In situ DRIFTS-MS studies on the oxidation of adsorbed NH_3 by NO_x over a Cu-SSZ-13 zeolite

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ABSTRACT

DRIFT spectroscopy combined with mass spectrometry was used to investigate the oxidation of adsorbed ammonia by NO_2, $NO + O_2$ and $NO_2 + O_2$ on a copper ion exchanged SSZ-13 (Cu-SSZ-13) zeolite. Compared with both NO_2 and NO, the adsorption of ammonia is much stronger on the Cu-SSZ-13 zeolite. Two adsorbed ammonia species were found over the Cu-SSZ-13 zeolite studied here, notably ammonia on Brønsted acid sites (proton) and ammonia on Lewis acid sites (copper ions). These adsorbed ammonia species present different activity profiles and selectivity to N_2 during NH_3 oxidation. The results obtained suggest that ammonia adsorbed onto copper ions in Cu-SSZ-13 is more active at low temperatures than proton-adsorbed NH_3, and give rise to a higher selectivity to N_2. The formation of N_2O is associated primarily with the reaction of NO_x with proton-adsorbed NH_3 via the formation and subsequent thermal decomposition of NH_4NO_3.

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1. Introduction

Ammonia selective catalytic reduction (SCR) of NO_x is one of the potential ways to reduce nitric oxide emissions from the exhaust of lean-burn engines (with better fuel efficiencies) in both automobile and stationary source applications [1–3]. Both vanadium oxide-based catalysts (for stationary sources) and metal ion exchanged zeolites (for mobile applications) have been reported with high activity and selectivity in this reaction [1]. However, insufficient hydrothermal stability of metal ion exchanged zeolites has sometimes limited their application.

Copper ion exchanged SSZ-13 zeolites (Cu-SSZ-13) have recently been reported to have higher activity and better selectivity to N_2 for the ammonia SCR reaction over a wide reaction temperature range than other copper ion exchanged zeolites, such as Cu-ZSM-5 and Cu-beta [4–6]. More importantly, Cu-SSZ-13 also displays better hydrothermal stability than other copper ion exchanged zeolites [7]. In order to understand the high activity/selectivity and high hydrothermal stability of this catalyst, increasing attention has been paid to studies of the structure and chemistry of Cu-SSZ-13 zeolites. For example, our group found two different copper sites in Cu-SSZ-13 zeolite exhibiting a large difference between their reducibility with H_2 [8]. The oxidation state of copper species in Cu-SSZ-13 zeolite has been shown to be very sensitive to pretreatment conditions [8]. Fickel and Lobo have determined the coordination structure of copper ions in calcined Cu-SSZ-13 zeolite by variable-temperature XRD measurement [7]. Their results suggest that copper ions are located in the six-member rings [7], which were also identified as the active species in NH_3-SCR reaction by Deka et al. [9]. However, unlike other copper exchanged zeolites, such as Cu-ZSM-5 and Cu-beta, the reaction mechanism of NH_3-SCR of NO_x over Cu-SSZ-13 zeolites is still poorly understood.

In this work, we investigated the oxidation of adsorbed NH_3 species by different oxidant gas mixtures (NO_2, $NO + O_2$ and $NO_2 + O_2$) in the temperature range of 423–673 K by using an in situ DRIFT spectroscopy and mass spectrometry system. The focus of this work is to understand the influence of reaction temperature and the composition of oxidation gas mixture on the activity and selectivity to N_2 of a Cu-SSZ-13 zeolite for the oxidation of adsorbed ammonia.

2. Experimental

The Cu-SSZ-13 sample used throughout this study was the same as that used in our previous work [6]. The synthesis of Cu-SSZ-13 was carried out by using the method reported by Fickel and Lobo [7]. The Si/Al_2 and Cu/Al ratio of the Cu-SSZ-13 sample is ~12 and ~0.4, and the copper ion exchange level of the Cu-SSZ-13 sample was 79% as determined by ICP analysis.

