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The first study of SCR of NO_x by acetylene in excess oxygen

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Acetylene as a reducing agent for the selective catalytic reduction (C_2H_2-SCR) of NO in the presence of excess oxygen on various Ce-exchanged zeolites was investigated for the first time. Under the conditions of 1600 ppm NO, 800 ppm C_2H_2, and 9.95 % O_2 in He, the Ce-H-ZSM-5 (Si/Al = 25) catalyst shows about 83% NO conversion to N_2 at the temperatures ranged from 300 to 350 °C. It is followed by the other zeolites in the activity order of Ce-H-Y (Si/Al = 2.5), Ce-H-_ (Si/A1 = 20~30), and Ce-H-SAPO (Si/Al = 34), Ce-H-5A (Si/Al = 12). Almost no NO conversion was obtained over Ce-Na-ZSM-5 (Si/Al = 25) and Na-ZSM-5 (Si/Al = 25) catalyst samples. The Conversion of NO to N_2 increased with O_2 concentration in the range of 0.1 ~ 9.95% over the CeH-ZSM-5 (Si/Al = 25) catalyst. It is suggested that O_2 plays an important role in the C_2H_2-SCR of NO reaction, by oxidizing NO to NO_2 on acid sites in assistant with cerium species of the catalyst. A large amount of CO, which seems to be in proportion with the NO conversion to N_2, was produced. Long-term experiments up to 56 h combined with a excursion of the reaction temperature up to 650 °C over the Ce-H-ZSM-5 (Si/A1 = 25) confirmed the catalyst's durable performance under the reaction conditions. It is found that the de-NO_x activity of Ce-H-ZSM-5 catalyst can be enhanced by the presence of 50 ppm of sulfur dioxide in the dry-feed reaction conditions.

KEY WORDS: acetylene; cerium-exchanged catalysts; De-NO_x; SCR.

1. Introduction

Removal of NO_x in excess oxygen conditions, such as from diesel or gasoline fueled leanburn engines' exhaust, has become one of the greatest challenges in environment protection. Since Iwamoto *et al.* [1] and Held *et al.* [2] have found alkenes and C_3-alkanes being capable of catalyzing the reduction of nitrogen oxides over Cu-ZSM-5 in the presence of oxygen, the selective catalytic reduction of SCR of NO_x by hydrocarbons (HC-SCR) was extensively investigated. However, higher activity and selectivity towards the reduction of NO_x under a lower temperature is essential to meet the practical exhaust treatment from lean-burn gasoline or diesel engines.

Among various hydrocarbons, methane has received great attention due to its widespread availability and easy handling. However, compared with the other hydrocarbons, it demands ca. 500 °C to activate the C-H bands in the HC-SCR of NO, e.g. over Co/ sulfated zireonia [3], Pd-Co/HZSM-5 [4], and indium or cerium incorporated zeolites [5]. Some researchers found that the temperature with maximum NO conversion in the SCR of NO by methane is at least 100 °C higher than that by C_3-hydrocarbons over Ga_2O_3/Al_2O_3 [6] and Cu-ZSM-5 [7] catalysts. In all of the HC-SCR investigations, methane gave the highest selectivity for NO reduction in lean-burn conditions, though it requires the higher reaction temperature, e.g. over Ce-In-H-MFI catalyst under a reaction system of 1000 ppm NO + 1000 ppm CH_4 + 10 vol.% O_2 + He, at 550 °C, the conversion of NO to N_2, 90%, was achieved [5].

On the other hand, some results being exciting with lower reaction temperature were obtained using higher hydrocarbons. For example, at 400 °C, a maximum conversion, 90% of NO to N_2 was obtained over SnO_2 doped Ga_2O_3–Al_2O_3 catalyst in reaction system of 900 ppm NO + 900 ppm C_3H_6 + 10%O_2 + 9.1%H_2O+ He [8], and ca. 90% conversion of NO was achieved at 350 °C over Ce (72)-H-FER catalyst under the reaction system of 400 ppm NO_x + 400 ppm C_3H_6 + 10%O_2 + 10%H_2O + N_2 [9]. However, the selectivity of the HC-SCR using alkenes or the alkanes (C > 2) seems not to be appreciated.

Up to date, no work has been reported using acetylene as reductant in SCR of NO reaction, though this industrial gas is convenient to be produced from methane or calcium carbide. There might be a worry that acetylene would strongly adsorbed on the surface of the catalyst, resulting in carbon deposition and catalyst deactivation. In this paper, however, aimed to increase the selectivity and activity for removal NO_x in excess oxygen at lower temperature, acetylene as reductant of the SCR of NO_x reaction (C_2H_2-SCR) was investigated over Ce-zeolites catalysts, and some significative results were obtained.

