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Eley-Rideal mode of formamide species formation in selective catalytic reduction of NO_x by C_2H_2 over ferrierite based catalysts

Na Xing, Xinping Wang *, Anfeng Zhang, Zhiguang Liu, Xinwen Guo

State Key Laboratory of Fine Chemicals, Dalian University of Technology, P.O. Box 288, Linggong Road 2, Dalian 116024, China

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ABSTRACT

It is found that formamide species as a crucial intermediate of the selective catalytic reduction of NO by C_2H_2 was produced by nitrate species reacting with acetylene in Eley-Rideal mode on H-ferrierite (HFER) based catalyst. The mode concerning the formamide intermediate formation was proposed for the first time in selective catalytic reduction of NO by hydrocarbons. Impregnation of 2% zirconium into HFER considerably favored the formation of formamide species, and therefore better catalytic activity for the title reaction was obtained on 2%Zr/HFER.

1. Introduction

Selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) is a potential method to remove NO_x from oxygen rich exhausts. In order to get high NO conversion, zeolites, e.g. ZSM-5 [1–4], ferrierite (FER) [5,6], mordenite [7,8], beta [5,9], Y [10,11], and the zeolites based catalysts were widely studied in the HC-SCR. Among them, FER based zeolites have been reported to be highly active and selective towards NO_x reduction to N_2 [7,8,12]. To have an insight into the reaction mechanism, study on the reaction intermediate and its formation route are very important. Nitrate species was reported to be active intermediate in the selective catalytic reduction of NO_x (SCR) by CH_4 over Co-HFER [10]. Nitroethylene, HCN and HNCO were also proposed to be active intermediates of SCR by C_2H_4 over HFER [9]. Recently, Ferreira et al. suggested that the intermediates are present in the form of R–NO_x for the SCR by CH_4 over cobalt/palladium based FER catalysts [13]. In this paper, we report that formamide species as a crucial intermediate of the SCR by acetylene can only be produced in Eley-Rideal mode over HFER based catalyst. The mode concerning the formamide intermediate formation was proposed for the first time in selective catalytic reduction of NO by hydrocarbons.

2. Experimental

2.1. Catalyst preparation

Commercial NH_4–FER zeolite (with SiO_2/Al_2O_3 ratio of 20) was purchased from Zeolyst Co. in USA. HFER was obtained by calcining the NH_4–FER zeolite at 500 °C in air for 5 h. 2%Zr/HFER catalyst was prepared by impregnating the related zeolites with a desired amount of $ZrOCl_2$ in aqueous solution overnight. The resulting materials were dried at 120 °C and calcined at 500 °C in air for 5 h before use. The content of zirconium in the catalysts was 2% in weight percent of zirconia.

2.2. Activity measurement

Selective catalytic reduction of NO_x by C_2H_2 reaction (C_2H_2-SCR) was carried out at atmospheric pressure in a quartz reactor (i.d. 4 mm). A gas mixture composed of 1600 ppm NO, 800 ppm C_2H_2, 10% O_2 in He with a total flow rate of 50 ml/min was fed through 0.2 g of catalyst. NO conversion was calculated from the amount of N_2 produced as analyzed by GC (HP 6890) using a capillary column (HP-PLOT/zeolite, 30 m × 0.32 mm, 12 μm).

2.3. Fourier transform infrared spectroscopy (FTIR)

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

* Corresponding author. Tel.: +86 411 84706323; fax: +86 411 83633080.
E-mail address: dllgwxp@dlut.edu.cn (X. Wang).

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desired temperature for taking a reference spectrum (S_r). The IR adsorption arising from every gas mixture (S_g) was recorded at each desired temperature. The in situ FTIR spectra of surface species formed on the catalyst in every gas mixture shown 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 gas reaction mixture was composed of 1000 ppm NO, 500 ppm C_2H_2 and 10% O_2 in N_2. A nitrogen stream containing 1000 ppm NO + 10% O_2, or 500 ppm C_2H_2 + 10% O_2 were used for the study of co-adsorption of reactants. The total flow rate was held at 50 ml/min. To compare the intensity of the bands characterizing the reaction intermediate in relative population over each catalyst samples, the sample wafers with 14 ± 0.7 mg were used and the same parameters of the IR spectrophotometer were adjusted.

3. Results and discussion

3.1. Catalytic activity of FER based catalysts for C_2H_2-SCR

Fig. 1 shows the NO conversion to N_2 in C_2H_2-SCR as a function of temperature over HFER and 2%Zr/HFER catalyst. As can be seen, the conversion of NO into N_2 over HFER and 2%Zr/HFER all reached their maximum at 300 °C, which corresponds to the total consumption of acetylene. Zirconium represented obvious doping effect on NO reduction in C_2H_2-SCR in the temperature rage of 250–450 °C. For instance, the NO conversion to N_2 at 300 °C was increased to 90.3% from 82.9% after 2% of zirconium was incorporated into HFER. The result coincides with the case of zirconium incorporated into HZSM-5 for the C_2H_2-SCR [14]. We believe that the doping effect of zirconium in the 2%Zr/HFER on NO reduction arose from the same reason as in the 2%Zr/HZSM-5 for the C_2H_2-SCR. Namely, highly dispersed zirconium species, especially amorphous ultrafine zirconium oxide, considerably enhanced NO_2 adsorption capacity of the catalysts, which have been confirmed both by NO_x-TPD and in situ FTIR (not shown), therefore increased the NO conversion to N_2.

