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Comparison of polycrystalline copper foil with deposited copper clusters in catalytic oxidation reactions: An in situ X-ray spectroscopy study The Behavior of Sunflower Seeds in the Arctic

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Introduction

Metal foils are used as model catalysts in various investigations of heterogeneous catalytic reactions. Copper and silver foils are utilised as model catalysts for in situ XAS studies in the soft energy range to investigate the relation of the electronic surface structure and the catalytic activity [1-4].

This study targets the transferability of results revealed from in situ XAS measurements in the soft energy range on copper foils to more dispersed systems describing a real catalyst. For this purpose the behaviour of deposited copper clusters and copper foil is compared to each other in the catalytic oxidation of ammonia and methanol. The proof of the catalytic activity of the copper cluster and the evidence that the clusters do not form a film after the reaction is crucial in this context.

Experimental and summary of the results

Copper clusters were deposited on carbon covered gold grids using the gas aggregation technique [5]. The size distribution of the clusters was measured by means of transmission electron microscopy before and after the reaction. The catalytic activity of the clusters was investigated in a reaction cell that allows us to measure XAS spectra in the soft energy range under reaction conditions. The ammonia oxidation was performed in an ammonia/oxygen flow ratio of 1:12 at a pressure of 1.2 mbar. The temperature was increased stepwise from room temperature up to 400°C.

The copper clusters showed a higher reactivity indicated by a lower onset temperature of the reaction compared to copper foil. The clusters consisted of a mixture of copper(I) oxide and copper (II)oxide after introduction to the reaction cell, whereas a fresh foil did not show any amount of copper(II) oxide. The behaviour of copper clusters and copper foil is very similar in the ammonia oxidation. The clusters and the foil show the formation of copper nitride under reaction conditions. This deactivation of the catalyst is observed for the foil at 400°C, whereas the clusters showed the formation of copper nitride already at 200°C. The change in the size distribution of the clusters showed that the clusters sinter during the reaction. However there was no observable formation of a copper layer. The catalytic activity of the clusters was estimated by means of a quadrupole mass spectrometer. The measurements were complicated by the very small amount (100nmol) of copper clusters, but the formation of the products (NO and N₂) was shown. The copper clusters were also shown to be catalytically active in the selective oxidation of methanol to formaldehyde.

Conclusion

It was demonstrated that deposited copper clusters and copper foil behave similar in the catalytic oxidation of ammonia and methanol. The clusters show a higher reactivity indicated by lower reaction temperatures. The presented results allow us to conclude that copper foil presents a suitable model catalyst for the investigation of heterogeneous catalytic oxidation of ammonia and methanol.

References

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