



Defect of HY as catalyst for selective catalytic reduction of NO in comparison with the pentasil zeolites

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ABSTRACT

The specific behavior of HY in some steps that possibly occurred in the selective catalytic reduction of NO by hydrocarbon (HC-SCR) was investigated. Experimental results indicated that the activity of HY for NO oxidation to NO₂ was much lower than those of the pentasil zeolites (HZSM-5, HFER and HMOR). In addition, FTIR measurements showed that both nitrosonium ions (NO⁺) and nitrate species were remarkably produced at 300 °C over the pentasil zeolites and they were highly active towards hydrocarbons at the temperature. On the contrary, no NO⁺ species could be detected over HY and the nitrate species produced over the zeolite were almost inactive towards reduction at the same reaction condition. It is proposed that the low amount of strong Brønsted acids of HY accounts for the above inferior functions of the zeolite required by HC-SCR, leading to the low NO reduction activity.

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1. Introduction

Selective catalytic reduction of NO by hydrocarbons (HC-SCR) in the presence of excess oxygen seems to be a feasible method to reduce NO_x emission from lean burn and diesel exhaust [1–4]. Since the pioneering work of Iwamoto et al. [5] and Held et al. [6], zeolite-based catalysts have been extensively studied on HC-SCR [7–10], due to their high selectivity towards the aimed reaction at low temperature. Up to now, many zeolites have been investigated as catalysts for the reactions. However, it seems that only limited types of zeolites including ZSM-5 [9,11–15], ferrierite [16–19] and mordenite [20–24], which are called as pentasil zeolites, displayed high selectivity to NO_x reduction in HC-SCR. For instance, Pieterse et al. [25] investigated the selective catalytic reduction of NO by methane (CH₄-SCR) over several zeolite-based catalysts and reported the activity order of Co-Pd-ZSM-5 > Co-Pd-MOR > Co-Pd-FER > Co-Pd-BEA. Sultana et al. [26] also found that the zeolites ordered in Pt-MOR (90%) > Pt-FER (77%) > Pt-ZSM-5 (74%) > Pt-BEA (70%) > Pt-HY (63%) in terms of NO conversion for the HC-SCR at ~300 °C using diesel as reductant. These results representing the catalytic performance of Y inferior to those of the pentasil zeolites in HC-SCR agreed well with the order of CuMFI (58%) > CuMOR (43%) > CuY (20%) reported by Torre-Abreu et al. [27] for selective

catalytic reduction of NO by propene (C₃H₆-SCR) at 400 °C. For the selective catalytic reduction of NO by propane (C₃H₈-SCR) assisted by H₂, a similar order of Ag-MFI (56%) > Ag-BEA (38%) > Ag-MOR (11%) << Ag-Y (2%) in NO conversion was obtained by Shibata et al. [28] at ~300 °C. Also, it was reported that Co-ZSM-5 [29] and Ni-ZSM-5 [30] were more active than the corresponding Co and Ni promoted Y zeolite in CH₄-SCR. Clearly, the pentasil zeolites exhibited higher catalytic activity for HC-SCR compared to Y zeolite.

Nevertheless, it seems that the gas hourly space velocity (GHSV) employed by the authors, at which high N₂ conversion level could be achieved over the pentasil zeolite-based catalysts [10–30], is far lower than that required by practical application. As is well known, the practical process for NO removal from lean burn and diesel exhaust needs a monolith catalyst working at 40,000–80,000 h⁻¹ that requires a real catalyst working well at a GHSV of 200,000–400,000 h⁻¹, out of consideration for engineering. Therefore, the NO removal activity of the catalysts must be largely enhanced to meet the application requirement.

Doping micro-zeolites was generally considered as a way to increase the catalytic activity of zeolites. However, the dynamic investigation results seem to be against the way for the catalysts used in HC-SCR. Shichi and co-workers [31–35] have emphasized intracrystalline diffusion of reductants limited by the zeolites' channels, based on their investigation results. They found that NO conversion over MFI and MOR appeared to be significantly influenced by both hydrocarbon molecular size and zeolite particle size in some instances. In our previous investigation of HC-SCR using

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acetylene as reductant (C_2H_2 -SCR), we found that the C_2H_2 -SCR over HZSM-5 is greatly affected by the intracrystalline diffusion of NO_2 as well [36]. Thus, we suppose that the limited diffusion of the reactants in narrow channels of the pentasil zeolites is the main reason leading to the low NO conversion at high GHSV in HC-SCR.