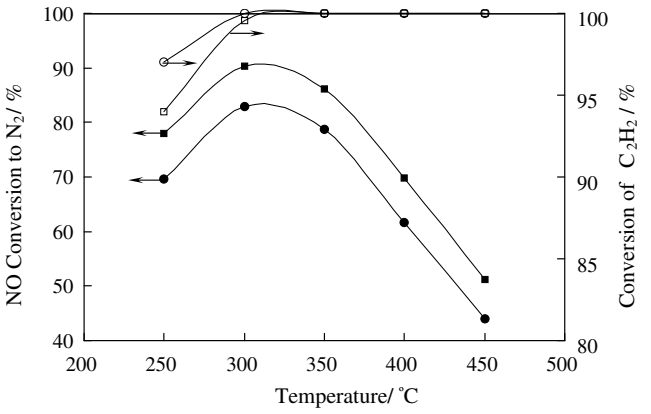
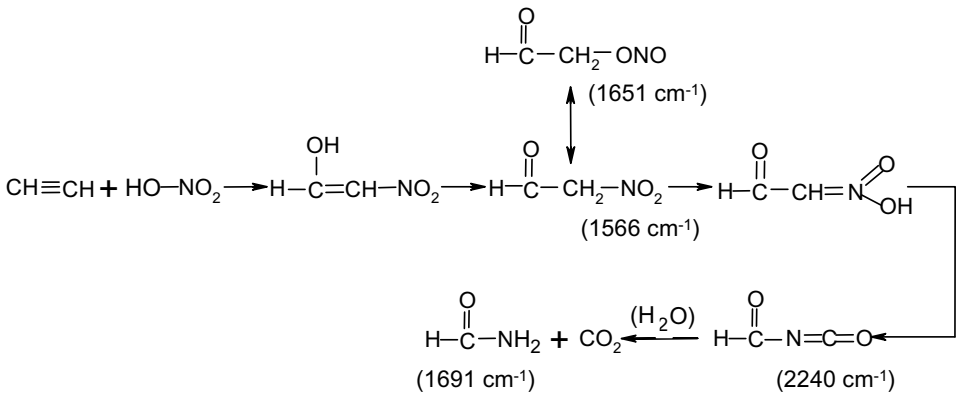


Fig. 1. NO conversion to N_2 (close symbols) and conversion of C_2H_2 (open symbols) in C_2H_2-SCR as a function of temperature over HFER (●, ○) and 2%Zr/HFER (■, □).

3.2. FTIR characterization of intermediate species in C_2H_2-SCR

Surface species formed on 2%Zr/FER by exposing the catalyst to NO + O_2 + N_2 at 250 °C for 30 min and subsequently to C_2H_2 + N_2 characterized by FTIR spectra are shown in Fig. 2. NO^+, bridging and bidentate nitrate species, which give the bands at 2188, 1629 and 1598 cm^{-1} [3,15–18] respectively, were presented by the co-adsorption of NO + O_2 in N_2 (spectrum a). The three bands rapidly decreased in intensity with an appearance of bands at 2240, 1691, 1651, 1580, 1566 and 1386 cm^{-1} after the gas mixture being exposed to the catalyst was switched to C_2H_2 + N_2. Apparently, the bands at 1651 and 1566 cm^{-1} due to –ONO and $-NO_2$ vibrations [19] increased with time, along with the band at 1691 cm^{-1}. The weak band at 2240 cm^{-1} due to –N=C=O vibration of isocyanate species [20] increased in intensity during the first several minutes, and decreased then after. Finally, it disappeared when the band at 1691 cm^{-1} reached its maximum in intensity. The result may imply that the species giving the band at 1691 cm^{-1} is produced by the isocyanate species.

In literature, Poignant et al. have found a band at 1694 cm^{-1} during the reaction of NO + C_3H_8 + O_2 over HZSM-5 at 350 °C [15] and assigned the band to acetamide species. Larrubia et al. also found a band at 1690 cm^{-1} in FTIR on Fe_2O_3–TiO_2 when they exposed the catalyst to acetamide vapor at 350 °C [21]. However, no band at around 1690 cm^{-1}, but at 1670 cm^{-1} was found when we exposed the 2%Zr/HFER catalyst sample to acetamide vapor in N_2 in the temperature range of 30–300 °C. Instead, a spectrum that much close to spectrum f (in Fig. 2) in shape, with the bands at 1691 and 1386 cm^{-1} along with 1651 cm^{-1} (–ONO vibration) was obtained when the catalyst was exposed to formamide vapor (spectrum g). In addition, the number of carbon in the amine species is also supported by a simultaneously formed formate species with the band at 1580 cm^{-1} [22] (spectra c–f). Hence, we propose that formamide species was formed during the reaction of C_2H_2-SCR over 2%Zr/FER catalyst by nitric species reacting with acetylene. Correspondingly, a possible formation route of the formamide species can be proposed as follows:



Formate species may be produced by the formamide species further reaction with nitric species: