



# An in situ Fourier transform infrared study on the mechanism of NO reduction by acetylene over mordenite-based catalysts

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## ABSTRACT

Selective catalytic reduction of NO with acetylene (C<sub>2</sub>H<sub>2</sub>-SCR) over mordenite-based catalysts (HMOR, 0.5% Mo/HMOR and NaMOR) was investigated by in situ Fourier transform infrared spectroscopy. A possible mechanism was proposed to explain catalytic performance of the mordenite-based catalysts in the C<sub>2</sub>H<sub>2</sub>-SCR: Nitrosonium ions (NO<sup>+</sup>) and bidentate nitrate are reactive nitric species towards acetylene at 250 °C. Isocyanate species thus formed are then hydrolyzed to acid amide species that are crucial intermediate of the C<sub>2</sub>H<sub>2</sub>-SCR. Bridging nitrate species become reactive towards the reductant when reaction temperature increased to 300 °C. Molybdenum loading on HMOR zeolite considerably increased the population of bridging nitrate species and therefore enhanced the title reaction above 300 °C.

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## 1. Introduction

Selective catalytic reduction of NO by hydrocarbons (HC-SCR) in presence of excess oxygen is a potential method to remove NO<sub>x</sub> from lean-burn exhausts [1]. Many kinds of catalysts have been investigated for the HC-SCR in the past years, such as noble-metal (e.g., Pt, Ir) supported catalysts [2,3], base metal oxide catalysts (e.g., Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO) [4,5] promoted by transition metals (e.g., Co, Ni, Cu, Fe, Sn, Ga, In, Ag) and zeolite-based catalysts (e.g., HZSM-5 doped by Co, Cu, Ce or MoO<sub>3</sub> [6–9], CuSAPO-5 [10], NiNaMOR [11], In-HBEA [12]). For all of the catalysts, no-one of them is sufficiently active, selective towards the desired reaction over a wide temperature range, as required by the practical application [2], despite some interesting results concerning the catalyst have been obtained.

To design a catalyst more active for the HC-SCR in real lean-burn conditions, extensive studies were also carried out on mechanism of the reaction. There have been different opinions concerning the mechanism of HC-SCR in literature, which can be roughly classified as “dissociative” [13,14] and “reduction” ones [11,15,16]. The “dissociative” mechanism proposed by Burch and Watling [14] has been widely accepted by the authors being concerned with noble metal catalysts in the HC-SCR field, and it can be expressed as follows [13]:



For the “reduction” mechanism of HC-SCR, some authors have claimed that activation of hydrocarbon occurs first, and some partially oxidized hydrocarbons (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>) produced by the step then react with NO and/or NO<sub>2</sub> to form the secondary intermediates [17]. For example, formate and acetate were proposed to be active species of HC-SCR over CoO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> [18], Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [19], Ag/Al<sub>2</sub>O<sub>3</sub> [4], SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [20], Cu–Al<sub>2</sub>O<sub>3</sub> catalysts [5,21], In<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [22], Ag/Al<sub>2</sub>O<sub>3</sub> [23] and Pd/Al<sub>2</sub>O<sub>3</sub> [24]. Acetaldehyde derived from propene was also proposed to be main active species of the HC-SCR over sulfated titania-supported rhodium catalyst [25]. However, some authors have claimed that activation of NO<sub>x</sub> occurs first, forming nitrous surface species, such as nitro [26], nitroso [8,27], nitrosonium ions [27,28], nitrate or nitrite [12,22] over the catalyst. For instance, bridging and bidentate nitrates were reported to be produced first by co-adsorption of NO + O<sub>2</sub> on Co/SO<sub>4</sub><sup>2-</sup>-ZrO<sub>2</sub> [29], BaY [30] and Ag/Al<sub>2</sub>O<sub>3</sub> [31]. Tsyntsarski et al. [29] have suggested that both bridging and bidentate nitrates are active species of the HC-SCR. Mihaylov et al. [16] have reported that monodentate nitrates on Ni-HZSM-5 are highly reactive towards methane. Lónyi et al. [32] have studied selective catalytic reduction of NO by CH<sub>4</sub> over Co-, Co,Pt-, and H-mordenite catalysts and suggested that nitrosonium ions are surface intermediates of the reaction. There are also some other suggestions about the reaction intermediate of HC-SCR in literature, including nitrile [8,33], isocyanate [11,16,18], R–NO<sub>x</sub> [6,11], amine [8], acetonoxime [34,35] and ammonia [32].

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Although most of the “reduction” mechanisms were supported by Fourier transform infrared (FTIR) identification of reaction intermediates [2], none of them has been widely accepted because of the complexity of the process [11] being concerned with different catalysts, reductants and reaction conditions. More investigation on the reaction mechanism is required for understanding the real reaction route of HC-SCR over different catalysts and reductants.

In the present work, selective catalytic reduction of NO with acetylene ( $C_2H_2$ -SCR) over mordenite-based catalysts was investigated by in situ FTIR. A possible mechanism was proposed to explain the behavior of the catalysts in the  $C_2H_2$ -SCR.

