Influence of CeO_2 morphology and initial Pd-Pt interaction degree on catalyst activity and stability

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Significance and Relevance

The impact of the support morphology and Pd-Pt interaction degree was systematically investigated during CO oxidation. Constant surface noble metal concentration (SNMC) ensured the same probability for noble metal (NM) aggregation/redispersion under reaction conditions on commercial CeO_2, nanocubes and nanorods. Ex *situ* and *in situ*/*operando* characterization tools revealed that the aggregation/redispersion of the NM is controlled by the morphology of ceria. On CeO_2-nanocubes a balanced NM-support interaction is obtained that promotes the formation of small and active clusters. In contrast, a high number of surface defects, as present for CeO_2-nanorods, foster the formation of highly dispersed and less active species.

Preferred and 2nd choice for the topic: *1) Automotive and stationary emission control, 2) Fundamental advances in understanding catalysis*

Preferred presentation: Oral preferred or short oral

Introduction and Motivations

Exploiting the interaction between the noble metals and reducible metal oxide supports has attracted a tremendous interest during recent decades for various catalytic applications including emission control[1,2], fine chemistry, electrocatalysis and energy-related processes[3]. Previous studies have shown that the activity, selectivity and stability of CeO_2-based catalysts is influenced by the porosity, reducibility and morphology/exposed facets of the support as well as by the interplay with the NM nanoparticles (NPs)[4,5]. On the latter aspect, we have recently shown for monometallic catalysts that the surface noble metal concentration (SNMC) influences the *in situ* formation of the active species and the onset of oxidation reactions[6,7]. As a next step, this study focuses on understanding the effect of Pd-Pt alloying extent and CeO_2 morphology by comparing bimetallic catalysts with the same SNMC supported on hydrothermally synthesized and morphologically pure CeO_2-nanocubes and nanorods. A commercial ceria support was used as a reference system for non-preferential exposed facets.

Materials and Methods

Different CeO_2 morphologies were obtained by hydrothermal synthesis. Bimetallic and alloyed Pd-Pt NPs were prepared by colloidal synthesis, and were afterwards deposited on the ceria supports via wet impregnation. To modify the Pd-Pt alloying degree, the noble metal precursors were varied during the synthesis process. The effect of the ceria morphology was highlighted by maintaining the same SNMC in all samples. The NM structural dynamics and the interactions between Pd, Pt and CeO_2 were then monitored by complementary characterization methods after synthesis, during catalyst pretreatment and under reaction conditions.

Results and Discussion

Ex-situ characterization of the bare CeO_2 supports revealed different exposed facets and oxygen vacancies concentrations depending on the ceria morphology. At the same time, alloyed nanoparticles or highly dispersed Pd-Pt species were identified for the differently prepared bimetallic catalysts. Accordingly, pronounced differences were measured in the CO oxidation activity and catalyst stability depending on the exposed facets of the CeO_2 support and noble metal state. In line with these results, *operando* XAS data obtained during consecutive light-off/light-out cycles and pre-treatment procedures indicate a higher structural stability for the alloyed Pd-Pt nanoparticles on CeO_2-nanocubes.

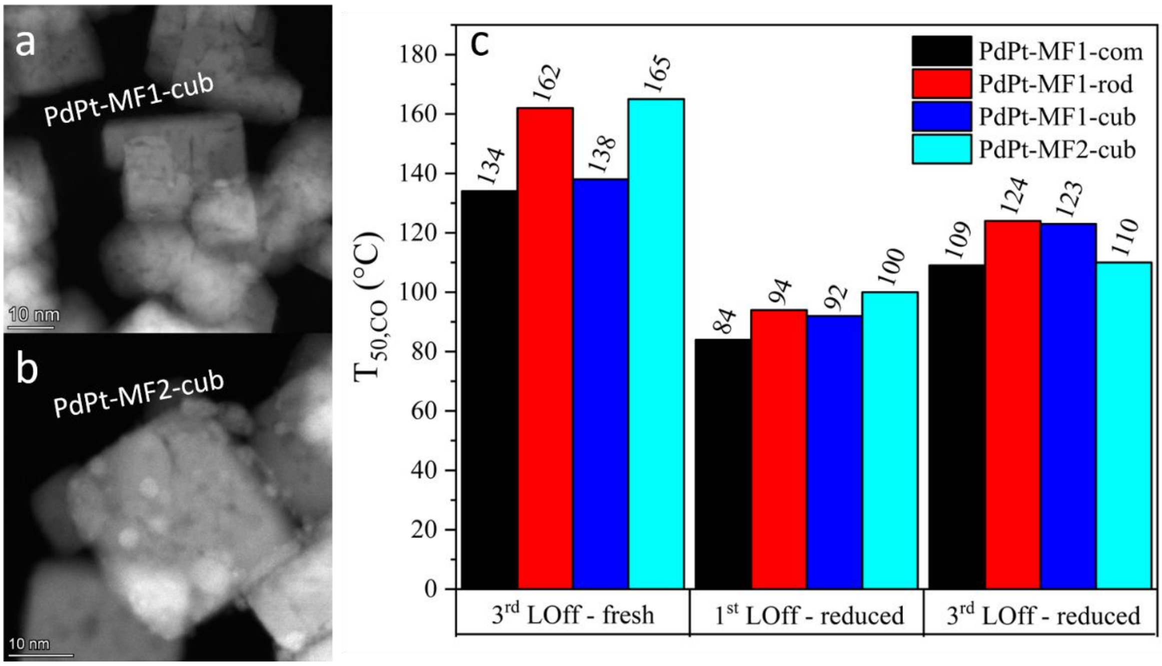

Figure 1: HAADF-STEM images of highly dispersed (a) and alloyed (b) Pd-Pt bimetallic catalysts after catalytic tests. (c) Temperatures of 50% CO conversion at different stages of the catalytic test for the investigated samples.

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