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Mechanism study of FeW mixed oxides to the selective catalytic reduction of NO_x with NH_3: *in situ* DRIFTS and MS

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ABSTRACT

In situ DRIFT spectroscopy and mass spectrometry techniques were employed to investigate the mechanisms of the selective catalytic reduction of NO with NH_3 on the FeW oxides catalysts. By integrating the adsorption peaks of NH_3 or NO_x, it was found that the coordinated NH_3 and NH_4^+ were the main active NH_3 ad-species, while the adsorbed NO_x was only obviously detected below 250 °C. That was to say that the reaction mechanisms were totally different at different temperature regions. At the low temperature region (< 250 °C), the reaction path was likely to be a "fast NO/NO_2-SCR" process, involving the formation of NO_2, complexes $NO_2(NH_3)_2$ and $NO_2(NH_4^+)_2$ as intermediates. These active complexes could react with gaseous NO to produce N_2 and H_2O. The oxidation of NO to NO_2 was probably the rate-determining step for the SCR reaction. At the high temperature region (≥ 250 °C), NH_2NO species formed from the reaction between surface coordinated NH_3/NH_4^+ species and gaseous NO were the key intermediates, which were further reduced to produce N_2 and H_2O.

1. Introduction

Selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) is one of the leading technologies for reducing NO_x emission from the exhaust of diesel engines. The NH_3-SCR reaction can be expressed in general as [1–3]:

Standard SCR reaction: $4NO + O_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O$

Fast SCR reaction: $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$

The presence of NO_2 in the feed could increase the NO_x reduction capacity of the SCR reaction. A large amount of literature exists on applied and fundamental studies on several SCR catalyst systems [4–6]. Recently, Fe-based catalysts are attractive as NH_3-SCR catalysts in diesel engines for their excellent moderate-low temperature activity, stable performance, and their high selectivity to N_2 [7–9]. We have achieved an excellent FeW oxides catalysts [3] which showed a higher activity and better selectivity to N_2 over a wide reaction temperature range than Fe_2O_3 and other Fe-based oxides catalysts, such as $FeTiO_x$ [10], Fe_2O_3/CNTs [11]. The introduction of W species facilitated the formation of NO_2 and NH_3/NH_4^+ species due to the increase of the amount of Lewis and Brønsted acid sites, in comparison with pure Fe_2O_3. However, the contribution of various adsorbed reactants species to the SCR reaction are not yet clear, and thus more attention should be paid to the study of NH_3-SCR mechanism over FeW oxides.

Concerning the reaction pathway of SCR reaction over metal oxide catalysts, most researchers suggested that NH_3 was adsorbed on the Lewis acid center to form intermediates like NH_2 or adsorbed NH_3, then they reacted with aerial NO or/and NO_2 through an Eley−Rideal (E−R) mechanism producing N_2, N_2O and H_2O [12–19]. In the studies of Kapteijn et al. [20], it was suggested that the initial step was the adsorption of NH_3, and then the NH_2 species from the abstraction of hydrogen could react with both gaseous NO and adsorbed NO*x* species over pure MnO_x and MnO_x/Al_2O_3 catalysts. However, other authors suggested a Langmuir−Hinshelwood (L−H) mechanism for this SCR reaction [21–23]. In terms of this reaction mechanism, the adsorbed NO_x could react with the NH_3/NH_4^+ species adsorbed on Lewis and Brønsted acid sites to form different intermediates and then produce N_2 and H_2O. On the basis of different intermediates formed during the reaction, two main types of pathways belonging to this L–H mechanism were proposed: (i) the reaction between the adsorbed NH_3/NH_4^+ and NO_2^- to form NH_4NO_2, which decomposed into N_2 and H_2O [12,23]; and (ii) the reaction between adsorbed NH_3/NH_4^+ and NO_3^- to form NH_4NO_3, and it subsequently reacted with NH_3/NO or decomposed to N_2O and H_2O [24–26]. Topsøe et al. [25] and Li et al. [27] have proposed a "Brønsted–NH_4^+" mechanism to form NH_4NO_3/NH_4NO_2 as intermediated species over V_2O_5-based catalyst and Cu/SSZ-13, respectively. Generally, two kinds of reaction pathways could occur on

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the same SCR catalysts.

To deepen the investigation about the NH_3-SCR of NO_x on the present FeW oxides, the fundamental mechanism information must be provided first and discussed in order to correctly relate the observed catalytic activity of the FeW oxides. In light of this, the SCR reaction mechanism for FeW oxides catalyst was studied by using *in situ* DRIFTS and mass spectra. On the basis of this knowledge we obtained, one of the further goals is to develop the novel Fe-based catalysts for NH_3-SCR in diesel applications.

2. Experimental section

2.1. Catalysts

FeW mixed oxides samples were synthesized by "stepwise urea-assisted" method [3]. Calculated amounts of $Fe(NO_3)_3{\cdot}9H_2O$, ammonium metatungstate and urea with mole ratio 4:1:50 were dissolved in the solution. The aqueous solution was aged at 90 °C for 24 h to form precipitate which was calcined at 500 °C for 5 h.

2.2. Techniques

In situ Diffuse Reflectance Infrared Fourier Transform spectra (*in situ* DRIFT) were recorded using on a Bruker Vector FTIR spectrometer (VERTEX 70) equipped with a high-sensitive MCT detector cooled by liquid nitrogen. The scans were collected from 4000 to 800 cm^{-1} at a spectral resolution of 4 cm^{-1}. Adsorption of NH_3 was performed by treating the samples with 500 ppm NH_3/He for 30 min and then purging with helium at 200 or 250 °C, while the adsorption of NO_x was performed by treating the samples with 500 ppm NO/He and 3 vol.% O_2 for 30 min and then purging with helium at 200 or 250 °C. Subsequent to NH_3 adsorption step, the helium was switched to different flows containing 500 ppm NO and 3 vol.% O_2 or 250 ppm NO and 250 ppm NO_2. Subsequent to NO_x adsorption step, the helium was switched to the flow of 500 ppm NH_3 at 200 or 250 °C. For each experiment, the mixed gas steam rate was fixed at 100 mL/min.