## 2. Experimental

### 2.1. Catalyst preparation

Mordenite in ammonium form ( $NH_4MOR$ ), supplied by Zeolyst Co. (America), was used as parent material. The fresh sample has a surface area of  $500\text{ m}^2/\text{g}$  and a  $SiO_2/Al_2O_3$  ratio of 20. Mordenite in H form (HMOR) was obtained by calcining the  $NH_4MOR$  at  $500^\circ\text{C}$  in air for 5 h. To obtain NaMOR zeolite, 4 g of HMOR was stirred in 20 ml of 1.0 M  $NaNO_3$  aqueous solution at  $80^\circ\text{C}$  for 10 h, then filtered, rinsed in deionized water, dried at  $120^\circ\text{C}$  overnight and calcined at  $500^\circ\text{C}$  in air for 5 h. The procedure was repeated three times to ensure that most of the protons in the HMOR were exchanged by sodium ions. 0.5% Mo/HMOR catalyst containing 0.5% of molybdenum in weight, was prepared by impregnation of the HMOR in ammonium heptamolybdate ( $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ ) aqueous solution overnight. The resulting sample was dried at  $120^\circ\text{C}$  for 5 h and calcined at  $500^\circ\text{C}$  in air for 5 h.

All of the catalyst samples were pressed into pellets, crushed and sieved to 20–40 meshes before use.

### 2.2. In situ FTIR measurements

In situ FTIR studies were carried out in a quartz IR cell equipped with  $CaF_2$  windows on a Nicolet 360 FTIR spectrophotometer. Prior to each experiment, the catalyst was pressed into a self-supporting wafer, pretreated at  $500^\circ\text{C}$  in  $N_2$  for 30 min, and then cooled to desired temperature in order to record a reference spectrum ( $S_r$ ). IR absorption arising from each gas mixture ( $S_g$ ) in the cell without catalyst sample was also recorded at the temperature. In situ FTIR spectra of surface species were obtained by subtracting the corresponding  $S_g$  and  $S_r$  from each spectrum. All spectra given in the figures were taken at a resolution of  $2\text{ cm}^{-1}$  for 32 scans. A nitrogen stream containing 1000 ppm NO + 10%  $O_2$ , or 500 ppm  $C_2H_2$  + 10%  $O_2$  were used for co-adsorption of reactants.

### 2.3. Catalytic activity test

$C_2H_2$ -SCR over the catalysts (0.1 g for HMOR and 0.5% Mo/HMOR, 0.2 g for NaMOR) was carried out at atmospheric pressure. The gas mixture composed of 1600 ppm NO, 800 ppm  $C_2H_2$ , and 9.95%  $O_2$  in He was passed through a quartz reactor (4 mm i.d.) at a total flow rate of 50 ml/min.  $N_2$  produced during the reaction was used to calculate the conversion of NO, which was analyzed by gas chromatography (HP6890) using a capillary column (HP-PLOT/zeolite,  $30\text{ m} \times 0.32\text{ mm}$ ,  $12\text{ }\mu\text{m}$ ) and TCD at  $50^\circ\text{C}$ . In the reaction, a nitrogen balance about 95% was obtained. No nitrogen containing species (including  $N_2O$ ) other than  $N_2$  and a little amount NO in the outlet of the reactor was detected by the GC.

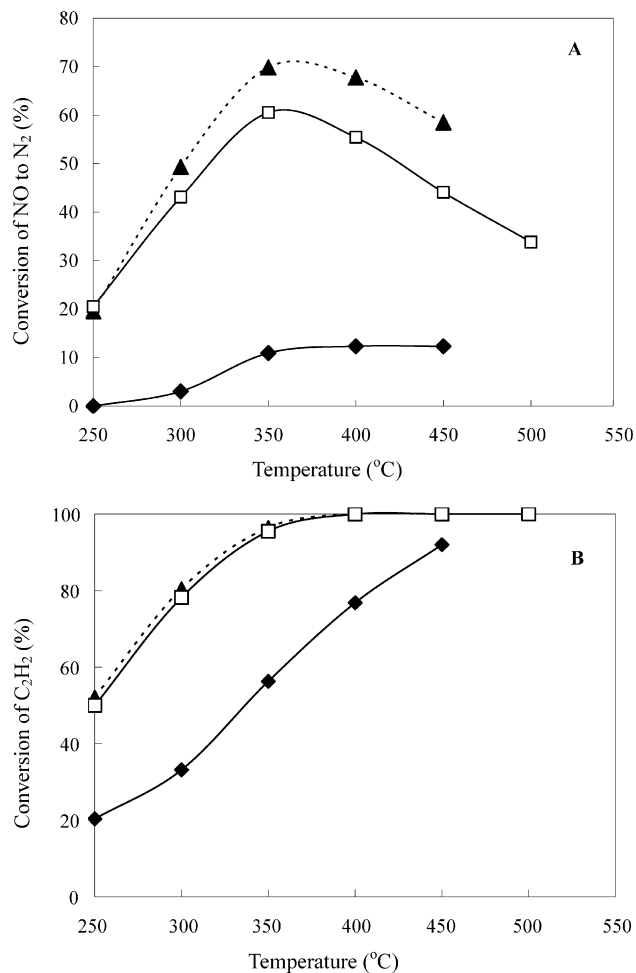


Fig. 1. Conversion of NO (A) and  $C_2H_2$  (B) as a function of reaction temperature in  $C_2H_2$ -SCR. Reaction condition: 1600 ppm NO, 800 ppm  $C_2H_2$ , 9.95%  $O_2$  in He with a total flow rate of 50 ml/min over HMOR 0.100 g (□), 0.5% Mo/HMOR 0.100 g (▲) or NaMOR 0.200 g (◆).

