub>. With increase in temperature, the intensity of nitrate species at 1240 cm<sup>-1</sup> (bidentate nitrate [2]) gradually increased, but the intensity of nitrate species at 1003 cm<sup>-1</sup> did not change until the temperature reached around 300 °C. Above 300 °C the nitrate species at 1003 cm<sup>-1</sup> (bridged nitrate [3]) disappeared. Fig. 4 (b) shows the change in the concentration of adsorbed NO<sub>x</sub> species at 1003 cm<sup>-1</sup> with increase in temperature. The spectra at 1003 cm<sup>-1</sup> were fitted using a Gaussian function to obtain the integrated areas to calculate the NO<sub>x</sub> concentration, using a previously reported NO<sub>x</sub> extinction coefficient  $\epsilon = 19.4 \text{ abs}/\mu\text{mol}$  [4]. Fig. 4 (b) shows that up to 250 °C the concentration of the bridged nitrate species (1003 cm<sup>-1</sup>) remained almost constant, and above this temperature the concentration of bridged nitrate species started to steadily decrease and disappear at around 300 °C. The activity test for CH<sub>4</sub> partial oxidation on Pt/Y<sub>2</sub>O<sub>3</sub> showed that the oxidation with NO+O<sub>2</sub> began close to 300 °C (Fig. 3). This indicated that the nitrate species at 1003 cm<sup>-1</sup> was involved in the reaction with CH<sub>4</sub> at around 300 °C. Hence the nitrate species at 1003 cm<sup>-1</sup> may be one of the key species for CH<sub>4</sub> partial oxidation on Pt/Y<sub>2</sub>O<sub>3</sub> by NO and O<sub>2</sub>.

### Synthesis of bimetallic catalyst

Silica-supported M<sub>A</sub>Pt (M<sub>A</sub> = Ni, Cu, Fe, Co) bimetallic catalysts with different molar ratios were prepared by varying the amounts of Ni or Cu while maintaining the loading of Pt constant at 2 wt.% (0.10 mmol/g<sub>support</sub>). Initially, 2.5 g of silica was dispersed in 100 mL of deionized water for 10 min. Then appropriate amounts of NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, or CoCl<sub>2</sub>·6H<sub>2</sub>O (0.25-1.0 mmol) were dissolved in deionized water and added to the silica/water mixture under continuous stirring. To reduce the M<sub>A</sub> precursor use was made of a stoichiometric amount of NaBH<sub>4</sub> (0.51-2.0 mmol) solution, added dropwise to the mixture under Ar. After stirring for 1.5 h, an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (0.25 mmol) was slowly added to the suspension and stirred for 1.5 h under Ar atmosphere. The solid samples were recovered by filtration and washed several times in order to remove sodium, chlorine, and boron ions. The solid sample was then dried overnight at 110 °C and then pelletized and

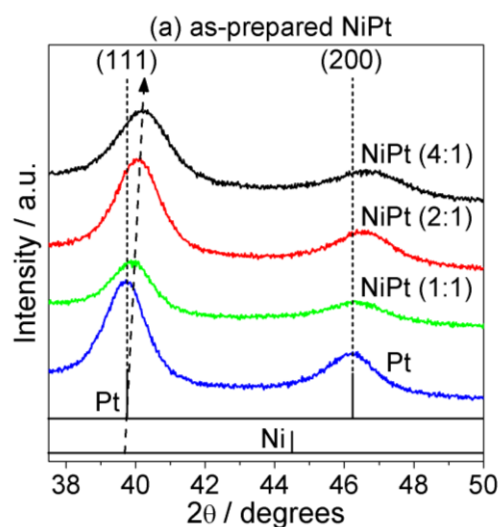


Fig. 5. Powder XRD patterns of silica supported NiPt bimetallic catalysts prepared by the redox deposition method

sieved to a size of 650-1180 μm. Fig. 5. shows the XRD patterns of the NiPt bimetallic samples prepared by redox deposition method. The shift in the diffraction angles indicate the formation of alloys.

