

HC-SCR reaction pathways on ion exchanged ZSM-5 catalysts

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ARTICLE INFO

Article history:

Received 14 March 2008

Received in revised form 30 June 2008

Accepted 11 July 2008

Available online 19 July 2008

Keywords:

Nitric oxide

SCR

Propane

Propene

DRIFTS

Competing adsorption

ABSTRACT

Metal cation (metal = Cu, In and La) ion exchanged ZSM-5 zeolites as catalysts for the NO selective reduction by propane and propene in excess oxygen. The surface reactions of HC-SCR over catalysts were investigated through in situ DRIFTS method. For C₃H₈-SCR, adsorbed nitrate species (–NO₃) were observed as main reaction intermediates and they could react with gaseous propane to produce N₂, H₂O and CO₂. While for C₃H₆-SCR, adsorbed amine species (–NH₂) were observed as main reaction intermediates and they could react with NO or NO₂ to produce the final products. The different reaction pathways for C₃H₈-SCR and C₃H₆-SCR over catalysts were proposed based on the DRIFTS results and the main factors controlling the activities of catalysts were discussed in details. The competing adsorption between NO–O₂ and HC–O₂ on the Brønsted acid sites of catalysts was responsible for the different reaction pathways in HC-SCR.

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1. Introduction

Nitric oxide, derived from transportation and power plants, is a major air pollutant that greatly contributes to the formation of photochemical smog and acid rain [1]. The selective catalytic reduction of NO by hydrocarbons (HC-SCR) is a potential method to remove NO from transportation sources [2,3]. Transition metal modified zeolites are regarded as promising HC-SCR catalysts due to their high catalytic activities as well as to high selectivity to the desired product N₂ [4]. During the past decade, extensive studies have been carried out on the HC-SCR with various zeolite-based catalysts, especially concerning the reaction pathways [5–10]. Generally speaking, several possible pathways have been proposed for HC-SCR reactions over modified zeolite catalysts [7]. Some authors suggested that the initial step should be the partial oxidation of hydrocarbons to C_xH_yO_z species, which would then reduce NO or NO₂ with high activity to produce N₂, CO₂ and H₂O. Some considered that NO was first oxidized to nitrite or nitrate species followed by the reduction by hydrocarbons. Others proposed that NO and hydrocarbons reacted to form organic N-containing species (for example R-NO_x) in excess oxygen, which could be converted to the final products through a series of degradation reactions. Although numerous researches of the HC-SCR reaction pathways have been carried out over certain kind of zeolite catalyst, few studies have been focused on the reaction pathways over a series

of catalysts [11–13]. Therefore, general HC-SCR reaction pathways over zeolite catalysts are not available. The lack of direct comparisons between similar kinds of catalysts makes it difficult to study the key factor controlling the deNO_x activity. Meanwhile, no exact explanations have been given to the cause of different reaction pathways in HC-SCR when alkane and alkene are used as different kind of reductant.

In this work, NO selective reduction by propane and propene in excess oxygen over a series of modified ZSM-5 catalysts will be studied. Three representative metal cations are selected as the modifier: main group metal indium, rare earth metal lanthanum and most studied VIII_B metal copper. The surface reactions of HC-SCR over ion exchanged ZSM-5 catalysts will be investigated through in situ DRIFTS method. The different reaction pathways of C₃H₈-SCR and C₃H₆-SCR over catalysts will be proposed based on the DRIFTS results, and key factors controlling the deNO_x activities will be discussed. Besides, it will also explain how different reaction pathways of HC-SCR reactions come into being.

2. Experimental section

2.1. Catalysts preparation

H-ZSM-5 (Si/Al = 25) was supplied by the Catalyst Plant of Nankai University. Metal-containing zeolites were prepared from H-ZSM-5 with conventional solution ion exchange method at room temperature. The detailed conditions of ion exchange and resulting metal contents were displayed in Table 1. The ion exchanged

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Table 1
List of catalysts and preparation methods

Catalyst	Precursor	Solution (mM)	Time (h)	Metal content (wt%) ^a	Ion exchange degree ^b
Cu-ZSM-5	H-ZSM-5	20 Cu(NO ₃) ₂	24 × 2	Cu 2.4%	108%
In-ZSM-5	H-ZSM-5	20 In(NO ₃) ₃	24 × 2	In 2.0%	78%
La-ZSM-5	H-ZSM-5	20 La(NO ₃) ₃	24 × 3	La 2.1%	69%

^a Measured by ICP (IRIS advantage, TJA solution).

^b Theoretical value.

samples were washed five times by an ultrasonic generator, 3 min each time, to completely remove the metal ions adhering on the surface and then the samples were dried and calcined at 550 °C for 4 h in the air.

2.2. Catalyst characterization

The acidity of metal cation ion exchanged ZSM-5 catalysts was determined by FT-IR spectra of pyridine adsorption. Prior to pyridine adsorption, the samples (ca. 0.1 g) were outgassed at 400 °C for 2 h and cooled down to room temperature under vacuum. Pyridine was then introduced to the sample at saturated vapor pressure. Physisorbed pyridine was removed through heating the samples at 150 °C for 2 h and then the IR spectrum was recorded.

The H₂-TPR experiments of samples were carried out on a chemisorption analyzer (Chemisorb 2720, Micromeritics) with 5 vol% H₂/Ar at a heating rate of 10 °C/min from 100 °C to 800 °C. Prior to reduction, the sample (100 mg) was treated in He at 500 °C for 2 h.

Chemical valence states of metal cations in the catalysts before and after reaction were measured by XPS on a PHI-5300 instrument with a Mg K α X-ray excitation source. Accurate binding energies (± 0.1 eV) were determined with respect to the position of the adventitious C 1s peak at 284.8 eV. The residual pressure in the analysis chamber was maintained below 10⁷ Pa during data acquisition.

