Can Iron Oxides Keep Up with Noble Metals in Carbon Monoxide Oxidation?

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Introduction

As a consequence of ongoing industrial growth, air pollution and the search for new ways of counteraction have never been a more relevant and yet challenging topic in scientific research. Every year large amounts of nitric oxides (NO_x), incompletely burnt hydrocarbons, carbon monoxide and carbon dioxide are emitted into the environment. Because of its toxic effect caused by the irreversible binding onto haemoglobin and hence decreasing the amount of oxygen transported through blood [1], carbon monoxide and its conversion to carbon dioxide play a primary role in the presented project.

By using catalysts based on palladium, platinum or rhodium it is possible to remove CO in exhaust gases by oxidation to carbon dioxide using residuary oxygen and thus to reduce its emission into the atmosphere. Unfortunately, the use of noble metals is limited due to low resources leading to extraordinary high and continuously increasing prices. Additionally, the harmful effect of these noble metal catalysts on the environment is still unknown and discussed controversially.

In previous work it could be shown that, by application of iron as catalytic centre, it is possible to oxidize a certain amount of CO in a defined gas stream completely at moderate temperatures [2]. To compensate lower activity in comparison to noble metal catalysts, the systems based on iron have to be optimized. Such an optimization is based on the elucidation of structure-activity correlations for a broad range of catalysts, which are tested under model conditions, as well as the determination of the reaction mechanism of carbon monoxide oxidation on iron catalysts.

Materials and Methods

The diversity of the tested catalysts presented in this contribution derives mainly from choice of support material and the metal precursor as well as the parameters applied within impregnation and calcination step. Catalysts from 0.01 wt% iron loading up to 50 wt% have been synthesized and tested. Typically γ-alumina is used as support and loaded with pure or pre-reduced iron (III) acetylacetonate by wetness impregnation and afterwards calcinated to yield in iron oxide more or less incorporated into the support lattice [3]. Differences in activity of the catalysts can be related to parameters like particle size of the iron species, the amount and distribution of active sites at the support surface and their accessibility as well as coordination geometry of the present iron species. To correlate these parameters with catalytic activity in carbon monoxide oxidation and to gain more insights into the mechanism of this reaction, analytics like Brunauer-Emmett-Teller adsorption isotherme (BET), X-ray diffraction (XRD), transmission electron microscopy (TEM), diffuse reflectance UV-Vis and *in-situ* diffuse reflectance infrared Fourier transformed spectroscopy (DRUVS & DRIFTS) are carried out as well as *ex-situ* and especially *in-situ* X-ray absorption spectroscopy performed in a self-designed reactor (fig. 1).

Results and Discussion

The normalized activity of the catalysts can be correlated to the ratio of isolated catalytic centers to oligomers and smaller particles on the surface of the support. This ratio decreases with increasing iron loading (fig. 1), which means that the amount of active iron species decreases, presumably because of inaccessibility. This leads to the goal to develop a better synthesis route so that more isolated and thus active iron centers can be obtained - ideally in tetrahedral coordination geometry which is considered to be even more active than octahedrally coordinated iron. One idea to achieve this is to successively increase the loading of the catalysts in small steps, to hinder agglomeration during the calcination step. Another idea is the variation of the temperature gradient used during calcination or even the application of a stepwise gradient. Results of catalytic tests and the above-mentioned analytical methods will be presented in this contribution.

In-situ X-ray absorption spectroscopy at the iron K edge was carried out in a specially designed XAS reactor. First experiments showed, that during carbon monoxide oxidation, the ratio of iron to aluminum backscatterers decreases with higher temperatures, which means that the observed iron species migrates into the support lattice (fig. 2).

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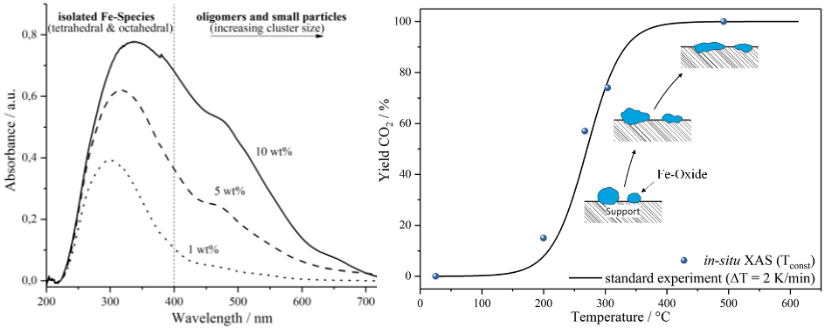
Figure 1. Diffuse reflectance UV-Vis spectroscopy (left) and structure concept based on XAS data obtained by *in-situ* experiments (right)



Significance

The structure-activity correlation and hence derived synthesis routes for the production of catalytically even more active iron species presented in this contribution constitute a new step towards the substitution of noble metals by earth abundant iron.

References

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