

2009

In situ DRIFTS study during C₂H₄-SCR of NO over Co-ZSM-5

Xiaomei Chen

Hong Kong Baptist University

Xuefeng Yang

Aimin Zhu

C.T. Au

Hong Kong Baptist University, pctaui@hkbu.edu.hk

Chuan Shi

This document is the authors' final version of the published article.

Link to published article: <http://dx.doi.org/10.1016/j.molcata.2009.07.010>

APA Citation

Chen, X., Yang, X., Zhu, A., Au, C., & Shi, C. (2009). In situ DRIFTS study during C₂H₄-SCR of NO over Co-ZSM-5. *Journal of Molecular Catalysis A: Chemical*, 312 (1-2), 31-39. <https://doi.org/10.1016/j.molcata.2009.07.010>

This Journal Article is brought to you for free and open access by the Department of Chemistry at HKBU Institutional Repository. It has been accepted for inclusion in Department of Chemistry Journal Articles by an authorized administrator of HKBU Institutional Repository. For more information, please contact repository@hkbu.edu.hk.

***In situ* DRIFTS study during C₂H₄-SCR of NO over
Co-ZSM-5**

Xiaomei Chen ^a, Xuefeng Yang ^a, Aimin Zhu ^a, C.T. Au ^c, Chuan Shi ^{a,b,*}

^a *Laboratory of Plasma Physical Chemistry, Dalian University of Technology,
Dalian 116024, P. R. China.*

^b *State Key Laboratory of Fine Chemicals, Dalian University of Technology,
Dalian 116012, P. R. China.*

^c *Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong*

*Corresponding author (Chuan Shi).

Tel: +86-411-84708548-803

Fax: +86-411-84708548-808.

E-mail address: chuanshi@dlut.edu.cn(C. Shi)

Postal address: Laboratory of Plasma Physical Chemistry, Box 288, Dalian University of
Technology, Dalian 116024, P. R. China

Abstract

The formation of surface intermediates and their reactivities with some reactant gases during the selective catalytic reduction of NO with ethylene (C₂H₄-SCR) over Co-ZSM-5 was investigated systematically by *in situ* Diffused Reflectance Infrared Fourier Transformed Spectroscopy. Some new IR bands relevant to the surface intermediates formed in the title reaction were identified. The results show that formate species, formed during the partial oxidation of ethylene over Co-ZSM-5, is reactive towards nitrates to yield formyl nitro compound, an intermediate critical for the formation of cyanide and isocyanate species by further reacting with nitrates. Kinetics analysis suggests that the cyanide and isocyanate at different sites vary in reactivity towards nitrates. The Co²⁺-CN and Al³⁺-NCO species subsequently react with nitrates for final production of N₂, CO₂ and H₂O, however, the -CN bound to Brønsted and Lewis acid sites show poor reactivity towards a flow of NO+O₂/He. On the basis of these investigations, a proposed reaction mechanism explains the formation and roles of all intermediates detected by IR spectroscopy in this study.

Keywords: Co-ZSM-5; Ethylene-SCR; Surface intermediates; *In situ* DRIFTS; Mechanism.

1. Introduction

The selective catalytic reduction of NO_x (denoted as NO_x -SCR hereinafter) in O_2 -rich exhaust streams of lean burn and diesel engines is a major challenge of environmental catalysis. The selective catalytic reduction of NO_x by hydrocarbons (denoted as HC-SCR hereinafter) was first reported in 1990 [1, 2]. In the past two decades, great efforts have been made to develop efficient catalytic systems and to study the related reaction mechanisms [3-8]. Among zeolite-based catalysts, Co-ZSM-5 has been found to be effective and thermally stable for HC-SCR of NO_x when CH_4 was used as reductant [6-10]. Besides CH_4 , higher hydrocarbons such as C_2H_2 [11], C_2H_4 [11, 12], C_2H_6 [13, 14], C_3H_6 [15], C_3H_8 [16] and *i*- C_4H_{10} [17] were also used as reducing agents over Co-ZSM-5. The general trends of hydrocarbon reducing activities are: (i) alkynes \sim alkenes $>$ CH_4 [11], and (ii) larger alkanes $>$ CH_4 [14, 16].

Mechanistic investigations of NO_x -SCR over Co-ZSM-5 revealed similarities with other types of catalysts used for HC-SCR of NO_x , whereby the addition of O_2 was found to enhance the efficiency of the process significantly [6, 18]. A common understanding about the mechanism of NO_x -SCR with hydrocarbons over Co-ZSM-5 is that in the co-adsorption of NO and O_2 , the first step is the formation of NO_y species ($y \geq 2$) at the active sites. There are a large number of *in situ* Fourier Transform Infrared (FTIR) studies conducted over Co-ZSM-5 to investigate the surface species formed in NO adsorption or $\text{NO}+\text{O}_2$ co-adsorption [13, 14, 19, 20]. In contrast, investigation on the adsorption of hydrocarbon is rare. Goryashenko *et al.* [15] reported the IR spectra of surface species formed in $\text{C}_3\text{H}_6+\text{O}_2$ co-adsorption on Co-ZSM-5, and assigned spectral profiles to surface $\text{C}_k\text{H}_l\text{O}_m$ ($m \geq 0$) species. It was suggested that the second step of the reduction process is very likely to be interaction between NO_y and $\text{C}_k\text{H}_l\text{O}_m$ ($m \geq 0$) species, resulting in the formation of initial

intermediates which may somehow convert into “stable” intermediates such as -CN [17, 21, 22], -NCO [15, 17], or possibly $\text{-NC}_a\text{O}_b\text{H}_c$ [12]. Within the temperature range for optimum reaction, the surface intermediates can be *in situ* probed or detected, sometimes even after purging the catalyst with inert gas. According to the experimental results of different groups, the final step would be the interaction of the intermediates with $\text{NO}+\text{O}_2$ or NO_2 , giving N_2 , CO_2 , CO and H_2O as final products. By means of *in situ* infrared spectroscopy, Lobree *et al.* [21] detected the presence of surface Co^{2+} -CN species during the reduction of NO by CH_4 at 450°C . The rate constants for the reaction of the -CN species with NO_2 , O_2 and NO at 450°C (accompanied by the formation of CO_2 and N_2) were found to be 8.5×10^{-5} , 1.9×10^{-6} and 3.3×10^{-7} $\text{s}^{-1}\text{ppm}^{-1}$, respectively. Goryashenko *et al.* [15] studied NO -SCR with propylene over Co-ZSM-5 using *in situ* FTIR and found that C_3H_6 and NO reacted readily above 200°C , leading to the formation of three different types of surface NCO species, i.e. NCO bonded to Co, Si and Al; the NCO species were found to be stable up to 400°C either in NO or O_2 atmosphere, but in a $\text{NO}+\text{O}_2$ mixture, they converted readily to N_2 and CO_2 below 400°C .

