

# Effect of Al<sub>2</sub>O<sub>3</sub> Crystalline Phase on Methane Combustion over Pd/Al<sub>2</sub>O<sub>3</sub>

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It is well known that a Pd/Al<sub>2</sub>O<sub>3</sub> is one of the most active catalysts for methane combustion. In this work, we investigated the effect of crystalline phase of alumina on methane combustion over Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

Various alumina supports used in this study were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-2, JRC-ALO-4, JRC-ALO5, JRC-ALO-8, JRC-ALO-9, boehmite calcinated at 500 °C),  $\theta$ -Al<sub>2</sub>O<sub>3</sub> (AKP-G07, JRC-ALO-10, boehmite calcinated at 1000°C), and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (AKP-50 and AES-12, boehmite calcinated at 1150°C). JRC-ALO-x were supplied from Catalysis Society of Japan. AKP-G07, AKP-50 and AES-12 were supplied from Sumitomo Chemical Co. Ltd. Supported palladium catalysts were prepared by impregnation method using aqueous solution palladium nitrate (Pd loading: 0.5-2wt%). The samples calcined at 500°C for 3 h. Some of the samples were further treated at 800, 850 or 900 °C under air for 10 h to vary Pd particle size. The methane combustion light-off test was performed in 0.4% CH<sub>4</sub>, 10% O<sub>2</sub> and N<sub>2</sub> balance as the temperature was ramped at 5 °C min<sup>-1</sup> from 200 to 600°C. TOF (at 300°C) was estimated as reaction rate of CH<sub>4</sub> per surface Pd atom measured by CO adsorption.

The light-off test showed that catalytic activity of Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> was the highest among the catalysts with various crystalline phases. Figure 1 shows dependence of TOF on Pd particle size. TOF of Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> and Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> were higher than that of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> regardless of Pd particle size. TOF of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> slightly increased as Pd particle size increased. In contrast, TOF of Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> and Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> increased as Pd particle size increased to approximately 7 nm, however they decreased with increasing Pd particle size above 7 nm.

We analyzed the structure of Pd particles using CO adsorption IR spectroscopy and TEM. Figure 2 shows IR spectra of adsorbed CO on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>. The bands of C-O stretching vibrations of linear a-top (2100-2000 cm<sup>-1</sup>) and bridging CO (1990-1970 and 1950-1850 cm<sup>-1</sup>) on Pd<sup>0</sup> were observed. The intensity of the band at 1990-1970 cm<sup>-1</sup> was stronger than that of the band at 2100-2000 cm<sup>-1</sup> in Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>. The intensity of both bands was nearly same in Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The intensity ratio of the bridge / (linear + bridge) of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> were 0.55 and 0.91, respectively. For the formation of a bridging CO, ensembles of Pd atoms are necessary. This result indicates that Pd particles on Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> have well-defined facets and edges. On the other hand, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has Pd particles with rough surface. These results were supported by TEM images of Pd particles on each sample (Fig. 2). We concluded that abundant Pd ensembles on Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> caused high methane combustion activity.

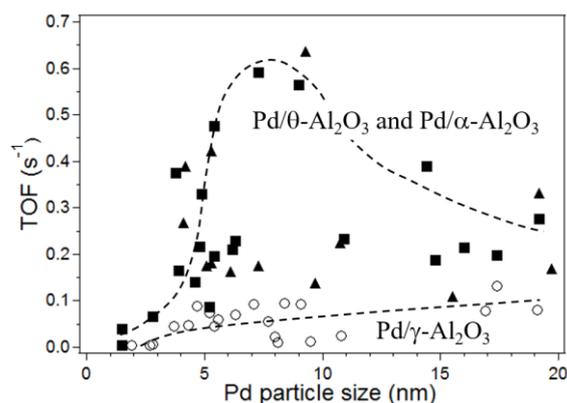


Fig. 1 Dependence of TOF (at 300°C) on Pd particle size. (○: Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ■: Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>, ▲: Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>)

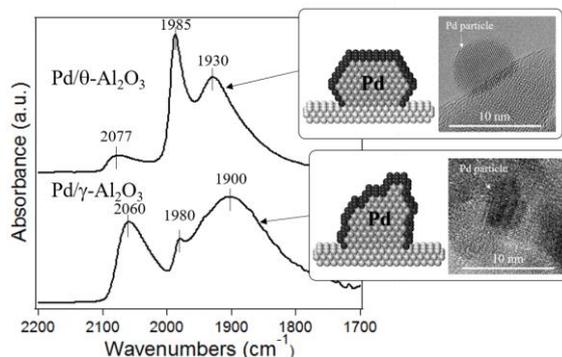


Fig. 2 IR spectra of adsorbed CO on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> with their TEM images and estimated Pd particle structure models.