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Microcalorimetry investigation on CNFs and metal supported CNFs for heterogeneous catalysis and electrocatalysis

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Introduction

Microcalorimetric methods, carried out under reaction conditions, provide insight into the interaction of adsorbates with the active surfaces, therefore, contributing to shed light on the nature of the active sites. In particular, the thermal effects during the chemisorption of a reactant over a solid under reaction condition provide information about the strength of the chemical bonds involved in the adsorption process and the transformations taking place as consequence of the adsorption process. In this work, microcalorimetry is applied to probe the active surface of CNF based materials for heterogeneously catalyzed and electro-catalyzed reaction.

In comparative study on differently active materials, a critical analysis of the reactivity data can be delineated with respect to the surface processes occurring under good catalyst performance. Two systems have been studied: O₂ chemisorption at reaction temperature on Pd nanoparticles/CNF based catalyst for the selective oxidation of alcohol to valuable compounds; CO₂ chemisorption at reaction temperature on Fe/CNFs based electrocatalysts used for the reduction of CO₂ to long chain hydrocarbon.

Experimental

A SETARAM MS70 Calvet calorimeter was combined with a custom-designed high vacuum and gas dosing apparatus, which has been described in detail [1]. The powder samples were pressed into pellets, crushed and sieved. CO₂ or O₂ were adsorbed at 313K and 353K, respectively. The gas was stepwise introduced into the cell, subsequently adsorption on the catalysts surface sites is observed. The corresponding adsorption heat signal was recorded for each dosing step. The Pd catalysts are obtained via sol-immobilization on the CNFs [2], while Fe-based electrocatalysts are prepared via incipient wetness impregnation [3].

Results and discussion

The differential heat of adsorption vs amount of gas uptake reveals the energetic of the chemisorption process related to the best catalytic or electrocatalytic performance. The Fe based electrocatalysts are characterized by heterogeneous distribution of energetically different chemisorption sites for CO₂. Different CO₂ differential heat profiles depending on the structural features of the Fe particles were observed. The best electrocatalytic performance correlated with the highest amount of chemisorption sites characterized by a reversible CO₂ chemisorption process at 313K. Irreversible chemisorption with probable metal phase transformation hinders the achievement of higher selectivity to long chain hydrocarbon. The microcalorimetric study of O₂ adsorption on Pd based catalysts at 353K has shown a very strong interaction between the probe molecule and the catalyst surface (initial differential heat of ~730kJ/mol, final heat of ~550kJ/mol). It became clear that the adsorption process is irreversible. Furthermore, the primary dissociative oxygen chemisorptions cannot be distinguished from the secondary reactions. This may include both oxidations of the Pd nanoparticles (-187 kJ/mol O₂ [4]) and of the polymer used as protective agent (PVA) for the nanoparticles possibly catalyzed by the palladium. However, higher differential heat release during the reaction of oxygen with the Pd surface correlate with the decrease of the selectivity toward hydrogenolysis reaction observed on this catalyst in the selective oxidation of alcohol.

Conclusions

In this work, we have used microcalorimetry to study the thermal effects occurring as a consequence of the interaction of the reactant with the solid surface under reaction condition. This approach is of relevance for assessing the energetics of the active sites towards the reactants and their correlation to the optimum in the catalytic performance.

References

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