Due to the wider channels (compared to the pentasil zeolites) [37], Y zeolite may be favorable for intracrystalline diffusion of reactants. Besides of this, Y zeolite is stable in severe hydrothermal conditions and economical [8]. Therefore, the zeolite will be expected to be a candidate for preparing a practical catalyst for HC-SCR working at high GHSV, if the required functions of Y can be effectively modified. For this purpose, it is necessary to clarify why Y zeolite gave much lower selectivity to the aimed reaction than the pentasil zeolites in HC-SCR, regardless of the doped metal [26–30]. Up to now, no report has given a reasonable interpretation for this problem and that is the reason why we take the subject in this paper.

In this investigation, H-form zeolites instead of metal-doped zeolites were employed to avoid possible interference resulted from the doped metal. To get a clear insight into reaction mechanism in Fourier transform infrared spectra (FTIR) study, the ideal system (free of H_2O and CO_2) rather than the real exhaust condition was chosen for the investigation [38–47]. The reason is that, H_2O and CO_2 greatly disturb the vibration signals in the region of 1500 – 2300 cm^{-1} which is sensitive to the nitrogen containing species.

2. Experimental

2.1. Catalysts preparation

HZSM-5 zeolite ($Si/Al=25$) was purchased from Nankai University. NH_4 -FER powder ($Si/Al=20$) and NH_4 -MOR zeolite ($Si/Al=24$) were purchased from Zeolite International Co. (America). HFER and HMOR zeolite were obtained by calcining the corresponding NH_4 -zeolites at 500°C in air for 5 h. NaY ($Si/Al=2.5$) was purchased from Wenzhou Huahua Corporation. To obtain HY from the parent zeolite, 100 g of NaY was stirred in 500 ml of 2.0 M NH_4NO_3 aqueous solution at 80°C for 10 h, then filtered and washed with deionized water, dried at 120°C overnight, and calcined at 500°C in air for 5 h. The procedures were repeated for several times to ensure that most sodium ions were exchanged by protons from the NaY.

All of the resulting materials were pelletized, crushed and sieved to a size of 20–40 mesh for activity measurements.

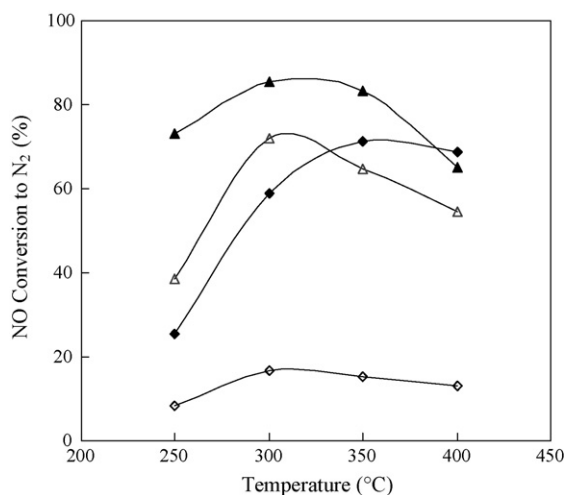


Fig. 1. Conversion of NO_x as a function of temperature over HZSM-5 (◆), HFER (▲), HMOR (△) and HY (◇). Reaction condition: 1600 ppm NO + 800 ppm C_2H_2 + 9.95% O_2 in He with a total flow rate of 50 ml/min over 0.2 g of catalyst.

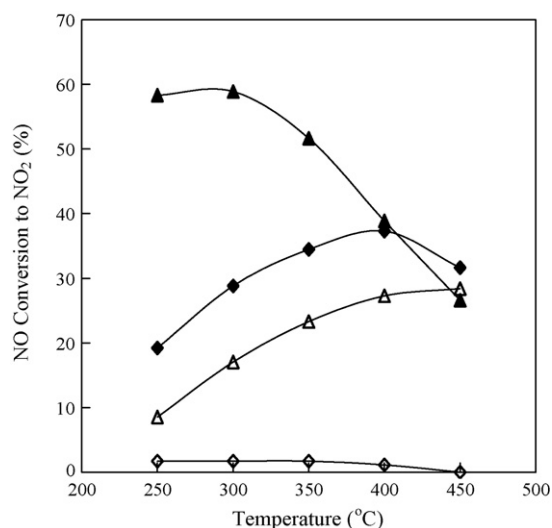


Fig. 2. Catalytic performance of HZSM-5 (◆), HFER (▲), HMOR (△) and HY (◇) in oxidation of NO with O_2 at different temperatures.