According to Wang *et al.* [17], the IR band of Co^{2+} -NCO species disappeared rapidly after exposure of the Co-ZSM-5 catalyst pretreated with $\text{NO}+\text{O}_2+i\text{-C}_4\text{H}_{10}$ to a $\text{NO}+\text{O}_2$ flow at 200°C , and there was concomitant formation of N_2 , CO and CO_2 . More recently, Shichi *et al.* [16] put forward a different explanation for the role of -NCO intermediates in the C_3H_8 -SCR of NO . They demonstrated that there was accumulation of -NCO species on the Co-ZSM-5 catalyst at 375°C in the absence of water vapor, resulting in catalyst deactivation; in the presence of water vapor, -NCO species readily hydrolyzed to NH_3 and CO_2 , leading to higher SCR activity. In a recent paper of ours [12], we reported that the surface species formed in exposing Co-ZSM-5 to a standard reactant

mixture (i.e. $\text{NO}+\text{C}_2\text{H}_4+\text{O}_2$ in Ar) produced much more N_2 upon exposure to $\text{NO}+\text{O}_2$ than upon exposure to either NO or O_2 at 275°C . The similarity in product ratios (i.e. $\text{N}_2:\text{CO}_x:\text{H}_2\text{O}$; CO_x stands for CO_2+CO) of the reaction of surface intermediates with $\text{NO}+\text{O}_2$ and that of a normal continuous flow reaction with $\text{NO}+\text{C}_2\text{H}_4+\text{O}_2/\text{Ar}$ as feed gas over Co-ZSM-5 suggests that the surface species of the former are very likely to be the primary long-lived reaction intermediates in the C_2H_4 -SCR of NO_x . The perception is corroborated by the fact that the average N:C:H atomic ratios of surface species as determined via transient product analysis in both cases were rather similar.

Due to the complexity of the NO-SCR process, consensus still has not been achieved in terms of the reaction mechanism. In view of this, we conducted detailed investigation on the formation and consumption of surface species formed in the C_2H_4 -SCR of NO over Co-ZSM-5. *In situ* Diffused Reflectance Infrared Fourier Transformed Spectroscopy (DRIFTS) was carried out to investigate the nature and structure of these surface intermediates based on our previous studies of the reactions of surface species formed in the C_2H_4 -SCR of NO over Co-ZSM-5 [12]. The spectra evolutions of the surface species reacting with some of the reactants were systematically examined. A possible reaction pathway was proposed to interpret the experiment results.

2. Experimental

The Co-ZSM-5 catalyst investigated in this work was prepared via a three-time repeated ion-exchange procedure at 80°C using H-ZSM-5 powders ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$, Nankai University, China) and aqueous cobalt acetate solutions, followed by drying at 120°C for 8 h and calcination at 500°C for 3 h after each ion exchange. The content of Co in the Co-ZSM-5 catalyst was determined to be 1.7 wt. % using an inductively coupled plasma emission spectrometry method.

The ground powder was placed in a DRIFT cell with CaF₂ windows and treated in a He flow at 500°C for 1 h. IR spectra were recorded (128-scan accumulation and 4 cm⁻¹ resolution) using Bruker Tensor 27 spectrometer equipped with a LATGS detector. In each experiment, the pretreated catalyst was exposed to reaction gas mixtures for 30 min at the desired temperature, and then spectra were recorded. The reactant gas mixture, containing NO (1.0% in He), O₂ (99.999%), C₂H₄ (5.0% in He) and He (99.999%) as balance gas, was introduced to the DRIFT cell via separate mass flow controllers. All gas mixtures were fed at a flow rate of 100 ml·min⁻¹. The reactivity of the surface adsorbed species was evaluated by the transient response of the IR spectra.

The non-steady-state experiments were performed to determine the rate constants of surface reaction of adsorbed species in a gas mixture of NO+O₂/He. The sample was pre-treated in NO+O₂+C₂H₄/He flow for 1 h, and then the flowing gas was switched to NO+O₂/He, while DRIFT spectra were recorded and the integrated intensities of bands were determined as a function of time at a particular temperature.

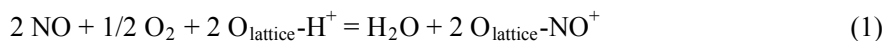
3. Results

3.1. Nitric oxides formed on Co-ZSM-5

Fig. 1 shows the DRIFT spectra of surface species formed in a gas mixture of 1000 ppm NO/He over Co-ZSM-5 catalyst at 200°C, 250°C and 300°C for 30 min, respectively. All of the three observed IR bands (1804-1807 cm⁻¹, 1890-1892 cm⁻¹ and 1931-1934 cm⁻¹) which were similar to those reported by other groups [13-15], were red-shifted with increasing temperatures, probably suggesting bond weakening at higher temperatures. For description simplicity, the IR bands of 1804, 1890 and 1931 cm⁻¹ at 300°C will be referred to in the rest of the text. The 1804 and 1890 cm⁻¹ bands were undoubtedly assigned to the *symmetric and asymmetric* N-O stretching modes of Co²⁺(NO)₂

dinitrosyl species, respectively, while the band at 1931 cm^{-1} was most probably due to Co^{3+} -NO mononitrosyl species [13-15]. From the data shown in Fig. 1, the intensities of the peaks at 1804 and 1890 cm^{-1} decreased sharply with rising temperature due to increasing dinitrosyl decomposition. In contrast, the intensity of the mononitrosyl band at 1931 cm^{-1} increased greatly with rising temperature and this led to the dramatic change of its intensity relative to that of the dinitrosyl bands at three temperatures.

The DRIFT spectra of Co-ZSM-5 after exposure to $\text{NO}+\text{O}_2/\text{He}$ at different temperatures are shown in Fig. 2A. The main bands in the range 1520 - 1625 cm^{-1} associated with nitric oxides were observed at 200 - 300°C . The band at 1575 and 1595 cm^{-1} are ascribed to bidentate nitrates, the band at 1520 and 1535 cm^{-1} to monodentate nitrates and that at 1557 and 1625 cm^{-1} probably to bridged nitrates and NO_2 species[13, 19]. Possible nitrites with bands below 1500 cm^{-1} could not be distinguished due to the significant noise level probably related to the zeolite framework. However, Most of nitrates species seemed to decline with temperature increasing, only a broad band at 1540 cm^{-1} attributable to monodentate nitrate species was observed at temperatures higher than 350°C . Thus, it can be observed obviously that the bidentate and bridged nitrates are predominant over Co-ZSM-5 at lower temperatures (300°C), instead of monodentate nitrates at higher temperatures (350 and 400°C). Moreover, Co^{3+} -NO species at 1931 cm^{-1} and a new band at 2130 cm^{-1} were formed along with the gradual decrease in intensity of Co^{2+} -dinitrosyl species. The 2130 cm^{-1} band which was also observed by a number of investigators over Co-ZSM-5 [17, 20, 22] has been assigned by Hadjiivanov *et al.* [23] to NO^+ species adsorbed on the cationic positions of H-ZSM-5. The enhancement of O_2 on the production of this NO^+ band was ascribed to the following surface species-involved reaction equilibrium [23]:



The subsequent He purge to the NO+O₂ pre-adsorbed catalyst at 300°C led to the disappearance of two IR bands at 1931 cm⁻¹ (Co³⁺-NO) and at 2130 cm⁻¹ (NO⁺ species) (Fig. 2B). In contrast, the bands in the region of 1500-1600 cm⁻¹ remained almost constant, suggesting that these nitrates were stable on Co-ZSM-5 at 300°C.