2. Experimental

2.1. Catalyst preparation

Commercial zeolites H-ZSM-5 (Si/Al = 25, 38, 50), H-_ (Si/Al = 20~30, 50~60), Na-ZSM-5 (Si/A1 = 25),

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Na-Y (Si/Al = 2.5), and Na-5A (Si/Al = 12) were used in this study as parent zeolites. For terseness, the Si/Al ratio in the parent zeolites was abbreviated to the value written in the parentheses hereafter. All Ce-H-zeolites were prepared from the proton form zeolites (H-zeolites) by the conventional ion-exchange method. To obtain H-Y and H-A zeolites, the Na-zeolites (Y, or 5A) 100 g was stirred in 500 mL of 1.0 M NH_4NO_3 aqueous solution at 80 °C for 10 h, filtered, and washed with demineralized water, then dried at 120 °C over night, calcined at 500 °C in air for 5 h. The procedures were repeated once more to obtain proton completely exchanged zeolites.

Ce-exchanged zeolites were prepared by stirring 4 g of the related H-zeolites (or Na-zeolites) in 50 mL of 0.04 M cerium nitrate aqueous solution at 80 °C for 10 h. After exchange, the sample was filtered, rinsed with deionized water and dried at 120 °C overnight in air. Besides the Ce-zeolites, a cerium-exchanged montmorillonite (Ce-H-MON) sample was also prepared in this way using a sulfuric acid treated montmorillonite as parent material.

For comparison, a sample of cerium oxide supported on commercial _-Al_2O_3 (with specific surface area 122.3 m^2/g), 1.6%Ce/-Al_2O_3, was prepared by incipient wet impregnation method.

All of the catalyst samples were finally calcined at 500 °C in air for 6 h and then pelletized, crushed to 20~40 mesh.

2.2. C_2H_2-SCR activity test

The C_2H_2-SCR tests were performed in a conventional fixed bed flow reactor (i.d. 4 mm) equipped with a temperature programmer–controller in the temperature range from 250 to 500 °C. Unless states differently, the reaction mixture typically containing 1600 ppm NO, 800 ppm C_2H_2, and 9.95%O_2, 0 or 50 ppm SO_2 in He was feed through the 0.2 g catalyst with a total flow rate of 50 mL min^{-1}. Catalytic activity was evaluated by the level of NO conversion to N_2, being analyzed by a gas chromatography (HP 6890) with a capillary column (HP-PLOT/zeolite 30 m_0.32 mm_12_m) and TCD at 50 °C. As a special performance of acetylene as the reductant compared with other hydrocarbons in the SCR of NO reduction, it produces large amount of CO, which was also analyzed by the same GC, while the C_2H_2 conversion was measured by another GC with a capillary (HP-PLOT/Al_2O_3 30 m_0.530 mm_15.00_m) and FID.

2.3. $NO + O_2$ activity test

The oxidation of NO to NO_2 over the catalyst was recorded at the temperatures ranging from 250 to 500 °C in a system of 200 ppm NO and 10%O_2 in N_2, by flowing the gas mixture with a total flow rate of 100 mL min^{-1} through 0.2 g catalyst in a quartz reactor with an inner diameter of 4 mm. Both the produced NO_2 and NO remaining in the outlet of the reactor were monitored by means of an electro-chemical NO_x analyzer ACY301-B, and the reaction data of NO were collected constantly over the one charge catalyst after the reaction being proceeded in a stable state for 40 min at each desired temperature.

2.4. C_2H_2-adsorption test

C_2H_2-adsorption on the catalyst was conducted at 40 °C on a set up after the sample had been pretreated at 500 °C in N_2 on-line for 60 min. The acetylene adsorption was started with a fourway valve turning, which inlets the gas mixture containing 2254 ppm C_2H_2 in N_2 through 0.2 g catalyst with a flow rate of 30 mL min^{-1}. Both of the by-passed gas before adsorption and the effluent from the sample were monitored by GC with FID.

3. Results and discussion

3.1. C_2H_2-SCR of NO over different Ce-zeolites

Figure 1 depicts NO and C_2H_2 conversion as a function of temperature over various Ce-exchanged catalyst samples in the C_2H_2-SCR. Obviously, in the reaction system of 1600 ppm NO, 800 ppm C_2H_2, and 9.95%O_2 in He, NO conversion to N_2 in the C_2H_2-SCR depends much on the kinds of zeolites which was ranked as Ce-H-ZSM-5 (25) > Ce-H-Y (2.5) > Ce-H-_ (20~30) > CeH-SAPO (34) > Ce-H-5A (12). Ce-H-ZSM-5 (25) shows the maximum conversion of 83%, in the temperature range of 300~350 °C, corresponding to the nearly total C_2H_2 consumption, as shown in figure 1b. The Ce-H-Y (2.5) and Ce-H-_ (20~30) displayed a moderate lower NO conversion to N_2, whereas in the case of Ce-H-SAPO (34) and Ce-H-5A (12), less than 10% of NO conversion to N_2 were obtained at 350 °C with a low C_2H_2 conversion.