The temperature programmed technique was carried in a fixed-bed flow reactor with a computer-interfaced quadruple mass spectrometer (MS, Pfeiffer OmniStar) as detector. Prior to each experiment, the catalyst was pretreated at 400 °C in Helium for 30 min to remove any impurities. NO_x-TPD experiment was pretreated by 500 ppm NO and 3 vol.% O_2 at room temperature and then was purged in He. With increasing temperature at 10 °C/min, the $m/e = 30$ was record to identify both NO and NO_2.

3. Results and discussion

3.1. Verification of the adsorbed reactant species

3.1.1. Confirmation of adsorbed NO_x

NO_x adsorbed species on FeW sample at various temperatures were investigated by FTIR spectroscopy, as shown in Fig. 1. After exposing 500 ppm NO and 3 vol.% O_2 to the catalyst at 200 °C, a major band attributed to NO_2 species at 1606 cm^{-1}, a broad shoulder assigned to nitrate species at 1431 cm^{-1} and a weak band ascribed to nitrite species at 1229 cm^{-1} were detected [28,29]. After the following purge with He, the band at 1229 cm^{-1} disappeared and meanwhile a mountain of NO_2 species were removed, suggesting that the NO_x species were weakly adsorbed on surface of FeW sample, especially for NO_2 species. Moreover, the broad shoulders around 2100–2200 cm^{-1} were also detected due to the formation of NO^+ species [30–37]. The NO^+ and NO_3^- species could be produced through NO_2 dimerization and disproportionation according to reaction (1–3): [36–38]

$$2NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(a)} \quad (1)$$

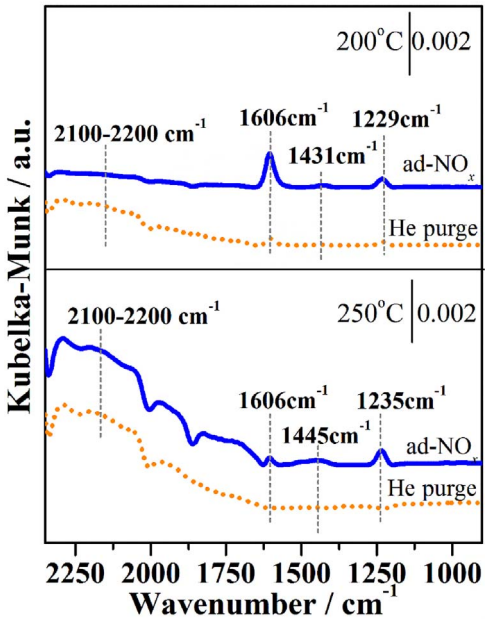

Fig. 1. *In situ* DRIFTS of NO_x adsorption on FeW mixed oxide catalysts at 200 and 250 °C.

$$2NO_{2(a)} \leftrightarrow N_2O_{4(a)} \quad (2)$$

$$N_2O_{4(a)} \leftrightarrow NO_3^-{}_{(a)} + NO^+{}_{(a)} \quad (3)$$

Furthermore, the formation of NO^+ could further incorporate with oxygen to form nitrite species in the light of reaction [36,39,40].

$$NO^+_{(a)} + O^{2-} \leftrightarrow NO_2^-{}_{(a)} \quad (4)$$

When the sample was treated with NO and O_2 at 250 °C, the band of NO_2 species (1606 cm^{-1}) decreased in intensity. Whereas, the bands attributed to NO^+ (2100–2200 cm^{-1}) and NO_2^- (1235 cm^{-1}) have a subtle upward trend. Simultaneously, the band assigned to NO_3^- was detected at 1450 cm^{-1} [41]. It was demonstrated that the dimerization and disproportionation of NO_2 were facilitated at the high temperatures. However, all the bands of NO_x derived species decreased in intensity and even disappeared after helium purge. The gaseous NO would be the main NO_x reactive species at the high temperature (≥ 250 °C). According to the NO_x–TPD result (Fig. S1), the desorption peaks were only observably detected below 250 °C. The peak below 200 °C could be due to the decomposition of chemical desorption of NO_x (such as NO_2 and nitrite), while the peaks above 200 °C could be ascribed to the decomposition of nitrate. In other words, for the synthesized FeW sample, only NO_x derived species with poor thermal stability were formed during the NO_x adsorption experiment (< 250 °C).

3.1.2. Confirmation of adsorbed NH_3

As for the NH_3 ad-species (Fig. 2), NH_4^+ species bound to Brønsted acid sites (1427 cm^{-1}) and coordinated NH_3 species (1200–1300 and 1606 cm^{-1}) were observed [21,42] when the FeW sample was pretreated with 500 ppm NH_3 at 200 °C. Meanwhile, the intensity of the band attributed NH_4^+ was greater than that of coordinated NH_3 species. However, raising the adsorption temperature to 250 °C, the band attributed to NH_4^+ was less intensely to the band assigned to coordinated NH_3 species. Their contributions to the SCR reaction are not yet clear. Based on the aforementioned results, the adsorbed reactant species state were different at the low or high temperatures, which might result in the different reaction mechanisms for the FeW mixed oxides samples at different temperature regions.