2.3. Catalytic test

The SCR reaction of NO by propane and propene at atmospheric pressure was carried out in a fixed-bed flow microreactor. The typical reactant gas mixture consisted of NO (1000 ppm), C₃H₈ or C₃H₆ (1000 ppm), O₂ (5.0%), H₂O (0% or 5%), balance with He to 100%. The total flow of the inlet gas was set at 60 mL min⁻¹ and 0.12 g catalyst sample was used to obtain a gas hourly space velocity (GHSV) of about 30,000 h⁻¹. The catalyst sample was pre-treated at 500 °C in He for 1 h and then the reactant gas mixture was introduced to the catalyst. The products were analyzed online using a gas chromatograph (HP 6890 series) equipped with a TCD detector. A molecular sieve 5A column served for separation of N₂, O₂ and CO, and a porapak Q column for separation of CO₂, C₃H₈, N₂O, NO and H₂O.

2.4. In situ DRIFTS study

In situ DRIFT spectra were recorded on a NEXUS 670-FTIR (Thermo Nicolet), equipped with a liquid N₂ cooled high sensitivity MCT detector. The samples for this study (0.2 g) were finely ground and placed in the in situ chamber. Prior to each experiment, the samples were heated in He flow at 600 °C for 1 h, and then cooled to the desired temperature for taking a reference spectrum. The gas mixtures were then fed and the spectra were recorded with a resolution of 4 cm⁻¹ and with an accumulation of 100 scans.

3. Results

3.1. Acidity characterization

FTIR analysis of adsorbed pyridine allows a clear distinction between Brønsted and Lewis acid sites. As a good Lewis base, pyridine molecules can interact with the Brønsted acid sites forming pyridinium ions, which are characterized by bands in the IR spectra from 1512 cm⁻¹ to 1567 cm⁻¹. Pyridine molecules can also adsorb on the surface of Lewis acid sites through their isolated electron pair on nitrogen atoms, characterized by bands in the IR spectra from 1423 cm⁻¹ to 1472 cm⁻¹. The band in the IR spectra within the range of 1470–1510 cm⁻¹ can be ascribed to the overlapping of Brønsted acid and Lewis acid sites [14,15]. Both Brønsted acid sites and Lewis acid sites can be observed for ion exchanged ZSM-5 samples, as displayed in Fig. 1. La-ZSM-5 processes the highest amount of Brønsted acid sites (0.45 mmol g⁻¹), followed by In-ZSM-5 (0.43 mmol g⁻¹) and then Cu-ZSM-5 (0.36 mmol g⁻¹).

3.2. Catalytic results

Catalytic performances of Cu-ZSM-5, In-ZSM-5 and La-ZSM-5 for NO reduction by propane and propene are shown in Figs. 2 and 3, respectively. Remarkably, the only product from NO was nitrogen, neither N₂O nor NO₂ was detected in the whole reaction process for all the three samples. There was a little CO yielded (<60 ppm) because of the incomplete oxidation of hydrocarbons, which was ignored in this study. When propane was employed as reductant, Cu-ZSM-5 exhibited the best deNOx activity followed by In-ZSM-5 and then La-ZSM-5. The presence of 5% water vapor in the reaction system showed distinct negative effect on NO reduction and ca. 30% decrease in NO conversion was observed. When propene was employed as reductant, Cu-ZSM-5 exhibited the best deNOx activity followed by La-ZSM-5 and then In-ZSM-5. Different to that in propane-SCR reaction, the existence of water vapor only show mild negative effect on NO reduction at temperatures below 500 °C in propene-SCR reaction. Notably, the catalytic activities of Cu-ZSM-5 and In-ZSM-5 in HC-SCR reactions were comparable with results reported in the literature under similar conditions [11,16].

3.3. In situ DRIFTS results

To achieve a better understanding of deNOx pathways over ion exchanged ZSM-5 catalysts, the reaction mechanism of

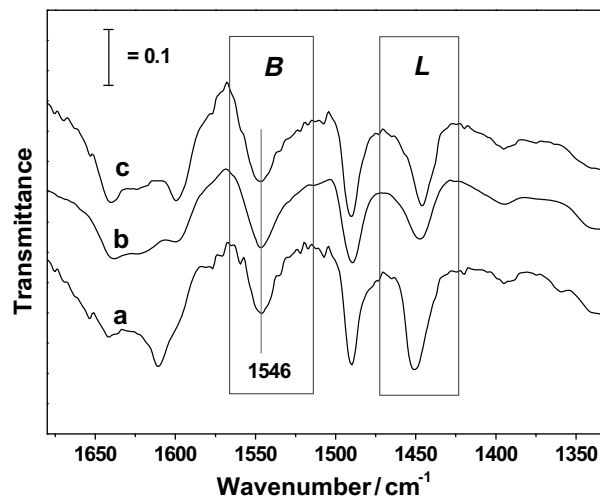


Fig. 1. FT-IR spectra of the adsorption of pyridine on (a) Cu-ZSM-5, (b) In-ZSM-5 and (c) La-ZSM-5.

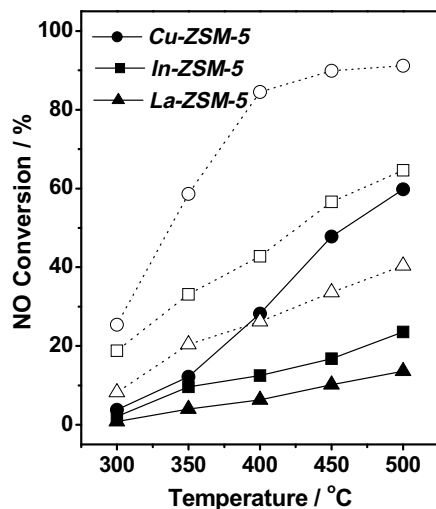


Fig. 2. SCR of NO by propane on Cu-ZSM-5, In-ZSM-5 and La-ZSM-5 in the absence (open symbols) and presence (solid symbols) of H₂O. Reaction conditions: 1000 ppm NO, 1000 ppm C₃H₈, 5% O₂, 0% or 5% H₂O, He balance, GHSV = 30,000 h⁻¹.

