Study on the adsorption and reaction performance of Fe/ZSM-5 catalyst on catalytic reduction of NO$_x$ with propylene

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Abstract

The adsorption performance of Fe/ZSM-5 catalyst has been investigated in the SCR of NOx with propylene as the reducing agent. Freudlich equation was found to fit the adsorption isotherm satisfactorily if the system dispersion is considered. Fe/ZSM-5 catalyst showed reasonable NO adsorption capacity. The study on the influence of reaction temperature, gas space velocity and gas composition on the Fe/ZSM-5 catalyst activity showed that, at T=350°C and GHSV=5000h^{-1}, the catalyst exhibited acceptable activity when O$_2$ concentration was controlled at some low level ($\leq$1%) and HC to NO molar ratio was kept on a reasonable ratio of about 2:1. Those performance data may be used for design the operating conditions of a newly proposed dual-zone continuous reactor for catalytic reduction of NOx under lean operating conditions.

Keywords: Nitric Oxide; Fe/ZSM-5; Adsorption; Reduction; Propylene

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1. Introduction

The selective catalytic reduction of nitrogen oxides by hydrocarbons (HC-SCR) has been proven effective in the treatment of model flue gases. As a key component of the flue gas under lean-burn conditions, the influence of excess oxygen has been widely investigated [1, 2]. One of the main NO reduction mechanisms states that NO is first oxidized to NO_2, followed by the reduction by the reducing agent [1]. The presence of O_2 is thus essential for the HC-SCR process. This mechanism appears to agree with many experimental findings that the presence of small amount of O_2 (e.g., <2%) is essential for HC-SCR [3, 4, 5, 6].

However, for most combustion processes, O_2 concentration in the flue gas is higher than 2%. That means O_2 will inhibit the activity/selectivity of most HC-SCR catalysts. In fact, many researchers treat O_2 as one of the major negative impacts in HC-SCR under lean-burn conditions [3, 7, 8, 9].

As a developing technology, the HC-SCR of NO_x is still in the first stage of research. Most studies have been focused on the development of catalysts, the selection of reducing agents, or the mechanism of the reaction process. For a technology to be of practical applications, so called "engineering" approach, where the focus is on the reactor design and application, needs to be considered.

We proposed a novel fluidized bed reactor in which the NO_x adsorption and reduction are carried out in two separate zones of the reactor to avoid the negative influence of the poisoning components and excess O_2 in the flue gas. In this process, the flue gas is injected into the adsorption zone where NO_x is adsorbed to the catalysts. The NO_x-rich catalyst particles then move into the reaction zone where NO_x is reduced by injected hydrocarbons. The regenerated catalyst particles are then recirculated back to the adsorption zone to keep a continuous operation. By controlling the bypassing of the flue gas to the adsorption zone, the O_2 concentration can be controlled to desired level.

