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Rate-determining Step of Selective Catalytic Reduction of NO by Acetylene Over HZSM-5

Xinping Wang · Qing Yu · Guangfeng Li · Zhiguang Liu

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Abstract Nitrate species is crucial intermediate of selective catalytic reduction of NO by acetylene (C_2H_2-SCR) over HZSM-5. It is proposed that formation of nitrate species on the zeolite is rate-determining step of C_2H_2-SCR. The proposition is supported by the experimental results: (1) No nitrate species could be detected by in situ FTIR in steady C_2H_2-SCR over HZSM-5 at 350 °C, while the bands due to nitrate species were clearly observed on the zeolite both in situ in $NO + O_2$ and after a brief evacuation at the temperature; (2) Yttrium incorporation into HZSM-5 zeolite considerably enhanced nitrate species formation on the catalyst and correspondingly the activity of the catalyst for C_2H_2-SCR was significantly increased. Both the promotional effect of yttrium on C_2H_2-SCR and the rate-determining step of C_2H_2-SCR being nitrate species formation over the catalyst were first reported herein.

Keywords Nitric oxide · Nitrate · Rate-determining step · Promotional effect · Selective catalytic reduction of NO

1 Introduction

Since the first reports on selective catalytic reduction of NO by hydrocarbons (HC-SCR) [1, 2], extensive research into the HC-SCR applications for the control of NO_x in exhaust gases of diesel and lean-burn engines has been carried out [3–9]. For the practical application of the HC-SCR, an active catalyst capable of reducing NO in large space velocity at ca. 300 °C is required, in addition to high selectivity of the reductant towards the target reaction. For this purpose, having an insight into the reaction mechanism of the HC-SCR is significantly of importance to the researchers investigating in this field. In the previous investigation, we reported that acetylene is highly active and selective towards NO reduction under lean-burn conditions over Ce-HZSM-5 [10] and Mo/HZSM-5 [11] in the temperature range 250–450 °C. In this paper, we report that yttrium incorporation into HZSM-5 can also significantly increase the activity of the zeolite for selective catalytic reduction of NO by acetylene (C_2H_2-SCR). NO removal with about same level as those over Ce-HZSM-5 and Mo/HZSM-5 could be obtained under same reaction conditions over 3% Y/HZSM-5 catalyst. As it is the first time to report the effect of yttrium on selective catalytic reduction of NO by hydrocarbons, the mechanism concerning the promotional effect of yttrium on C_2H_2-SCR was investigated. We found that nitrate species is a crucial intermediate of C_2H_2-SCR over HZSM-5 and that the nitrate species formation on the zeolite is rate-determining step of the C_2H_2-SCR. Yttrium incorporation into HZSM-5 promoted nitrate species formation and therefore considerably enhanced the activity of the catalyst for C_2H_2-SCR.

2 Experimental

Commercial HZSM-5 zeolite (with SiO_2/Al_2O_3 ratio of 25) was purchased from Nankai University in china. 3% Y/HZSM-5 containing 3% of yttrium in weight was prepared by impregnation of the zeolite overnight in aqueous yttrium nitrate solution. The resulting materials were dried at 120 °C, calcined at 500 °C in air for 6 h, and then pelletized, crushed and sieved to a size of 20–40 mesh before use.

X. Wang (✉) · Q. Yu · G. Li · Z. Liu
State Key Laboratory of Fine Chemicals, Dalian University of Technology, 288# Linggong Road 2, Dalian 116024, China
e-mail: dllgwxp@dlut.edu.cn

Temperature-programmed desorption of NO and NO_2 (NO_x-TPD) conducted on a home made setup using an electrochemical analyzer (ACY301-B). After the saturated co-adsorption of 200 ppm NO and 10% O_2 in N_2 at 40 °C and a purge with N_2 for 2 h, the sample (0.1 g) was heated to 500 °C in N_2 at 10 °C min^{-1}, during which the NO_x-TPD was recorded.

