

Nanofaceted Pd-O Sites in Surface Ce-Pd-O Superstructures Boost Activity in the Combustion of Methane

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Introduction

Catalytic combustion of methane is a leading technology in emission prevention and clean up [1]. The best catalyst for methane combustion is supported PdO, but it still suffers from inadequate activity at low temperature (<673K) and deactivation at high temperature (>973K) due to formation of metallic Pd from PdO particles [2]. Some authors reported that CeO₂ has a positive effect in stabilizing PdO at high temperature and in promoting Pd reoxidation, narrowing the hysteresis window between PdO decomposition and Pd reoxidation and enhancing catalytic activity [3,4]. In this work we describe a new Pd/CeO₂ material synthesized by solution combustion synthesis. This catalyst is more active for CH₄ combustion than Pd/CeO₂ catalysts prepared by traditional incipient wetness technique. The new material contains an ordered surface Ce-Pd-O superstructure (which has no precedent in noble metal-ceria systems) as revealed by HRTEM images and confirmed by DFT calculations.

Materials and Methods

Catalysts were prepared with 1% or 2% wt nominal Pd loading by solution combustion synthesis (SCS1, SCS2) or by incipient wetness from a Pd(NO₃)₂ solution on two different commercial CeO₂ supports (IW1a, IW1b – IW2a, IW2b). The catalysts were tested for the catalytic combustion of CH₄ under lean conditions (0.5% CH₄, 2% O₂ in He). Reaction rates were measured under differential conditions (CH₄ conversion was kept below 5%). HRTEM 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. DFT calculations were performed in the plane-waves pseudopotential framework [5].

Results and Discussion

The results presented in Table 1 indicate that SCS samples are always more active than the correspondent IW ones, with reaction rates on a per gram of noble metal basis 3 to 5 times higher. The microstructural study of the samples carried out by HRTEM evidenced the presence of an ordered surface superstructure. The lattice fringes observed in Figure 1a at 5.7 Å and 8.0 Å along the [110] and [001] directions individuate a (2x1)(110) surface supercell containing two cation and four anion sites per layer. The same superstructure was observed also after severe heating treatment (15 hours at 1173K). It results from a complex reconstruction of the (110) CeO₂ surface in which the Pd²⁺ ions substitute one out of two Ce⁴⁺ ions while the compensating oxygen vacancies form ordered arrays of open channels. The resulting active sites exposes strongly undercoordinated O atoms in front of square-planar PdO nanofacets (Figure 1b) which control the higher catalytic activity observed in the SCS catalysts.

Table 1. Physical properties and CH₄ combustion rates of the samples

Sample	Pd (wt%)	S.A. (m ² /g)	Reaction rate	
			(μmol/g _{PaS})	(μmol/m ² s)
IW1a	1,00	3,4	9,5	2,8
IW1b	0,98	11,8	9,7	0,8
SCS1	1,09	5,4	25,1	5,1
IW2a	1,72	3,3	5,5	2,9
IW2b	1,74	12,2	7,9	1,1
SCS2	1,71	5,9	27,6	10,4

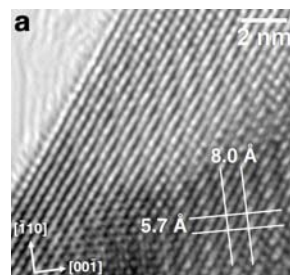


Figure 1a. Planar HRTEM raw image of SCS2 sample.

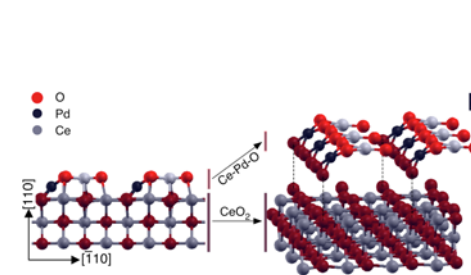


Figure 1b. Side view of the equilibrium surface superstructure predicted by DFT calculations.

Significance

Predictive rational design of new catalytic materials is a difficult task requiring interdisciplinary competences. We have prepared and characterized a novel catalyst formulation containing Pd and CeO₂ that displays high activity towards methane oxidation. This reactivity is directly correlated to the formation of a new nanostructured surface superstructure that we fully characterize at the atomic level. In addition, the local structure of the active Pd-O moiety displays striking similarities to that of Pd in solution-coordination chemistry. This link between solution chemistry and surface science allow us to put into a new perspective the predictive tailoring of heterogeneous catalysts.

References

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