論文の内容の要旨

論文題目

Methane partial oxidation on Pt based catalysts using an NO/NO_2 oxygen atom shuttle

(NO/NO_2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）

氏 名

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 ºC) 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_2 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_4 with NO and O_2 as the oxidant with Pt on different supports. It was found that Pt/Y_2O_3 was the best catalyst for DME synthesis and it was selected for further studies. A contact time study with Pt/Y_2O_3 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_2O_3 and

Y_2O_3 with NO+O_2 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..

Partial oxidation of methane

The direct partial oxidation of CH_4 on a Pt/Y_2O_3 catalyst was studied using a mixture of NO and O_2 as the oxidant. The reactions were carried out in a fixed bed reactor at 0.1 MPa and 275-400 ºC using 20 % CH_4, 1% NO, and 1% 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+O_2 gas mixture was necessary for DME formation as without NO only CO_2 was produced. During the methane partial oxidation reaction, NO and NO_2 were not reduced to N_2, indicating that they worked as a shuttle to transfer oxygen from O_2 to CH_4. In situ FTIR showed the formation of a bridged nitrate species on the Pt/Y_2O_3 catalyst which was associated with the reaction of 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).

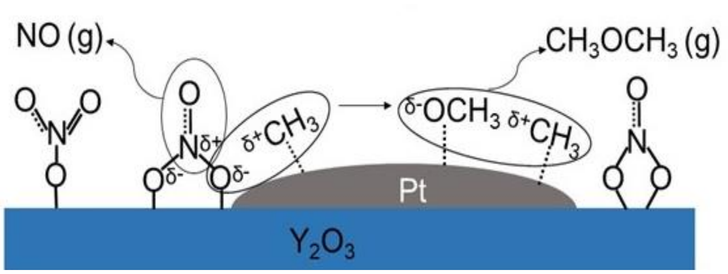

Fig. 1. A possible mechanism for the formation of DME during CH_4 partial oxidation by NO + O_2

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. 2 show the methane conversion and DME selectivity on Pt/Y_2O_3 and Y_2O_3 between 275-400 ºC 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 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

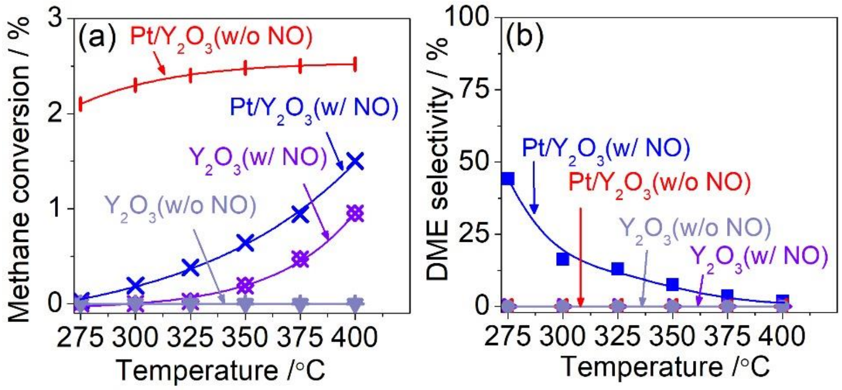

Fig. 2. (a) Methane conversion and (b) DME selectivity. Conditions: Pt/Y_2O_3 and Y_2O_3 with NO/O_2 (CH_4:NO:O_2:inert=20:1:1:78) and O_2 (CH_4:O_2:inert = 20:1:79) as oxidant at 0.1 MPa.

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 ºC). 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 ºC).

In situ FTIR study

Fig. 3 (a) shows a series of spectra of NO_x species on Pt/Y_2O_3 taken at increasing temperature to probe the reactions of surface nitrate species with CH_4. After the adsorption of NO_x species on Pt/Y_2O_3 at 100 ºC, the temperature was raised at 10 ºC min^{-1} to 400 ºC under a flow of 10% CH_4 in He (100 ml min^{-1}), the peak at 1300 cm^{-1} was due to the gas phase CH_4. With increase in temperature, the intensity of nitrate species at 1240 cm^{-1} (bidentate nitrate [2]) gradually increased, but the intensity of nitrate species at 1003 cm^{-1} did not change until the temperature reached around 300 ºC. Above 300 ºC the nitrate species at 1003 cm^{-1} (bridged nitrate [3]) disappeared. Fig. 3 (b) shows the change in the concentration of adsorbed NO_x species at 1003 cm^{-1} with increase in temperature. The spectra at 1003 cm^{-1} were fitted using a Gaussian function to obtain the integrated areas to calculate the NO_x concentration, using a previously reported NO_x extinction coefficient $\varepsilon = 19.4$ abs/μmol [4]. Fig. 3 (b) shows that up to 250 ºC the concentration of the bridged nitrate species (1003 cm^{-1}) remained almost constant, and above this temperature the concentration of bridged nitrate species started to steadily decrease and disappear at around 300 ºC. The activity test for CH_4 partial oxidation on Pt/Y_2O_3 showed that the oxidation with $NO+O_2$ began close to 300 ºC (Fig. 2). This indicated that the nitrate species at 1003 cm^{-1} was involved in the reaction with CH_4 at around 300 ºC. Hence the nitrate species at 1003 cm^{-1} may be one of the key species for CH_4 partial oxidation on Pt/Y_2O_3 by NO and O_2.