This study presents the adsorption and reaction performance of selected catalysts in a fixed bed reactor under various temperatures and flue gas compositions. The results will be used for the design of such an integrated dual-zone adsorption and reaction reactor.
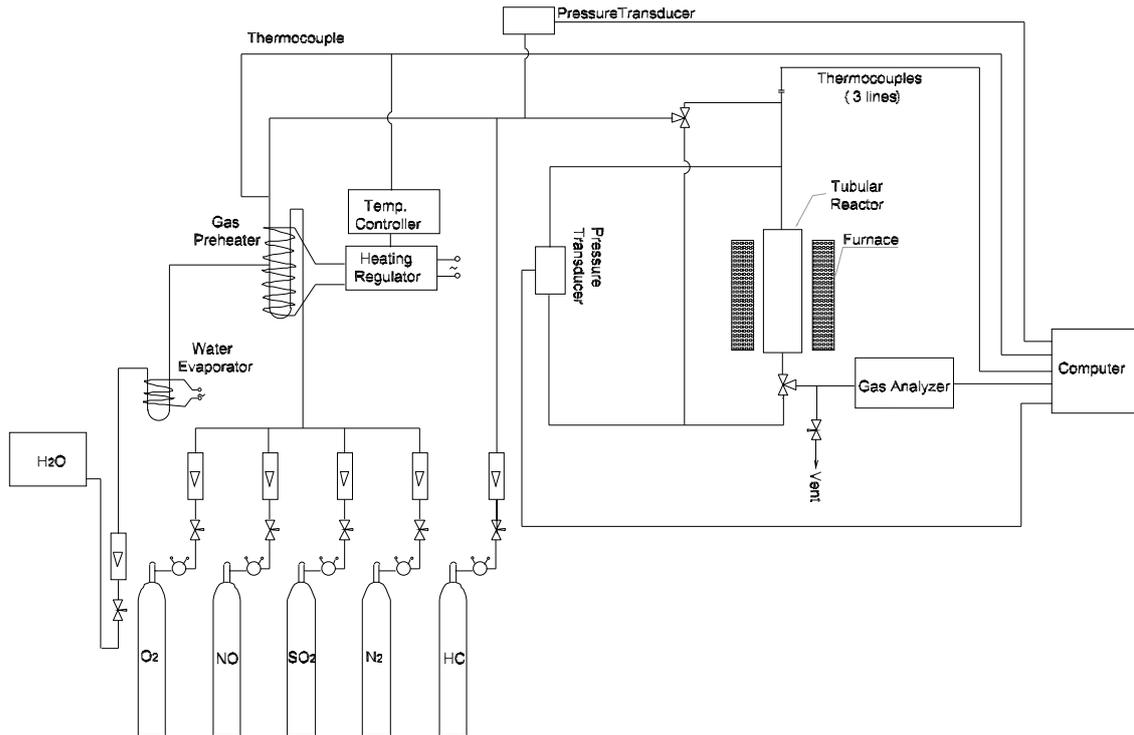
2. Experimental

2.1. Catalyst preparation

The catalyst used in the fixed bed experiment, Fe/ZSM-5, was prepared from the parent Na/ZSM-5 granular particles (Si/Al=23.5 mole/mole, Na_2O content=0.18%wt., S_{BET}=480m^2/g, bulk density=903 Kg/m^3, particle diameter range= 0.9-1.2mm). Na/ZSM-5 was first transformed to H/ZSM-5 by wet ion exchange (WIE) with a 0.5M NH_4Cl (99.5%, Fisher) solution, followed by calcinations at 550℃ for 4 hours. Thereafter, an iron (III) acetylacetate was used to prepare Fe/ZSM-5 according to the method described by Delahay et al. [10].

2.2. Reaction studies

The adsorption capacity and reaction kinetics of Fe/ZSM-5 catalyst was studied in a fixed bed reaction system, as shown in Fig. 1. A stainless steel tubular reactor with an inner diameter of 13.5mm was used in this experiment. The catalyst packing height was 50 mm. Propylene (HC) was used as the reducing agent in the experiment. The composition of the effluent gases was analyzed by a Horiba PG-250 flue gas analyzer.

Fig. 1 Schematic of fixed bed reaction system

The adsorption isotherm experiments were investigated under various temperatures and inlet NO concentrations using a model flue gas with 5% (v/v) O_2 balanced with N_2. The NO concentration of the model flue gas varied from 200 to 1000 ppm with an increment of 200 ppm and the temperature from 250°C to 400°C with an increment of 30°C. For each given temperature and gas composition, the breakthrough curve was determined experimentally, which was further used to calculate the equilibrium adsorption capacity q_e by integrating the breakthrough curve (the outlet concentration of NO vs. time). The Freudlich equation was applied to fit q_e as a function of C_0:

$$q_e = \alpha C_0^{\beta} \qquad (1)$$

With the relationship between α or β and temperature T derived, the equilibrium adsorption capacity q_e and breakthrough time t_B can be estimated.

To investigate the influence of temperature, gas space velocity, HC and O_2 concentration on the performance of the SCR catalyst, the selective catalytic reduction of NO was carried out in the same reactor with propylene as the reducing agent. The model gas composition was 600ppm NO, 1200ppm HC, 0.5% to 8% (v/v) O_2, balanced with N_2.