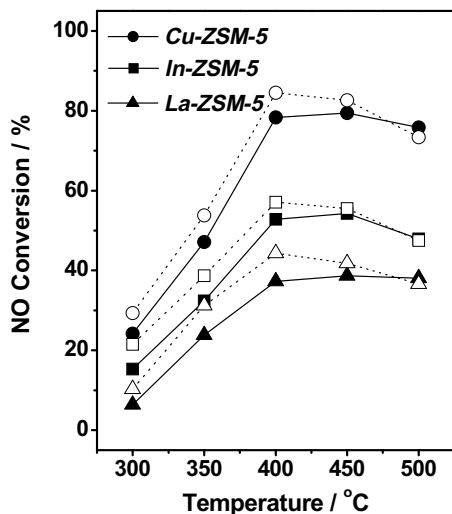


Fig. 3. SCR of NO by propene on Cu-ZSM-5, In-ZSM-5 and La-ZSM-5 in the absence (open symbols) and presence (solid symbols) of H₂O. Reaction conditions: 1000 ppm NO, 1000 ppm C₃H₆, 5% O₂, 0% or 5% H₂O, He balance, GHSV = 30,000 h⁻¹.

NO-C₃H₈-O₂ and NO-C₃H₆-O₂ systems were investigated with the in situ DRIFTS method. The reaction temperature selected for these DRIFTS studies was 400 °C, where apparent differences in catalytic activity could be observed (Ref. Figs. 2 and 3). FTIR spectra were monitored at in situ reaction conditions using the same reactant composition as in the catalytic tests, i.e., 1000 ppm NO, 1000 ppm propane or propene and 5% O₂ balance with He. FTIR spectra were recorded after 15 min of steady-state reaction.

3.3.1. C₃H₈-SCR

For Cu-ZSM-5, strong IR bands at 1625 cm⁻¹, 1598 cm⁻¹ and 1568 cm⁻¹ was observed in flowing NO/He as shown in Fig. 4. The bands at 1625 cm⁻¹ and 1598 cm⁻¹ were attributed to bridged nitrate species on the Cu²⁺ ions [17–19]; while the band at 1568 cm⁻¹ was attributed to chelating nitrate species also adsorbed on Cu²⁺ ions [20–22]. Simultaneously, two weak IR bands were observed: a band at 2133 cm⁻¹ attributed to adsorbed NO⁺ species on Brønsted acid sites of ZSM-5 zeolite [23,24], and a band at 1901 cm⁻¹ attributed to Cu²⁺-NO^{δ+} species [25,26]. When excess

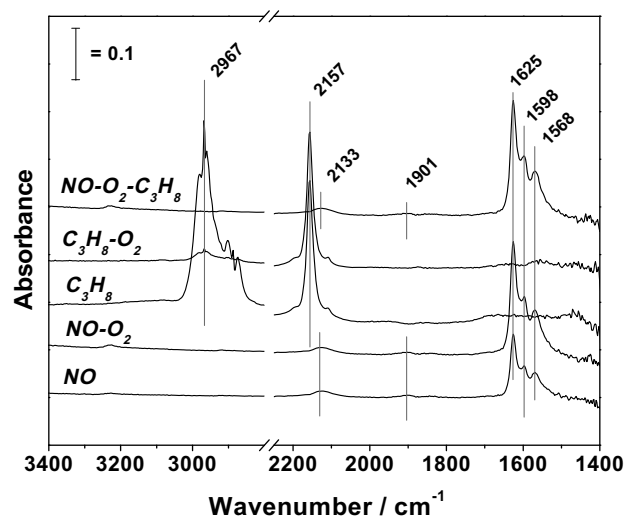


Fig. 4. DRIFTS study of adsorbed species formed on surface of Cu-ZSM-5 catalyst for NO reduction by propane under reaction conditions at 400 °C.

oxygen was introduced (NO-O₂/He), the intensities of IR bands corresponding to adsorbed nitrate species (bridged nitrate species and chelating nitrate species) increased greatly. Besides, no other obvious changes in IR bands could be observed. In flowing C₃H₈/He, a strong IR band assignable to CO adsorbed on Cu⁺ (2157 cm⁻¹) [27] and multi bands centered at 2967 cm⁻¹ assignable to adsorbed -C_xH_y species [28,29] were observed. On Cu-ZSM-5, propane was activated as -C_xH_y species, which could be oxidized by Cu²⁺ to CO. At the same time, Cu²⁺ was reduced to Cu⁺, leading to the formation of Cu⁺-CO. With the addition of excess oxygen to propane (C₃H₈-O₂/He), the intensity of IR bands corresponding to adsorbed -C_xH_y species decreased distinctly; while the intensity of IR band corresponding to Cu⁺-CO species did not show obvious changes. It was indicated that adsorbed -C_xH_y could be easily oxidized by the oxygen in the reaction system. Under SCR reaction condition (NO-C₃H₈-O₂/He), the adsorbed species observed over Cu-ZSM-5 catalyst was completely the same as that observed in flowing NO-O₂/He and the corresponding band intensities were quite similar. It should be mentioned that no adsorbed C-containing species, such as -CO and -C_xH_y [11,30] could be observed over Cu-ZSM-5 under our experiment conditions.

For In-ZSM-5 and La-ZSM-5, IR bands at 2133 cm⁻¹, 1895 cm⁻¹, 1628 cm⁻¹ and 1598 cm⁻¹ were observed in flowing NO, similar to those observed on Cu-ZSM-5. However, no band at 1568 cm⁻¹ assignable to chelating nitrate species was found, in contrast to that on Cu-ZSM-5. Weak bands at 1895 cm⁻¹ and 1852 cm⁻¹ were observed on In-ZSM-5 and La-ZSM-5, attributed to Me³⁺-NO^{δ+} and Me³⁺-O-NO^{δ+}, respectively [31]. Besides, other weak bands at 2333 cm⁻¹ and 2359 cm⁻¹, attributed to adsorbed CO₂ [32,33], were observed under SCR conditions (NO-C₃H₈-O₂). The DRIFTS results of adsorbed species formed on surface of In-ZSM-5 and La-ZSM-5 under reaction conditions at 400 °C are displayed in Figs. 5 and 6, respectively, and a proposed assignment of the IR bands is summarized in Table 2.