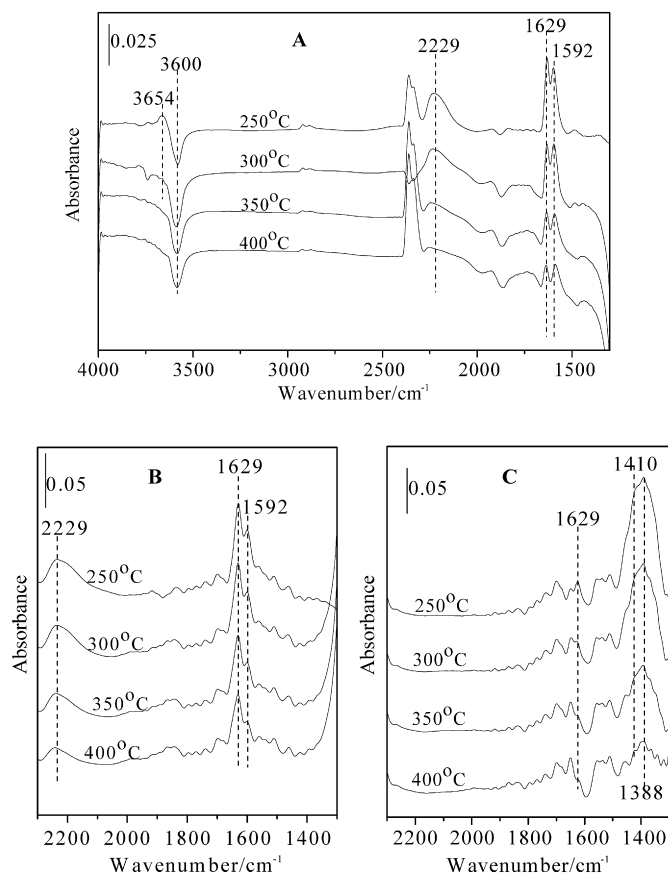
## 3. Results and discussion

### 3.1. Catalytic activity

Fig. 1 shows conversion of NO and  $C_2H_2$  in  $C_2H_2$ -SCR over the mordenite-based catalysts (HMOR, 0.5% Mo/HMOR, NaMOR) as a function of temperature. The activity of 0.5% Mo/HMOR for  $C_2H_2$ -SCR was considerably high compared to HMOR and NaMOR. 70% of NO conversion to  $N_2$  at  $350^\circ\text{C}$  over 0.5% Mo/HMOR catalyst was obtained. It indicates that molybdenum has a significant promotional effect on  $C_2H_2$ -SCR. For NO reduction by methane, decane or propene over HMOR zeolite, similar promotional effect of Co [36], Cu [37] and Ni [11,38] in temperature range  $450$ – $500^\circ\text{C}$  was reported. Obviously, the temperature ( $350^\circ\text{C}$ ) where the maximum NO conversion to  $N_2$  was obtained over 0.5% Mo/HMOR was lower than those reported in literature. The peak of the “volcano” curve in NO conversion to  $N_2$  versus reaction temperature seems to be in line with the temperature where  $C_2H_2$  was nearly completely consumed. Hence, the drop of NO conversion above  $350^\circ\text{C}$  can be considered arising from the lack of reductant.

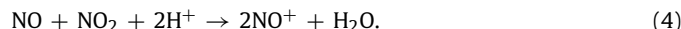
### 3.2. Nitric species on different mordenite-based catalysts

Fig. 2 shows steady state in situ FTIR spectra of nitric species formed by NO +  $O_2$  co-adsorption on the mordenite-based catalysts



**Fig. 2.** Steady state in situ FTIR spectra of surface species on HMOR (A), 0.5% Mo/HMOR (B) and NaMOR (C) in 1000 ppm NO + 10% O<sub>2</sub> + N<sub>2</sub> at different temperature.