## 3. Results and discussion

3.1. Adsorption isotherm

A typical adsorption breakthrough curve is shown in Fig.2.
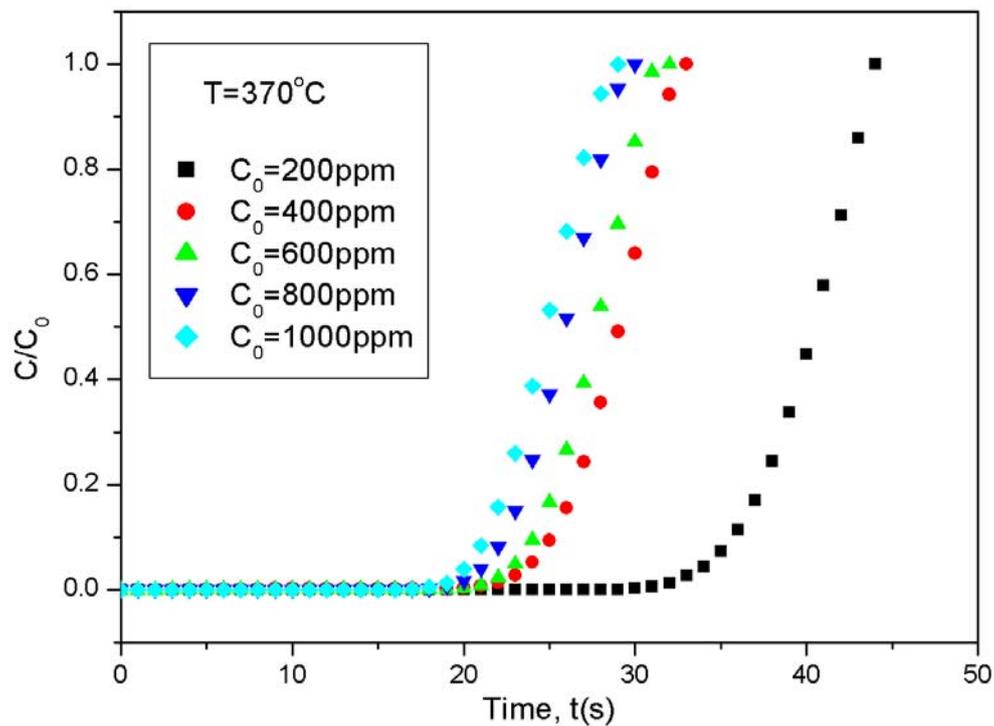
Fig. 2 Breakthrough curve of NO concentration at the reactor outlet.
Adsorption conditions: Feeding gas: NO+5%O_2+N_2;
Catalyst loading: 6.58g; GHSV=5000h^{-1}

Since there exists a delay in system response time for the analyzer, the delay time needs to be subtracted from the recorded adsorption time. Since the response time varied with the operating temperature, the delay time was determined separately for each operating temperature. After the adjustment of the adsorption time, the equilibrium adsorption concentration of NO on the catalyst can be integrated based on the breakthrough curve and fitted to the Freudlich equation, as shown in Fig.3.
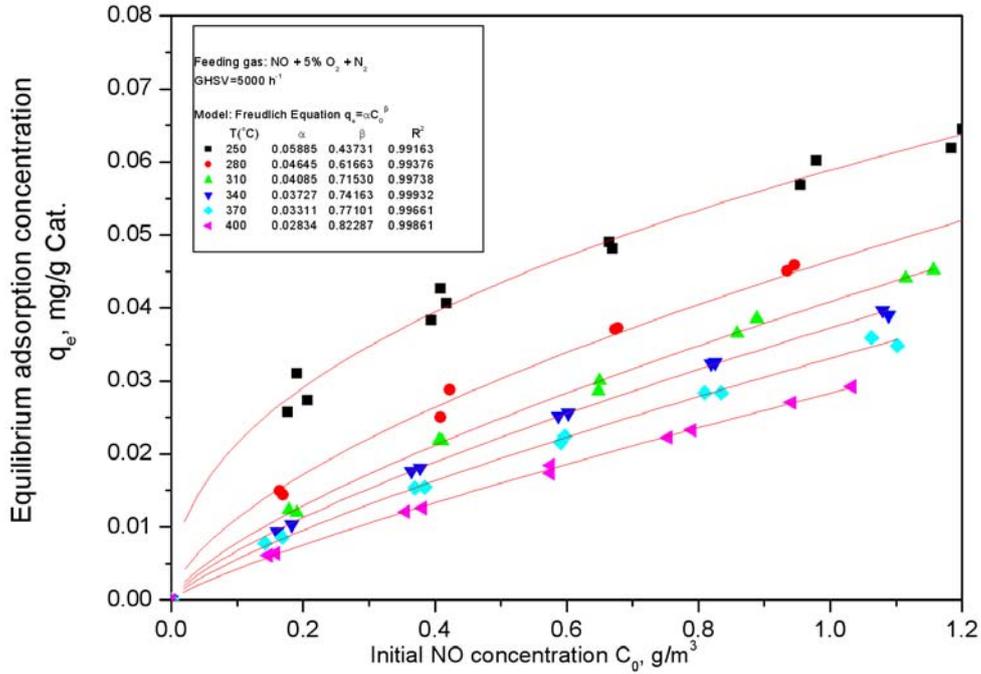
Fig. 3 Modelling of adsorption isotherm of NO by Freudlich equation