C_2H_2-SCR reaction was carried out in a quartz reactor (4 mm i.d.) by feeding gas mixture of 1,600 ppm NO, 800 ppm C_2H_2 and 9.95% O_2 in He at a total flow rate of 50 mL min^{-1} to 0.2 g of catalyst. NO conversion was calculated from the amount of N_2 produced, which was analyzed using a gas chromatograph (HP 6890) equipped with a capillary column (HP-PLOT/zeolite, 30 m × 0.32 mm, 12 μm).

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 °C in N_2 for 30 min, and then cooled to desired temperature for taking a reference spectrum (S_r). The IR absorption arising from every gas mixture (S_g) was recorded at each desired temperature. In situ FTIR spectra of surface species formed on the catalyst in every gas mixture given in the figures were obtained by subtracting the corresponding S_g and S_r from each spectrum. All spectra reported herein were taken at a resolution of 2 cm^{-1} for 32 scans. The reaction gas mixture was composed of 1,000 ppm NO, 500 ppm C_2H_2 and 10% O_2 in N_2. A nitrogen stream containing 1,000 ppm NO + 10% O_2, or 500 ppm C_2H_2 + 10% O_2 were used for co-adsorption of reactants.

3 Results and Discussion

3.1 NO_x-TPD

NO_x-TPD over HZSM-5 and 3% Y/HZSM-5 are compared in Fig. 1. Desorption of NO and NO_2 above 300 °C over HZSM-5 were almost negligible compared to those over 3% Y/HZSM-5, after a saturated co-adsorption of NO + O_2. Two new NO desorption peaks at 370 and 480 °C (Fig. 1a) being special for the yttrium-exchanged sample appeared over 3% Y/HZSM-5. Correspondingly, much more NO_2 desorption was observed over 3% Y/HZSM-5 compared to HZSM-5 (Fig. 1b) and the center of the peak shifted to 375 °C from 330 °C by yttrium (3%) loading on the zeolite. The results indicate that yttrium incorporation into HZSM-5 zeolite is favorable for NO_x storage and that yttrium species in the Y/HZSM-5 catalyst samples is the cause of the new desorption peak of NO and NO_2 in NO_x-TPD.

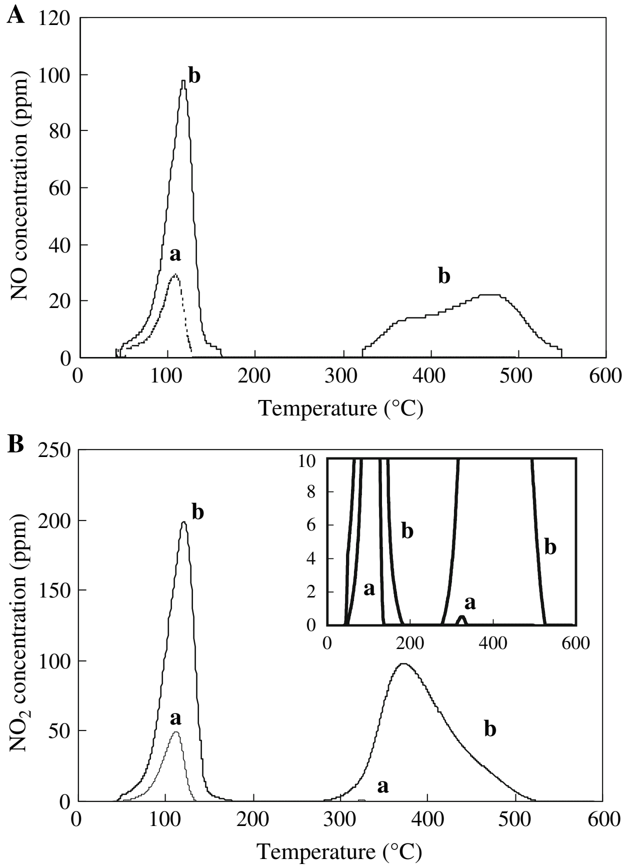

Fig. 1 TPD profiles of NO (**a**) and NO_2 (**b**) over HZSM-5 (a) and 3% Y/HZSM-5 (b) after co-adsorption of NO + O_2. The insert is the figure magnified to represent a clear desorption of NO_2 over HZSM-5 at higher temperature

3.2 FTIR

FTIR spectrum of nitrous species formed by co-adsorption of NO + O_2 on HZSM-5 and 3% Y/HZSM-5 measured at 250 °C are given in Fig. 2. It is evident that yttrium incorporation into HZSM-5 caused not only the appearance of the band at 1,609 cm^{-1}, but also a significant increase in intensity of the band at 1,585 cm^{-1} due to bidentate nitrates [12–16].