2.2. Activity test in C_2H_2 -SCR

The C_2H_2 -SCR reaction was carried out in a quartz reactor (i.d. 4 mm) at atmospheric pressure. First, the catalysts were heated at 500°C for 30 min in the flow of He to remove H_2O from zeolites, cooled to desired temperature, and then a gas mixture containing 1600 ppm NO + 800 ppm C_2H_2 + 10% O_2 in He with a total flow rate of 50 ml/min was fed into the reactor loading 0.2 g of catalyst (GHSV $\approx 8000\text{ h}^{-1}$). NO conversion was calculated from the amount of produced N_2 as analyzed by GC (HP 6890) using a capillary column (HP-PLOT/zeolite, 30 m \times 0.32 mm, 12 μm).

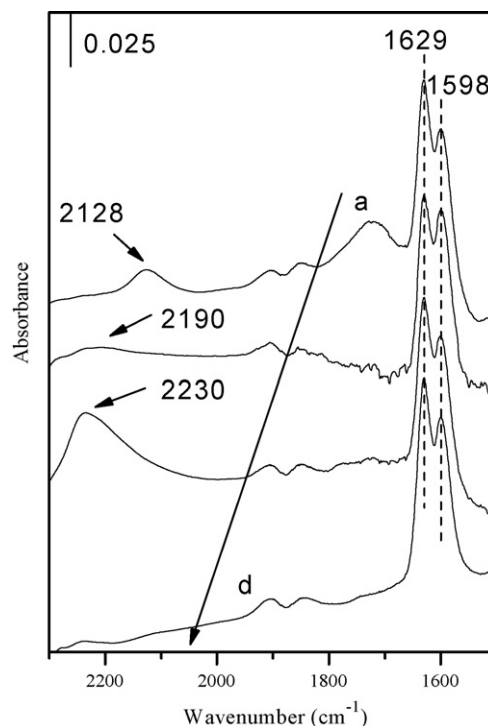


Fig. 3. Steady state of surface species recorded by in situ FTIR on HZSM-5 (a), HFER (b), HMOR (c) and HY (d) at 300°C in the gas mixture of 1000 ppm NO + 10% O_2 in N_2 .