Using α and β fitted in Fig.3, the expression of coefficient α or β as a function of T was derived as follows:

$$\alpha = 0.02406 + 0.66855e^{(-T/83.89312)} \qquad (2)$$

$$\beta = 0.82696 - 44.47198e^{(-T/52.55039)} \qquad (3)$$

The breakthrough time for the catalyst bed $t_{B, cal}$ is calculated by:

$$t_{B,cal} = \frac{(xq_{e,cal})W_{cat}}{FC_0} \qquad (4)$$

where $q_{e,cal}$ is the calculated equilibrium adsorption capacity of NO on the catalyst, mg/g cat.; x is the percentage of $q_{e,cal}$ when breakthrough is reached; W_{cat} is the catalyst loading, g; F is the gas flow rate (m^3/s) and C_0 is the inlet concentration of NO, mg/m^3.

Theoretically, x should be set to 99%. However, if x=99% was applied in this study, the error distribution of calculated t_B compared to experimental t_B was roughly around 20% to 40%. On the other hand, if x=80%, the error could be controlled within 10% (see Fig. 4).
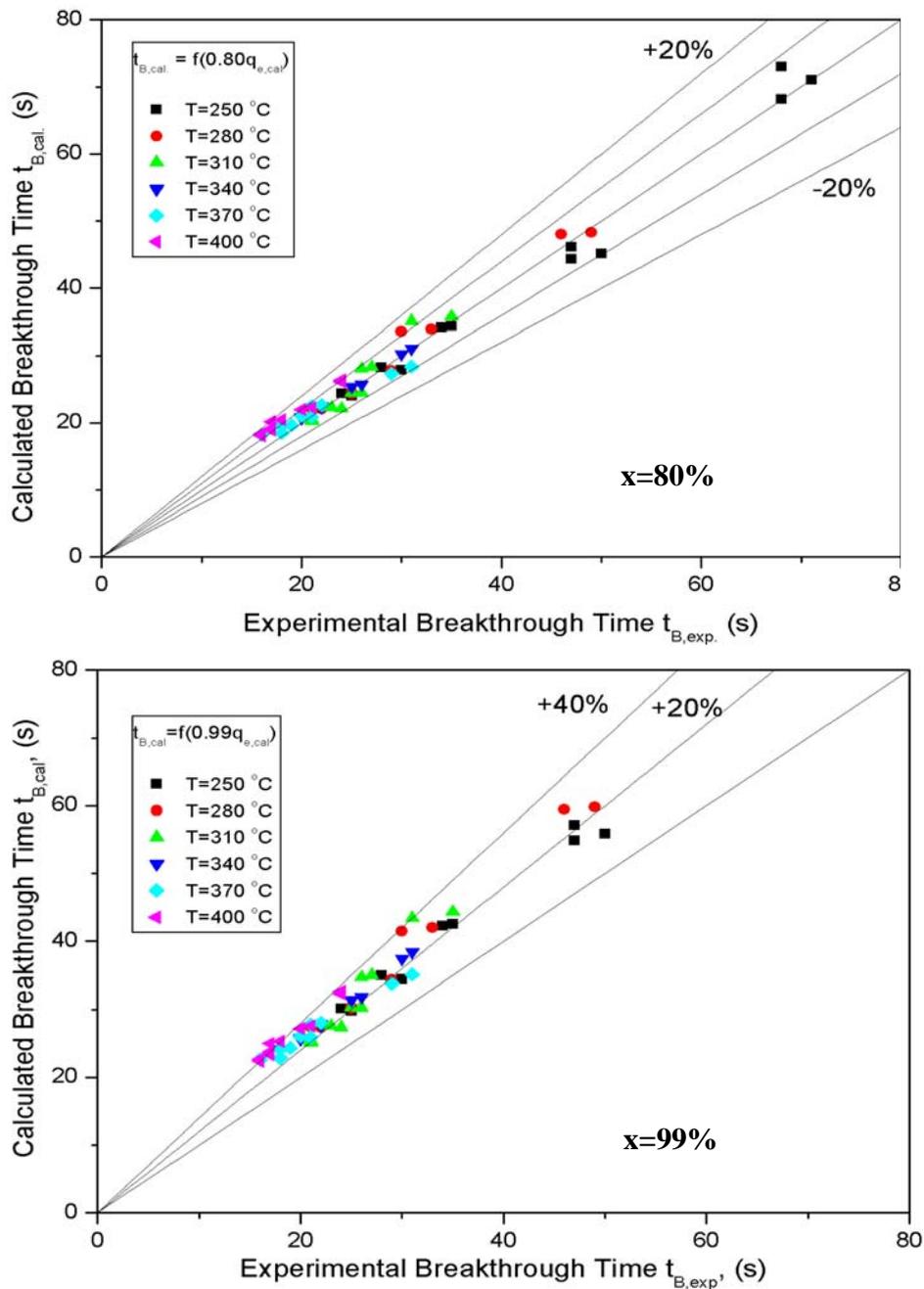
Fig. 4 Comparison of calculated and experimental breakthrough time, $t_{B,cal}$ and $t_{B, exp}$

Since the effect of gas dispersion is not considered in the calculation of breakthrough time, it is important to see how system dispersion can affect the breakthrough. An experiment was thus carried out to investigate the gas dispersion due to gas adsorption in the test system with the use of adsorbing catalyst and non-adsorbing glass bead particles of approximately same mean size, with the result shown in Fig. 5.
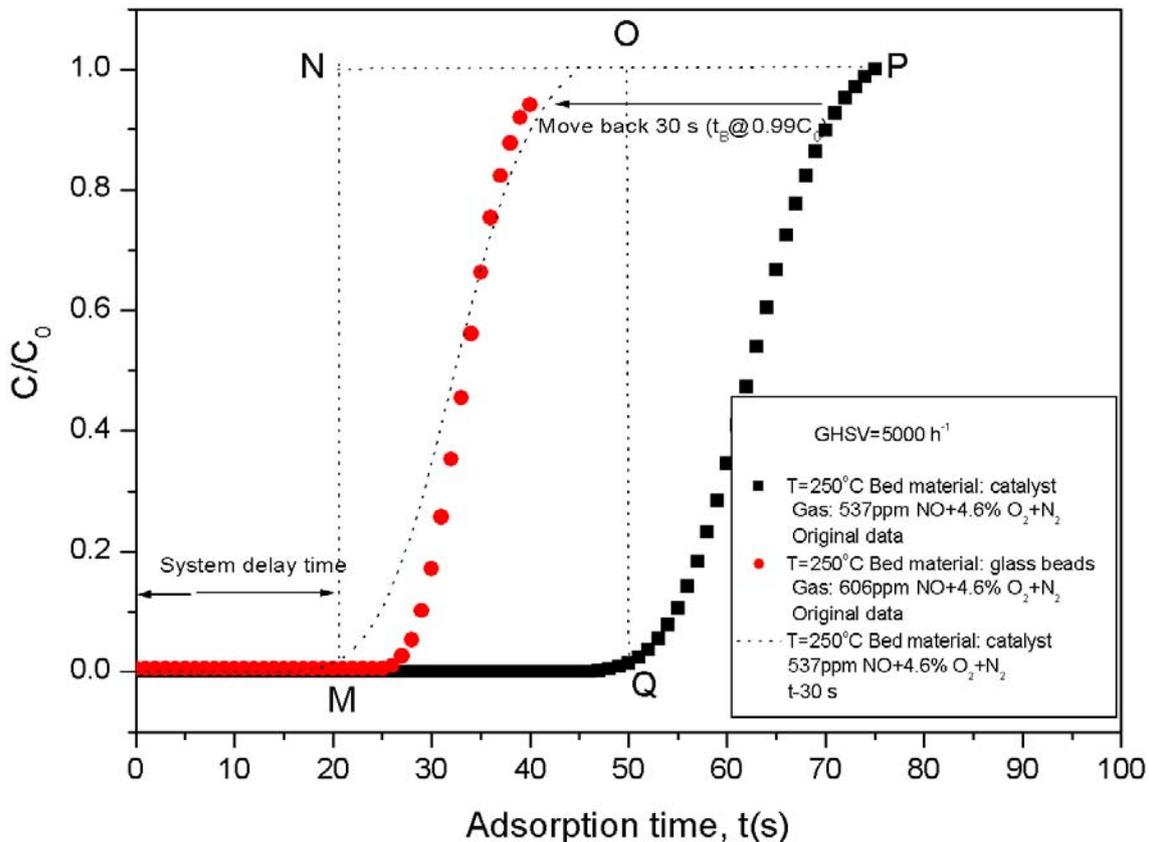
Fig.5 Influence of system dispersion on adsorption profile