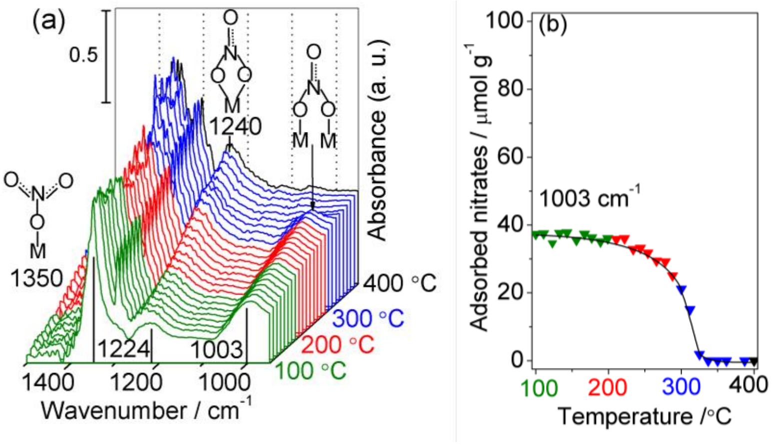

Fig. 3. In situ FTIR spectroscopy results under flow of CH_4 (a) for the treatment of adsorbed NO_x species on Pt/Y_2O_3 (b) concentration of adsorbed NO_x species at 1003 cm^{-1} with an increase in temperature. Conditions: 10 % CH_4 in He (50 ml min^{-1}) from 100 ºC to 400 ºC

Conclusions

The research here dealt with the selective oxidation of methane to dimethyl ether with supported platinum catalysts using NO/NO_2 as an oxygen transfer agent with molecular oxygen as the terminal oxidant.

The methane partial oxidation using $NO+O_2$ was studied on different Pt supported catalysts. Among these, Pt/Y_2O_3 was the most promising catalyst. Activity tests for Pt/Y_2O_3 results showed that DME was formed only in the presence of Pt and $NO+O_2$. The analysis of NO and O_2 conversion showed that at the beginning of the reaction almost all the NO converted to NO_2 and during the CH_4 partial oxidation NO_2 was reduced to NO. During this reaction, NO and NO_2 were the only nitrogen-containing products observed. So that they were acting as an oxygen atom shuttle for the partial oxidation of CH_4. An in situ FTIR study showed the formation of surface nitrate species on Y_2O_3 and the presence of Pt in Pt/Y_2O_3 enabled the formation of different nitrate species. The reaction of these nitrate species with CH_4 revealed the presence of reactive bridged nitrate species at 1224 cm^{-1} and 1003 cm^{-1}.

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

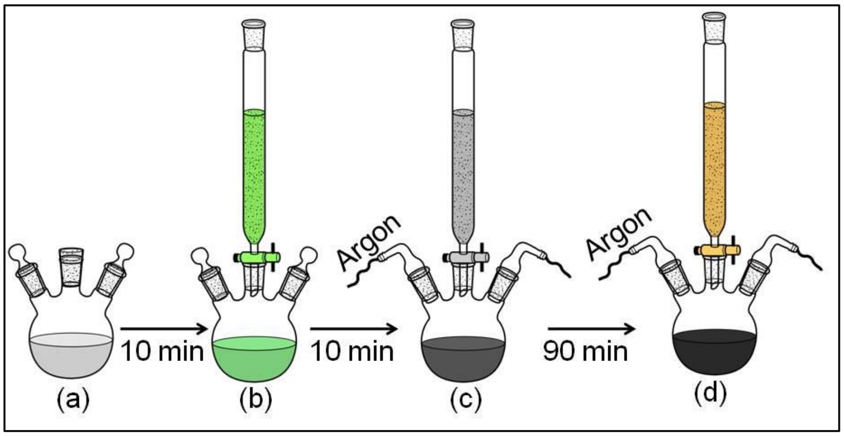

Fig. 4. One-pot synthesis of the bimetallic catalyst by redox deposition: (a) addition of silica in deionized water, (b) addition of nickel or copper precursor, (c) addition of $NaBH_4$ under argon atmosphere, and (d) addition of platinum precursor. This step is followed by filtration and drying at 110 °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_x 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_2 co-adsorption on ZrO_2 and sulfated ZrO_2: 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.