

## 論 文

### 担持白金触媒によるトリチウム化メタンの燃焼

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### Oxidation of Tritiated Methane by Supported Platinum Catalyst.

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#### Abstract

The oxidation reaction of  $\text{CH}_4$  and  $\text{CH}_3\text{T}$  by silica- and alumina-supported catalysts was studied. The oxidation rate of methane was pseudo-first order with respect to the methane pressure and the catalytic activity of  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst was higher than that of the  $\text{Pt}/\text{SiO}_2$  catalyst. A kinetic isotope effect was observed for the oxidation reaction on the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst; the activation energies for  $\text{CH}_4$  and  $\text{CH}_3\text{T}$  were 19.2 and 17.3 Kcal/mol, respectively.

A large part of the tritium in  $\text{CH}_3\text{T}$  was removed as the tritiated water, but some of it was trapped on the supported catalyst. Tritium was also found to be trapped on the surface of alumina, the amount being comparable to that observed for the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst. Thus, the exchange reaction between  $\text{CH}_3\text{T}$  and hydroxyl group on the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst is considered to a predominant role in the trapping of tritium on the catalyst.

In regard to waste handling, the above findings demonstrate contamination of the oxidation catalyst due to the captured tritium.

## Introduction

Development of the tritium decontamination systems is of great importance for safety handling of a large amount of tritium<sup>1)</sup>. When tritium leakage takes place, it must be removed as soon as possible by means of the decontamination systems in order to avoid the contamination of the laboratory rooms and the environment. Catalytic oxidation of tritium and subsequent capturing of tritiated water by an absorber is one of the available decontamination methods<sup>2)</sup>. For this purpose, supported noble metals are commonly used as oxidation catalyst because they are highly active for the oxidation reaction of hydrogen even at low temperatures, and silica or alumina is widely used as a support for them.

However, these supports have a large number of hydroxyl groups on their surfaces, and it is reported that heavy water easily exchanges with the hydrogen of the hydroxyl group existing on the surfaces, resulting in the formation of OD groups<sup>3)</sup>. Furthermore, the exchange reaction between deuterio-methane and the hydroxyl group takes place on alumina<sup>4)</sup>. These findings suggest that the contamination of the catalysts is caused by the oxidation reaction of tritium. Therefore, it would be important in view of the waste treatment to measure the degree of the contamination of the catalyst used for the tritium decontamination system.

This study is concerned with the relation between the oxidation reaction of tritiated methane and the degree of the contamination of alumina- and silica-supported platinum catalysts.

## Experimental

### 1) Catalysts

The supports of platinum, silica (JRC-SIO-1, 166 m<sup>2</sup>/g) and alumina (JRC-ALO-2, 285 m<sup>2</sup>/g), were obtained from the Catalysis Society of Japan. Alumina- and silica-supported platinum catalysts (Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>, respectively) were prepared from an aqueous solution of chloroplatinic acid (0.05 mol/l, 10 cm<sup>3</sup>) and the support (9.9 g) by means of the impregnation method. The solution was slowly added drop by drop to the alumina or silica powder being stirred at room temperature. The mixture was stirred further for 2 hours to disperse platinum uniformly after all of the solution was added. Subsequently, it was dried in a furnace at 80°C for 24 hours, and was calcinated in the atmosphere at 500°C for 1 hour. The weight fraction of the

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platinum was 1.0 wt% for both the catalysts; Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>. The catalyst, weighed out 0.1g, was put in the reaction vessel to measure the catalytic activity. Prior to the measurements, it was treated as follows: oxidation (P<sub>O<sub>2</sub></sub>=50 Torr, 450°C, 1 h), reduction (P<sub>H<sub>2</sub></sub>=50 Torr, 300°C, 1 h), and evacuation (450°C, 1 h).