It is seen that at the same temperature and feeding gas composition, if the adsorption breakthrough curve with catalyst loading was moved towards axis C/C_0 for 30 seconds (the experimental breakthrough time in this case), this curve overlapped with the one where glass beads were loaded instead of the catalyst. Because no NO was adsorbed on glass beads, the outlet concentration should be a step change for a step input concentration, if there is no dispersion. The area **OPQO** thus represents the system dispersion and must be subtracted from the total area **MNOPQM,** which is related to the experimental equilibrium adsorption capacity. The percentage of the area **OPQO** over the total area is 21% (around 20%). This probably explains why the breakthrough time can only be fitted to 80% of the calculated equilibrium adsorption capacity $q_{e,cal}$.

3.2. Effect of reaction temperature on catalytic activity

Using 600ppm NO + 1200ppm HC + 1% O_2 + N_2 as the reaction gas mixture, the effect of temperature on the catalytic activity of Fe/ZSM-5 was investigated in the time-on-stream test at a gas space velocity, GHSV=5000h^{-1}, with the results shown in Fig.6.

The peak NO conversions at different reactor temperatures were 70.52% (250°C), 74.42% (275°C), 70.18% (300°C), 68.24% (325°C) and 65.64% (350°C), respectively. The highest

NO conversion was achieved at 275°C. With the further increase of the temperature, the peak NO conversion decreased. However, at lower temperatures (<325°C), the catalytic activity was obviously unstable and the conversion decreased very quickly with time. The catalytic activity couldn't be recovered if the catalyst was not calcined in air or 20% O$_2$+N$_2$ at 500°C or higher temperatures, as shown in Fig. 7.
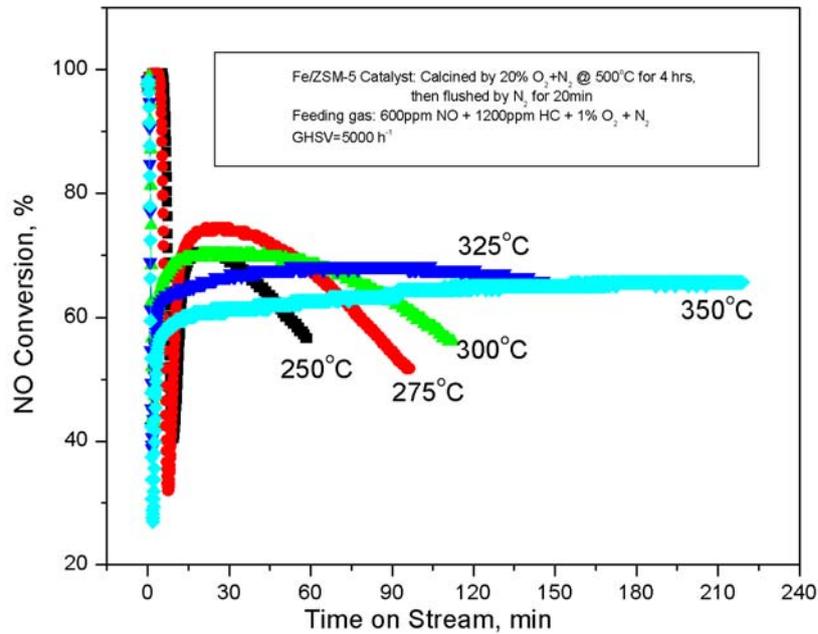