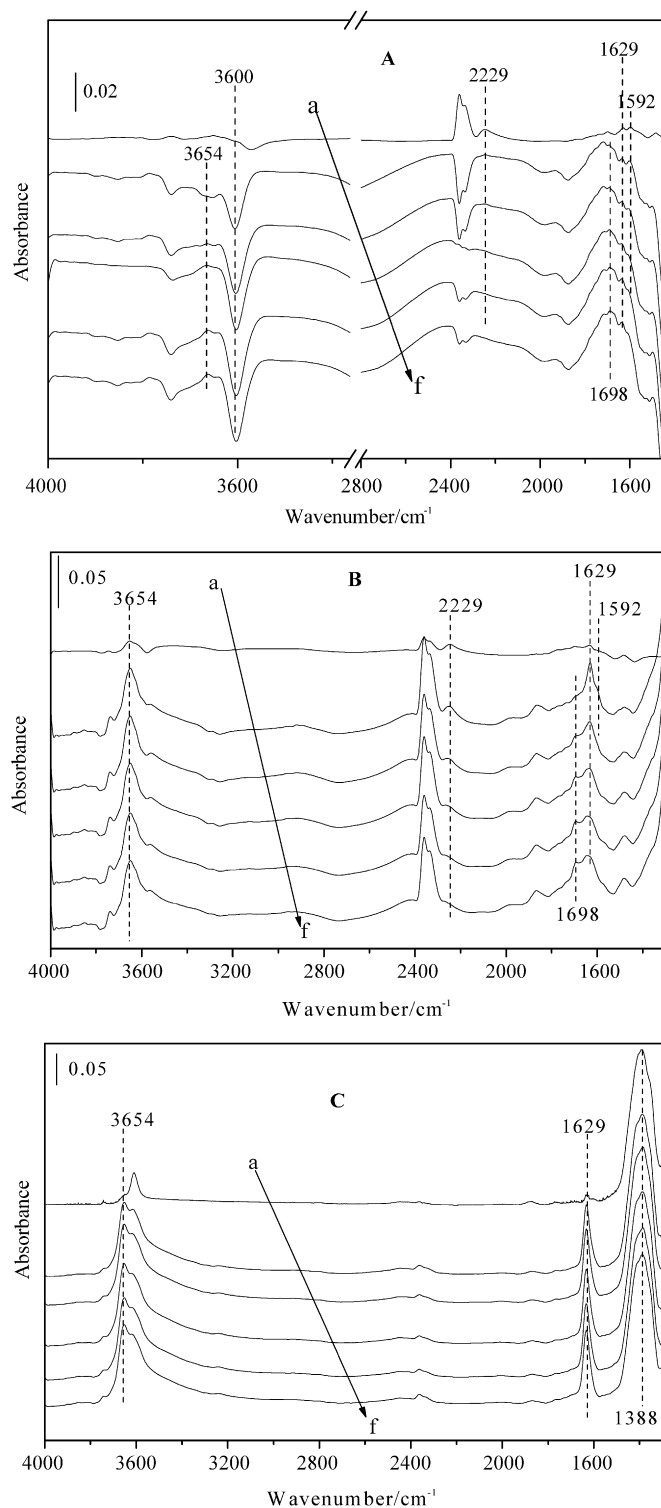
at different temperatures. Three main bands at 2229, 1629 and 1592 cm<sup>-1</sup> associated with nitric species were observed on HMOR (Fig. 2A). The band at 2229 cm<sup>-1</sup> is due to N–O stretching mode in NO<sup>+</sup> [27,39,40], and the bands at 1629 and 1592 cm<sup>-1</sup> can be assigned to bridging and bidentate nitrates [8,30,40,41], respectively. The NO<sup>+</sup> (2229 cm<sup>-1</sup>) species was also detected by Gerlach et al. [27] at 120 °C when NO<sub>x</sub> was adsorbed on the zeolite. As shown in Fig. 2A, a positive band at 3654 cm<sup>-1</sup> due to adsorbed water [16,43] and a negative band at 3600 cm<sup>-1</sup> due to Brønsted acid sites [16,44] were observed after co-adsorption of NO and O<sub>2</sub> on the zeolite at 250 °C. It can be well interpreted by the NO<sup>+</sup> formation pathway proposed by Hadjiivanov et al. [42] and Gerlach et al. [27]:



Band at 1629 cm<sup>-1</sup> due to bridging nitrate and band at 2229 cm<sup>-1</sup> due to NO<sup>+</sup> on 0.5% Mo/HMOR are obviously greater in intensity respectively compared to those on HMOR, particularly above 300 °C. It indicates that molybdenum loading on the HMOR zeolite have a promotional effect on the nitric species formation at higher temperature. On NaMOR (Fig. 2C), band (1629 cm<sup>-1</sup>) due to this type of bridging nitrate was rather weak, and bands due to bidentate nitrates (1592 cm<sup>-1</sup>) and NO<sup>+</sup> species (2229 cm<sup>-1</sup>) even could not be observed. Instead, a broad band at 1410–1388 cm<sup>-1</sup> due to nitrate ions attached to Na<sup>+</sup> sites [16,40,41] appeared after NO + O<sub>2</sub> co-adsorption on the sample under same condition.

### 3.3. Reactivity of the nitric species

Reactivity of the nitric species towards C<sub>2</sub>H<sub>2</sub> + O<sub>2</sub> over the mordenite-based catalysts was examined by in situ FTIR at 250 °C



**Fig. 3.** In situ FTIR spectra on HMOR (A), 0.5% Mo/HMOR (B) and NaMOR (C) at 250 °C: a brief evacuation after saturation adsorption of NO + O<sub>2</sub> (a), and subsequently exposing to C<sub>2</sub>H<sub>2</sub> + O<sub>2</sub> for: 1 min (b), 3 min (c), 5 min (d), 8 min (e), 30 min (f).

