



Quantitative sorption of oxygen and CO₂ on metal supported nanocarbons for catalysis and electrocatalysis

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Introduction

In the present work, microcalorimetry is applied to characterize the surface chemical properties of nanocarbon (NC) and NC-based materials for heterogeneously catalyzed and electro-catalyzed reaction.

By a comparative study of differently active materials, the reactivity data can be analyzed with respect to the surface processes occurring on these materials during adsorptive microcalorimetry. Three reaction systems have been studied: O₂ chemisorption on Pd /CNF catalysts for the selective oxidation; O₂ chemisorption on Pd/Au /CNF catalysts for the synthesis of H₂O₂, CO₂ chemisorption on Fe/CNFs based electrocatalysts for the reduction of CO₂ to long chain hydrocarbon. Additionally, the surface basicity of NC and N-NC was investigated by CO₂ chemisorption.

Experimental

A SETARAM MS70 Calvet calorimeter was combined with a custom-designed high vacuum and gas dosing apparatus [1]. CO₂ or O₂ were stepwise adsorbed at reaction temperature 313 K and 353 K, respectively. The Pd and Pd/Au catalysts are obtained via sol-immobilization on the CNFs [2], while Fe-based electrocatalyst are prepared via incipient wetness impregnation [3].

Results and discussion

The microcalorimetric titration of basic sites on N-CNF by CO₂ adsorption at 313K shows the presence of heterogeneously distributed and energetically different basic sites on the CNF surface, which depend on the amination temperature (Fig.1) [4]. The impact of surface chemistry of the CNF supports on the metal/CNF electro/catalytic performance can be evaluated through the thermal effect due to the interaction of the reactant at the surface under reaction condition.

In the case of the Fe based electrocatalysts, the best performance is observed for sample presenting few very small Fe nanoparticles among the majority of big Fe particles inside and outside the N-CNF. This sample is characterized by heterogeneously distributed and energetically different chemisorption sites with a very strong and irreversible interaction with CO₂ (280 kJ/mol) limited to very few sites

while mainly reversible CO₂ chemisorption process occurs. Smaller Fe nanoparticles on the outer surface of oxidized CNF shows contribution of reaction to the heat released. Such reaction imparts instability to the catalyst which lowers the electrocatalytic activity and selectivity.

The most active Pd N-CNF presents a relatively low amount of surface sites for the oxygen chemisorption characterized by an activated process (~750 kJ/mol). The oscillating differential heat accounts for the dissociative oxygen chemisorption and for the oxidation reactions of the protective agent (PVA) covering the Pd nanoparticles. The determined accessible Pd by oxygen (0.7 m²/g) is significant higher that by CO (0.4 m²/g) indicating the penetration of oxygen into the Pd subsurface [5]. In contrast, the lower catalytic activity observed for the Pd/N-CNF473K correlates to the lower differential heat of reaction accounting for a smaller contribution of reaction involving the PVA (Fig. 2).

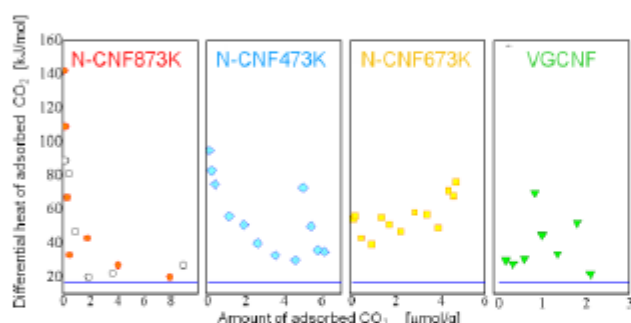


Figure 1: Differential heats of CO₂ adsorption versus amount of CO₂ uptake at 313 K.

Conclusion

This work shows the high potential of microcalorimetry for the characterization of nanocarbon based materials for catalysis and electrocatalysis. It shows the importance of strong basic sites on the CNF surface for improving the Metal/CNF performance.

The nature of the chemisorption process relevant for high performance was correlated to the surface structural features of the sample. Such informations are of relevance in the view of designing a catalyst or an electrocatalyst. Furthermore, the calorimetric data are relevant for comparing theoretical and experimental hypotheses about reaction pathways.

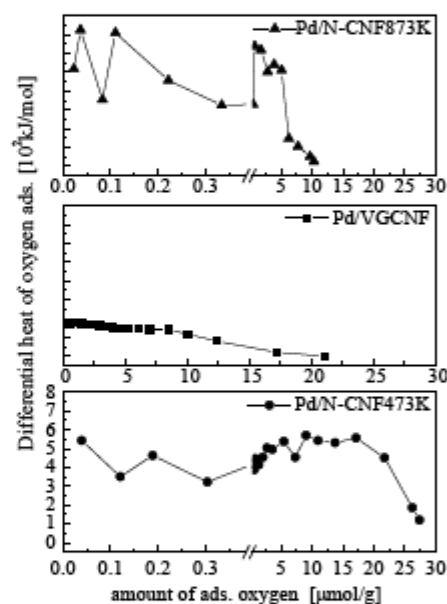


Figure 2: Differential heats of O₂ adsorption versus amount of O₂ uptake at 353 K.

References

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