3.2. Formation of surface oxygenates

Figure 3 shows the DRIFT spectra of Co-ZSM-5 catalyst after exposure to 1000 ppm C₂H₄/He and 1000 ppm C₂H₄+10% O₂/He at 300°C for 30 min. In agreement with the results reported by us [24], adsorption of C₂H₄/He on CoH-ZSM-5 led to the appearance of a strong band at 1576 cm⁻¹ with two shoulder bands at 1645 and 1680 cm⁻¹. The broad band centered at 1576 cm⁻¹ has been assigned to the ν(-COO) of formate species, and the bands at 1645 and 1680 cm⁻¹ to the C=C and -C=O stretching mode of oxygenates, as well as the bands at 2899, 2935 and 2977 cm⁻¹ corresponding to the C-H stretching vibrations of formate species. In addition, the last three bands at 3610, 3745 and 3680 cm⁻¹ have been assigned to ν(OH) of terminal Si-OH, Si-OH-Al and Al-OH. When 10% O₂ was present in the C₂H₄ stream (Fig. 3A-b), there was a significant increase in intensity of the formate band at 1576 cm⁻¹, whereas the bands at 1680 and 1645 cm⁻¹ almost disappeared (Fig. 3b). It is likely that these oxygenates were further oxidized by gas phase oxygen and more formate species were generated.

3.3. Reactivity of surface nitric oxides

The stable surface nitric oxides on Co-ZSM-5 catalyst are usually various nitrates, which are potential candidates for HC-SCR intermediates. For this reason, we studied the reactivity of nitrates towards gas mixtures of C₂H₄/He and C₂H₄+O₂/He at 300°C. Surface nitrates were accumulated on

Co-ZSM-5 in a flow of NO+O₂/He for 30 min followed by He purge for 10 min. (Fig. 4-a). After exposure of the catalyst surface with nitrate species to C₂H₄/He, the variation in intensity of nitrate species could not be determined because these bands were masked by the broad band of formate at 1576 cm⁻¹. However, new bands at 1670, 2178, 2260, 2290, 2315 and 2356 cm⁻¹ were observed. Similar result was obtained when switched gas to C₂H₄+O₂/He. There are only quantitative differences in both IR spectra of new-formed adsorbed species. Referring to the results of Lobree and Shichi [16,21], the new-formed band at 2178 cm⁻¹ can be assigned to -CN species bound to Co²⁺(Co²⁺-CN), and the band at 2260 cm⁻¹ to -NCO bound to Al³⁺(Al³⁺-NCO). The band at 2356 cm⁻¹ is undoubtedly due to CO₂. Additionally, the 2290 and 2315 cm⁻¹ peaks have been attributed to -CN species bound to Brønsted and Lewis acid sites(denoted as -CN_B and -CN_L) according to the literatures [16, 25].

It is worth pointing out that we observe a weak band at 1670 cm⁻¹ after exposing the catalyst with nitrate species to a flow of C₂H₄/He or C₂H₄+O₂/He. This band was also detected when fresh Co-ZSM-5 was exposed to a flow of NO+O₂+C₂H₄/He (spectrum *a*, inset of Fig. 4). Since we do not detect such a band when Co-ZSM-5 is exposed to NO+O₂/He (Fig. 2) or C₂H₄+O₂/He (Fig. 3), it is reasonable to believe that this band (at 1670 cm⁻¹) is due to an entity that contains carbon, nitrogen and oxygen atoms. Despite species such as organic nitrates and nitrites [26, 27], NO_x-hydrocarbon adduct [19], oxime or amide [9] have been suggested to be important intermediates for HC-SCR of NO, experimental evidences for their existence are lacking. Reported here by us is the first time that the 1670 cm⁻¹ band was observed in HC-SCR of NO over Co-ZSM-5. Since we did not detect signals of ν(-OH) or ν(-NH) stretching mode, we excluded the possibility of having oxime or acid amide species. In a comparison experiment, we detected the 1670 cm⁻¹ band

(spectrum *b*, inset of Fig. 4) that corresponded to the $\nu(\text{N}=\text{O})$ vibration of nitro species [26] upon exposure of fresh Co-ZSM-5 to gas phase CH_3NO_2 . Despite we could not exclude the possibility of forming nitroso-containing organic species during the C_2H_4 -SCR of NO over Co-ZSM-5, we tentatively assigned the band at 1670 cm^{-1} to formyl nitro compound (HCONO_2), and its formation pathway was depicted in Scheme 1.

3. 4. Reactivity of surface oxygenate species

The reactivity of adsorbed formate over Co-ZSM-5 towards different oxidizing agents was evaluated by time-dependent changes of the DRIFT spectra. In these experiments, the catalyst was first exposed to a flow of $\text{C}_2\text{H}_4+\text{O}_2/\text{He}$ for 30 min and followed by He purge for 10 min, then the feed gas was switched to different gas mixtures of O_2/He , NO/He or $\text{NO}+\text{O}_2/\text{He}$ at 300°C (Fig. 5). After switching the gas to a flow of O_2/He , the intensity of the bands at 1645 and 1680 cm^{-1} decreased with the simultaneous production of considerable CO_2 (Fig. 5-b). It is noteworthy that the formate species were consumed greatly accompanied by the formation of compounds that contained nitrogen and carbon atoms when switched gas to $\text{NO}+\text{O}_2/\text{He}$ flow (Fig. 5-c). In contrast, only a weak band at 2178 cm^{-1} was observed during NO/He exposure (Fig. 5-d).

3. 5. Surface species detected during the C_2H_4 -SCR reaction

In situ DRIFT spectra of Co-ZSM-5 after exposure to $\text{NO}+\text{C}_2\text{H}_4+\text{O}_2/\text{He}$ under steady state conditions at various temperatures are shown in Fig. 6. At 200 , 250 or 300°C , the spectra showed well-defined bands at 1576 , 1670 , 2178 , 2290 , 2315 and 2260 cm^{-1} . A band at 2141 cm^{-1} ascribable to weakly bonded CO was also detected [28] (Fig. 6-a,b,c). Subsequent heating of the sample resulted in the decline in intensity of the bands at 1576 , 1670 , 2178 and 2260 cm^{-1} as well as those in the $2800\text{-}3000\text{ cm}^{-1}$ region. However, there was a significant rise in intensity of the bands at 2290

and 2315 cm^{-1} with rising temperature (Fig. 6-d, e). Heating the sample under $\text{NO}+\text{C}_2\text{H}_4+\text{O}_2/\text{He}$ to 400°C resulted in further enhancement of the intensity of $-\text{CN}_\text{B}$ (2290 cm^{-1}) and $-\text{CN}_\text{L}$ (2315 cm^{-1}) bands, as well as the complete disappearance of the band corresponding to formyl nitro compound (1670 cm^{-1}).

3.2.6 Reactivity of surface species formed during $\text{NO}+\text{C}_2\text{H}_4+\text{O}_2$ reaction

The reactivity of surface species formed during $\text{NO}+\text{C}_2\text{H}_4+\text{O}_2/\text{He}$ reaction was also examined in different oxidizing atmosphere in order to elucidate the roles of surface intermediates. After exposure of catalyst to $\text{NO}+\text{C}_2\text{H}_4+\text{O}_2/\text{He}$ for 30 min at 300°C , the sample was purged with He for 10 min to eliminate the gaseous and weakly adsorbed species (Fig. 7-a). After switching the feed gas to NO/He or O_2/He , a slight decline in intensity of all the bands was observed (Fig. 7-b, c). In contrast, there was a complete disappearance of the bands at 1670 , 2178 and 2260 cm^{-1} after switching gas to $\text{NO}+\text{O}_2/\text{He}$ (Fig. 7-d). At the same time, the formation of nitric oxides and a little decrease in intensity of the 2290 and 2315 cm^{-1} were also observed. It is apparent that the consumption of cyanide on acid sites (2290 and 2315 cm^{-1} bands) is slow in comparison with that of other species in a flow of $\text{NO}+\text{O}_2/\text{He}$.