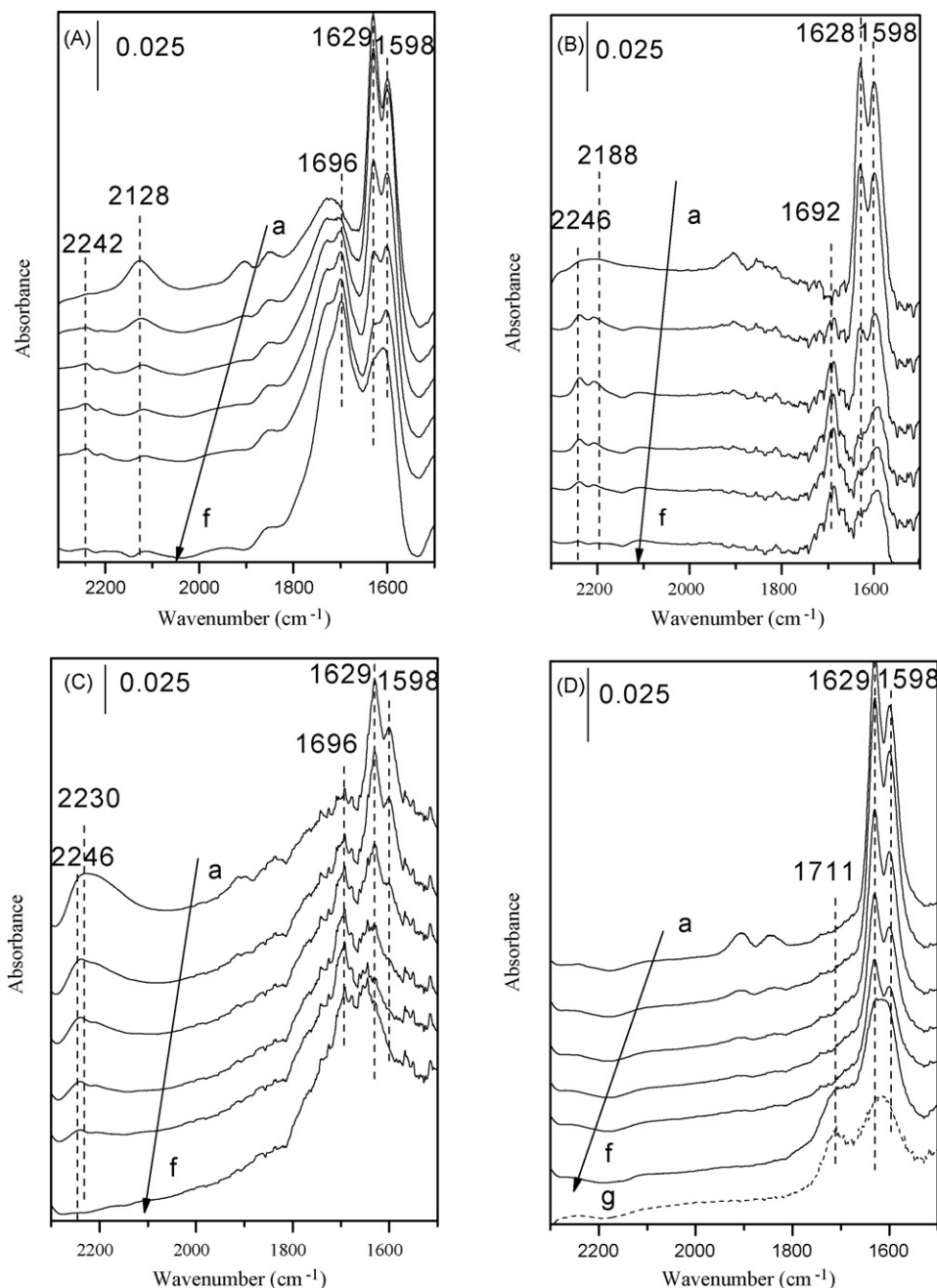


Fig. 4. FTIR spectra of surface species on HZSM-5 (A), HFER (B), HMOR (C) and HY (D) at 300 °C: saturated co-adsorption of 1000 ppm NO + 10% O₂ in N₂ (a) and then exposed to 500 ppm C₂H₂ + 10% O₂ in N₂ for 1 min (b), 2 min (c), 3 min (d), 4 min (e), 8 min (f); fresh HY zeolite in 500 ppm C₂H₂ + 10% O₂ in N₂ for 30 min at 300 °C (g).

2.3. Activity test in NO oxidation to NO₂

Activity of the zeolites (0.2 g) for NO oxidation was tested in a quartz reactor (4 mm i.d.). First, the catalysts were heated at 500 °C for 30 min in the flow of N₂ to remove H₂O from zeolites, cooled to desired temperature, and then a gas mixture of 200 ppm NO + 10% O₂ in N₂ was fed into the reactor at a total flow rate of 100 ml/min. Produced NO₂ and unreacted NO in the outlet gas were monitored by a NO_x analyzer (ACY301-B).

2.4. Fourier transform infrared spectra (FTIR) measurement

FTIR studies were carried out in a quartz IR cell equipped with CaF₂ windows on a Nicolet 360 FTIR spectrophotometer. Prior to each experiment, the catalyst was pressed into a self-supporting

wafer (with 14 ± 0.7 mg in weight), pretreated at 500 °C in N₂ for 30 min, and then cooled to the desired temperature for taking a reference spectrum (S_r). All of the in situ FTIR spectra of surface species on the catalyst shown in the figures were recorded at a resolution of 2 cm⁻¹ for 32 scans and obtained by subtracting the corresponding S_r from each spectrum.

3. Results

3.1. Activity for C₂H₂-SCR

Fig. 1 shows NO conversion to N₂ in C₂H₂-SCR as a function of temperature over HY and the pentasil zeolites. The pentasil zeolites gave much higher NO conversion to N₂ in the range of 250–400 °C, compared to HY. Stable NO conversions obtained over the zeolites