Some parent zeolite samples were also used as catalysts for the reaction. As shown in figure 2a, H-ZSM-5 (25) gives 58.9% of NO conversion to N_2 at 300 °C, which is much lower than that of the Ce-H-ZSM-5 (25), indicating that the cerium ion in the zeolite plays an important function in the SCR of NO reaction. The enhancement of cerium on the NO conversion to N_2 appears on the H-Y (2.5) and H-5A (12) as well, upon cerium ion being exchanged into the zeolite catalysts, which is clear by comparing figure 1a, and figure 2a. Especially in the case of the H-Y (2.5) zeolite which shows 15.3% NO reaction to N_2 at 350 °C, while a dramatic increase of the NO reduction up to 75.0% over the Ce-H-Y (2.5) was achieved, in accordance with an acetylene conversion increase from 37.9 to 100% as shown in figure 1b, and figure 2b. To investigate the role of cerium species in zeolites for the C_2H_2-SCR, the performance of the H-ZSM-5 (25) and Ce-H-ZSM-5

(25) for C_2H_2 adsorption was compared. As shown in figure 3, no considerable difference was observed, indicating that the promotion effect of cerium for the C_2H_2-SCR cannot attribute to any modified C_2H_2 adsorption. In some previous studies [10–12], an enhanced NO conversion to N_2 by incorporating cerium to zeolites in the HC-SCR using C_3H_6 or CH_4 as reluctant has been reported, and the major function of cerium suggested in those studies was to initiate the SCR reaction by converting NO to NO_2 [11,12]. In the C_2H_2-SCR, the function of cerium is also clearly manifested by the following two investigations.

In a system of 200 ppm NO, 10% O_2 in N_2, Ce-H-ZSM-5 is far more active for NO oxidation with O_2 than the H-ZSM-5 at the elevated temperatures, as shown in figure 4, which is well in agreement with the activities for NO reduction to N_2 displayed in the C_2H_2-SCR. By this correlation, the maximum activity of the catalysts at the temperature ranged in 300-350 °C for the C_2H_2-SCR can be well interpreted.

In the conditions of 0 ppm NO, 800 ppm C_2H_2, 9.95% O_2 in He, acetylene conversion was rather low at each reaction temperature over the Ce-H-ZSM-5 (25) compared with those in the presence of 1600 ppm NO, as shown in figure 5. This result implies that the acetylene consumption is initiated mainly by the NO_x species, most probably being concerned with the NO_2 formation, especially at the lower reaction temperature, though the NO concentration is much lower than that of O_2 in the C_2H_2-SCR conditions. Here, the result that Ce-H-SAPO (34) and Ce-H-5A (12) show both lower conversions of NO and C_2H_2 in the C_2H_2-SCR, as described above, could be explained by the lack of activity for the oxidation of NO to NO_2.

The C_2H_2-SCR of NO was also investigated over a cerium oxide supported sample, 1.6%Ce/_-Al_2O_3, as shown in figure 2. The catalyst gave a very low activity for the aimed reaction, leading to only 8.3% NO conversion to N_2 at 400 °C, with 92% C_2H_2 consumption, which is in good agreement with the rather lower activity for the oxidation of NO to NO_2, as shown in figure 4. It seems that the cerium component mainly enhances the NO_x reduction only when it exists in the tunnels of H-ZSM-5 zeolite, while dominantly accelerates the combustion of the reducing agent in the reaction conditions when it is supported on the _-Al_2O_3. The very low activity may also be related with its different cerium species state on the support, besides with the support's nature itself. It was suggested previously by the researchers that the isolated cation in zeolites' tunnels is more active species than aggregated oxide clusters for the HC-SCR [12].

It should be noticed here that as a special performance of the C_2H_2-SCR, which is quite different from other HC-SCR of NO reported before in literatures, is that about a same moles level of CO as that of NO undergoing reduction to N_2 was produced in the C_2H_2-SCR over the most of catalysts as shown in Table 1. This result implies that the CO is produced quantitatively with the NO reduction to N_2, according to some special mechanism, which is to be investigated.

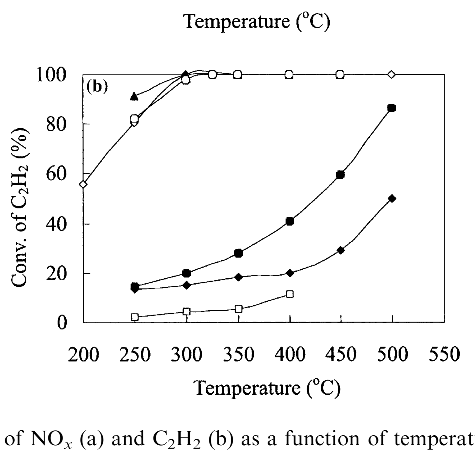

Figure 1. Conversion of NO_x (a) and C_2H_2 (b) as a function of temperature over Ce-H-zeolites.

