

The promotion effect operated by CeO₂ on Pd-PdO transformation in CH₄ combustion catalysts

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Introduction

Palladium-based catalysts are the most active systems for the catalytic combustion of methane [1]. It is widely recognized that the active phase is palladium oxide [2,3], which undergoes decomposition at about 1000K with 20 mbar P_{O₂} [4]. This behavior is reflected in a poor catalytic performance in a wide range of temperature, since Pd reoxidation takes place only at about 850K [5]. It has been reported that the addition of CeO₂ as a dopant onto the support can effectively promote Pd reoxidation [6,7].

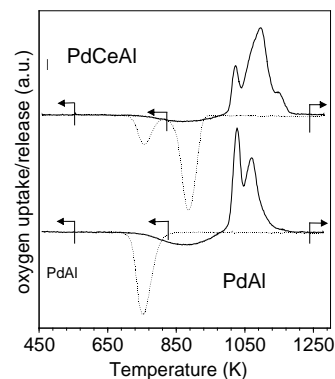
Purpose of this work is the study of the promotion of Pd reoxidation in the presence of CeO₂. This has been realized by the coupling of two different experimental techniques: HRTEM and TPO experiments. HRTEM analysis has been carried out on samples that underwent partial decomposition/reoxidation during TPO experiments.

Materials and Methods

Catalysts consisted of 3% wt Pd supported on either stabilized Al₂O₃ (PdAl) or 10% CeO₂/Al₂O₃ (PdCeAl). Supports and catalysts have been calcined at 1273K for 6 h in flowing air. TPO experiments have been carried out in a quartz tubular reactor loaded with 150 mg of catalyst with inlet gas composition of 2% O₂ in N₂ (total flowrate of 0.06 l/min @ STP). For each sample three heating/cooling cycles from 473K up to 1273K have been performed (heating ramp 10K/min) and during the third cycle samples for HRTEM analysis have been collected at three reference temperatures (1248K heating, 833K and 553K cooling). High-resolution transmission electron microscopy studies were carried out with a field emission gun microscope JEOL 2010F working at 200 kV with a point-to-point resolution of 0.19 nm.

Results and Discussion

In Figure 1 the third TPO cycle for both samples is reported with collection points. It can be observed that when CeO₂ is present, Pd reoxidation takes place in two steps: one at high temperature and one at the same temperature as the non-doped catalyst. Figure 2 shows a low magnification HRTEM image of PdCeAl catalyst collected at 833K during cooling. At this point only the high temperature reoxidation peak is detected by TPO in the PdCeAl sample. It appears clearly that at this temperature only Pd particles in contact with CeO₂ are reoxidized, while Pd particles in contact with Al₂O₃ are still in the metallic state. This indicates that, in order to obtain anticipated Pd reoxidation, a deep contact between the promoter and the noble



metal is required. From further HRTEM investigations, it has also been possible to attribute the O₂ uptake peak observed during heating (see Figure 1) to the reoxidation of two-domain particles in which both Pd and PdO are present. These particles have been detected in the samples collected at 553K, and only in contact with Al₂O₃. For the particles in contact with ceria at this temperature PdO reformation was already completed.

Figure 1. TPO profiles for PdAl and PdCeAl. Solid line: heating; dotted line: cooling. Arrows indicate collection points for HRTEM analysis.

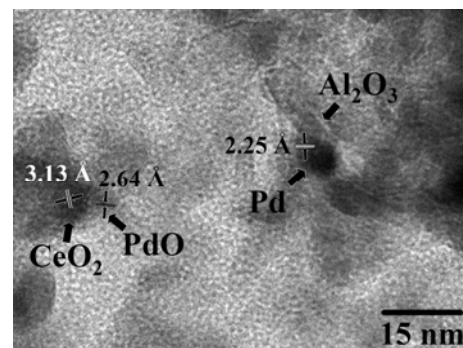


Figure 2. HRTEM image of PdCeAl sample collected during cooling at 833K.

Significance

For the first time, to our best knowledge, the dynamics of reoxidation of Pd in Pd/Al₂O₃ and Pd/CeO₂/Al₂O₃ catalysts has been clarified and correlated to the geometrical contact between metal, promoter and support. Moreover, these results could provide a useful tool to determine by simple TPO profile whether the

noble metal is in contact with the promoter or with the support.

References

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