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Report:

Pd-supported catalysts are of importance for the catalytic combustion of methane for energy production. PdO-based catalyst materials are composed of a thermally stable support (such as stabilised alumina or zirconia) and of the active phase PdO. They have been recognized as the most effective catalysts for methane combustion, because they have the unique property to be a chemical thermostat at 850-900°C in the presence of adiabatic reaction temperature exceeding 1300°C. The property of temperature control has been associated with the reversible Pd-PdO transformation: at low temperature active PdO is stable and ignites the reaction; the temperature increase (due to combustion) causes PdO reduction to metallic Pd. Due to its low activity, the reaction will switch off, with a decrease in temperature. Therefore, Pd re-oxidizes to PdO, that in turn re-ignites the combustion. At a steady state, a stable temperature will be reached; its value will be related to the thermodynamics of Pd-PdO reaction. Some of the features of this reaction are still not completely clear. A large hysteresis occurs between decomposition and reformation of palladium oxides; the width of the hysteresis depends on the support used, as CeO_2 promotes PdO formation, thus reducing the width of the hysteresis. Furthermore, temperature of decomposition/formation of PdO are influenced by pO_2.

Based on preliminary results on home diffractometer, a series of experiments were performed at BM8 on PdO supported on different materials, particularly La-doped alumina and Y-stabilised Zirconia with the Pd-containing material precalcined at different temperatures. The aim was the comprehension of the mechanism of the hysteresis, and the influence of the nature of the support and of the precalcination temperature on the PdO-Pd transformation.

Refinement of the collected data are still in progress, however the following preliminary evidences have been found:

1. The PdO-Pd decomposition reaction is easily followed by XRD. On increasing the temperature PdO progressively desappear and Pd forms. However on allumina samples small amounts of Pd are always detected. This suggests that Pd oxidation in this conditions is not completed.

2. Support recrystallisation occurs in minor amount in La-stabilised alumina.

3. Temperature (and width) of PdO-Pd hysteresis is influenced by the nature of the support.

4. In the allumina based samples the formation of an unknown phase have been observed. Such a phase does not show any hysteresis behaviour and is favoured by low temperature and low pO2.

5. An example of the hysteresis in the oxidation/reduction is shown in the figure.