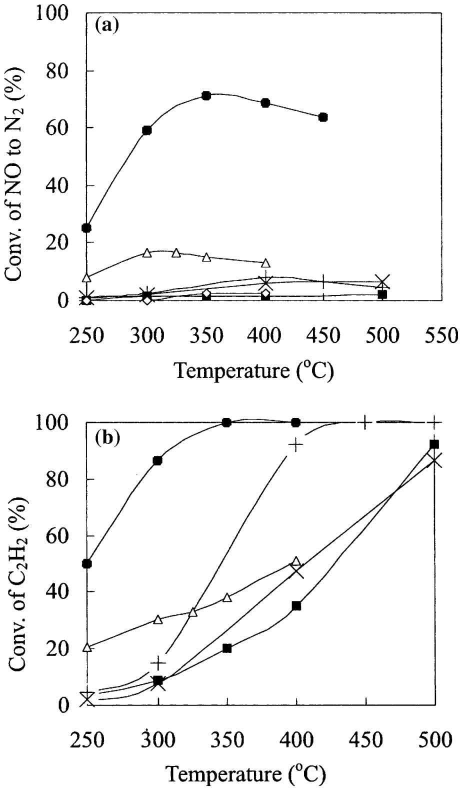

Figure 2. Conversion of NO_x (a) and C_2H_2 (b) as a function of temperature over H-zeolites.

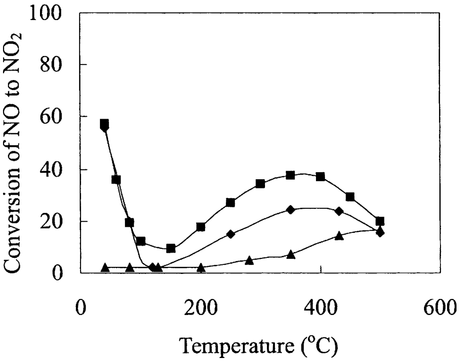

Figure 4. Oxidation of NO to NO_2 by O_2 over 0.2 g Ce-H-ZSM-5 (25) (_), H-ZSM-5 (25) (_), Ce/ _Al_2O_3 (_) catalysts in the feed of 200 ppm NO, 10%O_2, and balanced in N_2 at the flow rate of 50 mL min^{-1}.

3.2. Synergetic effect of proton with Ce^{3+} in the C_2H_2-SCR

Comparing the catalytic performance of Ce-H-ZSM-5 (25) and Ce-Na-ZSM-5 (25) shown in figure 1, a dramatic different effectiveness of Ce^{3+} could be observed for the C_2H_2-SCR upon it being incorporated to the proton or sodium form zeolite. Almost no detectable NO conversion to N_2 could be observed over the Ce-Na-ZSM-5 (25) in 300~350 °C with no more than 20% of acetylene consumption, though the Ce-H-ZSM-5 (25) shows the highest activity for the NO selective reduction in the temperature range. Correspondingly, no activity for the C_2H_2-SCR was observed over the Na-ZSM-5 (25) as shown in figure 2. This result indicates that proton in the zeolites plays a decisive role in the C_2H_2-SCR, and the doping effect of Ce^{3+} for the C_2H_2-SCR could exert only in the proton assistance. In other words, there is a synergetic effect for C_2H_2-SCR between Ce^{3+} and proton. Using methane as reducing agent in the SCR of NO reaction, similar result was reported previously by E. kikuchi [13].

As discussed above, both proton and the cerium ion were suggested to play significant role in the C_2H_2-SCR, that is the reason why we prepared the Ce-H-zeolites from H-zeolites in this study. Accordingly, some acidic materials with large surface area seem to be expected as better support candidates for the C_2H_2-SCR, if they disperse cerium in ion level. As an attempt, a montmorillonite treated with sulfuric acid was investigated for the C_2H_2-SCR, after exchanged with cerium. Unfortunately, however, it gives only 2% of NO conversion to N_2 at 300 °C, as shown in figure 2a. The less activity may be resulted from the disappearance of the intervals between the aluminosilicate layers, which was