### 2) Gases

Tritium gas was obtained from New England Nuclear Co. and high purity methane and oxygen gases were bought from Takachiho Chemicals Co. They were used without further purification. Tritiated methane was prepared by means of the exchange reaction between the tritium gas (1 Ci : 300 Torr cm<sup>3</sup>) and the methane gas (2.7 × 10<sup>5</sup> Torr cm<sup>3</sup>) at 100°C for 7 days. A palladium evaporated-film was used as the catalyst<sup>9</sup>. The tritiated methane was purified by using a molecular sieve (5A) cooled at the liquid nitrogen temperature. The purity of the resultant mono-tritiated methane was found to be 99.6% (CH<sub>3</sub>T/T<sub>2</sub>). The specific activity was ca. 7 Ci/mol.

### 3) Equipment and Procedures

A glass made circulating system (516 cm<sup>3</sup>), shown schematically in Fig. 1, was used to measure the oxidation rate. The circulation rate was 300 cm<sup>3</sup>/min. After the pretreatments of the catalyst mentioned above, the mixture of the tritiated methane and oxygen (1 : 4) was introduced into the system. The initial pressure of the mixture was about 200 Torr in each run. The reaction temperature was varied in a range from 300 to 520°C. The amount of the tritiated water produced by the oxidation reaction and that trapped on the catalyst surface were measured by a liquid scintillation counter. The change in the total pressure was followed by a mercury manometer, and the amount of the tritiated methane presenting in the gas phase was measured by means of the radio-gas chromatography.

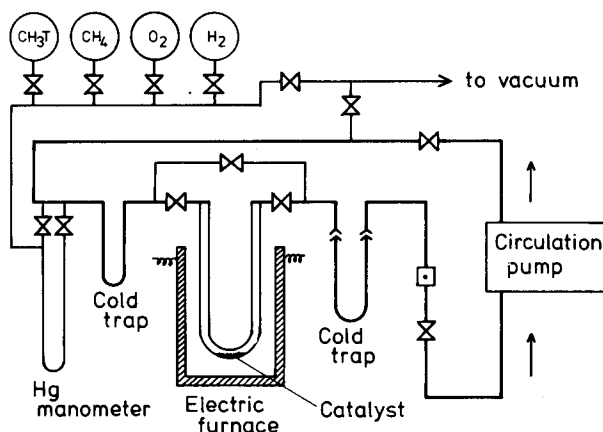


Fig. 1 Schematic diagram of the experimental apparatus.

### Results and Discussion

Figure 2 shows the variations of the amounts of  $\text{CH}_4$  and  $\text{CH}_3\text{T}$  existing in the reaction vessel with time at 300, 400, and 460°C. These amounts decreased exponentially against time, indicating that the oxidation reaction of methane was pseudo-first order concerning the methane pressure. Consequently, the slopes of these lines give the rate constants of the oxidation reaction.

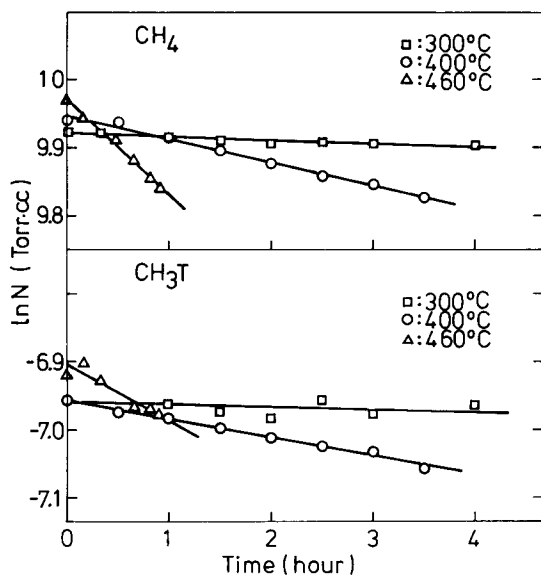


Fig. 2 Experimental kinetics of the oxidation reaction for  $\text{CH}_4$  and  $\text{CH}_3\text{T}$ .