Reactivity of nitrous species on 3% Y/HZSM-5 towards acetylene was studied at 350 °C. After saturated co-adsorption of NO + O_2 and a brief evacuation at 350 °C, the 3% Y/HZSM-5 catalyst sample gave a FTIR spectrum of nitrous species on the sample at 350 °C as shown in Fig. 3a. The spectrum changed little with time when 10% of O_2 in N_2 was flowed through the FTIR cell at the temperature. However, the bands at 1,609 and 1,585 cm^{-1} due to nitrate species rapidly decreased in intensity upon exposure of the catalyst sample to C_2H_2 + O_2 in a same condition. They almost disappeared within 5 min. The results indicate that the both types of nitrous species

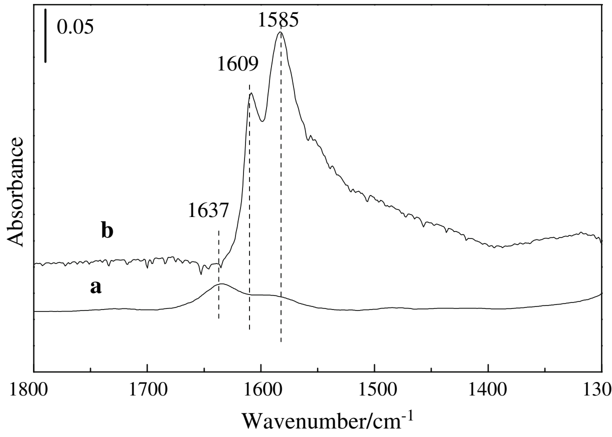

Fig. 2 FTIR spectra of nitrous species formed on HZSM-5 (a) and 3%Y/HZSM-5 (b) at 250 °C after NO + O_2 saturated co-adsorption

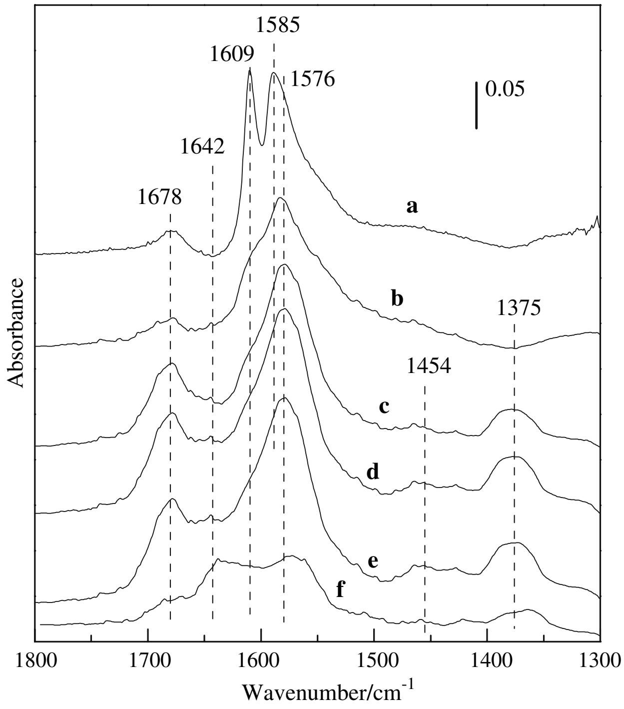

Fig. 3 FTIR spectra of adsorption species on 3%Y/HZSM-5 at 350 °C: brief evacuation after saturated coadsorption of NO + O_2 (a), and subsequently exposing to C_2H_2 + O_2: 1 min (b), 5 min (c), 20 min (d), 30 min (e); In situ in 500 ppm C_2H_2 + 10% O_2 (f)

