Structure-activity relation of iron oxide catalysts in soot oxidation

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Introduction

Diesel particulate filters (DPF) represent a state-of-the-art technology for the removal of soot from diesel exhaust. However, the continuous regeneration of these filters remains a considerable challenge, as the trapped soot causes backpressure effects potentially decreasing the engine efficiency. While the DPF regeneration with NO_2 is already established for heavy duty vehicles, the catalytic soot oxidation by O_2 is considered to be a promising procedure for passenger cars, ships and working machines. Since iron based catalysts are known to reveal high potential for soot oxidation [1], the present paper addresses the targeted design of efficient iron oxide samples implying the evaluation of physical-chemical characteristics driving the catalytic activity.

Materials and Methods

Seven bare iron oxide catalysts were evaluated towards their soot oxidation activity under oxygen-rich conditions. The catalytic studies were performed by temperature programmed oxidation (TPO) using tight contact mixtures of catalyst and soot. A home-made carbon black originated from propene combustion was taken as model soot. The catalysts were thoroughly characterised by employing powder X-ray diffraction (PXRD), N_2 physisorption, high resolution transmission electron microscopy (HRTEM), temperature programmed reduction by H_2 (HTPR), temperature programmed desorption of NH_3 (NH_3-TPD), temperature programmed desorption of O_2 (O_2-TPD) and thermogravimetry coupled with difference thermal analysis (TG/DTA). Special notice was put on the NH_3-TPD data, which were used for the modelling of the NH_3 adsorption and desorption. This model included elementary reactions and implied the specific number of Bronsted and Lewis acid sites.

Results and Discussion

For the assessment of the catalytic performance, the temperature of maximum CO_2 production (T_{max}) was taken. T_{max} of the catalysts appeared between 330 and 415°C, whereas the Fe_2O_3 sample prepared by flame spray pyrolysis (FSP) indicated highest activity (T_{max} = 330°C). For reference, $T_{CO2,max}$ of bare soot was found at 570°C clearly demonstrating the effect of the catalysts.

In the correlation of the soot oxidation efficiency and determining physical-chemical characteristics, a connection between proportion of Lewis acid sites as well as relative crystallinity of the catalysts was deduced as shown in **Figure 1**. This contour diagram demonstrates highest activity for moderate crystallinity (ca. 0.5) and a high amount of specific Lewis acid sites, whereas a moderate quantity of specific Lewis bond NH_3 and high (1.0) or low (ca. 0) crystallinity reveal poor activity. The importance of Lewis acid surface sites is ascribed to their capability of transferring oxygen, whereas the constructed NH_3 adsorption/desorption model points to very similar nature of these surface sites for the iron oxides investigated.

Moreover, our mechanistic studies with $^{18}O_2$ reported lately [2] suggest that oxygen is pumped from the iron oxide to the soot by physical contact points thus leaving oxygen vacancies on the catalyst surface, i.e. Lewis acid sites. These vacancies are refilled by diffusion of surface and bulk oxygen. In surface diffusion, oxygen migrates from neighbouring Lewis acid sites, whereas diffusion of bulk oxygen occurs along lattice vacancies. The present structure-activity study confirms the importance of the transport of crystalline oxygen, as the amorphous iron oxide sample shows rather low catalytic activity, although it exhibits a medium surface concentration of Lewis acid sites. This finding is associated with faster oxygen diffusion in crystalline structures as referred to amorphous domains.

Hence, the derived correlation of Lewis acid sites, crystallinity and catalytic activity coincides with the mechanistic suggestions thus accounting for the highest efficiency of the Fe_2O_3 sample originated from FSP. This catalyst implies the largest number of surface defect sites as well as moderate crystallinity both evoking fast diffusion of oxygen to contact points. This knowledge on determining characteristics identified in this paper is considered to be an important tool for the rational development of advanced iron oxide catalysts for soot oxidation.

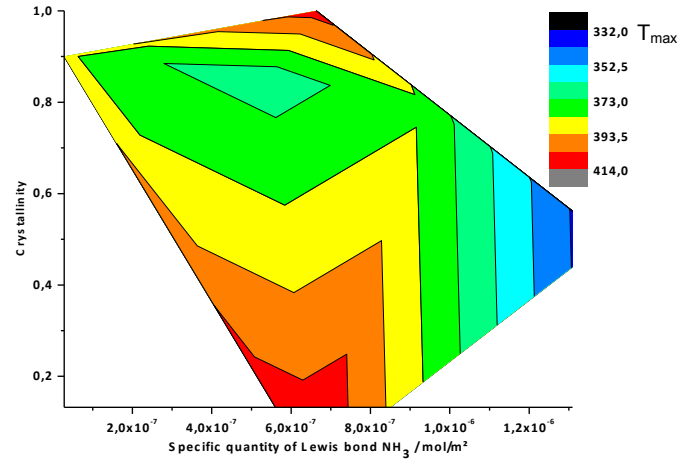

Figure 1. Correlation of T_{max}, quantity of specific Lewis bond NH_3 and crystallinity of the iron oxide catalysts.

Significance

The correlation of structure and activity of iron oxides for soot oxidation shows Lewis acid sites and moderate crystallinity of the catalysts to be crucial. These results coincide with mechanistic studies thus representing the base for the targeted design of advanced catalysts.

References

1. Zhang, Z.; Han, D.; Wei, S.; Zhang, Y. *Journal of Catalysis* **2010**, *276*, 16.
2. Wagloehner, S.; Kureti, S. *Applied Catalysis B: Environmental* **2012**, *125*, 158.