(Fig. 3). When C<sub>2</sub>H<sub>2</sub> + O<sub>2</sub> was introduced into the FTIR cell, bands due to bidentate nitrates (1592 cm<sup>-1</sup>) and NO<sup>+</sup> species (2229 cm<sup>-1</sup>) on HMOR arose from NO + O<sub>2</sub> pre-adsorption (Fig. 3A) rapidly decreased. Concomitantly, a new band at 1698 cm<sup>-1</sup> appeared and reached its maximum intensity within 3 min with disappearance of bands at 2229 and 1592 cm<sup>-1</sup>. Similar result was obtained when C<sub>2</sub>H<sub>2</sub> was used instead of C<sub>2</sub>H<sub>2</sub> + O<sub>2</sub> in the above

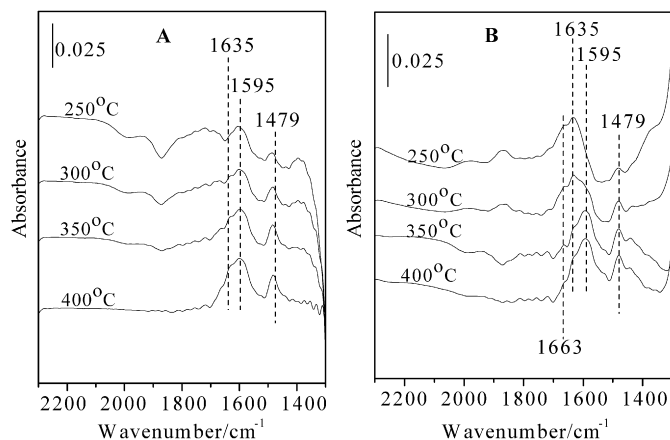


Fig. 4. Steady state in situ FTIR spectra of adsorbed species in 500 ppm  $C_2H_2$  + 10%  $O_2$  +  $N_2$  on HMOR (A), 0.5% Mo/HMOR (B) at different temperature.

experiment. The results indicate that  $NO^+$  and bidentate nitrate species are fairly reactive towards acetylene at this temperature. It was evidenced by the following change of bands associated with water formation during the process: A positive band at  $3654\text{ cm}^{-1}$  due to water appeared, and at the same time, a negative band at  $3600\text{ cm}^{-1}$  arose from water adsorption on Brønsted acid sites correspondingly increased in intensity. Unfortunately, the corresponding reactivity of bridging nitrate species ( $1629\text{ cm}^{-1}$ ) could not be directly evaluated on the zeolite because of water formation. The band due to bending mode of water appears at the identical wave number with that of bridging nitrate species at  $1629\text{ cm}^{-1}$ . Similar experimental results as that on HMOR was obtained on 0.5% Mo/HMOR (Fig. 3B). However, quite different results were obtained on NaMOR. The nitrate species attached to  $Na^+$  seem to be completely inert towards the reactant. No change in intensity of band at  $1388\text{ cm}^{-1}$  due to the species could be observed on NaMOR (Fig. 3C). Meanwhile, as expected, band at  $1698\text{ cm}^{-1}$  did not appear on NaMOR. Instead, strong bands at  $3654$  and  $1629\text{ cm}^{-1}$  due to water adsorbed on the Na-form zeolite were observed, which may simply result from combustion of acetylene.

### 3.4. Species with band at $1698\text{ cm}^{-1}$

Fig. 4 shows steady state in situ FTIR spectra of the surface species on HMOR and 0.5% Mo/HMOR in gas mixture of 500 ppm  $C_2H_2$  + 10%  $O_2/N_2$  at different temperatures. No band at  $1698\text{ cm}^{-1}$  could be observed on the catalysts. Instead, bands at  $1635$ ,  $1595$  and  $1479\text{ cm}^{-1}$  due to  $\nu(C=O)$ ,  $\nu_{as}(COO)$  and  $\nu_s(COO)$  of carboxylic groups [42,45] appeared. Combined the result with that observed in Fig. 3, the band at  $1698\text{ cm}^{-1}$  can be attributed to nitrogen containing organic species, because this band could appear only in the following conditions: both the nitric species (nitrogen oxides and/or nitric surface species) and the reductant were present together in the reaction system.

Fig. 5 shows the steady state in situ FTIR reaction spectra of the surface species on HMOR and 0.5% Mo/HMOR in gas mixture of 1000 ppm  $NO$  + 500 ppm  $C_2H_2$  + 10%  $O_2/N_2$  at different temperatures. Two overlapped bands respectively centered at  $2242$  and  $2208\text{ cm}^{-1}$  were appeared in the spectra, in addition to the bands at  $1698$ ,  $1629$  and  $1592\text{ cm}^{-1}$ . The band at  $2242\text{ cm}^{-1}$  can be assigned to  $-NCO$  vibration of isocyanate ( $2242\text{ cm}^{-1}$ ) [21,46] and that at  $2208\text{ cm}^{-1}$  can be assigned to  $N-O$  stretching of  $NO^+$  [27,39]. It was reported that the stretching frequency of  $NO^+$  on HMOR is influenced by an interaction between  $NO^+$  and some other surface species formed on the zeolite [27]. Herein, it should be noticed that although the band at  $1698\text{ cm}^{-1}$  for 0.5% Mo/HMOR (spectrum a) was slightly weaker