Fig. 8 shows the integrated area of bands of surface species versus time after exposure to $\text{NO}+\text{O}_2/\text{He}$. One can see that the intensities of the bands at 1576 cm^{-1} (HCOO^-) and 1670 cm^{-1} (HCONO_2), as well as that at 2178 cm^{-1} ($\text{Co}^{2+}\text{-CN}$) decreased rapidly with exposure time, whereas those at 2290 cm^{-1} ($-\text{CN}_\text{B}$) and 2315 cm^{-1} ($-\text{CN}_\text{L}$) rose in the first 4 min, and then declined gently to a constant value within 40 min. Regarding the 2260 cm^{-1} band which can be related to $\text{Al}^{3+}\text{-NCO}$ species, the changing trend is similar to that of the 2290 and 2315 cm^{-1} bands but shows more rapid decline after the first 4 min. We performed similar experiments at 250 , 320 and 350°C to

estimate the rate constants of -CN and -NCO consumption in NO+O₂/He flow as given in Table 1.

The apparent rate constants of -CN and -NCO consumption can be determined based on the kinetic dependence of intensities of the absorption bands due to surface intermediates obtained in the course of non-steady-state measurements, denoted as k' . The rate equation of -CN or -NCO consumption can be derived:

$$r_A = -\frac{dC_A}{dt} = k' C_A^\alpha C_{NO_x}^\beta \quad (2)$$

where C_A denotes the concentration of -CN or -NCO species. Since the amount of NO_x is in large excess, it is a good approximation to consider a constant NO_x concentration throughout the reaction and to write $k = k' C_{NO_x}^\beta$; then the consumption rate equation (2) becomes:

$$r_A = -\frac{dC_A}{dt} = k C_A^\alpha \quad (3)$$

Supposed that the consumption of -CN or -NCO is a first-order reaction ($\alpha=1$), the integrated form of rate equation can be expressed in the following form:

$$kt = \ln \frac{C_{A,0}}{C_{A,t}} = \ln \frac{1}{1-x} \quad (4)$$

(x denotes the conversion of -CN or -NCO at a time t , calculated by using the variation of integrated area as a function of reaction time)

This equation shows that if $\ln C_{A,0}/C_{A,t}$ is plotted against t , it will give a straight line, and the value of k can be obtained from the slope (the slope is k). The calculated results show that the plot is straight, suggesting the -CN or -NCO consumption is a pseudo first-order reaction. The values of consumption rate constants k are given in Table 1. It can be seen that the consumption rate constants follow an order of: $k(\text{Co}^{2+}\text{-CN}) > k(\text{Al}^{3+}\text{-NCO}) > k(\text{-CN}_L) > k(\text{-CN}_B)$.

4. Discussion

Selective catalytic reduction of NO by hydrocarbons is a very complex reaction concerning

several parallel and/or consecutive reaction steps. In this study, we followed the accumulation and consumption of surface intermediates as a function of different feed gases at different temperatures. Based on the variation in intensity of surface species (shown in Fig. 4, Fig. 5 and Fig. 7), it was found that nitrates, formate and *N, C*-containing species (-CN, -NCO, HCONO₂) were considered as important intermediates involving in the C₂H₄-SCR of NO reaction.

As shown in Fig. 2B, under He flushing, the nitrates (bands in the region of 1520-1625 cm⁻¹) formed from NO+O₂/He over Co-ZSM-5 remained almost constant, suggesting that these stable nitrates probably acted as reactive intermediates to participate in the selective reduction process. Furthermore, some formate species were found to accumulate on the surface of Co-ZSM-5 when exposed to a flow of C₂H₄/He and/or C₂H₄+O₂/He (Fig. 3). The investigations on the reactivity of adsorbed nitrates suggested that they were highly reactive towards either C₂H₄/He or C₂H₄+O₂/He, leading to the formation of *N, C*-containing species, such as -CN, -NCO and HCONO₂ species. It is clear that the interaction of surface nitrate species with formate is a crucial step for the formation of intermediates that contain N and C atoms (Figs. 4, 5). We found that the bands observed after exposing Co-ZSM-5 to NO+O₂/He and then to C₂H₄+O₂/He were similar to those detected after exposing Co-ZSM-5 to NO+O₂/He and then to C₂H₄/He (Fig. 4b, c), the only difference being that more formate, cyanide, isocyanate species and formyl nitro compounds were generated in the former case. The results suggest that rather than reacting with C₂H₄, the adsorbed nitrate species react with formate to yield the intermediates that contain N and C atoms. As indicated by the results of this study, C₂H₄ is oxidized to formate species at 300°C even in the absence of gaseous O₂ (Fig. 3-a), and being strong oxidants, nitrates species promote the oxidation of ethylene. Similarly, based on the data given in Fig. 5, it is deduced that adsorbed formate can react with nitrates or NO₂ to form -CN,

-NCO and HCONO₂. The Co²⁺-CN species detected in Fig. 5-d may be due to the reaction between formate and a small amount of nitrates that were generated from NO oxidation by residual O₂ and/or lattice oxygen. Thus, the results demonstrate the high oxidation ability of nitrates in comparison to that of NO or O₂, and also confirm the essential role of surface oxygen in the C₂H₄-SCR of NO over the Co-ZSM-5.

It is well known that the intensity of IR bands commonly decrease with rising temperature due to bond weakening, as observed for the variation of bands at 1576, 1670, 2178 and 2260 cm⁻¹ in Fig. 6. Therein, the bands at 2178 and 2260 cm⁻¹ disappeared at 400°C, whereas the intensities of bands at 2290 and 2315 cm⁻¹ increased greatly and exhibited excellent stability under the same condition. As discussed previously, these N, C-containing species were produced from the reaction between formate and some nitrate species. In consideration of the same formate species detected in a flow of C₂H₄+O₂/He at different temperatures, although the intensity of these species decreased with rising temperatures, it is speculated that this different change trend in intensity of above species may result from the formation of various nitrate species at different temperatures. Recalling the fact that only a band at 1540 cm⁻¹ assignable to monodentate nitrate species was observed when exposed Co-ZSM-5 catalyst to NO+O₂/He at 400°C, which was different from the surface bidentate and bridged nitrates formed at lower temperatures in the flow of NO+O₂/He(Fig. 2A). This fact may be explained by the following considerations: this conflicting intensity variation of different surface species is owing to their inconsistent formation pathway. The cyanide species on Bronsted and Lewis sites(2290 and 2315 cm⁻¹) may be produced by the reaction of formate with monodentate nitrate species, whereas cyanide species on Co²⁺ sites and isocyanate may be formed from the reaction between formate and bidentate/bridged nitrates.