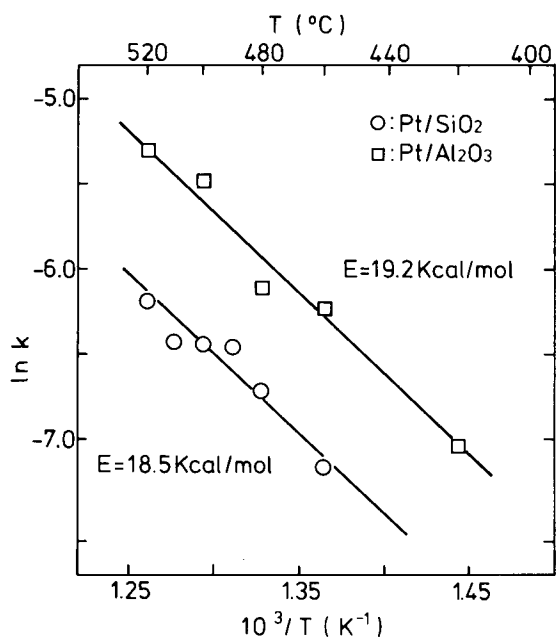


Fig. 3 Temperature dependence of the oxidation rate constants for  $\text{CH}_4$  on the  $\text{Pt}/\text{Al}_2\text{O}_3$  and  $\text{Pt}/\text{SiO}_2$  catalysts.

The temperature dependence of the oxidation rates was measured for both the Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub> catalysts to examine the roles of the supports. The results were shown in Fig. 3. The catalytic activity of Pt/Al<sub>2</sub>O<sub>3</sub> was larger than that of Pt/SiO<sub>2</sub>, and the activation energies were 19.2 and 18.5 Kcal/mol for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>, respectively. The activation energies did not differ much from each other. However, a substantial difference in the frequency factors was observed between the Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub> catalysts. It may result from the difference in the crystal size of the platinum between both the catalysts.

Figure 4 shows the Arrhenius plots of the oxidation rate constants for CH<sub>4</sub> and CH<sub>3</sub>T on the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The activation energy for the oxidation of CH<sub>4</sub> was 19.2 Kcal/mol, whereas that of CH<sub>3</sub>T was 17.3 Kcal/mol. The former was about 2 Kcal/mol greater than the latter. On the other hand, the frequency factors were 21 and 3.7 sec<sup>-1</sup> for CH<sub>4</sub> and CH<sub>3</sub>T, respectively. Hence, the ratio of them was 5.7 which was larger than the root of the inverse mass ratio. Since the zero point energy of C-H bond evaluated from the IR data is about 1.7 Kcal/mol greater than that of C-T bond<sup>6)</sup>, assuming that the ratio of  $\nu_{C-H}/\nu_{C-T}$  is  $\sqrt{3}$ , the larger activation energy for the oxidation of CH<sub>4</sub> may indicate that the bonding involving hydrogen bond becomes stronger in the activated complex.

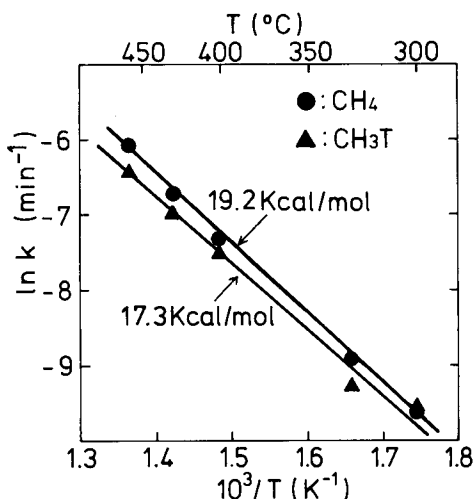


Fig. 4 Temperature dependence of the oxidation rate constants for CH<sub>4</sub> and CH<sub>3</sub>T on the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

Table 1 shows the amounts of the tritium residing on the catalysts. When the tritiated methane was oxidized by using the supported catalysts, a large portion of the tritium in CH<sub>3</sub>T was removed as the tritiated water. A part of it, however, remained on the catalyst even at 460°C.