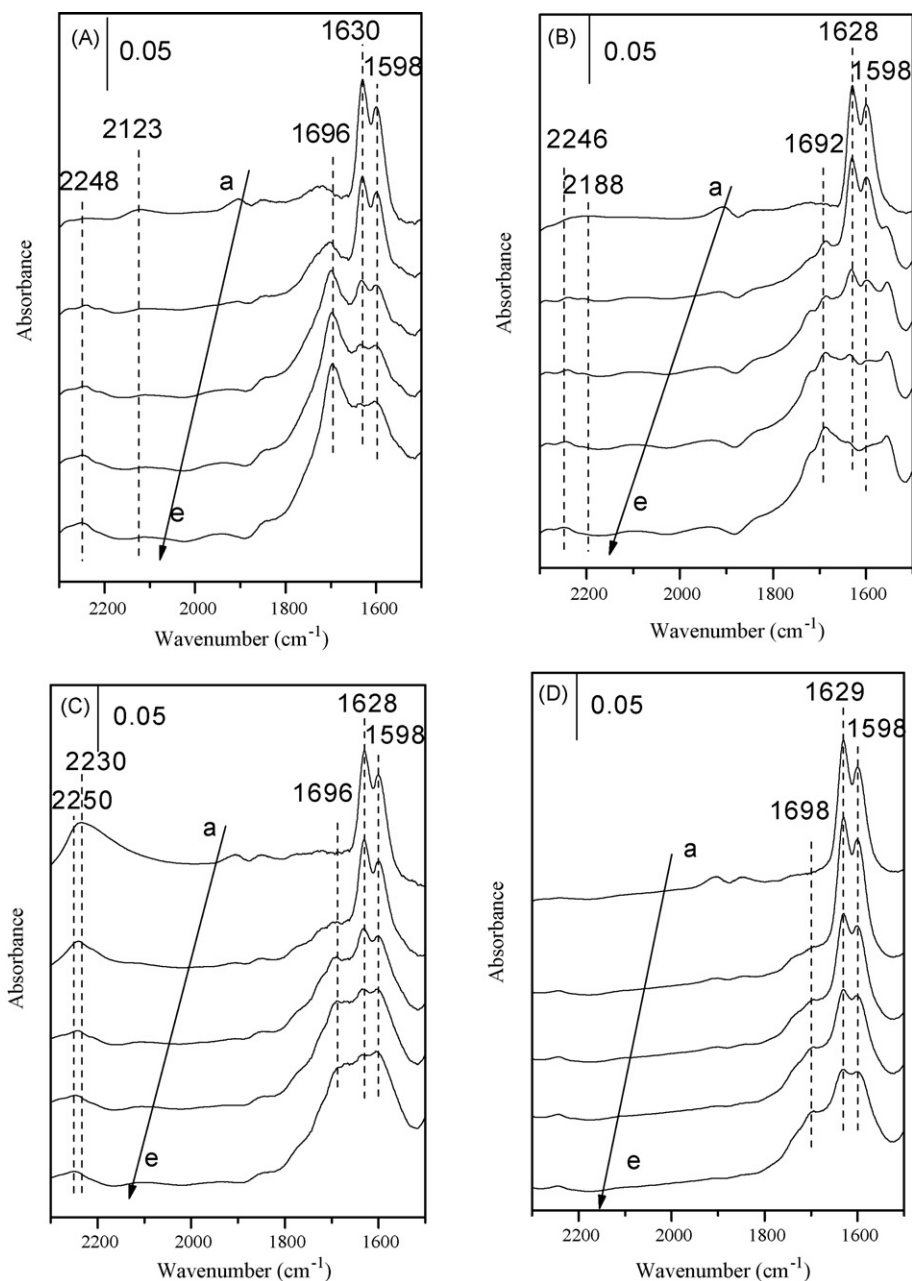


Fig. 5. FTIR spectra of surface species on HZSM-5 (A), HFER (B), HMOR (C) and HY (D) at 300 °C: saturated co-adsorption of 1000 ppm NO + 10% O₂ in N₂ (a) and then exposed to 333 ppm C₃H₆ + 10% O₂ in N₂ for 1 min (b), 2 min (c), 3 min (d), 4 min (e).

at 300 °C were in the order of HFER (85.5%) > HMOR (71.9%) > HZSM-5 (58.9%) << HY (16.8%), which is in good accordance with those reported in the literature as mentioned in the Section 1 [25–28].

3.2. Activity for NO oxidation to NO₂

For HC-SCR, NO oxidation to NO₂ was generally accepted to be its crucial step over zeolite-based catalysts [12–14,19–20]. To elucidate the mechanism leading to the quite different behavior of HY from the pentasil zeolites in C₂H₂-SCR, the activity of the zeolites for NO oxidation to NO₂ was studied. As shown in Fig. 2, all of the pentasil zeolites exhibited considerably higher activity compared to HY, in particular, in the case of HFER at 250 °C. More interestingly, it can be seen that the patterns of NO oxidation to NO₂ vs reaction temperature resemble much to those of NO conversion to N₂ in C₂H₂-SCR by comparing Fig. 2 with Fig. 1. The results led us to

speculate that the performance of the zeolites in C₂H₂-SCR is determined to some extent by the activity of the zeolites for catalyzing NO oxidation.