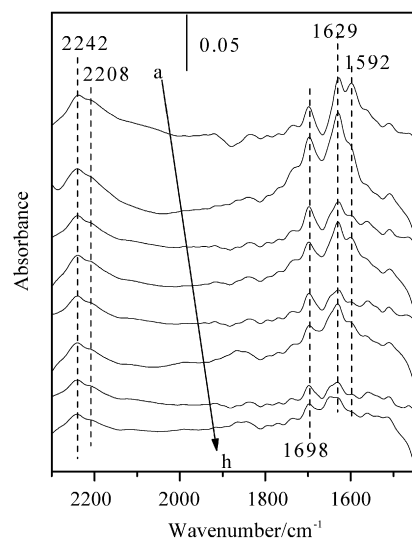


Fig. 5. Steady state in situ FTIR spectra of adsorbed species on 0.5% Mo/HMOR in gas mixture of 1000 ppm  $NO$  + 500 ppm  $C_2H_2$  + 10%  $O_2$  +  $N_2$  at  $250^\circ\text{C}$  (a),  $300^\circ\text{C}$  (c),  $350^\circ\text{C}$  (e),  $400^\circ\text{C}$  (g) and that on HMOR at  $250^\circ\text{C}$  (b),  $300^\circ\text{C}$  (d),  $350^\circ\text{C}$  (f),  $400^\circ\text{C}$  (h).

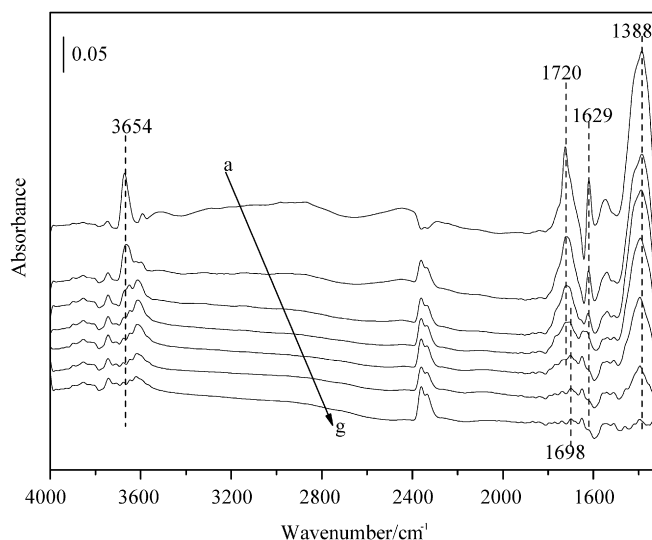
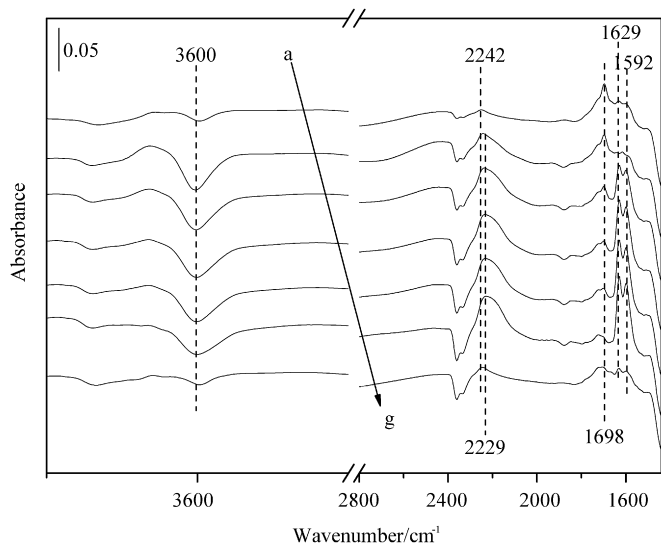


Fig. 6. Steady state in situ FTIR spectra of adsorbed species in gas mixture of 1000 ppm  $NO$  + 500 ppm  $C_2H_2$  + 10%  $O_2$  +  $N_2$  on NaMOR at different temperature:  $150^\circ\text{C}$  (a),  $200^\circ\text{C}$  (b),  $250^\circ\text{C}$  (c),  $300^\circ\text{C}$  (d),  $350^\circ\text{C}$  (e),  $400^\circ\text{C}$  (f),  $450^\circ\text{C}$  (g).

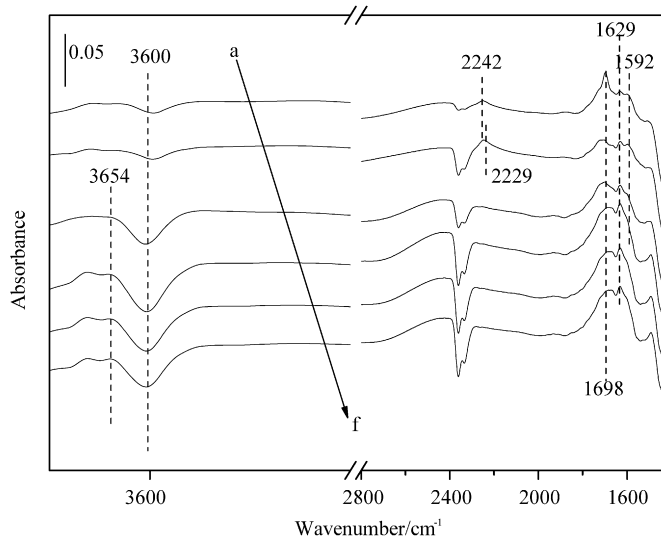
in intensity in comparison with that of HMOR (spectrum b) at  $250^\circ\text{C}$ , it became much stronger than that on of HMOR above  $300^\circ\text{C}$ . The relative intensity of the band observed on HMOR and 0.5% Mo/HMOR at different temperatures could be correlated well with the relative activity of the catalysts for  $C_2H_2$ -SCR (Fig. 1). Good accordance of  $NO$  reduction with the band at  $1698\text{ cm}^{-1}$  could also be obtained on NaMOR (Fig. 6). The band at  $1698\text{ cm}^{-1}$  just appeared at the temperature (spectrum e), where  $NO$  conversion to  $N_2$  became significant over the zeolite in  $C_2H_2$ -SCR. Based on the above findings, we believe that the species with the band at  $1698\text{ cm}^{-1}$  is a crucial intermediate for  $C_2H_2$ -SCR over the mordenite-based catalysts.