There are many hydroxyl groups (3-4 OH/Å<sup>2</sup>) on alumina or silica surface<sup>7)</sup>; it has been reported that the hydrogen atom of the hydroxyl group on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst easily exchanges with hydrogen isotopes<sup>8)</sup>. It is also reported that the deuterium atom in deuterio-methane exchanges with the hydrogen atom of the hydroxyl group on alumina and/or silica alumina surfaces without supported metal catalyst<sup>4)</sup>.

Table 1 The amounts of the tritium residing on the supported catalysts.

Run No.	Catalyst	Temp. (°C)	Conv. (%)	C <sub>0</sub> (mCi)	C (μCi)	C/C <sub>0</sub> (x10 <sup>-3</sup> )
1	Al <sub>2</sub> O <sub>3</sub>	400	—	7.45	68.7	9.2
2	Pt/Al <sub>2</sub> O <sub>3</sub>	300	8.7	7.60	137	18
3		330	14	8.06	123	15
4		400	7.5	6.57	61.2	9.3
5		400	53	8.50	110	13
6		400	100	8.06	44.0	5.6
7		430	28	8.38	81.6	9.7
8		460	13	8.43	97.9	12
9	Pt/SiO <sub>2</sub>	460	78	7.75	21.9	2.8

C<sub>0</sub>: Amount of tritium introduced as CH<sub>3</sub>T.

C: Amount of tritium resided on the catalyst.

In addition Teichner et al<sup>9</sup>. have reported that the hydrogen adsorbed on supported-metal migrates onto the support; this phenomenon is known as “hydrogen spillover”. These facts and the present observations suggest that the tritium released by the dissociative adsorption of tritiated methane on platinum migrates onto the support, being captured on the support surface as OT.

The ratio of the amount of the tritium residing on the catalyst to that of the tritium initially introduced into the system decreased slowly with increasing reaction temperature for the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. It was also observed that the ratio of the residing tritium for alumina (without Pt) was about the same as that observed for the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Hence, it is considered that the tritium residing on the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst mainly resulted from the direct exchange reaction between the tritiated methane and the hydroxyl group on the alumina surface, and that the platinum on the alumina contributed little to the exchange reaction. This is also supported by the observation that the ratio increased with increasing conversion of the tritiated methane at 400°C.

The amount of the tritium residing on Pt/SiO<sub>2</sub> was smaller than that on Pt/Al<sub>2</sub>O<sub>3</sub>. This is closely related to a fact that the direct exchange reaction between CH<sub>3</sub>T and the hydroxyl group on the silica hardly occurred<sup>10</sup>. Therefore, it is considered that the tritium residing on Pt/SiO<sub>2</sub> might arise from the tritium adsorbed on the platinum.

### References

- 1) V.P. Gede and P.D. Gildea, "Tritium Technology in Fission, Fusion and Isotopic Applications", Dayton, p.334 (1980)
- 2) J.L. Anderson and R.H. Sherman, "Tritium Systems Test Assembly, Design for Major Device Fabrication Review", Report No. LA-6855-P (1977)
- 3) J.B. Peri and R.B. Hannan, J. Phys. Chem., **64**, 1526 (1960)
- 4) J.G. Larson and W.K. Hall, J. Phys. Chem., **69**, 3808 (1965)
- 5) C. Kemball, Pro. Roy. Soc., **A217**, 376 (1953)
- 6) G. Herzberg, "Molecular Spectra and Molecular Structure, (II) Infrared and Raman Spectra of Polyatomic Molecules", D. van Nostrand Comp. Inc., (1960)
- 7) V.Ya. Davydov, A.V. Kiselev, and L.T. Zhuravlev, Trans. Faraday Soc., **60**, 2254 (1964)
- 8) R.P. Eichens and W.A. Pliskin, "Advances in Catalysis", Academic Press Inc., New York, **10**, 1 (1958)
- 9) G.E.E. Gardes, G.M. Pajonk, and S.J. Teichner, J. Catal., **33**, 145 (1974)
- 10) O. Takayasu, private communication (1982)