3.3. NO + O₂ co-adsorption over the zeolites

Fig. 3 shows steady state in situ FTIR spectra recording nitric species of the zeolites in NO + O₂ at 300 °C. No obvious differences between HY and the pentasil zeolites could be observed in nitrate species formation capacity. The bands at 1629 and 1598 cm⁻¹ (due to bridging and bidentate nitrates [38,39], respectively) were observed in similar intensity on the four zeolites after saturated co-adsorption of NO + O₂, indicating that Y zeolite has the same capacity as that of the pentasil zeolites for producing the nitrate species. However, a large difference between HY and the pentasil zeolites was detected in nitrosonium ions (NO⁺) formation. Over

the pentasil zeolites, NO^+ species were considerably produced, which were characterized by the bands at 2128 cm^{-1} for HZSM-5, 2190 cm^{-1} for HFER and 2230 cm^{-1} for HMOR [40–42]. On the other hand, no bands due to NO^+ species could be observed over HY. The poor NO^+ producing ability may be one of the causes leading to the inferior catalytic performance of HY in C_2H_2 -SCR in comparison with the pentasil zeolites. The speculation is supported by literatures in which NO^+ species were proposed to be important intermediates of C_3H_6 -SCR over H-form zeolites [29,40].

3.4. Reactivity of nitric species towards $\text{C}_2\text{H}_2 + \text{O}_2$ over the zeolites

Reactivity of the nitric species towards $\text{C}_2\text{H}_2 + \text{O}_2$ over the zeolites was investigated at 300°C . As shown in Fig. 4, both bands due to nitrates (1598 and 1629 cm^{-1}) and bands due to NO^+ species (2128 cm^{-1} for HZSM-5, 2188 cm^{-1} for HFER and 2230 cm^{-1} for HMOR) rapidly decreased in intensity on the pentasil zeolites when the zeolites were subsequently exposed to $\text{C}_2\text{H}_2 + \text{O}_2$. Concomitantly, new bands at $\sim 1692\text{ cm}^{-1}$ (1696 cm^{-1} for HZSM-5, 1692 cm^{-1} for HFER and 1696 cm^{-1} for HMOR) due to formamide species [43] and at $\sim 2240\text{ cm}^{-1}$ (2242 cm^{-1} for HZSM-5, 2246 cm^{-1} for HFER and 2246 cm^{-1} for HMOR) due to NCO species [44–46] appeared. The results indicated that both nitrate and NO^+ species are rather reactive towards acetylene over the pentasil zeolites at the reaction temperature.

On the other hand, quite different results were obtained over HY (Fig. 4 D). No bands due to formamide species (at $\sim 1692\text{ cm}^{-1}$) or NCO species (at $\sim 2240\text{ cm}^{-1}$) could be observed in the transient FTIR spectra over HY when the gas mixture of $\text{NO} + \text{O}_2$ was switched to $\text{C}_2\text{H}_2 + \text{O}_2$. Instead, only a band at 1711 cm^{-1} belonged to carbonyl species [23,47] slowly appeared. The same band could be also observed when fresh HY was exposed to $\text{C}_2\text{H}_2 + \text{O}_2$ (spectrum h) at the same temperature. Based on these results, it can be considered that the nitrate species on HY are inert towards the aimed reaction.

3.5. Reactivity of nitric species towards $\text{C}_3\text{H}_6 + \text{O}_2$ over the zeolites

To validate that the activity of nitrate species on HY are quite different from those on the pentasil zeolites, the reactivity of nitric species over different zeolites towards $\text{C}_3\text{H}_6 + \text{O}_2$ was also compared. As shown in Fig. 5, when the gas mixture of $\text{C}_3\text{H}_6 + \text{O}_2$ (instead of $\text{C}_2\text{H}_2 + \text{O}_2$) was introduced into the cell, the following quite different results between HY and the pentasil zeolites were also observed. Bands at $\sim 1692\text{ cm}^{-1}$ (1696 cm^{-1} for HZSM-5, 1692 cm^{-1} for HFER, 1696 cm^{-1} for HMOR) due to acylamide [39,43,48] rapidly appeared on the pentasil zeolites. However, the increasing of the band at 1698 cm^{-1} was rather slow on HY. The results indicate again that the reactivity of nitric species towards the reductants is much lower on HY compared to those on the pentasil zeolites.