To further study the reaction route of  $C_2H_2$ -SCR over the catalysts, reactivity of the intermediate ( $1698\text{ cm}^{-1}$ ) was investigated. After a pre-exposure of HMOR to 1000 ppm  $NO$  + 500 ppm  $C_2H_2$  + 10%  $O_2/N_2$  at  $250^\circ\text{C}$  and a followed brief evacuation, then the catalyst was exposed to gas mixture of 1000 ppm  $NO$  + 10%  $O_2/N_2$ . As a result, the intensity of the band at  $1698\text{ cm}^{-1}$  rapidly



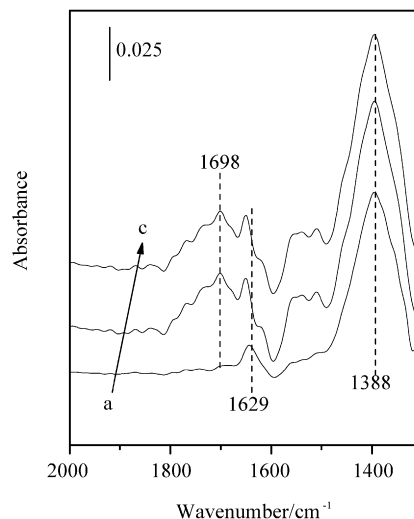


**Fig. 7.** In situ FTIR spectra of surface species on HMOR at 250 °C: a brief evacuation after a pre-exposure of the catalyst to NO + C<sub>2</sub>H<sub>2</sub> + O<sub>2</sub> for 30 min (a), and then when the catalyst was exposed to NO + O<sub>2</sub> for: 1 min (b), 3 min (c), 5 min (d), 8 min (e), 30 min (f), and finally evacuated briefly (g).



**Fig. 8.** FTIR spectra of the surface species on HMOR at 250 °C: a brief evacuation after exposing the catalyst to NO + C<sub>2</sub>H<sub>2</sub> + O<sub>2</sub> for 30 min (a), a brief evacuation after exposing the catalyst to NO + O<sub>2</sub> for 30 min (b), then exposed the catalyst to C<sub>2</sub>H<sub>2</sub> + O<sub>2</sub> for 1 min (c), 3 min (d), 5 min (e), 30 min (f).

decreased (Fig. 7, spectrum a). It indicates that the intermediate is rather reactive towards NO + O<sub>2</sub> at the temperature. On the other hand, no decrease in intensity of the band at 2242 cm<sup>-1</sup> due to -NCO species could be observed during the period (Fig. 7), indicating that -NCO species is inert towards NO + O<sub>2</sub>. When the sample was then exposed to gas mixture of 500 ppm C<sub>2</sub>H<sub>2</sub> + 10% O<sub>2</sub> in N<sub>2</sub>, as shown in Fig. 8 (spectra c–f), the bands both at 2242 cm<sup>-1</sup> due to -NCO and at 2229 cm<sup>-1</sup> due to NO<sup>+</sup> disappeared within one minute. Concomitantly, a band at 1698 cm<sup>-1</sup> and bands at 3654 and 1629 cm<sup>-1</sup> due to adsorbed water appeared. It should be noticed that the intensity of the three bands as well as that of the negative band at 3600 cm<sup>-1</sup> continued to increase within three minutes. The result agrees well with the proposition in literature that isocyanate species can be easily hydrolyzed to amines [8,47]. Thus, the band at 1698 cm<sup>-1</sup> can be reasonably assigned to acid amide species on the zeolite. It is in accordance with that reported by Poignant et al. [8], who found the species with band



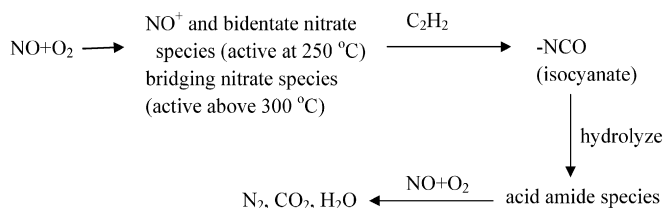
**Fig. 9.** In situ FTIR spectra of surface species on NaMOR at 350 °C: the catalyst was subjected a brief evacuation after saturation adsorption of 1000 ppm NO and 10% O<sub>2</sub> in N<sub>2</sub> (a), and then exposed to 500 ppm C<sub>2</sub>H<sub>2</sub> + 10% O<sub>2</sub>/N<sub>2</sub> for 1 min (b), 10 min (c).

at 1694 cm<sup>-1</sup> in reaction of NO + C<sub>3</sub>H<sub>8</sub> + O<sub>2</sub> over HZSM-5 at 350 °C.