In situ IR spectra were collected on a Mattson Research Series 1 FT-IR instrument equipped with a DRIFT accessory and a high temperature/high pressure reaction cell (Thermo Fisher Scientific). Each spectrum was recorded at $4\,cm^{-1}$ resolution, and was the
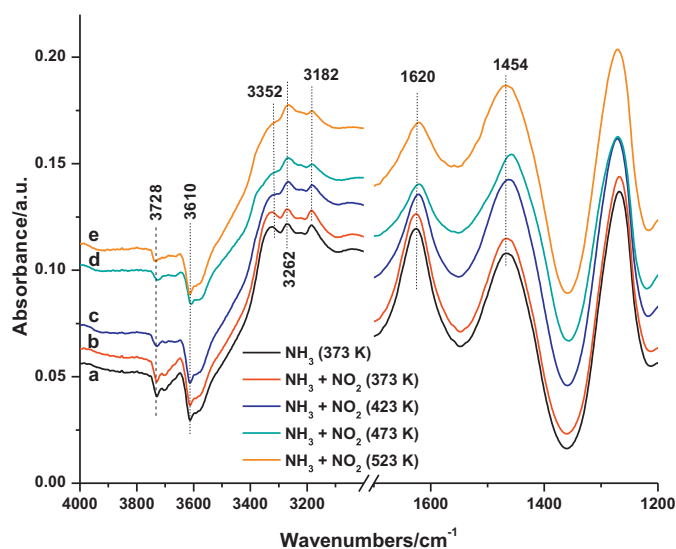
Fig. 1. DRIFT spectra after NH$_3$ adsorption at 373 K (a), and after NH$_3$ and NO$_2$ co-adsorption at 373 K (b), 423 K (c), 473 K (d) and 523 K (e) on Cu-SSZ-13.

average of 256 scans. After the Cu-SSZ-13 sample was loaded into the ceramic sample holder cup of the high temperature/high pressure cell, it was activated at 773 K for 1 h in flowing helium (10 mL/min). After activation, the Cu-SSZ-13 sample was cooled to the desired reaction temperature under flowing helium. Then a background IR spectrum was taken at reaction temperature. (IR spectra recorded from the adsorbate-free zeolite samples at the temperature the subsequent reaction studies were carried out were used as background.) Ammonia adsorption on the Cu-SSZ-13 sample was carried out by exposing the activated sample to an NH$_3$/He (0.5% of NH$_3$) gas mixture (10 mL/min) for 1 h. Before the introduction of the oxidizing gas mixture, the sample was purged by helium (10 mL/min) for another 1 h. The mixtures of NO$_2$ in He (0.25% of NO$_2$), NO and O$_2$ in He (0.25% of NO, and 3.8% of O$_2$) and NO$_2$ and O$_2$ (0.125% of NO$_2$, and 3.8% of O$_2$) in He were used as oxidation gases to react with surface ammonia species at a flow rate of 10.7 mL/min. When O$_2$ was present during the NH$_3$ oxidation (i.e., in NO + O$_2$ and NO$_2$ + O$_2$ mixtures) the NO$_x$ was mixed with O$_2$ prior to entering the IR reactor cell. Meanwhile, mass spectrometry was used to continuously record the signals of selected masses in the effluent gas during the oxidation reaction.

3. Results and discussion

3.1. Adsorption of NH$_3$ and NO$_2$ + NH$_3$

Fig. 1 shows a series of DRIFT spectra obtained after the adsorption of ammonia at 373 K (spectrum a), and the co-adsorption of NO$_2$ and NH$_3$ at different temperatures on Cu-SSZ-13 (spectra b–e). The IR features observed after NH$_3$ adsorption represent two distinct ammonia species: bands at 3352, 3182, and 1620 cm^{-1} can be assigned to Lewis acid (copper ion) site-adsorbed ammonia; while the features at 3262 and 1454 cm^{-1} are those of Brønsted acid site-adsorbed ammonia species [10]. The presence of these two adsorption sites in our Cu-SSZ-13 sample is the consequence of the incomplete ion exchange of the catalyst (ICP analysis revealed that the Cu ion exchange level in the sample studied here was ~80%). Generally, the features at high wavenumbers (>3000 cm^{-1}) originate from the stretching vibrations of the N—H bonds, and the features in low wave number region (1400–1650 cm^{-1}) represent the N—H bending vibrations in adsorbed ammonia. The features of the same ammonia species in both the high and low wavenumber

regions should change in a parallel fashion during ammonia oxidation. Accordingly, the discussion below will focus on the changes occurring in the 1200–1800 cm^{-1} spectral region only. In addition to the bands discussed above, negative features at 3728 and 3610 cm^{-1} appeared after ammonia adsorption. These two features are the OH stretching bands of surface silanol and structural hydroxyl groups in Cu-SSZ-13, respectively. These results suggest that the adsorption of ammonia consumed both surface silanol and structural hydroxyl groups in Cu-SSZ-13.