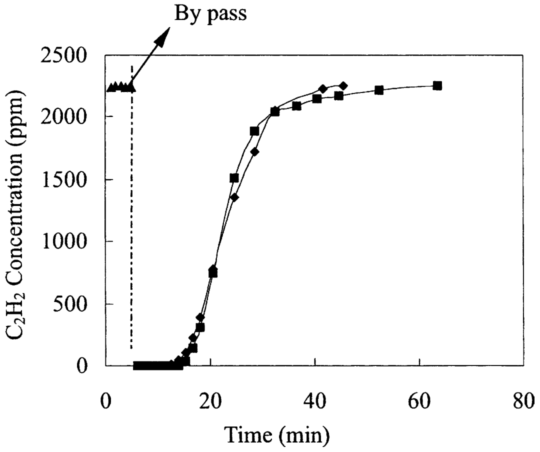

Figure 3. C_2H_2 absorption over Ce-H-ZSM-5 (25) (_) and H-ZSM-5 (25) (_) in the feed of 2254 ppm C_2H_2, bal. in N_2.

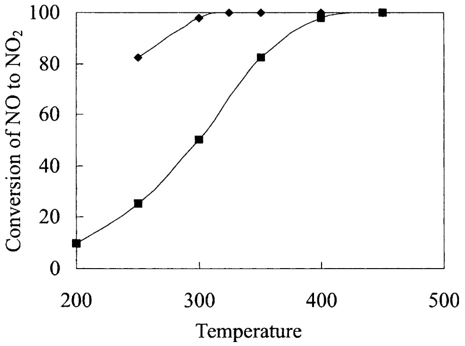

Figure 5. Comparison of C_2H_2 conversion over 0.2 g Ce-H-ZSM-5 (25) in the feed of 800 ppm C_2H_2, 9.95%O_2 in He with 1600 ppm NO(_) and without NO (_).

Table 1
By-product of CO over different zeolites*

Sample	NO conv. to N_2 (%)	C_2H_2 conv. to CO (%)	Total conv. of C_2H_2 (%)
Ce-H-ZSM-5 (25)	83	59.7	98.9
Ce-Na-ZSM 5 (25)	0	15.3	2.9
H-ZSM-5 (25)	58.9	54.6	86.6
Na-ZSM-5 (25)	0	6.9	15.3
Ce- H-_ (20∼30)	39.5	61.7	100
Ce-H- 5A (12)	1.0	1.3	4.3
H- 5A (12)	1.4	2.3	9.0
Ce-H-Y (2.5)	75.4	60.8	100
H-Y (2.5)	16.9	17.2	30.6
Ce-H-SAPO (34)	6.6	9.4	19.9
Ce-H-MON	2.0	4.8	7.5
Ce/Al_2O_3	2.4	3.4	15.0

*Reaction conditions: 300 °C, 1600 ppm NO, 800 ppm C_2H_2, and 9.95% O_2 in He with a total flow rate of 50 mL min^{-1} over 0.2 g catalyst.

characterized by the XRD of the samples calcined at temperature above 300 °C. The study using some pillared montmorillonites as the catalyst material for the C_2H_2-SCR is in progress.

3.3. The effect of Si/Al ratio of the zeolites

To further check the effect of acidity of the zeolite on the C_2H_2-SCR, we investigated the catalytic performance of Ce-H-ZSM-5 zeolites with different Si/Al ratios, as one expected that the zeolite with higher Si/Al ratio provide less acid sites for the reaction. As shown in figure 6a, being sensitive to the Si/Al ratio, the activity of the Ce-H-ZSM-5 for the C_2H_2-SCR acutely decreased with the Si/Al ratio increase, even no NO conversion to N_2 was observed over the Ce-H-ZSM-5 (50), which is in good agreement with the acid amount order being expected in the zeolites. In addition, Ce-H-_ catalysts with different Si/Al ratios also gave the similar order as that of the CeH-ZSM-5 catalysts, though the absolute activity of two kinds of zeolites is different each other due to their diverse structure. On the other hand, as shown in figure 6b, except for the Ce-H-ZSM-5 (50), all of the catalysts with higher Si/Al ratio show comparable acetylene consumption as that of the catalysts with lower Si/Al ratio, though they give much lower NO conversion level. The results indicate that, in the competitive reactions between the NO_x reduction and the useless combustion of C_2H_2, the former one could be largely facilitated by the acidity of the Ce-H-zeolite catalysts, and consequently, the latter one could be suppressed.