3.3.2. C₃H₆-SCR

The results of IR bands observed on Cu-ZSM-5 under C₃H₆-SCR conditions are shown in Fig. 7 and their assignment is shown in Table 3. In flowing C₃H₆/He, strong IR bands corresponding to adsorbed -CH_x and -R=CH₂ species were observed at high wavenumbers [28,36] and IR bands corresponding to adsorbed -C=O and -COO species were observed at low wavenumbers [41–43]. It was indicated that the adsorbed propene could be partially

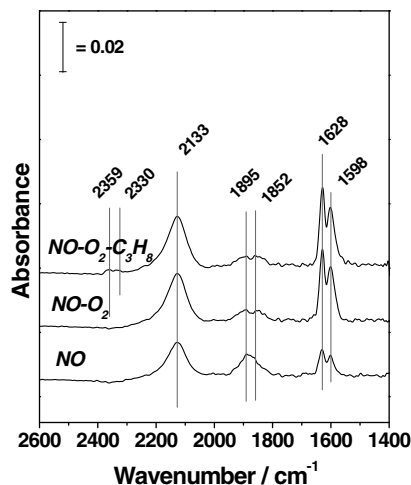


Fig. 5. DRIFTS study of adsorbed species formed on surface of In-ZSM-5 catalyst for NO reduction by propane under reaction conditions at 400 °C.

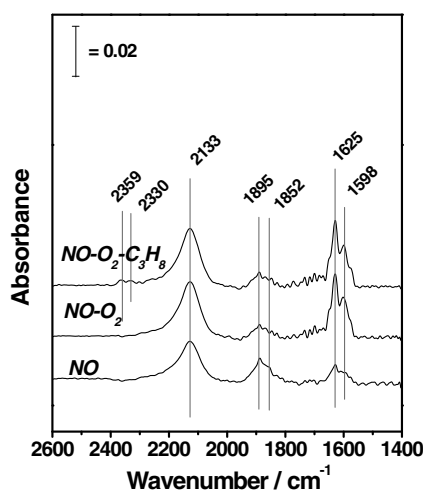


Fig. 6. DRIFTS study of adsorbed species formed on surface of La-ZSM-5 catalyst for NO reduction by propane under reaction conditions at 400 °C.

Table 2
Assignment of IR bands during C₃H₈-SCR over In-ZSM-5 and La-ZSM-5

Wavenumber/cm ⁻¹	Assignment
2359 and 2330	ν CO ₂
2133	ν_{NO} of -NO ⁺
1895	ν_{NO} of Me ³⁺ -NO ^{δ+}
1852	ν_{NO} of Me ³⁺ -O-NO ^{δ+}
1625	ν_{NO_2} of Me ³⁺ -NO ₃
1598	ν_{NO} of Me ³⁺ -NO ₃

oxidized to produce carbonyl or carboxyl species, probably by residual oxygen. When excess oxygen was added, the intensities of IR bands ascribed to -CH_x and -R=CH₂ species decreased greatly while the intensities of bands ascribed to -C=O and -COO increased a little. Meanwhile, IR band ascribed to adsorbed Cu⁺-CO appeared. The oxidation of propene to CO and the reduction of Cu²⁺ to Cu⁺ took place even in excess oxygen. Under C₃H₆-SCR conditions (NO-C₃H₆-O₂/He), the intensities of IR bands ascribed to -C=O and -COO increased to a great extent compared to those observed in flowing C₃H₆-O₂/He. The addition of NO greatly promoted the partial oxidation of propene. At the same time, an increase in the intensity of IR band ascribed to -R=CH₂ was observed, while the intensity of IR band corresponding to

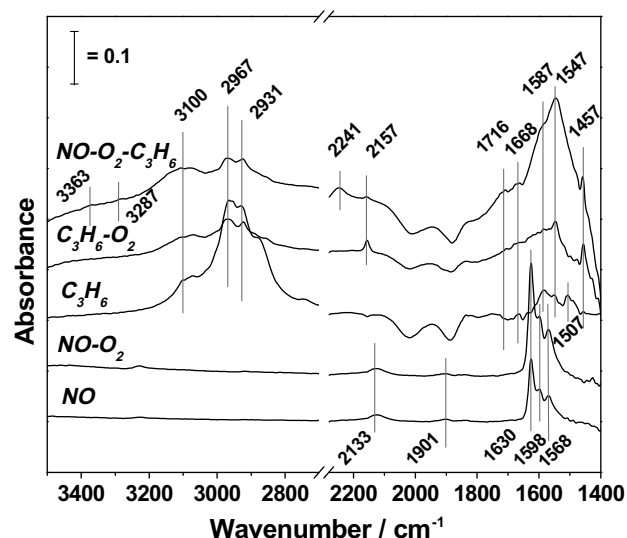


Fig. 7. DRIFTS study of adsorbed species formed on surface of Cu-ZSM-5 catalyst for NO reduction by propene under reaction conditions at 400 °C.

Table 3
Assignment of IR bands during C₃H₆-SCR over Cu-ZSM-5

Wavenumber/cm ⁻¹	Assignment	References
3363 and 3287	ν_{NH} of -NH ₂	[34,35]
3100	ν_{CH} of R=CH ₂	[36]
2967	ν_{CH} of R-CH ₃	[28,29]
2931	ν_{CH} of R-CH ₂	[28,29]
2241	ν_{CN} of -NCO	[37,38]
2157	ν_{CO} of Cu ⁺ -CO	[27]
2133	ν_{NO} of -NO ⁺	[23,24]
1901	ν_{NO} of Cu ²⁺ -NO ⁺	[21,23]
1716 and 1668	ν_{CO} of -C=O	[39,40]
1625	ν_{ONO} of bridged Cu ²⁺ -NO ₃	[17–19]
1598	ν_{NO} of bridged Cu ²⁺ -NO ₃	[17–19]
1587 and 1547	Asymmetric ν_{CO} of CH ₃ -COO	[41,42]
1568	ν_{NO} of chelating Cu ²⁺ -NO ₃	[20–22]
1507	Asymmetric ν_{CO} of H-COO	[41]
1457	Symmetric ν_{CO} of CH ₃ -COO	[42,43]

Cu⁺-CO species decreased dramatically and almost disappeared. Moreover, several new IR bands were observed in flowing NO-C₃H₆-O₂/He: a band at 2236 cm⁻¹ attributed to adsorbed -NCO [37,38] and very weak bands at 3363 cm⁻¹ and 3287 cm⁻¹ attributed to adsorbed -NH₂ [34,35]. The -NH₂ came from the hydrolysis of -NCO species (-NCO + H₂O → -NH₂ + CO₂) [3]. -NCO and -NH₂ species were generally regarded as important reaction intermediates for HC-SCR reactions [3,44].

The results of IR bands observed over In-ZSM-5 and La-ZSM-5 under C₃H₆-SCR conditions can be found in Figs. 8 and 9, respectively. As shown in the figure, the IR bands observed on In-ZSM-5 and La-ZSM-5 were quite similar to those observed on Cu-ZSM-5, except that no -CO was found on the reduced cation sites of In-ZSM-5 and La-ZSM-5. It is supposed that the C₃H₆-SCR reactions on In-ZSM-5 and La-ZSM-5 operated in essential the same way as that on Cu-ZSM-5 catalyst. The detail assignment of IR bands observed on In-ZSM-5 and La-ZSM-5 is displayed in Table 4.

4. Discussion

4.1. Mechanism of C₃H₈-SCR

Under C₃H₈-SCR conditions at 400 °C, only adsorbed inorganic N-containing species could be observed and the activation of

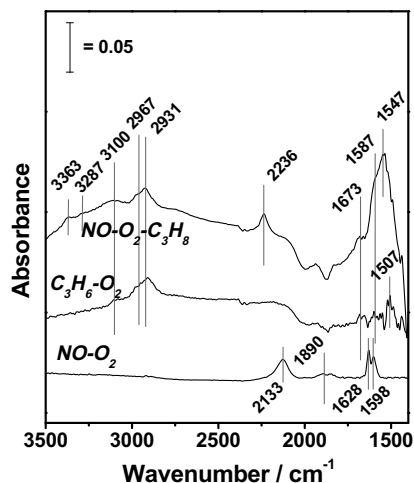


Fig. 8. DRIFTS study of adsorbed species formed on surface of In-ZSM-5 catalyst for NO reduction by propene under reaction conditions at 400 °C.

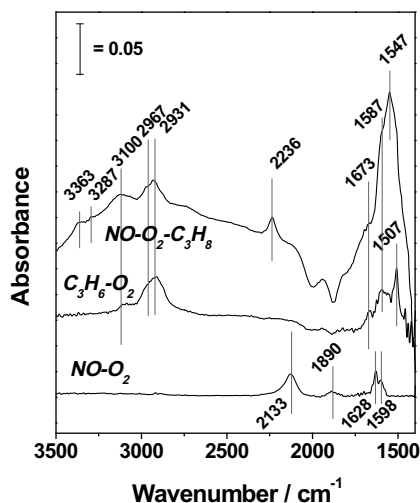


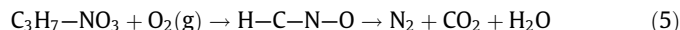
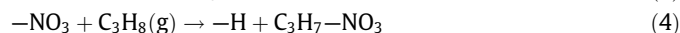
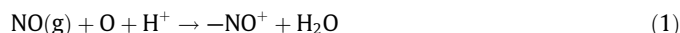
Fig. 9. DRIFTS study of adsorbed species formed on surface of La-ZSM-5 catalyst for NO reduction by propene under reaction conditions at 400 °C.

Table 4
Assignment of IR bands during C₃H₆-SCR over In-ZSM-5 and La-ZSM-5

Wavenumber/cm ⁻¹	Assignment
3363 and 3287	ν_{NH} of $-\text{NH}_2$
3100	ν_{CH} of $\text{R}=\text{CH}_2$
2967	ν_{CH} of $\text{R}-\text{CH}_3$
2931	ν_{CH} of $\text{R}-\text{CH}_2$
2236	ν_{CN} of $-\text{NCO}$
1673	ν_{CO} of $-\text{C}=\text{O}$
1587 and 1547	Asymmetric ν_{CO} of CH_3-COO
1507	Asymmetric ν_{CO} of $\text{H}-\text{COO}$

C₃H₈ on the catalysts under discussion seemed impossible. These inorganic N-containing species should be responsible for NO reduction. All inorganic N-containing species ($-\text{NO}^+$, $-\text{NO}^{\delta+}$ and $-\text{NO}_3$) could react with C₃H₈ to produce N₂, CO₂ and H₂O in different ways. Adsorbed nitrate species, with highest oxidation activities [45], should be the most active ones to be reduced by gaseous propane. In this study, the highest peak intensities of IR bands corresponding to adsorbed nitrate species was observed on

Cu-ZSM-5 followed by In-ZSM-5 and then La-ZSM-5, in great consistent with the order of their deNO_x activities. From this point of view, adsorbed nitrate species could be regarded as main reaction intermediate for NO reduction by propane in excess oxygen. A simple reaction pathway is proposed as follows (The presented mechanisms have to be understood as principal schemes of the species involved but without true stoichiometry, which is in any case difficult to establish for reactions of surface species.):



In the first step, gaseous NO and oxygen adsorbed as $-\text{NO}^+$ species on Brønsted acid sites of ZSM-5 zeolite in a similar way as reported in the literature [23,24]. Then, $-\text{NO}^+$ species on Brønsted acid sites migrated to neighboring cation sites as $\text{Me}^{\text{n+}}-\text{NO}^{\delta+}$, probably with charge transfer. $-\text{NO}^{\delta+}$ was not a stable species and could be further oxidized by O to $\text{Me}^{\text{n+}}-\text{NO}_3$. Once $\text{Me}^{\text{n+}}-\text{NO}_3$ was formed, it would react with gaseous C₃H₈, accompanied by the recovery Brønsted acid sites (see Figure 1S in the supporting information). Organic N-containing compound C₃H₇-NO₃ may react with oxygen to form H-C-N-O intermediate and then decompose to final product N₂, CO₂ and H₂O (Eq. (5)). The possible H-C-N-O intermediates have been well summarized by Gorce et al. [44]. However unfortunately, the information of H-C-N-O intermediate is missing in the IR spectra in this work. The formation of H-C-N-O deposit on the surface of catalyst may be hindered by the strong surface acidity of catalyst, as suggested by Tsyntarski et al. [46]. During NO-C₃H₈-O₂ reactions, there should be certain equilibrium between all adsorbed N-containing species on the surface of the catalysts. When $\text{Me}^{\text{n+}}-\text{NO}_3$ was consumed, NO and oxygen would adsorb as $-\text{NO}^+$ on Brønsted acid sites and converted to $\text{Me}^{\text{n+}}-\text{NO}_3$ through $\text{Me}^{\text{n+}}-\text{NO}^{\delta+}$. The main reaction intermediate $\text{Me}^{\text{n+}}-\text{NO}_3$ was thus consumed and again formed, and in such a way NO could be continuously reduced to N₂.

As discussed above, the formation of nitrate species has essential effect on the catalytic activity in the NO-C₃H₈-O₂ reactions, but the question is what controls the formation of nitrate species? Brønsted acidity of samples is viewed as an important factor. In the first step for NO reduction, gaseous NO and oxygen should adsorb on the Brønsted acid sites to form $-\text{NO}^+$. Brønsted acid sites are necessary and strong Brønsted acidity favors the formation of NO^+ . Na-ZSM-5 is completely inactive for NO-C₃H₈-O₂ reaction [47], which can be explained from the lack of Brønsted acid sites. However, too strong Brønsted acidity also hinders the transformation of $-\text{NO}^+$ species to $-\text{NO}^{\delta+}$ species (Eq. (2)), due to the stabilization of $-\text{NO}^+$ species on Brønsted acid sites. So, it is concluded that Brønsted acid sites are necessary for NO selective reduction by propane and appropriate Brønsted acidity are propitious to the formation of main reaction intermediate nitrate species ($-\text{NO}_3$).

The oxidative activity of exchanged cations in the catalyst is another important factor that greatly influences the formation of nitrate species. Higher oxidative activity favors the formation of nitrate species because it accelerates the step of $-\text{NO}^{\delta+} + \text{O} \rightarrow -\text{NO}_3$ and generates more adsorbed nitrate species. H₂-TPR profiles were used to study the oxidative activity of metal cations in the catalyst (Fig. 10). Two reduction at ca. 240 °C and 480 °C were observed on Cu-ZSM-5, corresponding to the reduction of intrazeolite Cu (II) to Cu (I) and Cu (I) to metallic Cu [48,49], respectively. The reduction peak of intrazeolite In (III) was observed on In-ZSM-5 at ca. 390 °C [50] and the reduction peak of La (III) was observed on

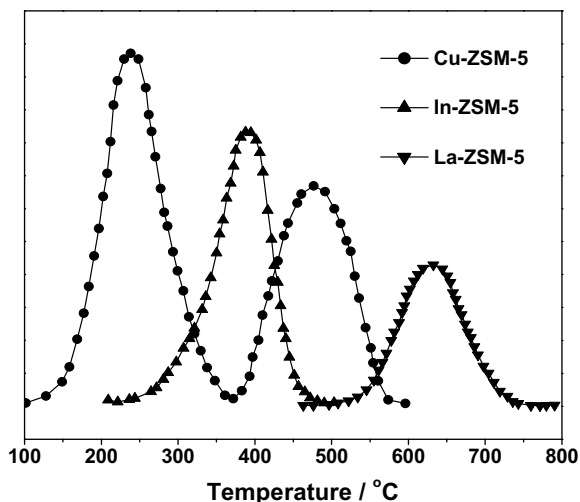


Fig. 10. H_2 -TPR profiles of Cu-ZSM-5, In-ZSM-5 and La-ZSM-5.

La-ZSM-5 at ca. 630 °C. Generally speaking, a low reduction temperature was equivalent to high oxidation capacity, so Cu-ZSM-5 processed the highest oxidative activity, followed by In-ZSM-5 and then La-ZSM-5.

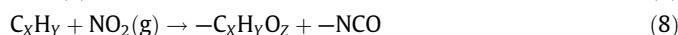
The Brønsted acidity and the oxidative activity of exchanged cations are two key factors controlling the formation of main reaction intermediates nitrate species. So, they are the two key factors controlling the deNO_x activity in NO–C₃H₈–O₂ reaction. As for this work, the oxidative activity of exchanged cations may played a decisive role on the activity, since similar Brønsted acidity was observed on the catalysts studied (Fig. 1). As a result, Cu-ZSM-5 with the highest oxidative activity showed the best deNO_x activity in NO–C₃H₈–O₂ reaction. From above discussion, it is proposed that the activity of catalysts in C₃H₆-SCR can be improved by turning their Brønsted acidity and oxidative activity. IrCu-ZSM-5, as an example, have been reported to be more active than Cu-ZSM-5 [9].

The existence of excess water vapor showed distinct negative effect on NO reduction, as shown in Fig. 2. Water vapor would compete with NO in adsorption on the Brønsted acid sites and prohibit the formation of –NO⁺ species. More important, the existence of water vapor greatly depressed the oxidative activity of metal cations [51] and the oxidation of –NO^{δ+} to –NO₃ was also prohibited. On a whole, the formation of reaction intermediate nitrate species was greatly prohibited by the existence of water vapor.

4.2. Mechanism of C₃H₆-SCR

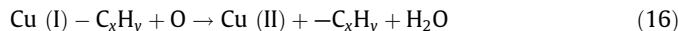
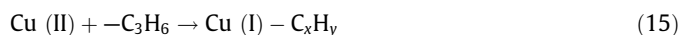
Compared with C₃H₈-SCR, the mechanism of C₃H₆-SCR is much more complicated. In the first step, propene was adsorbed on Brønsted acid sites and was activated as –C_xH_y (–CH₃, –CH₂ or –R=CH₂). The –C_xH_y species could be oxidized to –C_xH_yO_z species by an oxidant (NO, NO₂ or O₂). Since NO₂ showed the highest oxidative activity, followed by O₂ and then NO [52], we suggest that adsorbed –C_xH_y species were preferred oxidized by NO₂. When –C_xH_y was oxidized, NO₂ was simultaneously reduced to –NCO species. These –NCO species were highly active reaction intermediates and they could react with NO or O to produce N₂ and CO₂ [53,54]. In a more reasonable way, the –NCO species hydrolyzed to produce –NH₂ species [55,56], as observed in the DRIFT spectra. The adsorbed –NH₂ species were more active reaction intermediates, which could react with NO or NO₂ to give the final product N₂ and H₂O [57,58]. The –C_xH_yO_z could be further oxidized to CO₂ and H₂O by adsorbed oxygen, which

made the SCR reaction proceed continuously. A concise deNO_x mechanism for the C₃H₆-SCR reaction is described as following:



As for C₃H₆-SCR reactions, –NH₂ species are the reaction intermediates with high activity and they are ready to react with oxidants (NO or NO₂) once formed. Amine species come from the hydrolysis of isocyanate species (Eq. (10)) via a very quick reaction [3]. So, the formation of –NCO species from –C_xH_y and NO₂ is a key step for NO reduction. The peak intensities of IR bands corresponding to all adsorbed –C_xH_y species (–CH₃, –CH₂ and –R=CH₂) on catalysts were observed as Cu-ZSM-5 > La-ZSM-5 > In-ZSM-5, in great consistent with the catalytic activities for C₃H₆-SCR reaction (Fig. 3). So, the activation of C₃H₆ (in excess oxygen) on catalyst, which was the initial step of the C₃H₆-SCR reaction, had an essential effect on the deNO_x activities of catalysts.

The activation of C₃H₆ on catalysts is determined by the intrinsic properties of the catalysts. The chemical valence states of the exchanged cations in the catalysts before and after the C₃H₆-SCR reactions were investigated by XPS, as displayed in Fig. 11. It shows that the states of In species and La species in ZSM-5 zeolite did not change after C₃H₆-SCR reaction: In existed in the form of In (III) [59] and La existed in the form of La (III) [60], respectively. While for Cu-ZSM-5 catalyst, Cu species existed in the form of intrazeolite Cu (II) (BE = 935.5 eV) [61] before reaction and after C₃H₆-SCR reaction, Cu species existed in the form of both intrazeolite Cu (II) (BE = 935.6 eV) [61] and intrazeolite Cu (I) (BE = 934.3 eV) [62]. The interconversion of Cu (II) to Cu (I) and Cu (I) to Cu (II) is shown as following [63,64]:



It is proposed that propene on the Brønsted acid sites could be oxidized by the adjacent Cu (II), accompanied by the reduction of Cu (II) to Cu (I). The formed Cu (I) can be re-oxidized to Cu (II) by the oxygen. Obviously, Cu species involved in the process of propene activation, probably through transitional Cu (I)–C_xH_y species. The participation of Cu species promoted the activation of propene and accelerated the whole deNO_x reaction. Hence, the highest deNO_x activity for the C₃H₆-SCR reaction was obtained over Cu-ZSM-5 catalyst. As for In-ZSM-5 and La-ZSM-5, the activation of propene could only be achieved on Brønsted acid sites of the zeolites through the function of adsorbed oxygen on metal cations (–C₃H₆ + O → –C_xH_y + H₂O). Since oxygen adsorbed more easily on the rare earth metal La (III) than on the main group metal In (III), La-ZSM-5 showed better activity than In-ZSM-5.

Different from that in C₃H₈-SCR reaction, the existence of water vapor only showed very mild negative effect on NO reduction in C₃H₆-SCR reaction at relative low temperatures. On one side, water vapor competed with propene in adsorption on the Brønsted acid sites and prohibited the activation of propene. On the other side, the existence of water vapor would promote the hydrolysis of –NCO species and favored the formation of highly active –NH₂ species.

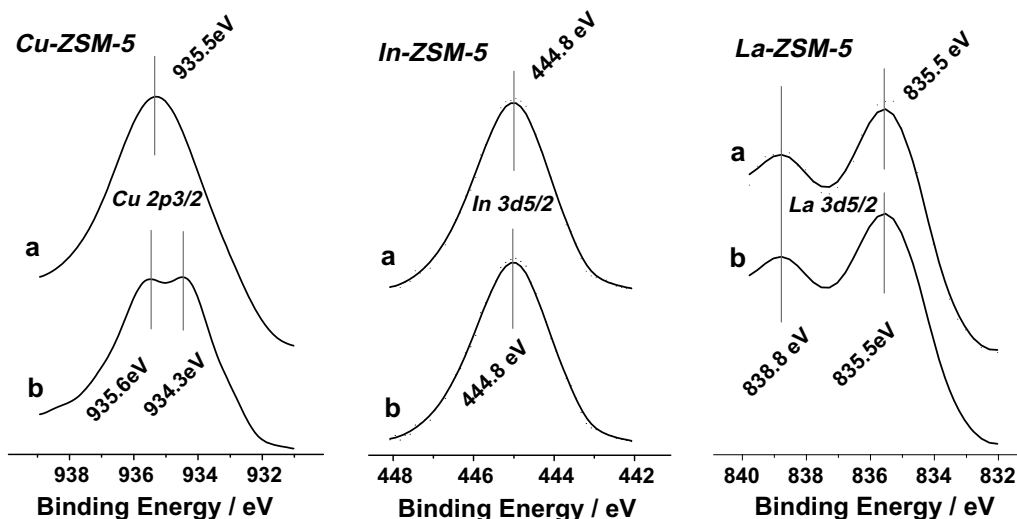


Fig. 11. XP spectra of Cu-ZSM-5, In-ZSM-5 and La-ZSM-5 catalyst before (a) and after (b) C_3H_6 -SCR reaction.

4.3. Comparison between C_3H_8 -SCR and C_3H_6 -SCR

The reaction pathways for C_3H_8 -SCR and C_3H_6 -SCR over ion-exchanged ZSM-5 catalysts are proposed in Fig. 12. The adsorption of NO and hydrocarbons (propane and propene) on the catalysts is the initial step for the whole reaction, and the competing adsorption between NO and hydrocarbons determines the different reac-

tion pathways. The following discussion will be made based on Cu-ZSM-5 as an example catalyst.