Recently, Savva *et al.* [29] emphasized the different reactivity of active NO_x in the H_2 -SCR of nitrogen oxides over Pt/MgO-CeO₂ catalyst, the volcano-type profile of reaction rate (catalytic activity) versus temperature under steady-state reaction conditions was not attributed to the variation of surface concentration of active NO_x but the different reactivity of active NO_x with rising temperature. In the temperature range of 120-200°C, bidentate or monodentate nitrate and nitrosyl (NO^+) coadsorbed with a nitrate (NO_3^-) species were considered as reactive NO_x intermediates. Raising the temperature to 200-300°C, the bidentate or monodentate nitrate became inactive, whereas chelating nitrite (NO_2^-) and nitrosyl (NO^+) coadsorbed with a nitrate (NO_3^-) appeared to be new active reaction intermediates. However, the volcano-type profile of catalytic activity versus temperature in the SCR reaction was often attributed to the lack of reductant due to the high temperature combustion in oxygen [30-32]. Moreover, based on the temperature-programmed desorption (TPD) and in situ DRIFTS studies, the thermal stability and reactivity of surface nitrate species in HC-SCR of nitrogen oxides were evaluated by many researchers [33, 34]. These results revealed the decomposition of different surface nitrates with temperature increasing, which agreed well with the DRIFTS results obtained in this work. However, it still deserves further investigation to ascertain whether the decomposition of nitrates will have effect on the catalytic activity of catalysts in HC-SCR of nitrogen oxides.

The results in Fig. 7 indicate that these N, C-containing intermediates are reactive towards $\text{NO}+\text{O}_2/\text{He}$ but not towards NO/He or O_2/He . The phenomenon can be explained in terms of the higher oxidation ability of nitrate species compared to that of NO or O_2 , in good agreement with the conclusion drawn by Goryashenko *et al.* [15], Weingand *et al.* [35], and Niu *et al.* [12]. It is noteworthy that the formyl nitro compounds were rapidly consumed in a flow of $\text{NO}+\text{O}_2/\text{He}$,

whereas the intensities of bands of Al^{3+} -NCO, -CN_B and -CN_L species went through a maximum in 4 min and then decreased to a constant value within 40 minutes (Fig. 8). This result shows that the formyl nitro compound can react further with $\text{NO}+\text{O}_2/\text{He}$ to form -CN and -NCO species. In other words, this formyl nitro compound acts as a precursor for the formation of -CN and -NCO species. Furthermore, we do not detect prominent increase in intensity of the 2178 cm^{-1} band (Co^{2+} -CN) in this study, probably owing to the rapid consumption of the Co^{2+} -CN under the same conditions.

According to the order of reaction rate constants depicted in Table 1, the -CN located at Co^{2+} sites is more reactive towards $\text{NO}+\text{O}_2/\text{He}$ than the Al^{3+} -NCO species. Also, the -CN_B and -CN_L species are considered to be inactive towards $\text{NO}+\text{O}_2/\text{He}$ at 300°C due to the small rate constants. These results suggest that the cyanide species on different adsorbed sites vary in the reactivity towards nitrate species. In fact, results of previous studies on three-way catalysts indicated that cyanide and isocyanate species may be formed on surface metal sites, and be stabilized after migration to the support material [36]. On the other hand, according to Obuchi *et al.* [37] and Zuzaniuk *et al.* [38], -CN species are more stable than -NCO species on supports at higher temperatures.

It is worth mentioning that the rate constant k for Al^{3+} -NCO species (2260 cm^{-1}) increases from 250 to 300°C and then decreases with rising temperature in Table 1. The same behavior is true for the -CN_B species (2290 cm^{-1}). According to the Arrhenius equation, the apparent rate constant k should increase with increasing temperature. As the temperature rise above 300°C , the surface coverage of -CN or -NCO species may be lowered, resulting in the decreasing of k values.

Consequently, based on the above experimental results and the relevant studies of other groups, a possibly reaction pathway for the C_2H_4 -SCR of NO over Co-ZSM-5 is proposed in scheme 2.

Three reactants (NO, O₂, C₂H₄) are suggested to be adsorbed on the active cobalt adsorption sites. As reported earlier [24], three types of Co species were co-existed on the Co-ZSM-5: Co³⁺-oxides, Co²⁺-oxo and ion exchanged Co²⁺ species. Besides being completely oxidized, C₂H₄ can be adsorbed on the Co³⁺ sites and partially oxidized to formate species in the presence of active oxygen species such as O₂, O₂⁻ and O⁻. NO adsorbs on the Co²⁺ sites to form nitrosyl species, the latter species can be oxidized to nitrates (NO_x) by active oxygen species. The reaction between nitrates and formate species gives rise to a formyl nitro compound (HCONO₂), a precursor for formation of -CN and -NCO species by reacting with NO_x species. Subsequently, reactive -CN and -NCO species react with NO_x for final production of N₂, CO_x and H₂O. Although acid protons may play a negligible role for the selective catalytic reduction of NO with hydrocarbons when Co is present [39], the unique channel structure of ZSM-5 zeolite can supply appropriate environment for formation of active cobalt species. In addition, the framework of zeolites can function as a huge ligand to coordinate and stabilize the cobalt ions, preventing the latter from oxidation or reduction [40, 41].

4. Conclusion

The formation and consumption of surface intermediates formed during the C₂H₄-SCR of NO reaction over Co-ZSM-5 have been investigated by *in situ* DRIFTS technique. The results show that the main adsorbed species detected by IR are surface nitrates, formate, cyanide, isocyanate and formyl nitro compound. Investigations on the reactivity of the detected surface species suggest that the formate species act as an efficient reductant and are reactive towards nitrates to form a crucial intermediate of formyl nitro compound which can react further with various nitrates to yield cyanide and isocyanate. Simple kinetics analysis suggest that Co²⁺-CN and Al³⁺-NCO show good reactivity towards NO+O₂/He, whereas the -CN species bound to Brønsted and Lewis acid sites exhibit

inactive under the same conditions. Our findings showed the behaviors of reactive intermediates in the HC-SCR reaction, and provided useful information on the nature and structure of surface intermediate species for gaining further insight into the reaction mechanism.

Acknowledgements

The present work was supported by the National Natural Science Foundation of China (No.20573014 and 20077005) and by the Program for New Century Excellent Talents in University (NCET-07-0136), as well as by the National High Technology and Development Program (863 program) of China (Grant No.2007AA06Z311).

References

- [1] M. Iwamoto, H. Yahiro, S. Sundo, Y. Yu-u, N. Mizuno, *Shokubai (Catalyst)* 32 (1990) 430-433.
- [2] W. Held, A. Koenig, T. Richter, L. Puppe, *Soc. Aut. Eng.*, 1990, Paper 900496.
- [3] M. D. Fokema, J. Y. Ying, *Catal. Rev. Sci. Eng.* 43 (2001) 1-29.
- [4] R. Burch, *Catal. Rev. Sci. Eng.* 46 (2004) 271-334.
- [5] Z. Liu, S. I. Woo, *Catal. Rev. Sci. Eng.* 48 (2006) 43-89.
- [6] Y. Li, J. N. Armor, *Appl. Catal. B* 1 (1992) L31-L40.
- [7] Y. Li, J. N. Armor, *Appl. Catal. B* 2 (1993) 239-256.
- [8] J. N. Armor, T. S. Farris, *Appl. Catal. B* 4 (1994) L11-L17.
- [9] N. W. Cant, I. O. Y. Liu, *Catal. Today* 63 (2000) 133-146.
- [10] A. Boix, E. E. Miro, E. A. Lombardo, M. A. Banares, R. Mariscal, J. L. G. Fierro, *J. Catal.* 217 (2003) 186-194.
- [11] J. H. Niu, X. F. Yang, A. M. Zhu, L. L. Shi, Q. Sun, Y. Xu, C. Shi, *Catal. Commun.* 7 (2006) 297-301.
- [12] J. H. Niu, A. M. Zhu, C. Shi, H. Y. Fan, X. M. Chen, X. F. Yang, *Res. Chem. Intermed.* 33 (2007) 549-566.
- [13] K. Hadjiivanov, B. Tsyntarski, T. Nicolova, *Phys. Chem. Chem. Phys.* 1 (1999) 4521-4528.
- [14] K. Hadjiivanov, B. Tsyntarski, E. Ivanova, D. Klissurski, T. Morinova, *Surf. Inter. Anal.* 32 (2001) 205-209.
- [15] S. S. Goryashenko, Y. K. Park, D. S. Kim, S. E. Park, *Res. Chem. Intermed.* 24 (1998) 933-951.
- [16] A. Shichi, T. Hattori, A. Satsuma, *Appl. Catal. B* 77 (2007) 92-99.
- [17] X. Wang, H. Y. Chen, W. M. H. Sachtler, *J. Catal.* 197 (2001) 281-291.
- [18] M. C. Campa, S. D. Rossi, G. Ferraris, V. Indovina, *Appl. Catal. B* 8 (1996) 315-331.
- [19] K. Hadjiivanov, *Catal. Rev. Sci. Eng.* 42 (2000) 71-144.
- [20] K. Hadjiivanov, E. Ivanova, M. Daturi, J. Saussey, J. C. Lavalley, *Chem. Phys. Lett.* 370 (2003) 712-718.
- [21] L. J. Lobree, A. W. Aylor, J. A. Reimer, A. T. Bell, *J. Catal.* 169 (1997) 188-193.
- [22] T. Montanari, O. Marie, M. Daturi, G. Busca, *Appl. Catal. B* 71 (2007) 216-222.

- [23] K. Hadjiivanov, J. L. Freysz, J. Saussey, J. C. Lavalley, *Catal. Lett.* 52 (1998) 103-108.
- [24] X. M. Chen, X. F. Yang, A. M. Zhu, H. Y. Fan, X. K. Wang, Q. Xin, X. R. Zhou, C. Shi, *Catal. Commun.* 10 (2009) 428-433.
- [25] C. Resini, T. Montanari, L. Nappi, G. Bagnasco, M. Turco, G. Busca, F. Bregani, M. Notaro, G. Rocchini, *J. Catal.* 214 (2003) 179-190.
- [26] Y. Ukisu, S. Sato, A. Abe, K. Yoshida, *Appl. Catal. B* 2 (1993) 147-152.
- [27] D. E. Sparks, P. M. Patterson, G. Jacobs, N. Dogimont, A. Tackett, M. Crocker, *Appl. Catal. B* 65 (2006) 44-54.
- [28] X. Wang, H. Y. Chen, W. M. H. Sachtler, *Appl. Catal. B* 29 (2001) 47-60.
- [29] P. G. Savva, A. M. Efstathiou, *J. Catal.* 257 (2008) 324-333.
- [30] G. F. Li, X. P. Wang, C. Y. Jia, Z. G. Liu, *J. Catal.* 257 (2008) 291-296.
- [31] A. G. Vargas, G. Delahay, B. Coq, E. Lima, P. Bosch, J. C. Jumas, *Catalysis Today* 107-108 (2005) 94-99.
- [32] G. D. Lionta, S. C. Christoforou, E. A. Efthimiadis, I. A. Vasalos *Ind. Eng. Chem. Res.* 35 (1996) 2508-2515.
- [33] S. Kameoka, Y. Ukisu, T. Miyadera, *Phys. Chem. Chem. Phys.*, 2 (2000) 367-372.
- [34] X. L. Zhang, H. He, H. W. Gao, Y. B. Yu, *Spectrochimica Acta Part A* 71 (2008) 1446-1451.
- [35] T. Weingand, S. Kuba, K. Hadjiivanov, H. Knozinger, *J. Catal.* 209 (2002) 539-546.
- [36] D. K. Captain, C. Mihut, J. A. Dumesic, M. D. Amiridis, *Catal. Lett.* 83 (2002) 109-114.
- [37] A. Obuchi, C. Wögerbauer, R. Köppel, A. Baiker, *Appl. Catal. B* 19 (1998) 9-22.
- [38] V. Zuzaniuk, F. C. Meunier, J. R. H. Ross, *J. Catal.* 202 (2001) 340-353.
- [39] M. C. Campa, V. Indovina, *J. Porous Mater.* 14 (2007) 251-261.
- [40] D. Kauchy, A. Vondrova, J. Dedecek, B. Wichterlova, *J. Catal.* 194 (2000) 318-329.
- [41] T. Sun, M. L. Trudeau, J. Y. Ying, *J. Phys. Chem.* 100 (1996) 13662-13666.

Figure, table and scheme captions:

Fig. 1 DRIFT spectra of Co-ZSM-5 after exposure to a gas mixture of NO (1000 ppm)/He for 30 min at 200, 250 and 300°C, respectively.

Fig. 2 A: DRIFT spectra of Co-ZSM-5 after exposure to a gas mixture of NO (1000 ppm)+O₂(10%)/He for 30 min at 200, 250, 300, 350 and 400°C, respectively; B: DRIFT spectra of Co-ZSM-5 after exposure to a gas mixture of NO (1000 ppm)+O₂ (10%)/He for 30 min(a), followed by He purge for 10 min(b).

Fig. 3 DRIFT spectra of Co-ZSM-5 after exposure to C₂H₄(1000 ppm)/He (a); C₂H₄(1000 ppm)+O₂(10%)/He (b) for 30 min.

Fig. 4 DRIFT spectra of Co-ZSM-5 after exposure to a flow of NO(1000 ppm)+O₂(10%)/He for 60 min, followed by He purge for 10 min (a), then switched feed gas to C₂H₄(1000 ppm)/He(b), C₂H₄(1000 ppm)+O₂(10%)/He(c) for 30 min. Inset of Fig. 4: DRIFT spectra of Co-ZSM-5 catalyst after exposure to a flow of NO+O₂+C₂H₄/He (a), and after adsorption of gas phase CH₃NO₂ (b), at 300°C.

Fig. 5 DRIFT spectra of Co-ZSM-5 after exposure to a flow of C₂H₄(1000 ppm)+O₂(10%)/He, followed by He purge for 10 min(a), then switched to O₂(10%)/He(b); NO(1000 ppm)+O₂(10%)/He(c); NO (1000 ppm)/He (d)for 30 min.

Fig. 6 DRIFT spectra of Co-ZSM-5 catalyst after exposure to a flow of NO(1000 ppm)+O₂(10%)+C₂H₄ (1000 ppm)/He at different temperatures: (a) 200°C, (b) 250°C, (c) 300°C, (d) 350°C, (e) 400°C.

