

On the role of the support in platinum on carbon nanofiber catalysts for cinnamaldehyde hydrogenation - support-assisted catalysis?

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Introduction

Catalyst supports based on carbon nanofibers (CNF) combine the advantages of both active carbons and graphite i.e., CNF have a large surface area, are well defined, inert, non microporous and can potentially be prepared without contaminants. Moreover the surface of CNF can be modified by chemical treatments like oxidation. These treatments result in the formation of oxygen-containing groups on the surface of the CNF and play an important role both in catalysis and catalyst preparation. In general, while preparing catalysts the oxygen groups serve as deposition sites for the metal precursors, in addition sintering of the metallic particles is prevented. In catalysis the oxygen-containing groups can have a pronounced effect on the activity and selectivity of the materials. It was shown earlier by our group that the activity of Ru/CNF for the hydrogenation of cinnamaldehyde could be increased with a factor of 22 by the removal of 97% of the initially present acidic oxygen-containing groups [1]. In the current contribution we will show that similar trends were observed for Pt/CNF catalysts. Moreover a model is developed which can explain the catalytic behavior of Pt/CNF catalyst for cinnamaldehyde hydrogenation, (for a overview of this reaction see e.g. [2]), as function of the concentration of oxygen containing groups on the CNF surface.

Experimental

In order to be able to investigate the influence of the surface oxygen groups different catalysts having the same Pt particle size but with varying concentrations of oxygen containing groups were prepared. First the CNF were grown from CO/H₂ over a Ni/SiO₂ catalyst, next the prepared fibers with the Ni/SiO₂ growth catalyst still in it were treated in refluxing 1M NaOH to remove the SiO₂. After washing with water the CNF-Ni mixture was treated in refluxing HNO₃ for 2 hours to remove the Ni and introduce oxygen-containing groups on the CNF surface. After the deposition of Pt (3.6wt%) by Homogeneous Deposition Precipitation (HDP [3]) the samples were treated at different temperature (none, 573, 773 and 973 K) under a nitrogen atmosphere to remove part of the oxygen-containing groups from the CNF surface.

The hydrogenation of cinnamaldehyde (13.7-344.5 mol.m⁻³) was executed in a slurry reactor at 383K in H₂ (3.0-7.0 MPa) in order to obtain data for kinetic modeling

Results and Discussion

TEM, EXAFS and chemisorption studies showed the presence of a narrow and stable platinum particle-size distribution (1-2 nm) on all catalysts. The temperature treatment, after metal deposition, did not change the metal particle size but it modified the number of oxygen-containing groups on the CNF surface. This had a pronounced effect on the catalytic behavior of the catalyst as can be seen in Figure 1. Clearly the overall initial activity increased by a factor of 25 after treatment at 973 K compared to that with no temperature treatment. This increased activity is related to the

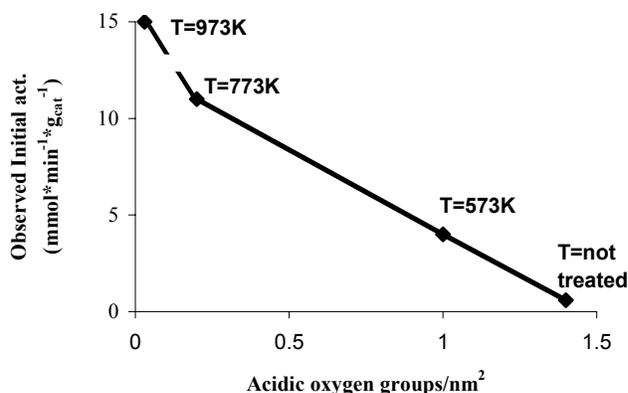


Figure 1: Activity for cinnamaldehyde hydrogenation of Pt/CNF catalysts treated at the indicated temperature

decreased amount of oxygen groups on the fibers. Please note that here the amount of acidic oxygen groups are plotted on the x-axis which was determined by titration. However also the total number of oxygen groups, as determined by TGA [4], relate to the catalytic activity. The differences in intrinsic activity are even larger, since internal diffusion limitation slowed down the reaction for the catalyst treated at 973 K (indicated by de dashed line in Figure 1). This enhanced activity is mainly caused by a strong increase in hydrogenation rate of the C=C bond, while only a slight increase in C=O bond hydrogenation rate is observed.

In the network of elementary steps of a hydrogenation reaction, the dissociative adsorption of hydrogen, the adsorption of the organic reactants and the reaction between sorbed intermediates are of crucial importance. These steps can be influenced by the number and type of oxygen containing groups on the CNF surface in two ways, namely indirectly via the metal or directly by influencing (the mode of) reactant adsorption. Using XPS and H₂-chemisorption no evidence has been found demonstrating that the amount of oxygen in the support influences the electronic properties of the platinum particles. Using a model including both Langmuir-Hinselwood kinetics

and mass

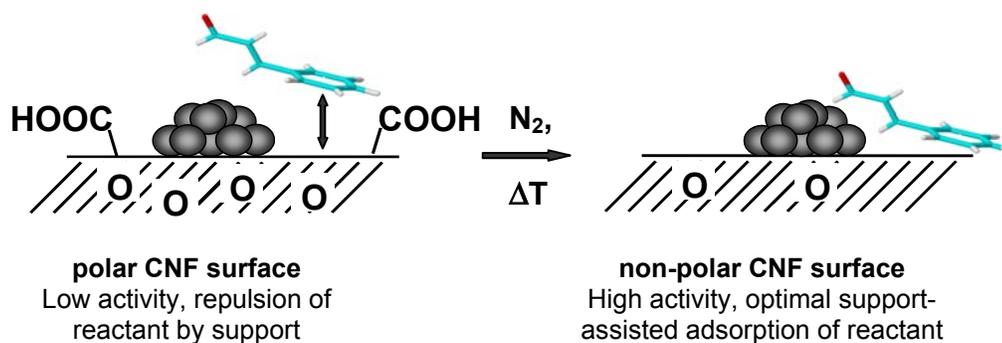


Figure 2: Proposed model for the support assisted catalysis in Pt/CNF catalysts for cinnamaldehyde hydrogenation.

transfer effects we have compared the reaction rate constants and adsorption constants of a CNF-supported platinum catalyst with a large and with a much smaller number of oxygen-containing groups on the surface. These results suggest that hydrogenation is assisted by adsorption of the cinnamaldehyde on the CNF support surface after removal of the oxygen surface groups, as is depicted in Figure 2.

Conclusions

The hydrogenation activity of Pt particles supported on carbon nanofibers (CNF) for cinnamaldehyde strongly depends on the chemical composition of the support. The intrinsic activity increases with a factor of 300 when 97% of the initially present oxygen groups on the support were removed. Based on physico-chemical characterization and kinetic studies a reaction pathway is proposed in which the adsorption of cinnamaldehyde on the metal support perimeter is a key to catalytic activity. After removal of the oxygen groups the support is less polar resulting in an enhanced adsorption of the substrate via the phenyl-ring which increases the catalytic activity.

References

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