

CO-induced dynamic behavior of supported PGM nanoparticles in mild conditions

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Significance and Relevance

This study investigates the interaction of CO at room temperature with Platinum Group Metal (PGM) nanoparticles (NPs) supported on alumina, using gas-volumetry, adsorption microcalorimetry, and IR spectroscopy. Unique step-shaped adsorption isotherms, accompanied by an unexpected increase in the heat of adsorption, is observed for both Pd/Al₂O₃ and Pt/Al₂O₃ catalysts. This observation is correlated with a drastic change in the relative population of carbonyl species, indicating the occurrence of CO-induced surface modifications. The methodology, based on characterization techniques largely available in modern laboratories, can be extended also to PGM NPs on activated carbons, which are crucial in various industrial and environmental applications.

Preferred and 2nd choice for the topic: Fundamental advances in understanding catalysis Preferred presentation: Oral only

Introduction and Motivations

The interaction of CO with Platinum Group Metal (PGM) nanoparticles (NPs) is a topic of wide fundamental interest and also of high practical relevance. Indeed, PGM-based systems are involved in the thermo- and electro-catalytic conversion of CO in a variety of valuable chemical compounds, and have a prominent role also in the field of hydrogen purification and pollution abatement. Last, but not least, CO is the most used probe in the characterization of Pd NPs, and it is widely adopted for a rapid and efficient evaluation of the metal dispersion through pulsed chemisorption methods. It is well assessed that CO adsorption at high temperature can cause important surface and structural modification in PGM NPs, with evident consequences on the activity and selectivity of many catalytic processes.¹⁻³ In contrast, the occurrence of such kind of phenomena at lower temperature is by far less documented, despite its importance for a correct interpretation of the characterization data or for understanding the behavior of Pd-based catalysts in milder condition (e.g., in electrocatalytic reactions). Identifying these environment-dependent phenomena requires a full characterization of the surface sites and of their evolution upon interaction with CO, but accessing this information is not straightforward and requires multiple in situ and operando techniques.

Materials and Methods

A series of catalysts consisting in PGM NPs supported either on alumina or on activated carbons were provided by Chimet S.p.A. Each catalyst was prepared with the metal loading of 5 wt% using the deposition-precipitation method, differing only in the metal type and support material. The catalysts were activated following a standardized protocol, involving heating under dynamic vacuum and subsequent reduction in H₂. Activation temperatures were selected based on prior H₂-TPR measurements to ensure the complete reduction of the metal oxide phase.

The CO adsorption process was monitored by coupling three complementary experimental techniques, i.e. gas-volumetry, adsorption microcalorimetry and IR spectroscopy, applied in the same



experimental conditions. Small incremental doses of CO were put in contact with the reduced catalysts in isothermal conditions until a first adsorption run was completed (primary adsorption). After a desorption step by simple evacuation of the cell, a secondary adsorption run was performed to investigate the reversibility of the process.

Results and Discussion

For the Pd/Al₂O₃ catalyst, a peculiar step in the adsorption isotherm was observed for the first time at a relative pressure corresponding approximately to 80% of the maximum coverage. This was accompanied by an unexpected increase in the heat of adsorption. Both observations were correlated with an important modification in the relative abundance of the Pd-carbonyls species, as revealed by IR spectroscopy (Figure 1). In particular, a significative increase in the amount of linear carbonyls at defective sites was detected, at the expense of bridged carbonyls.⁴ These synergistic experimental observations provided an unprecedent insight into a CO-induced corrugation of the (100) surface in small supported Pd NPs. This phenomenon is driven by the strong adsorption energy of CO, which lowers the surface energy and promotes atomic rearrangement, creating new, defective and more energetic adsorption sites. Interestingly, a similar phenomenon is observed for CO adsorbed on Pt/Al2O3. Preliminary measurements suggest also a potential role of residual hydride species in affecting the CO adsorption phenomenon.

In perspective, this approach has the potential to provide a methodological benchmark in the field of characterization of adsorbate-induced phenomena in supported metal NPs on realistic catalysts of industrial and environmental relevance. It is important to notice that, while application of IR spectroscopy is restricted to samples transparent in the Mid-IR region, volumetric and micro-calorimetric measurements have no limitations and can be performed on every type of samples. This paves the way to the investigation of adsorbate-induced surface phenomena at metal NPs on activated carbons, which represent a big fraction of PGM-based catalysts employed in the chemical industry and for environmental applications.



Figure 1 Combination of gas-volumetry, adsorption microcalorimetry and IR spectroscopy provided an unprecedent insight into a CO-induced surface reconstruction of Al_2O_3 -supported Pd NPs involving the (100) surface and entailing the creation of new, defective, adsorption sites.

References

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Acknowledgements

We acknowledge support from the Project CH4.0 under the MUR program "Dipartimenti di Eccellenza 2023-2027" (CUP D13C22003520001).