Highly efficient iron oxide catalysts for emission control

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Introduction

For the abatement of pollutants from the exhaust of gasoline and diesel engines precious metals are the most frequent catalytic materials. Three Way Catalysts composed of Pd/Rh or Pt/Rh mixtures are used for the simultaneous conversion of hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO_x) in gasoline cars. Additionally, Diesel Oxidation Catalysts (DOC) imply Pt and Pd to remove HC and CO from the exhaust. However, due to the worldwide increasing number of automobiles the limited resources of precious metals become more and more an issue indicated by their rising market price. Thus, alternative materials with higher natural abundance and harmlessness are of growing interest. In this concern, iron oxide catalysts are increasingly noticed within the last few years for a couple of reactions being of environmental relevance, i.e. oxidation of CO, C_3H_6, NH_3 and NO [1-3]. Therefore, the present paper addresses the structure-activity correlation of Al_2O_3-supported iron oxide samples for the above-mentioned conversions to provide a contribution for the knowledge-based development of advanced Fe based catalysts.

Materials and Methods

A systematic series of model catalysts with iron loadings between 0.1 and 20 wt.% was prepared by using the incipient wetness method. The catalysts were characterized by powder x-ray diffraction (PXRD), diffuse reflectance UV-vis spectroscopy (DRUV-Vis), high resolution transmission electron microscopy (HRTEM) and N_2 physisorption. The experiments were performed in a tube reactor with fixed-bed at total flow of 500 ml/min (STP) and a catalyst mass of 1 g (GHSV = 25,000 h^{-1}). The oxidation of CO, C_3H_6, NH_3 and NO was investigated by using a respective feed gas fraction of 500 ppmv in the presence of 5 vol.% O_2, while taking N_2 as balance. Gas analysis was carried out by a hot measuring FTIR spectrometer (MULTI-GAS Analyzer Mg 2030, MKS Instruments).

Results and Discussion

Iron oxide catalysts developed in our research group exhibit CO oxidation performance above 200°C and therefore they reveal high potential for practical application, for instance for non-road diesel engines such as hand-guided machinery. **Fig. 1 (left)** demonstrates the light-off behavior of a laboratory powder catalyst starting CO oxidation at about 200°C. Interestingly, the correlation between mass and performance of catalyst significantly differs between precious metals and iron oxide. For precious metal catalysts, it is well known that the light-off shift to lower temperatures with increasing metal load, whereas for iron oxide this effect does not appear, since specific Fe oxo entities form in dependency of the loading. For evaluation of the specific Fe oxo sites, detailed spectroscopic characterization was performed implying three different types of Fe oxo species present on the catalysts. As shown in **Fig. 1 (right)** the respective fraction of these Fe oxo species strongly depends on the load of iron. Based on these results a structure activity correlation was established indicating highest activity for isolated Fe oxo sites in the above mentioned oxidation reactions. In addition, a model was developed to estimate more accurate turnover frequencies for catalysts which predominately consist of particulate Fe oxo sites. These improved turnover frequencies were used to get an advanced structure activity correlation. However, both calculations evidence superior activity for isolated Fe oxo sites. This knowledge represents a fundamental base for the targeted development of highly efficient iron oxide catalysts for emission control.

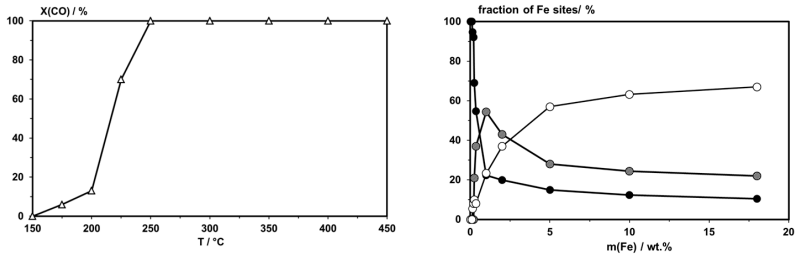

Figure 1. Left: CO oxidation activity of iron oxide catalyst. Conditions: 500 ppmv CO, 5 vol.% O_2, 0 or 5 vol.% H_2O, N_2 balance, $m_{catalyst}$ 1g, 50'000 h^{-1}. Right: Effect of Fe load on the relative fraction of the three different types of Fe oxo species (isolated sites ●, oligomeric sites, particulate sites ○)

Significance

Iron based catalysts provide a high potential for emission control. The relationship between iron load and catalytic activity shows a different behavior as compared to precious metal catalysts. The active sites of iron based catalysts basically consist of three types of Fe oxo species, which can be identified by several spectroscopic methods. The relative fraction of the three Fe oxo entities strongly depends on the load of iron. With respect to all the reactions studied in this paper the TOF values evidence superior activity for the isolated Fe oxo sites.

References

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