### 3.5. Reactivity of bridging nitrate towards acetylene

In Fig. 2, we showed that molybdenum loading on HMOR zeolite considerably promoted the formation of bridging nitrate species. However, neither higher NO conversion to N<sub>2</sub> in C<sub>2</sub>H<sub>2</sub>-SCR nor stronger band due to the acid amide species (1698 cm<sup>-1</sup>) could be observed on 0.5% Mo/HMOR compared to HMOR at 250 °C. It leads us to speculate that bridging nitrate species (1629 cm<sup>-1</sup>) may make no contribution to C<sub>2</sub>H<sub>2</sub>-SCR at the lower temperature (<250 °C) over the mordenite-based catalysts. The speculation was validated by the following experimental result: Although the bridging nitrate species (1629 cm<sup>-1</sup>) was detected by FTIR after co-adsorption of NO + O<sub>2</sub> on NaMOR at 250 °C (Fig. 2C, spectrum a), no NO conversion to N<sub>2</sub> could be obtained at the temperature (Fig. 1).

Above 300 °C, both C<sub>2</sub>H<sub>2</sub>-SCR activity (Fig. 1) and the intensity of the band due to acid amide species detected by FTIR (1698 cm<sup>-1</sup>, in Fig. 5) were larger for 0.5% Mo/HMOR compared to HMOR, which corresponds well with the larger population of bridging nitrate species (1629 cm<sup>-1</sup>, in Fig. 2) given by 0.5% Mo/HMOR in comparison with HMOR at the temperature. The results indicate that bridging nitrate species (1629 cm<sup>-1</sup>) are also involved in C<sub>2</sub>H<sub>2</sub>-SCR at higher temperature. Same conclusion can be drawn on NaMOR. The band at 1629 cm<sup>-1</sup> due to bridging nitrate species arose from NO + O<sub>2</sub> pre-adsorption on the zeolite at 350 °C (Fig. 9, spectrum a) rapidly disappeared when gas mixture of 500 ppm C<sub>2</sub>H<sub>2</sub> + 10% O<sub>2</sub>/N<sub>2</sub> was introduced to the FTIR cell at this temperature. Correspondingly, band at 1698 cm<sup>-1</sup> due to acid amide species appeared (Fig. 9, spectrum b). No change of the band at 1388 cm<sup>-1</sup> in intensity could be observed during this procedure. The results again indicate that bridging nitrate species are involved in the desired reaction at the higher temperature, whereas nitrate species attached to Na<sup>+</sup> have no contribution to C<sub>2</sub>H<sub>2</sub>-SCR under the reaction condition. It explains why the C<sub>2</sub>H<sub>2</sub>-SCR activity of NaMOR became significant when the reaction temperature increased to 350 °C. Thus, the considerably larger activity of 0.5% Mo/HMOR compared to HMOR for C<sub>2</sub>H<sub>2</sub>-SCR above 300 °C (Fig. 1) can be rationally attributed to the larger bridging nitrate formation capacity of the catalyst than HMOR.



**Scheme 1.** A possible reaction pathway of the  $\text{C}_2\text{H}_2$ -SCR over the mordenite-based catalysts.

### 3.6. A possible reaction mechanism of $\text{C}_2\text{H}_2$ -SCR over the mordenite-based catalysts

On the basis of above discussion, a possible reaction mechanism of  $\text{C}_2\text{H}_2$ -SCR over the mordenite-based catalysts can be outlined in Scheme 1. Nitrosonium ions ( $\text{NO}^+$ ), bidentate and bridging nitrate species formed by  $\text{NO} + \text{O}_2$  co-adsorption react first with  $\text{C}_2\text{H}_2$ , leading to isocyanate species ( $2242 \text{ cm}^{-1}$ ) formation. The isocyanate species is then rapidly hydrolyzed to the acid amide species ( $1698 \text{ cm}^{-1}$ ) that is a crucial intermediate for  $\text{C}_2\text{H}_2$ -SCR over the mordenite-based catalysts.

## 4. Conclusions

For  $\text{C}_2\text{H}_2$ -SCR over the mordenite-based catalysts, following conclusions can be drawn: The nitric species, including nitrosonium ions ( $\text{NO}^+$ ) and bidentate nitrate, are fairly active towards the desired reduction in the temperature range of  $250\text{--}450 \text{ }^\circ\text{C}$ . However, bridging nitrate species begin to make its significant contribution to the reaction above  $300 \text{ }^\circ\text{C}$ . Molybdenum incorporated into HMOR zeolite considerably improved the bridging nitrate formation capacity of the catalyst. It explains the promotional effect of molybdenum on  $\text{C}_2\text{H}_2$ -SCR at the higher temperatures. Isocyanate ( $-\text{NCO}$ ), as an active species produced from the reaction of the nitric species with  $\text{C}_2\text{H}_2$ , can be rapidly hydrolyzed to the acid amide species ( $1698 \text{ cm}^{-1}$ ) that is a crucial intermediate for  $\text{C}_2\text{H}_2$ -SCR over the mordenite-based catalysts.

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