## Conclusions

The research here dealt with the selective oxidation of methane to dimethyl ether with supported platinum catalysts using NO/NO<sub>2</sub> as an oxygen transfer agent with molecular oxygen as the terminal oxidant. The methane partial oxidation using NO+O<sub>2</sub> was studied on different Pt supported catalysts. Among these, Pt/Y<sub>2</sub>O<sub>3</sub> was the most promising catalyst. Activity tests for Pt/Y<sub>2</sub>O<sub>3</sub> results showed that DME was formed only in the presence of Pt and NO+O<sub>2</sub>. The analysis of NO and O<sub>2</sub> conversion showed that at the beginning of the reaction almost all the NO converted to NO<sub>2</sub> and during the CH<sub>4</sub> partial oxidation NO<sub>2</sub> was reduced to NO. During this reaction, NO and NO<sub>2</sub> were the only nitrogen-containing products observed. So that they were acting as an oxygen atom shuttle for the partial oxidation of CH<sub>4</sub>. An in situ FTIR study showed the formation of surface nitrate species on Y<sub>2</sub>O<sub>3</sub> and the presence of Pt in Pt/Y<sub>2</sub>O<sub>3</sub> enabled the formation of different nitrate species. The reaction of these nitrate species with CH<sub>4</sub> revealed the presence of reactive bridged nitrate species at 1224 cm<sup>-1</sup> and 1003 cm<sup>-1</sup>.

A new one-pot method for the synthesis of bimetallic catalysts at room temperature was developed. The XRD patterns of these bimetallic catalysts showed the formation of phase-pure bimetals at room temperature. Conversely, multiphase species were present in the reference silica-supported NiPt and CuPt

catalysts prepared by incipient wetness impregnation. A proposed redox formation mechanism, in which a fraction of Ni or Cu acts as sacrificial seed metal atoms to reduce Pt, was supported by XRF results

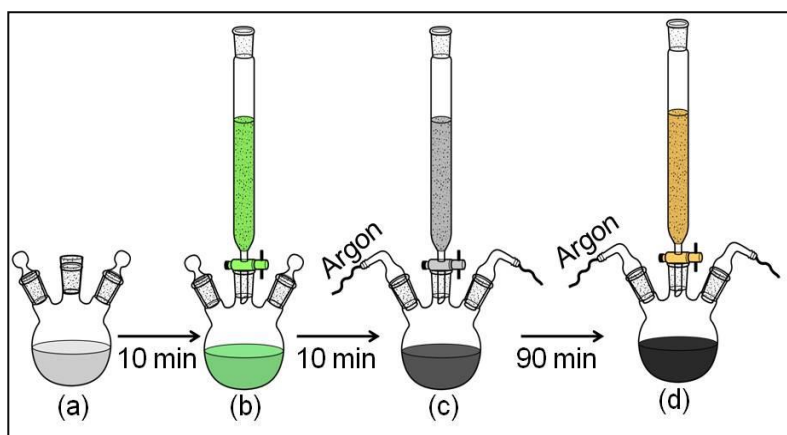


Fig. 6. One-pot synthesis of the bimetallic catalyst by redox deposition: (a) addition of silica in deionized water, (b) addition of nickel or copper precursor, (c) addition of NaBH<sub>4</sub> under argon atmosphere, and (d) addition of platinum precursor. This step is followed by filtration and drying at 110 °C.

## References

- [1] R. Horn, R. Schlögl, Methane activation by heterogeneous catalysis, *Catal. Lett.* 145 (2015) 23–39.
- [2] C. Sedlmair, K. Seshan, A. Jentys, J. A. Lercher, Elementary steps of NO<sub>x</sub> adsorption and surface reaction on a commercial storage–reduction catalyst, *J.Catal.* 214 (2003) 308–316.

- 
- [3] K. Hadjiivanov, V. Avreyska, D. Klissurski, T. Marinova, Surface species formed after NO adsorption and NO + O<sub>2</sub> co-adsorption on ZrO<sub>2</sub> and sulfated ZrO<sub>2</sub>: An FTIR spectroscopic study, *Langmuir* 18 (2002) 1619-1625.
- [4] K. Shimizu, Y. Saito, T. Nobukawa, N. Miyoshi, A. Satsuma, Effect of support on formation and reduction rate of stored nitrates on NSR catalysts as investigated by in situ FTIR, *Catal. Today* 139 (2008) 24-28.