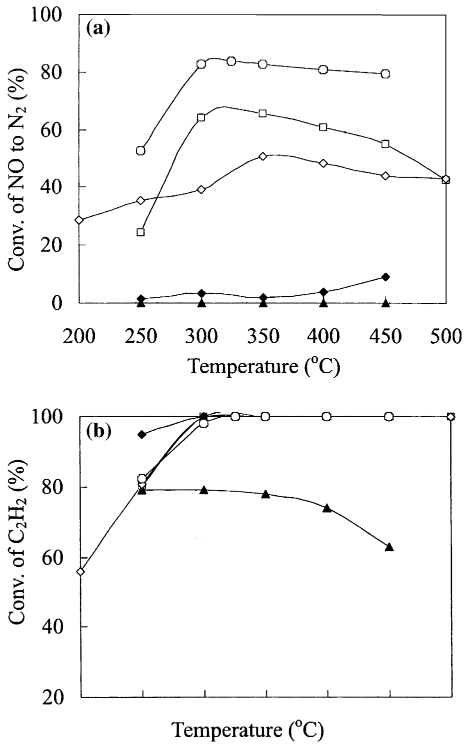

Figure 6. Conversion of NO_x (a) and C_2H_2 (b) as a function of temperature over Ce-H-zeolites with different Si/Al ratios.

3.4. Effect of O_2 concentration

The catalytic performance of Ce-H-ZSM-5 (25) was studied with different O_2 concentration ranged of 0.1% $\sim$ 9.95 %, as the concentration of O_2 in the reaction gas is an important variable for the reaction mechanism studying. As shown in figure 7, almost no N_2 produced from NO was observed in the 0.1% O_2, The conversion of NO to N_2 strongly dependeds on the O_2 concentration, especially in the lower O_2 concentration range, 0.1% $\sim$ 1.18% O_2, the NO conversion increased sharply from $\sim$0 to 47.4%. It is clear that in the C_2H_2-SCR process, some reaction steps, in which O_2 participates in, controls the apparent NO reduction rate in the lower O_2 concentration conditions. This result indicates that O_2 has a crucial contribution to the NO reduction, though it also competes the reductant C_2H_2 in some extent for combustion over the Ce-H-ZSM-5 (25) catalyst. We believe that the oxidation of NO to NO_2 is the

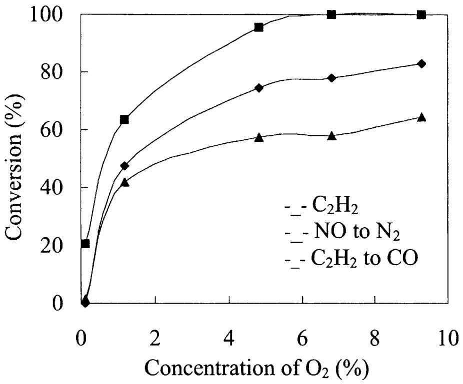

Figure 7. The dependence of C_2H_2-SCR of NO reaction upon O_2 concentration in the feed gas over the Ce-H-ZSM-5 (25).

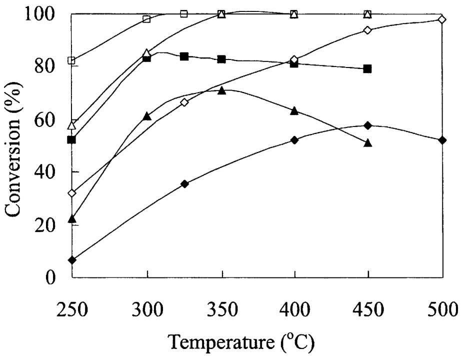

Figure 8. Conversion of NO to N_2 (filled symbols) and C_2H_2 (open symbols) as a function of temperature over Ce-H-ZSM-5 (25) at SV = 8000 h^{-1} (_, _) 16,0001 h^{-1} (_, Δ), and 40,000 h^{-1} (_,◇).

rate-determining step of NO reaction to N_2, in the O_2 concentration range of 0~10% over the Ce-HZSM-5 (25), with which the role of cerium component was well understand as discussed in the section 3.1.

O_2 is essential for the NO reduction, the previous result was reported by Shimizu *et al.* [6] in the CH_4-SCR over Ga_2O_3/Al_2O_3, and Long and Yang [14] over Pt/MCM-41. Chen and Kawi [15] suggested that the role of oxygen over the Pt/MCM-41 in the C_3H_6-SCR below 250 °C is to assist the activation of C_3H_6, forming the oxidized hydrocarbon intermediates to react with NO on the catalyst, and by this way facilitating the NO reduction. Another speculation in the literatures is that O_2 reacts with NO to form NO_2, which is then reduced to N_2 by the hydrocarbon or oxidized hydrocarbon [5,16,17]. In the case of C_2H_2-SCR, the former speculation seems to be excluded. In the 0.1% O_2 conditions, as shown in figure 7, ca. 20.7% of C_2H_2 was converted at 300 °C, from which a considerable partially oxidized hydrocarbons and carbonaceous deposits thus could be expected as the products in the reaction conditions, besides the observed ca. 1.7% CO. However, almost no N_2 arising from the NO removal could be detected.

