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Importance of the Cu oxidation state for the SO_2-poisoning of a Cu-SAPO-34 catalyst in the NH_3-SCR reaction

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ABSTRACT

Cu-exchanged zeolites of the CHA structure are state-of-the-art catalysts for selective catalytic reduction of NO_x with NH_3 in diesel aftertreatment systems. However, these catalysts deactivate in the presence of SO_2, which is a constituent of diesel exhaust gas. In this article, the deactivation behavior and mechanisms of a Cu-SAPO-34 catalyst were studied with reactor tests and DFT calculations. Exposure of the catalyst to two different SO_2 concentrations and durations, but with the same total SO_2 exposure, calculated as the product of partial pressure of SO_2 and exposure time, lead to the same degree of deactivation. Exposure of the Cu-SAPO-34 catalyst to SO_2 in the presence and absence of NO and NH_3 at different temperatures between 200–600 °C showed different trends for the deactivation. Below 400 °C, the S/Cu ratio on the catalyst increased with temperature in absence of NO and NH_3, while it decreased with increasing temperature in the presence of NO and NH_3. This is explained by the ability of NO and NH_3 to reduce Cu(II) to Cu(I). DFT calculations show that SO_2 adsorbs more strongly on Cu(I) than on Cu (II). Above 400 °C, the S/Cu ratio decreased with temperature irrespective of the presence of NO and NH_3. In all cases, the S/Cu ratio is lower than 1. This is not compatible with extensive deposition of ammonium sulfate when co-feeding SO_2, H_2O and NH_3. A more likely explanation for the deactivation is that SO_2 is mainly related to the Cu sites. This is further corroborated by DFT calculations showing that SO_2 and SO_3, which is possibly formed by oxidation of SO_2 over Cu sites, interact similar with Cu in Cu-SAPO-34 and Cu-SSZ-13.

1. Introduction

Diesel engines operate with excess air in the combustion, leading to production of nitrogen oxides (NO_x). NO_x emissions from diesel engines are a source of air pollution and are therefore regulated. To meet legislation requirements for NO_x emissions, a modern aftertreatment systems for diesel engines contain one or more catalysts for the reduction of NO_x to N_2 by selective catalytic reduction with NH_3 (NH_3-SCR). The NH_3-SCR proceeds according to the reaction: $4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O$. Urea injected in the exhaust gas stream is commonly used as a source for NH_3, and, if properly controlled, the NH_3-SCR reaction can reach very high degrees of NO_x removal. The currently applied catalysts for NH_3-SCR are based on V-oxide, Fe-zeolites or Cu-zeolites.

Current zeolite state-of-the-art NH_3-SCR catalysts are based on the CHA structure due to its better hydrothermal stability than other commercial zeolite structures [1]. The CHA structure exists with an overall chemical composition of $H_nAl_nSi_{1-n}O_2$ (SSZ-13) or $H_nSi_nAlP_{1-n}O_4$ (SAPO-34), under the assumption that only P is substituted by Si. Cu ions are introduced into the ion-exchange positions in these materials, and these Cu sites are the source of the catalytic activity of Cu-CHA catalysts. Compared to Fe-zeolites and vanadia-based SCR catalysts, the main advantages of the Cu-CHA catalysts are superior low-temperature SCR activity and lower N_2O selectivity [2,3]. A disadvantage of the Cu-CHA catalysts is their susceptibility towards poisoning by SO_2 [4,5]. SO_2 is an inevitable compound in diesel exhausts, and even at concentration levels below 15 ppm, as in ultra-low sulfur diesel [4,6], the resulting SO_2 in the exhaust gas, typically about 1–2 ppmv, has a significant impact on the performance of Cu-CHA catalysts. It is therefore important to understand how SO_2 affects the Cu-CHA catalysts.

The gas stream that the SCR catalyst is exposed to in a diesel exhaust system consists of several other compounds than SO_2, including but not limited to O_2, H_2O, NO and NH_3. These compounds may affect the

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interaction of SO_2 with the Cu-CHA catalyst. Several SO_2-poisoning studies have been carried out in gas compositions where NO and NH_3 are omitted [4–11]. Such experiments have shown that the deactivation is due to SO_2 interactions with Cu, which is dependent on the temperature of SO_2 exposure. Adsorption of SO_2 mainly takes place at temperatures around 200 °C [5], while chemical reactions between SO_2 and Cu become more dominating at temperatures around 400 °C [5]. SO_2 reacts at the Cu sites in the CHA, resulting in (Cu,S) species with S in oxidation state +6, which are assigned to isolated Cu-sulfates [4,12]. This assignment is corroborated by their decomposition temperature of around 650 °C, which is consistent with the decomposition of bulk $CuSO_4$ [4,11,13], and by an observed 1:1 correlation between the S/Cu ratio of these species and the deactivation [11]. The formation of sulfates implies that SO_2 is oxidized over the catalyst, and the rate of oxidation increases with temperature [10]. The effect of the gas composition on the deactivation by SO_2 is not fully understood, and therefore, it is important to improve the understanding in order to be able to transfer results to the SO_2-poisoning occurring in real exhausts.

It has been argued that the effect of NO and NH_3 on SO_2-poisoning is the formation of ammonium sulfate, which may infer mass transfer limitations by pore-blocking [14–16]. However, ammonium sulfate decomposes at about 350 °C, and can therefore feasibly be removed [16]. Moreover, the presence of NO and NH_3, or release of NH_3 from ammonium sulfate, has a suggested beneficial effect on the regeneration of SO_2-poisoned catalysts, due to the reducing properties of the SCR gas mixture and NH_3 [8,16].

In this article the SO_2 deactivation behavior of a Cu-SAPO-34 catalyst was investigated. The Cu-SAPO-34 was chosen because of its high hydrothermal stability so that high-temperature regeneration did not result in deterioration of the zeolite structure; something that cannot always be avoided with SSZ-13. We investigated the effect of SO_2 exposure time, SO_2 concentration, and the presence of NO and NH_3 on the deactivation by SO_2. DFT calculations were used to evaluate the interactions between Cu, SO_2 and SO_3 in order to obtain a better understanding of the temperature dependence, and effect of NO and NH_3, on the deactivation.

2. Experimental

2.1. Catalyst material and reactor testing conditions

In this study, we used a Cu-SAPO-34 catalyst with a (P + Al)/Si of 6.5 and a Cu-loading of 1.9 wt%, as determined by ICP-OES. The steady-state conversions of NO in the NH_3-SCR reaction were measured in a fixed-bed quartz reactor with an inner diameter of 2 mm, using 5 mg catalyst on dry matter basis, and a sieve fraction of 150–300 μm. The SCR-feed gas for the activity measurements consisted of 500 ppmv NO, 530 ppmv NH_3, 10% O_2 and 5% H_2O, in N_2 at a total flow of 225 N mL/min- The inlet and outlet gas composition was determined using a Gasmet CX4000 FTIR analyser. Prior to the NH_3-SCR activity measurements, the catalyst was heated for 1 h in the SCR-feed gas at 550 °C. The effect of SO_2 on the NH_3-SCR activity was determined from a comparison of the NO_x conversion before and after exposure of the catalyst to an SO_2-containing feed gas in the same reactor setup.

The catalyst was exposed to SO_2 in a flow with either SCR-feed gas, or with 10% O_2 and 5% H_2O, balanced by N_2 to a total flow rate of 225 N mL/min. The inlet concentrations of SO_2 were 1.5 or 15 ppmv. The temperature and duration of SO_2 exposure were varied and are stated specifically with the results.