4. Discussion

As given in Figs. 1–5, all of the three types of pentasil zeolites, which are rather active for HC-SCR, possess the following common features: (1) they are highly active for the oxidation of NO to NO_2 , (2) they have strong NO^+ producing capability and nitrate formation ability, and (3) both nitrate and NO^+ species are quite active towards reduction over the zeolites, i.e. the zeolites are capable of activating the nitric species for reduction. However, in the case of HY, the low activity of the zeolite for HC-SCR together with the features of low activity towards NO oxidation to NO_2 , lack of the ability to generate NO^+ species and to activate nitrate species were given. Thus, it can

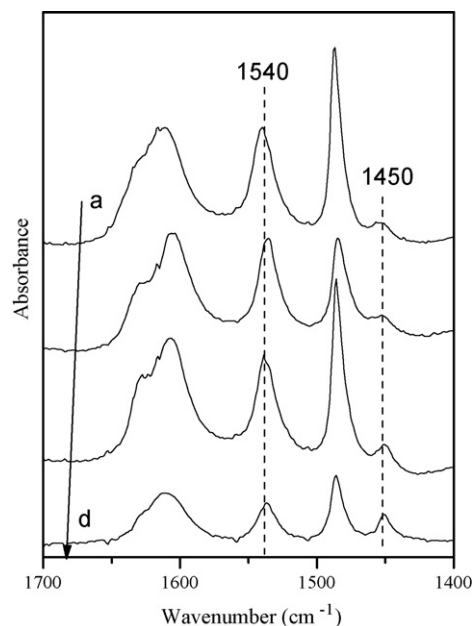
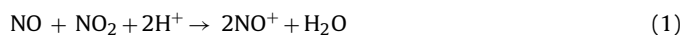


Fig. 6. FTIR spectra of pyridine adsorbed on HZSM-5 (a), HFER (b), HMOR (c) and HY (d) at 500°C in evacuation.

be considered that the functions of the zeolites to catalyze oxidation of NO to NO_2 , to produce the nitric species (particularly, the NO^+ species from the co-adsorption of $\text{NO} + \text{O}_2$), and to activate the nitric species for reduction are much significant for zeolite-based catalysts. It means that, these functions of Y must be substantially strengthened for designing a practical HC-SCR catalyst based on the zeolite. The deduction was supported by the following propositions dealing with HC-SCR over zeolite-based catalysts: (1) NO oxidation to NO_2 is an important step of HC-SCR [12–14,19–20]. (2) The active nitric species (nitrates and NO^+) formation is the rate-determining step of C_2H_2 -SCR over the pentasil zeolites [43].

To interpret the different features of HY from those of pentasil zeolites, acidity of the zeolites was characterized by pyridine adsorption FTIR at 500°C . As shown in Fig. 6, the band at 1540 cm^{-1} due to Brönsted acid sites was much weaker in intensity for HY compared to the pentasil zeolites, indicating that strong Brönsted acids over HY are much less than those of the pentasil zeolites in amount. In literature, protons in Ga- and In-ZSM-5 zeolite were proposed to be active sites for catalyzing NO oxidation to NO_2 [49]. Active NO^+ species formation was also associated with protons in the zeolites [40,50], as shown in Eq. (1).



Thus, the poor functions of HY for catalyzing NO oxidation (Section 3.2) and producing NO^+ species (Section 3.3) could be attributed to the deficiency in strong Brönsted acids of the zeolite. As for the function of the zeolites to activate nitrate species for reduction, it can be also correlated well with protons in the zeolites. As reported in our previous observation, nitrate species are much active towards C_2H_2 over HZSM-5, whereas those over NaZSM-5 are almost inert for the aimed reaction [38].

5. Conclusions

The low activity of HY for HC-SCR lies in the poor functions of the zeolite to catalyze the oxidation of NO to NO_2 , to produce NO^+ species and to activate nitrate species for reduction. Therefore, to design a practical HC-SCR catalyst based on Y zeolite, how to strengthen the functions of the zeolite should be first taken into account, besides the consideration of intracrystalline diffusion.

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