3.5. *Catalytic performance Ce-H-ZSM-5 (25) in different space velocity*

The performance of the Ce-H-ZSM-5 (25) catalyst for SCR of NO was studied at different space velocity (SV), as shown in figure 8. When space velocity increased from 8,000 to 40,000 h^{-1} which was carried out by decreasing the catalyst loading from 0.2g to 0.04g, the NO conversion to N_2 sharply decreased, especially at the lower temperature in the range of 250~350 °C. For instance, at 325 °C, the NO conversion to N_2 lowed down from 83 to 35.7%, corresponding to the space velocity variation from 8,000 to 40,000 h^{-1}. Meanwhile, the acetylene conversion was also drastically decreased, indicating that the activity of the Ce-H-ZSM-5 (25) catalyst is strongly affected by the SV.

3.6. *Efficiency of the C_2H_2-SCR over the Ce-H-ZSM-5 (25)*

Based on the C_2H_2-SCR results obtained in the excess O_2 (9.95%) over the Ce-H-ZSM-5 (25) catalyst, the total amount of O_2 consumed both in the NO reduction process according to the reaction (1), and in the possible C_2H_2 combustion process according to the reaction (3)

$$NO + O_2 \longrightarrow NO_2 \qquad (1)$$

$$C_2H_2 + NO_2 \longrightarrow N_2 + CO + CO_2 + H_2O \qquad (2)$$

$$C_2H_2 + O_2 \longrightarrow CO + CO_2 + H_2O \qquad (3)$$

could be deduced as follows:

$$NO + C_2H_2 + O_2 \xrightarrow{\text{Ce-H-ZSM-5}} N_2 + CO + CO_2 + H_2O$$

Experimental data in ppm (Consumed or produced): 1340 800 670 1017 Calculated data in ppm deriving from the experimental data: 822 583 800

If the C_2H_2-SCR of NO reaction occurs exactly *via* the intermediate NO_2, and no combustion of the reducing agent takes place, the moles of O_2 consumed in the reaction will be half as many as the NO in moles being reduced to N_2. Interestingly, the amount of O_2 calculated from the experimental data based on oxygen balance turns out to be 822 ppm which is much close to 670 ppm expected to react with the 1340 ppm of NO, forming the intermediate NO_2 in the C_2H_2-SCR reaction. Thus, among the practically consumed O_2 in the reaction, only 152 ppm of O_2 being deduced to react with C_2H_2 for combustion, i.e. in the C_2H_2-SCR, with reducing 1340 ppm NO_2 to N_2 over the Ce-H-ZSM-5 (25) catalyst, C_2H_2 reacts with 152 ppm of O_2 for combustion in the 9.95% O_2 reaction condition. Accordingly, it could be further deduced that the C_2H_2-SCR reaction proceeded with 90% selectivity based on C_2H_2 over the Ce-H-ZSM-5 (25) catalyst at 325 °C, assuming that one mole of NO_2 and of O_2 consume the same amount of C_2H_2 for the aimed reaction and the competitive combustion, respectively.

Comparing with the recent results reported in literatures, it is interesting here to evaluate the efficiency of the C_2H_2-SCR over the Ce-H-ZSM-5 catalyst. It seems that acetylene is much more selective to NO_x reduction than propene, as it gives the nearly same level of NO_x conversion to N_2 as that of propene reported in the literatures [8,9,18–20], using one third of the reducing agent in carbon moles. Moreover, in the C_2H_2-SCR, it was noticed that a large part of carbons in acetylene was not converted to CO_2, but CO which is still a sort of reductant for the SCR of NO in the lean bum conditions over some catalyst being responsible for reducing NO_x with the reductant, though it seems to be ineffective over the cerium based zeolites.

3.7. Durability of the Ce-H-ZSM-5 in the C_2H_2-SCR

For all the Ce-exchanged catalyst samples tested in C_2H_2-SCR, no color change was observed after the reaction. It indicates that no carbon deposition accumulated on the catalysts during the C_2H_2-SCR of NO reaction under the lean burn conditions. To estimate the durability of the Ce-H-ZSM-5 (25) catalyst in the C_2H_2-SCR, the reaction was carried out continuously for 56 h at 325 °C combined with some cycled temperature variation. As shown in figure 9, deactivation evidence of the catalyst could not be observed neither in the temperature cycle of 325–400–350–325–300–325 °C nor in the reaction period of 48 h at 325 °C prolonged afterwards, implying its better durability for the C_2H_2-SCR application. No deterioration could be observed as well in the NO conversion to N_2 at 325 °C as the Ce-H-ZSM-5 catalyst experienced the temperature excursion up to 650 °C, as given in figure 10, indicating that the catalyst is capable of withstanding the thermal impact which is possibly occurred in the practical application.

