Effect of Al$_2$O$_3$ Crystalline Phase on Methane Combustion over Pd/Al$_2$O$_3$

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It is well known that a Pd/Al$_2$O$_3$ 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$_2$O$_3$ catalyst.

Various alumina supports used in this study were γ-Al$_2$O$_3$ (JRC-ALO-2, JRC-ALO-4, JRC-ALO5, JRC-ALO-8, JRC-ALO-9), boehmite calcinated at 500°C, θ-Al$_2$O$_3$ (AKP-G07, JRC-ALO-10), boehmite calcinated at 1000°C, and α-Al$_2$O$_3$ (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$_4$, 10% O$_2$ and N$_2$ balance as the temperature was ramped at 5°C min$^{-1}$ from 200 to 600°C. TOF (at 300°C) was estimated as reaction rate of CH$_4$ per surface Pd atom measured by CO adsorption.

The light-off test showed that catalytic activity of Pd/θ-Al$_2$O$_3$ was the highest among the catalysts with various crystalline phases. Figure 1 shows dependence of TOF on Pd particle size. TOF of Pd/θ-Al$_2$O$_3$ and Pd/α-Al$_2$O$_3$ were higher than that of Pd/γ-Al$_2$O$_3$ regardless of Pd particle size. TOF of Pd/γ-Al$_2$O$_3$ slightly increased as Pd particle size increased. In contrast, TOF of Pd/θ-Al$_2$O$_3$ and Pd/α-Al$_2$O$_3$ 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/γ-Al$_2$O$_3$ and Pd/θ-Al$_2$O$_3$. The bands of C-O stretching vibrations of linear a-top (2100-2000 cm$^{-1}$) and bridging CO (1990-1970 and 1950-1850 cm$^{-1}$) on Pd$^0$ were observed. The intensity of the band at 1990-1970 cm$^{-1}$ was stronger than that of the band at 2100-2000 cm$^{-1}$ in Pd/0-Al$_2$O$_3$. The intensity of both bands was nearly same in Pd/γ-Al$_2$O$_3$. The intensity ratio of the bridge / (linear + bridge) of Pd/γ-Al$_2$O$_3$ and Pd/θ-Al$_2$O$_3$ 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/θ-Al$_2$O$_3$ have well-defined facets and edges. On the other hand, Pd/γ-Al$_2$O$_3$ 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/θ-Al$_2$O$_3$ caused high methane combustion activity.