The evaluation of the NH_3-SCR activity is based on the rate constant for the NH_3-SCR reaction. The rate constants (k) are derived from measured steady state NO_x conversions, as shown in Eq. (1), assuming plug flow of the gas and that the NH_3-SCR reaction is first order in NO.

$$k = -\frac{F}{W}\ln(1-X) \quad (1)$$

F is the total molar flow rate, W is the total mass of catalyst on a dry matter basis, and X is the NO_x conversion.

The deactivation of the catalyst is calculated from a comparison of rate constants after SO_2 exposure or regeneration with the corresponding rate constant of the fresh catalyst. In this article, we define the deactivation as:

$$\text{Deactivation} = 1-\frac{k}{k_{fresh}} \quad (2)$$

2.2. Computational

Spin polarized Density Functional Theory (DFT) calculations were used to obtain adsorption energies of O_2, SO_2 and SO_3 on Cu species in SAPO-34 and SSZ-13. The calculations were performed with the GPAW package [17,18] using a real space grid-based projector augmented wave method. A grid spacing of h = 0.2 Å and a Fermi smearing of 0.1 K were found sufficient to obtain a satisfactory convergence of the relative energies. To account for Van der Waals interactions the BEEF-vdW functional was used [19]. This functional has shown to produce reliable results for the interaction of molecules with zeolites [20,21]. Both SSZ-13 and SAPO-34 were represented by periodic cells with hexagonal symmetry containing 36 T-atoms (SSZ-13 cell parameters: a,b = 13.886 Å, c = 15.116 Å, α = 120°, β, γ = 90° and SAPO-34 cell parameters: a,b = 14.602 Å, c = 15.287 Å, α = 120°, β, γ = 90°).

3. Results

3.1. Deactivation by SO_2 exposure and scalability

Fig. 1A shows the measured steady state NO_x conversions for the fresh catalyst, after exposure to SO_2, and after regeneration at 550 °C. For the SO_2 exposure, 1.5 ppmv of SO_2 was added to the SCR-feed, which is in the SO_2 concentration range expected in automotive diesel exhaust, and the catalyst was held at 300 °C for 8 h. The regeneration of the catalyst was performed at 550 °C for 1 h in SCR-feed gas without SO_2. Exposure to SO_2 leads to significantly lower steady state NO_x conversions in the temperature range 150–300 °C. Regeneration at 550 °C restores most of the original NO_x conversion in this temperature range. This behavior has also been observed for an aluminosilicate Cu-CHA catalyst, and can be understood in terms of irreversible and reversible deactivation [11]. According to the definitions in [11], the deactivation measured after regeneration at 550 °C is the irreversible deactivation, and the difference in deactivation after SO_2 exposure and regeneration at 550 °C is the reversible deactivation.

For practical reasons when investigating SO_2 deactivation, it is often useful to accelerate the SO_2-poisoning by increasing the SO_2 concentration and proportionally shortening the exposure time. The results are then interpreted in terms of the total SO_2 exposure, calculated as the product of the SO_2 partial pressure and the exposure time, rather than the SO_2 concentration. This interpretation requires that a direct proportionality exists between the exposure time and SO_2 concentration, such that these two parameters can be scaled with respect to SO_2-poisoning. This scalability was investigated by comparing the results of the non-accelerated SO_2 exposure, i.e. exposure to 1.5 ppmv SO_2, to the results from a catalyst exposed to an accelerated SO_2 exposure. For the accelerated SO_2 exposure, the SO_2 concentration was increased by a factor 10 and the exposure time was correspondingly decreased, thus exposing to 15 ppmv SO_2 in SCR-feed gas for 48 min at 300 °C. The steady state NO_x conversions before and after the accelerated SO_2 exposure, and after 1 h regeneration at 550 °C in SCR-feed gas, are plotted in Fig. 1B.

The appearance of the NO_x conversion curve for the accelerated SO_2 exposed catalyst in Fig. 1B, is very similar to that shown in Fig. 1A. The NO_x conversions of the fresh catalyst shown in Fig. 1B are slightly lower than those of the fresh catalyst in Fig. 1A, which is due to small