Modeling of the CO oxidation on Fe_2O_3 model catalyst

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Introduction

For the abatement of CO from the exhaust of gasoline and diesel vehicles three way catalysts (TWC) and diesel oxidation catalysts (DOC) are used, which both imply precious metals (Pt, Pd) as active components. These components reveal high catalytic performance, but their natural resources are limited. Therefore, the development of TWC and DOC free from noble metals is currently a challenging issue. From the literature it is known that iron oxide catalysts exhibit promising CO oxidation activity [1]. Additionally, iron oxides are not of toxicological concern, which has to be considered due to mechanical abrasion effects of automotive catalysts.

The present paper deals with the reaction mechanism and the elementary kinetics of the CO oxidation under lean conditions using an α-Fe_2O_3 model catalyst. This study represents a crucial part of the knowledge-based design of efficient iron oxide catalysts for the CO oxidation in automotive exhaust.

Reaction mechanism and modeling

Based on DRIFTS studies, a reaction mechanism has been postulated implying the reaction of CO with surface oxygen of the Fe_2O_3 catalyst to form carbonates. In the second step the carbonates desorb producing CO_2. Finally, the catalyst surface is re-oxidized by dissociative adsorption of oxygen [1,2].

For the construction of an elementary kinetic model reflecting this mechanism, the CO_2 adsorption/desorption on a bare α-Fe_2O_3 model catalyst is investigated using independent CO_2-TPD studies (temperature programmed desorption of CO_2). The corresponding model is based on the mean field approach assuming all active iron oxo sites to be equivalent. The present approach considers the Arrhenius based rates of adsorption (r_5) as well as desorption of CO_2 (r_6) on the active sites corresponding to formation and decomposition of the surface carbonates. Also, the model implies the mass balances of gas-phase as well as surface species, as demonstrated in **Figure 1**, while the kinetic parameters are obtained by fitting calculations as well as by kinetic gas theory.

Parameter fitting was done simultaneously for two measured desorption signals in order to include the influence of the adsorption temperature. As a result, the obtained parameters implemented into the model are able to describe and predict the experimental data very well. Furthermore, the model also provides the development of the surface coverage by CO_2. As expected, the carbonate coverage increases with decreasing saturation temperature upon TPD (Figure 1).

In our current work, the elementary kinetic model is extended in order to describe the entire CO oxidation in detail. Data from literature [1] as well as kinetic studies measured in a gradient-free loop reactor are used for this purpose.
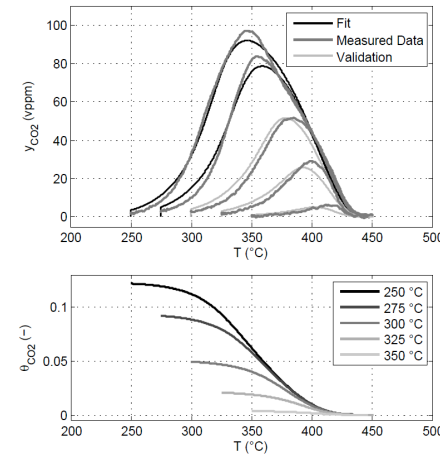

$$CO_2(g) + * \underset{r_6}{\overset{r_5}{\rightleftharpoons}} CO_2*$$

$$1 = \theta_* + \theta_{CO_2}$$

$$r_5 = A_5 \exp\left(-\frac{E_5}{RT}\right) c_{CO_2}\theta_*$$

$$r_6 = A_6 \exp\left(-\frac{E_6 - \alpha_6\theta_{CO_2}}{RT}\right)\theta_{CO_2}$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - u\frac{\partial c}{\partial z} + R_{gas\ phase} \cdot S$$

$$\frac{\partial \theta}{\partial t} = 0 \quad - \quad 0 \quad + R_{surface}/\Gamma$$

Figure 1. Elementary kinetic mean field model of the adsorption and desorption of CO_2 on the α-Fe_2O_3 model catalyst, as well as the mass balances for the gas phase and on the catalyst surface.

Significance

Iron oxides are promising catalysts for the CO oxidation in automotive exhaust gas, which might substitute the precious metals in future. For the targeted design of highly efficient iron oxide catalysts the mechanism and elementary kinetics of the CO oxidation are unraveled using an Fe_2O_3 model catalyst, whereas the present paper gives deep insights into the interaction of CO_2 with the catalyst surface as a crucial part of the entire reaction mechanism.

References

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