Fig. 1 also shows DRIFT spectra for the co-adsorption of NO$_2$ and NH$_3$ on a Cu-SSZ-13 zeolite in the temperature range of 373–523 K. After the co-adsorption of NO$_2$ and NH$_3$ at a molar ratio of 3:4, only the features for adsorbed ammonia species were observed at these temperatures, indicating that the adsorption of ammonia is much stronger than that of NO$_2$ on the Cu-SSZ-13 zeolite. During these experiments the formation of N$_2$ was clearly detected by the online mass spectrometer, underlining the fact that these experiments (especially those conducted at sample temperatures higher than 523 K) cannot be strictly considered as "coadsorption" ones. However, even at a 523 K sample temperature (where NH$_3$ SCR is known to proceed at a high reaction rate [7,8]), the only adsorbed species observed by IR are the two types of ammonia. In addition, the DRIFT spectra collected during co-adsorption of NO and NH$_3$ (spectra not shown here) also indicated that the adsorption of NH$_3$ is much stronger than that of NO.

In the following, the oxidation of adsorbed ammonia with NO$_2$, NO + O$_2$ and NO$_2$ + O$_2$ gas mixtures was investigated by in situ DRIFT spectroscopy and mass spectrometry.

3.2. Oxidation with NO$_2$

DRIFT spectra in the range of 1200–2300 cm^{-1} recorded during the oxidation of adsorbed ammonia by NO$_2$ on Cu-SSZ-13 as a function of reaction time are displayed in Fig. 2 for sample temperatures of 423 K (panel A), 573 (B), and 673 K (C). Prior to NO$_2$ exposure the sample was saturated with NH$_3$ at the oxidation reaction temperature, and then purged with He. Saturation of the sample with NH$_3$ resulted in the appearance of two features in the IR spectra at each sample temperature, corresponding to adsorbed ammonia on Lewis (1620 cm^{-1}) and Brønsted (1454 cm^{-1}) acid sites, as discussed above. Note that the initial NH$_3$ coverage at these three sample temperatures are not identical, as the intensities of the IR features of adsorbed NH$_3$ (in particular the Lewis acid-bound ones) decreased with increasing sample temperature. (The appearances of the intense bands at ~1350 cm^{-1} (negative) and the feature at ~1270 cm^{-1} (positive) are due to the influence of the adsorbed ammonia on the framework vibrations of the zeolite.)

The series of IR spectra in panel A of Fig. 2 clearly shows the very different rate of NH$_3$ oxidation for the two types of adsorbed NH$_3$ species (i.e., Lewis and Brønsted sites-bound NH$_3$) at 423 K. The feature at 1620 cm^{-1} (ammonia adsorbed onto copper sites) decreased rapidly with reaction time and disappeared completely after 40 min of NO$_2$ exposure. On the other hand, the feature at 1454 cm^{-1}, representing Brønsted acid site-adsorbed ammonia species, actually increased with reaction time initially (up to 40 min). Parallel to this intensity gain, the position of this feature shifted from 1454 to 1467 cm^{-1} with reaction time, and also there was a change in the shape of the broad IR absorbance at ~1270 cm. At reaction times longer than 20 min, several new features could be detected at ~1512, 1573 and 1600 cm^{-1}, which can be attributed to the formation of differently coordinated nitrate species onto the copper sites that are now free of ammonia. The shift in the position of the IR feature for Brønsted acid site-adsorbed ammonia species might be due to either the interaction between adsorbed ammonium ions and the newly formed nitrate species or to the formation of ammonium nitrate. These observations clearly indicate that Lewis acid (copper