Fig. 7 DRIFT spectra of CoH-ZSM-5 sample after exposure to a flow of NO+O₂+C₂H₄/He for 60 min, followed by He purge for 10 min (a), and subsequent switch to a flow of NO (1000 ppm)/He (b), to a flow of O₂ (1000 ppm)/He (c), to a flow of NO (1000 ppm) +O₂ (10%)/He (d) for 30 min, respectively.

Fig. 8 The integrated area of bands of surface species versus time after exposure to NO (1000 ppm) + O₂ (10%)/He.

Table 1 Kinetic parameters of the reaction of cyanide and isocyanate species with nitrates over Co-ZSM-5.

Scheme 1 A possible pathway for the formation of formyl nitro compound.

Scheme 2 Proposed reaction pathway for NO reduction in C₂H₄-SCR over Co-ZSM-5 catalyst

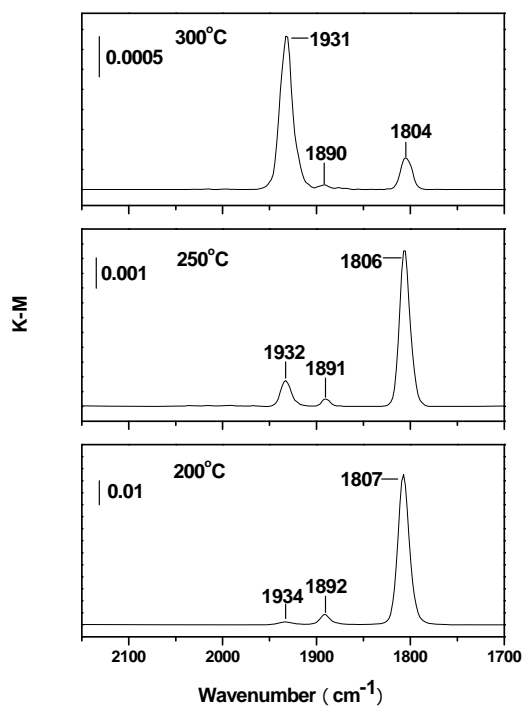


Fig. 1

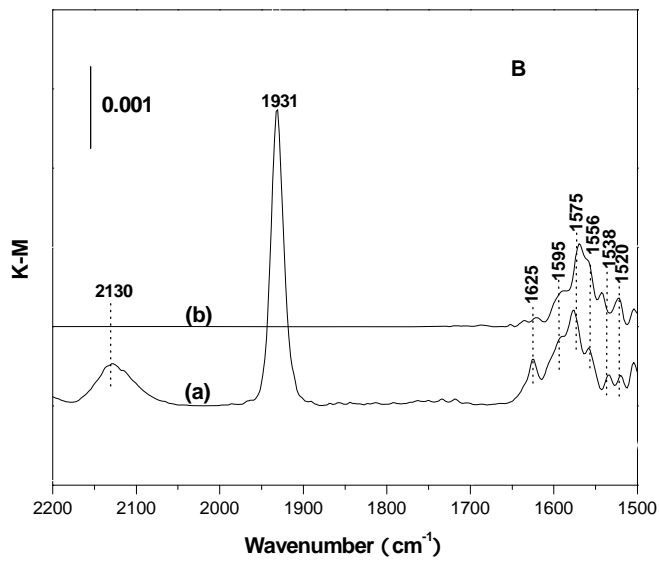
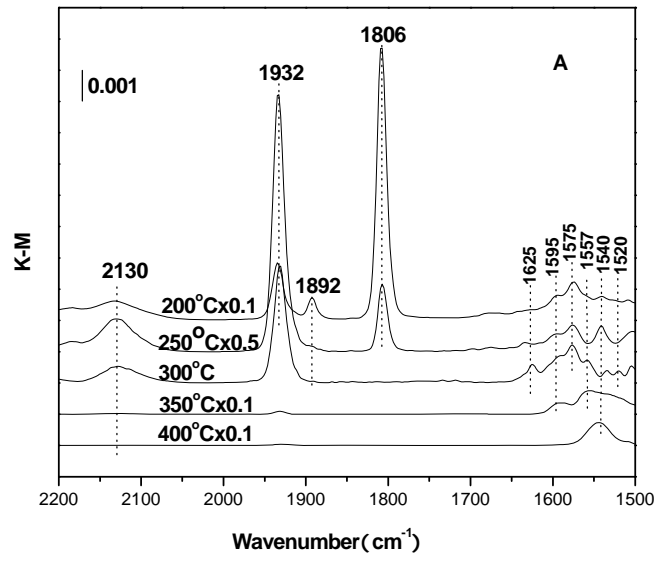