DRIFTS study of co-adsorption of $C_3H_8-O_2$, $C_3H_6-O_2$ and $NO-O_2$ on Cu-ZSM-5 is displayed in Fig. 13. As is known, three kinds of hydroxyl groups exist in ion-exchanged ZSM-5 zeolites and they can be distinguished clearly in the FTIR spectra [18,65,66]: terminal silanol groups (Si-OH) represented by the band at 3740 cm^{-1} ,

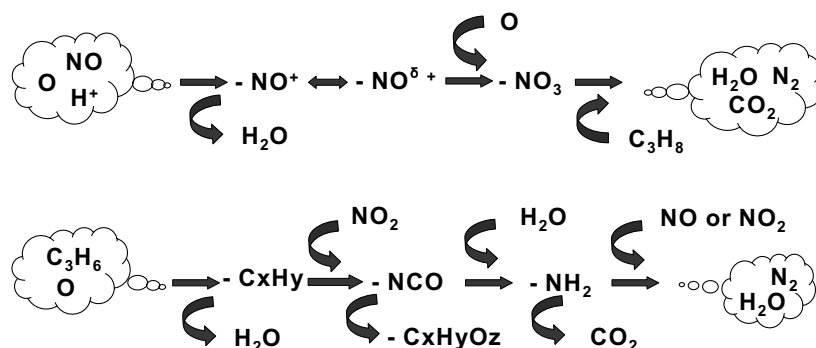


Fig. 12. Different reaction pathways proposed for C_3H_8 -SCR and C_3H_6 -SCR over Me-ZSM-5 catalyst.

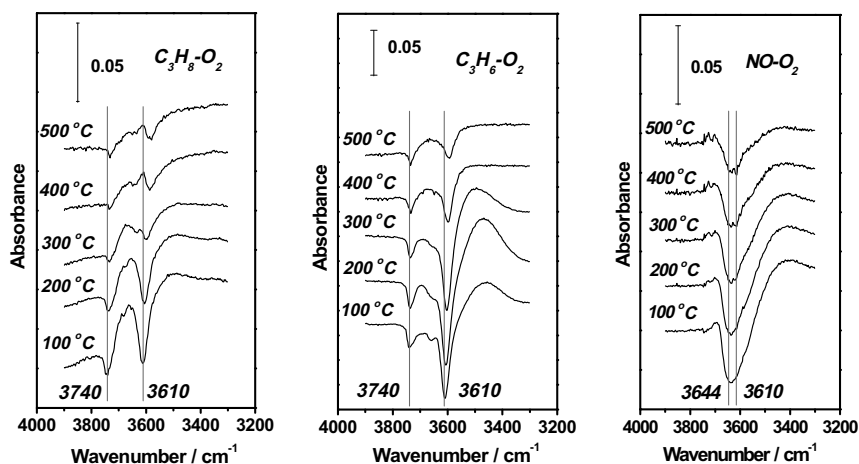


Fig. 13. DRIFTS study of co-adsorption of $C_3H_8-O_2$, $C_3H_6-O_2$ and $NO-O_2$ on Cu-ZSM-5 catalyst at different temperatures.

Al–OH by a band at 3644 cm^{-1} and bridging hydroxyl groups (Si–OH–Al) by a band at 3610 cm^{-1} . The band of bridging hydroxyl groups at 3610 cm^{-1} is typical for Brønsted acid sites in zeolites. From the co-adsorption results of $\text{C}_3\text{H}_8\text{--O}_2$ and $\text{C}_3\text{H}_6\text{--O}_2$, it could be seen that in excess oxygen propane and propene adsorbed on the Si–OH and Si–OH–Al, as indicated by the consumption of the bands of Si–OH (3740 cm^{-1}) and Si–OH–Al (3610 cm^{-1}). By comparing the intensities of the negative peaks at 3740 cm^{-1} and 3610 cm^{-1} , we believed that both propane and propene preferred adsorption on the Si–OH–Al, the Brønsted acid sites. At all temperatures range from $100\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$, propene adsorbed much stronger than propane in excess oxygen (note the different scales of the y-axis). For NO--O_2 co-adsorption, the consumption of Si–OH–Al (3610 cm^{-1}) as well as of Al–OH (3644 cm^{-1}) was observed, indicating the adsorption of NO on Brønsted acid sites and Al–OH.

NO, propane and propene all adsorb on the Brønsted acid sites, and the results of competing adsorption may determine the subsequent reaction pathway. At $400\text{ }^\circ\text{C}$, the adsorption of $\text{C}_3\text{H}_6\text{--O}_2$ predominated on Brønsted acid sites under $\text{C}_3\text{H}_6\text{--SCR}$ condition, so the Brønsted acid sites were occupied by propene and the initial step for the reaction is the adsorptive activation of propene. In contrast, the adsorption of NO--O_2 predominated under $\text{C}_3\text{H}_8\text{--SCR}$ condition, and here the Brønsted acid sites are occupied by NO--O_2 . As a consequence, the initial step for the $\text{C}_3\text{H}_8\text{--SCR}$ reaction is the formation of NO^+ species on Brønsted acid sites and the activation of propane was completely prohibited.

It should be mentioned that even for a given catalyst, the results of competing adsorption might be dependent on the reaction conditions, e.g., reaction temperatures and reactant composition. These might be the reason for the different reaction pathways for HC–SCR proposed in literature.

5. Conclusion

NO selective reduction in excess oxygen by propane and propene were studied over Cu–ZSM-5, In–ZSM-5 and La–ZSM-5 catalysts. The surface reactions of HC–SCR were studied using the in situ DRIFTS method. For $\text{C}_3\text{H}_8\text{--SCR}$ reaction, adsorbed nitrate species were observed as main reaction intermediates. The Brønsted acidity and oxidative activity of catalyst were key factors controlling the deNO_x activity. For $\text{C}_3\text{H}_8\text{--SCR}$ reaction, adsorbed amine species were observed as main reaction intermediates and the adsorptive activation of propene was key step for the whole reaction. Different reaction pathways for $\text{C}_3\text{H}_8\text{--SCR}$ and $\text{C}_3\text{H}_6\text{--SCR}$ reactions were found to be dependent on the competing adsorption of HC--O_2 and NO--O_2 on the Brønsted acid sites of catalysts.

Acknowledgment

This work was financially supported by National Natural Science Foundation of China (20573059, 20703057).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2008.07.021.

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