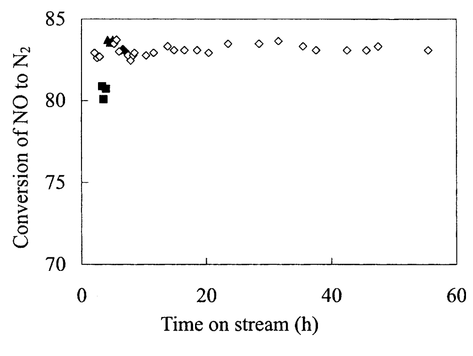

Figure 9. Time on stream of the Ce-H-ZSM-5 (25) catalyst (0.2 g) in the feed of 1600 ppm NO, 800 ppm C_2H_2, 9.95% O_2 in helium with a total flow rate of 50 mL min^{-1}, at 300 °C_; 325 °C◇; 350 °C_; 400 °C_.

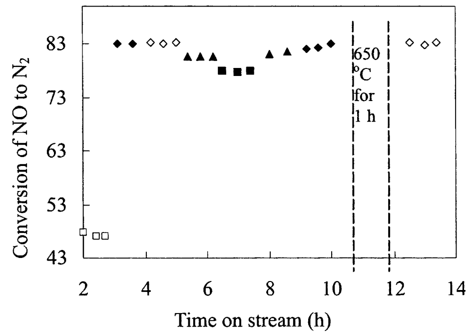

Figure 10. Catalytic performance of Ce-H-ZSM-5 (25) in C_2H_2-SCR at 250 °C_; 300 °C _; 325 °C◇; 350 °C–; 400 °C– before and after experienced 650 °C.

3.8. Tolerance of the Ce-H-ZSM-5 (25) to sulfur dioxide

The presence of sulphur in fuel usually plays a detrimental role in the performance of HC-SCR catalysts as a method to control emissions from engines operated under lean burn conditions. It was found that the activity of NO reduction over the Pt and Pd catalyst was completely suppressed even in the presence of low levels of SO2 (20 ppm) [21]. Therefore, improving the tolerance of the catalysts towards SO_2 is an important prerequisite for its application in the SCR of NO. In this paper, favorable result was achieved over Ce-H-ZSM-5 (25) catalyst by the presence of 50 ppm SO_2, as shown in figure 11. About 3% increase in terms of NO conversion to N_2 in the reaction temperature range of 250∼450 °C was observed compared with the SO_2-free conditions. The result obtained in the C_2H_2-SCR is consistent with that reported in the literature [22] regarding the presence of SO_2 in the C_3H_6-SCR and C_3H_8-SCR study.

4. Conclusion

Acetylene as reducing agent used for the selective catalytic reduction of NO has the character of both being effective at the lower reaction temperature as that of alkenes and being efficiency as selective as methane

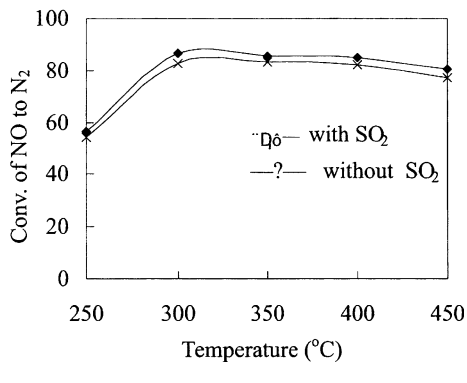

Figure 11. The effect of SO_2 on the C_2H_2-SCR over the Ce-H-ZSM-5 (25) Feed gas: 1600 ppm NO, 800 ppm C_2H_2, 9.95% O_2, 0 or 50 ppm SO_2 in He.

for the aimed reaction. It is clear from the result that about 83% NO conversion to N_2 was achieved over Ce-H-ZSM-5 (25) catalyst at the temperature ranged in 300~350 °C, under the condition of 1600 ppm NO, 800 ppm C_2H_2, and 9.95% O_2 in He. No deterioration could be observed at 325 °C in the long-term experiments up to 56 h combined with a temperature excursion up to 650 °C. The presence of SO_2 in the feed has a promotional effect on the C_2H_2-SCR. In the C_2H_2-SCR, about a same moles level of CO as that of NO undergoing reduction to N_2 was produced in the C_2H_2-SCR over the most of catalyst. This result implies that the CO is produced quantitatively with the NO reduction to N_2, according to some special mechanism.

O_2 plays an important role in the C_2H_2-SCR of NO reaction, by oxidizing NO to NO_2 over the Ce-H-ZSM-5 (25) catalyst, in which a synergetic effect between cerium species and proton exerts in the C_2H_2-SCR. The activity of the catalyst for C_2H_2-SCR depends much on the kinds of zeolites showing the order of Ce-H-ZSM-5 (25) > Ce-H-Y (2.5) > Ce-H-_ (20~30) > Ce-H-SAPO (34) > Ce-H-5A (12). Lower Si/Al ratio of the zeolite is favorable for the aimed reaction.

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