Fig. 2

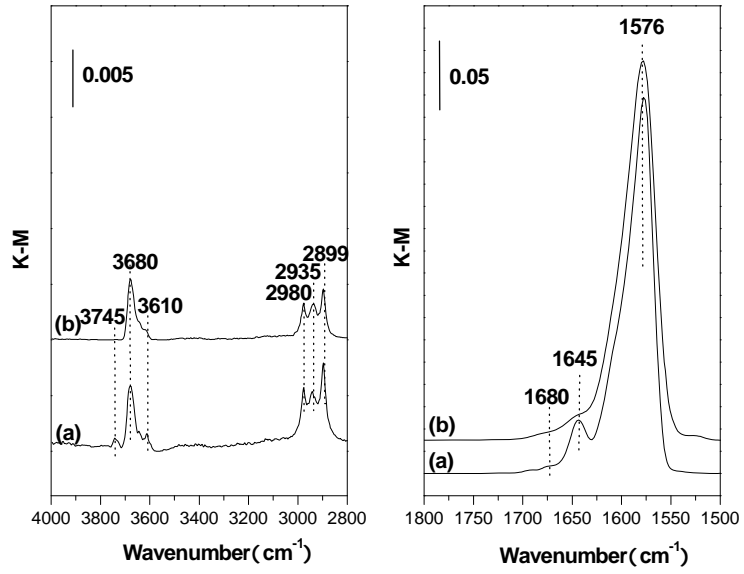


Fig. 3

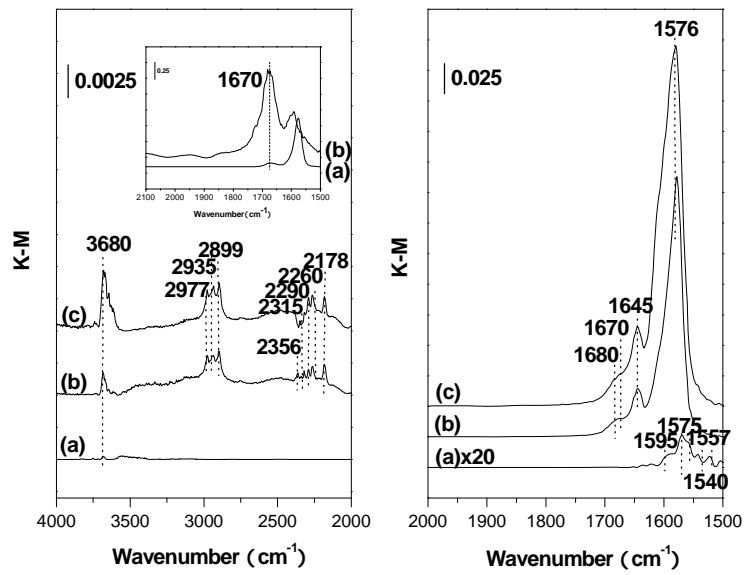


Fig. 4

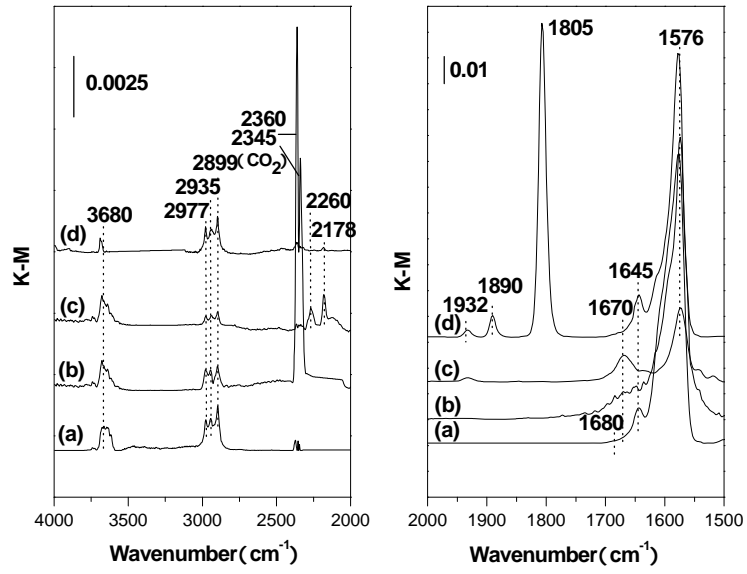


Fig. 5

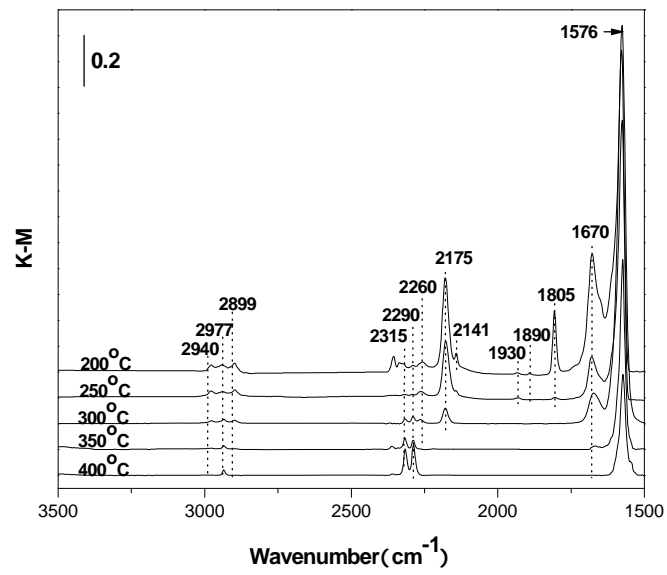


Fig. 6 (°C换成字母)

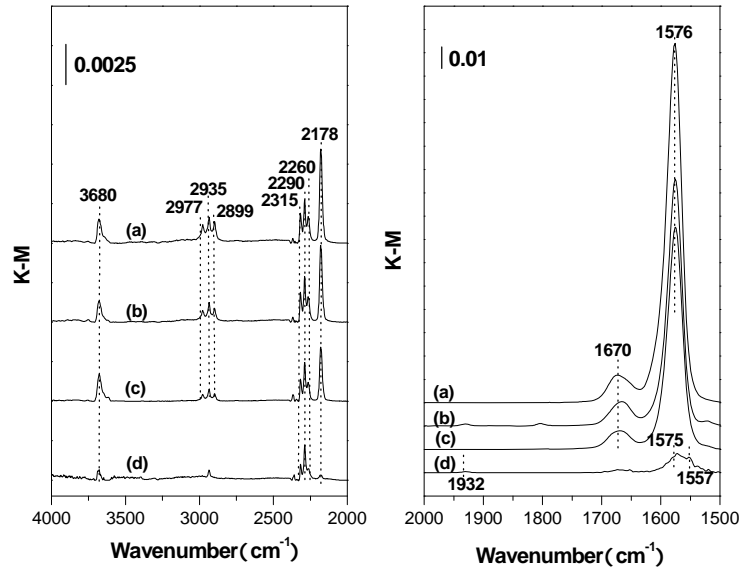


Fig. 7

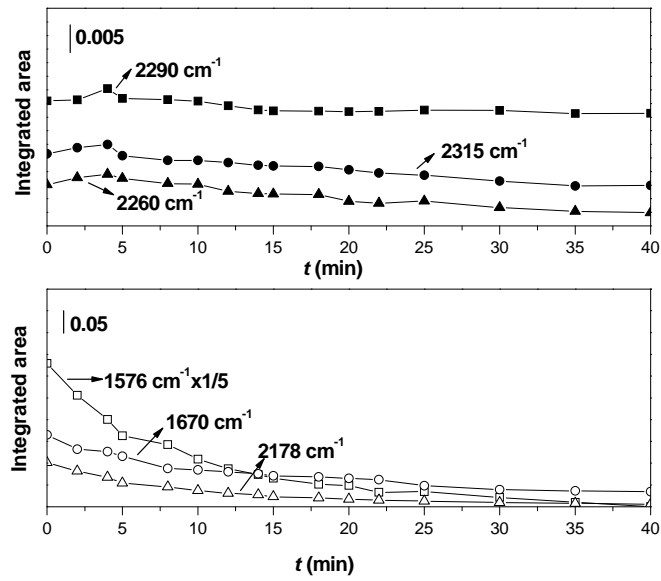
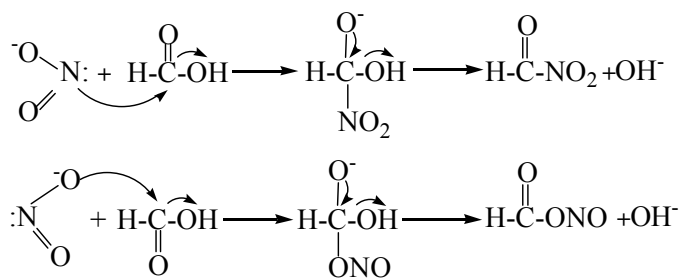


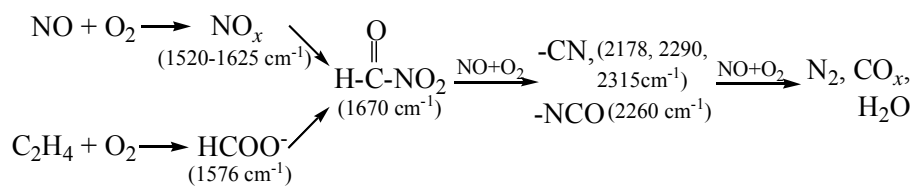
Fig. 8

Table 1

Consumption rate constant of the cyanide and isocyanate compounds, $k(\text{min}^{-1})$				
$T(^{\circ}\text{C})$	2178 cm^{-1} band	2260 cm^{-1} band	2290 cm^{-1} band	2315 cm^{-1} band
250	0.0146	~0	~0	~0
300	0.0768	0.046	0.0042	0.013
320	0.0742	0.0214	0.0045	0.0104
350	0.0842	—	0.0193	0.0181



Scheme 1



Scheme 2

(a) 1st line: "Recently, Savva et al. [29] emphasized ..."

(b) 4th line: "of surface concentration of active NOx but it can be related to the different reactivity ..."