formed on the catalyst surface are rather active towards the reductant and/or some derivates of the reductant. On the contrary, a band at 1,678 cm^{-1} increased in intensity upon exposure of the catalyst to C_2H_2 + O_2 in the first 5 min. This indicates that a new species have formed, which led to the band at 1,678 cm^{-1}. Concomitantly, bands at 1642, 1576, 1454 and 1375 cm^{-1} appeared with the reaction progress, which are most probably due to some oxygen-containing species formed by partial oxidation of acetylene over the catalyst, as the four bands were also observed when the catalyst sample was exposed to C_2H_2 + O_2 at the same reaction temperature (spectrum f). According to literature [12, 14, 15, 17–19], the bands at 1,576 and 1,454 cm^{-1} can be assigned to ν_{as}(COO) and ν_s(COO), respectively, for carboxyl surface species. Recently, Shimizu et al. [20] reported that acetic acid exhibited an intense and sharp band at 1,676 cm^{-1}, together with a band at 1,642 cm^{-1}, when it was introduced to Ag-MFI catalyst at 300 °C. The authors assigned these bands to acetate species adsorbed on the catalyst surface. Clearly, results in our case fit well with the literature.

3.3 Surface Species in Steady-state Reaction

Figure 4 shows the steady state in situ FTIR spectrum of surface species on 3% Y/HZSM-5 catalyst under reaction condition and the transient in situ FTIR spectra changed with reaction condition. Interestingly, the sample exhibited predominant bands due to acetate species at 1678, 1576 and 1454 cm^{-1}, but no band due to nitrate species could be detected by the in situ FTIR on the catalyst during the reaction of 500 ppm C_2H_2 + 1,000 ppm NO + 10% O_2 in N_2 at 350 °C (spectrum a). The result reveals an extreme deficiency of nitrate species, whereas there was an

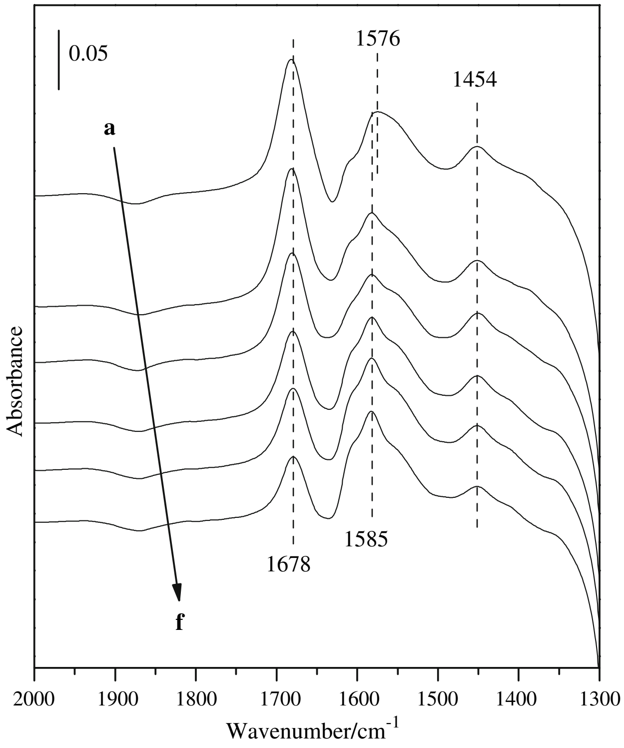

Fig. 4 Spectra of surface species on 3%Y/HZSM-5 at 350 °C: in situ in 500 ppm C_2H_2 + 1,000 ppm NO + 10% O_2 (a), a brief evacuation (b), then exposing to NO + O_2 for 1 min (c), 5 min (d), 10 min (e), 30 min (f)

abundance of acetate intermediate species on the catalyst. When C_2H_2 was removed from the reaction system at this temperature, band at 1,585 cm^{-1} due to bidentate nitrates appeared, which was accompanied by a slow decrease in intensity of the bands due to acetate species (at 1678, 1576 and 1454 cm^{-1}). It should be noted that the band at 1,609 cm^{-1} due to nitrate species connected to Y^{3+} ions did not appear, even when the sample was then continuously exposed to gas mixture of NO + O_2 for 30 min after C_2H_2 was cut off from the reaction system. The result indicates that this type of nitrate species is much active towards acetate species than that attributed to the band at 1,585 cm^{-1}.

3.4 Catalytic Activity for HC-SCR

The catalytic performance of HZSM-5 and 2%Y/HZSM-5 in C_2H_2-SCR is depicted in Fig. 5. The 3% Y/HZSM-5 catalyst yielded significantly higher NO conversion to N_2 compared to that of the parent HZSM-5. For example, NO conversion to N_2 obtained over HZSM-5 at 350 °C was 71% and drastically increased to 85% over the 3% Y/HZSM-5 catalyst. The results indicate that yttrium have promotional effect on the target reaction when incorporated into HZSM-5 zeolite. Combined the result with those obtained in sections 3.1 and 3.2, it is reasonable to propose that the higher activity of 3% Y/HZSM-5 for C_2H_2-SCR is associated with the larger NO_x adsorption capacity of the catalyst at higher temperature (>300 °C) compared to HZSM-5. The proposal was validated in the following logical decisions: (1) Maximum NO conversion to N_2 was obtained over HZSM-5 and 3% Y/HZSM-5 catalysts at 300–350 °C, therefore the nitrous species contributing to the target reaction should be capable of remaining on the catalyst at the reaction temperature. (2) The nitrous species increased by yttrium incorporation into HZSM-5 should be active towards the reductant under the reaction conditions. (3) The nitrous species on HZSM-5 should be in much deficiency under the steady C_2H_2-SCR condition. As revealed by the FTIR, the bands due to nitric species (1,585 and 1,609 cm^{-1}) were substantially increased in intensity by yttrium incorporation into the zeolite. It is very interesting that no nitrate species could be detected by in situ FTIR on 3% Y/HZSM-5 under steady reaction condition, and the band at 1,585 cm^{-1} due to bidentate nitrates could be observed only when acetylene was cut off from the reaction system at the reaction temperature. It is demonstrated that the nitrate species on 3% Y/HZSM-5 are so active towards the reductant and short for C_2H_2-SCR that they were reduced right away once produced, under the reaction condition.

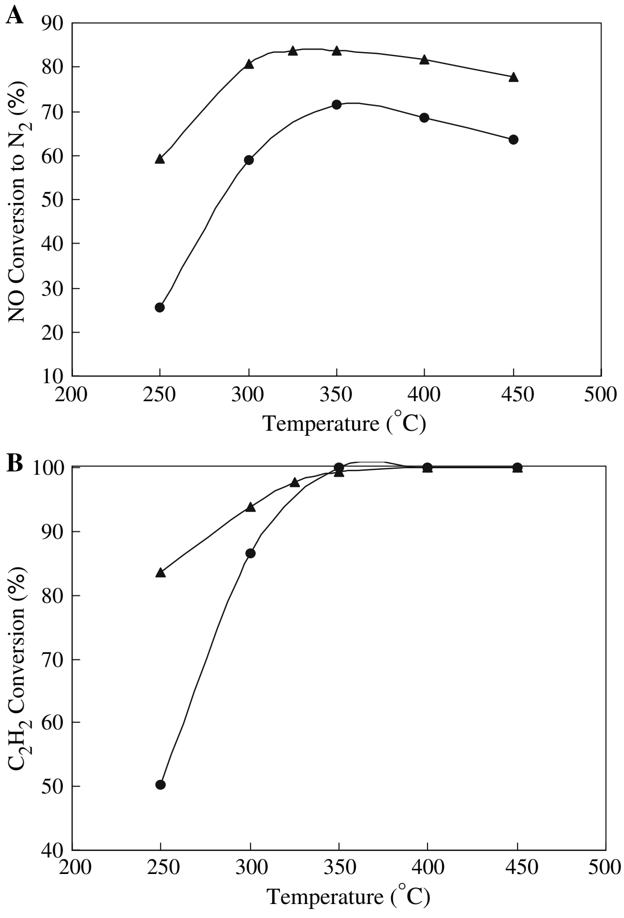

Fig. 5 NO conversion to N_2 (**a**) and acetylene conversion (**b**) as a function of reaction temperature over HZSM-5 (●), and 3%Y/HZSM-5 (▲). Reaction condition: 1,600 ppm NO, 800 ppm C_2H_2, 9.95% O_2 in He with a total flow rate of 50 mL min^{-1} over 0.2 g of catalyst

4 Conclusions

Yttrium exhibited a significant promotional effect on C_2H_2-SCR when incorporated into HZSM-5 zeolite. NO_x-TPD of catalyst samples indicated that the amount of nitrous species capable of remaining on 3% Y/HZSM-5 at reaction temperature was considerably greater than that on HZSM-5 zeolite. The 3% Y/HZSM-5 catalyst gave much stronger bands at 1,585 cm^{-1} due to active bidentate nitrate species and a band at 1,609 cm^{-1} due to bonding of a new active nitrate species to Y^{3+} ions compared to HZSM-5 zeolite. In situ FTIR measurements confirmed an extreme deficiency of nitrate species on the catalyst surface under steady-state C_2H_2-SCR condition. Therefore, it can be concluded that the formation of nitrate species on HZSM-5 is rate-determining step of the C_2H_2-SCR.

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References

1. Iwamoto M, Yahiro H, Yu-u Y, Shundo S, Miauno N (1990) Shokubai (Catalyst) 32:430
2. Held W, Konig A, Ritcher T, Puppe L (1990) SAE Paper 900496
3. She X, Flytzani-Stephanopoulos M (2006) J Catal 237:79
4. Chupin C, van Veen AC, Konduru M, Després J, Mirodatos C (2006) J Catal 241:103
5. Lónyi F, Valyon J, Gutierrez L, Ulla MA, Lombardo EA (2007) Appl Catal B 73:1
6. Bautista P, Faraldos M, Yates M, Bahamonde A (2007) Appl Catal B 71:254
7. Konova P, Arve K, Klingstedt F, Nikolov P, Naydenov A, Kumar N, Murzin D Yu (2007) Appl Catal B 70:138
8. García Cortés JM, Illán Gómez MJ, Salinas Martínez de Lecea C (2007) Appl Catal B 74:313
9. Zhang F, Zhang S, Guan N, Schreier E, Richter M, Eckelt R, Fricke R (2007) Appl Catal B 73:209
10. Wang X, Xu Y, Yu S, Wang C (2005) Catal Lett 103:101
11. Wang X, Yu S, Yang H, Zhang S (2007) Appl Catal B 71:246
12. Yu Y, Hong He, Feng Q, Gao H, Yang X (2004) Appl Catal B 49:159
13. Ivanova E, Hadjiivanov K, Klissurski D, Bevilacqua M, Armaroli T, Busca G (2001) Micropor Mesopor Mat 46:299
14. Shimizu K, Shibata J, Yoshida H, Satsuma A, Hattori T (2001) Appl Catal B 30:151
15. He H, Zhang C, Yu Y (2004) Catal Today 90:191
16. Poignant F, Freysz JL, Daturi M, Sauaaey J (2001) Catal Today 70:197
17. Haneda M, Bion N, Daturi M, Saussey J, Lavalley J-C, Duprez D, Hamada H (2002) J Catal 206:114
18. He C, Paulus M, Find J, Nickl JA, Eberle H-J, Spengler J, Chu W, Köhler K (2005) J Phys Chem B 109:15906
19. Shimizu K, Kawabata H, Satsuma A, Hattori T (1999) J Phys Chem B 103:5240
20. Shimizu K, Sugino K, Kato K, Yokota S, Okumura K, Satsuma A (2007) J Phys Chem C 111:6481