Fig.6 Effect of reaction temperature on catalytic activity
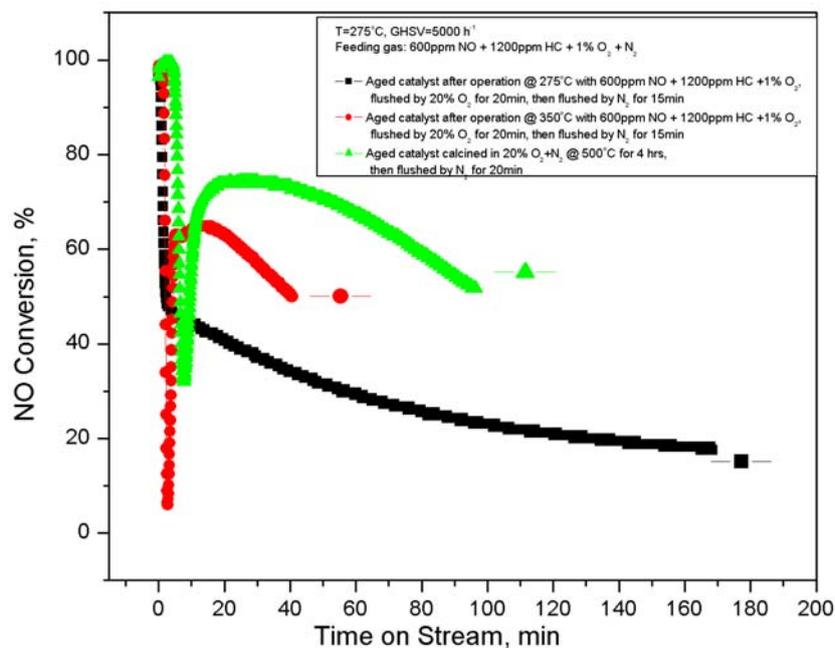

Fig. 7 Effect of catalyst regeneration condition

The durability or stability of the catalyst improved with the increase of temperature (Fig. 6). At T=350°C, the catalyst showed stable yet lowest NO conversion. That means that to reach a high peak NO conversion, lower temperature is preferred. On the other hand, the stable catalytic activity is favoured at higher temperatures. Considering the requirement of time durability for the catalyst in practical applications, coupling with the reduction efficiency of NO, the optimal reaction temperatures should be equal to or higher than 350°C.

Further investigation (Fig. 8) showed that the catalyst deactivation might be induced by the incomplete oxidation of hydrocarbons. When the O_2 concentration in the flue gas was increased from 1% to 4%, the peak NO conversion decreased to 67.26%, but the catalytic activity remained for a much longer stable period. We may infer that, the intermediate species of the hydrocarbon which was produced in the reduction gradually covered the active sites of the catalyst in the reaction process, and resulted in catalyst deactivation at lower O_2 concentrations. For higher O_2 concentrations, the incompletely reacted intermediate species was oxidized by excessive O_2 and thus left the sites active for the adsorption of NO. Similarly, higher temperatures can result in the complete combustion of the HC species, and had the same impact as higher O_2 concentration.
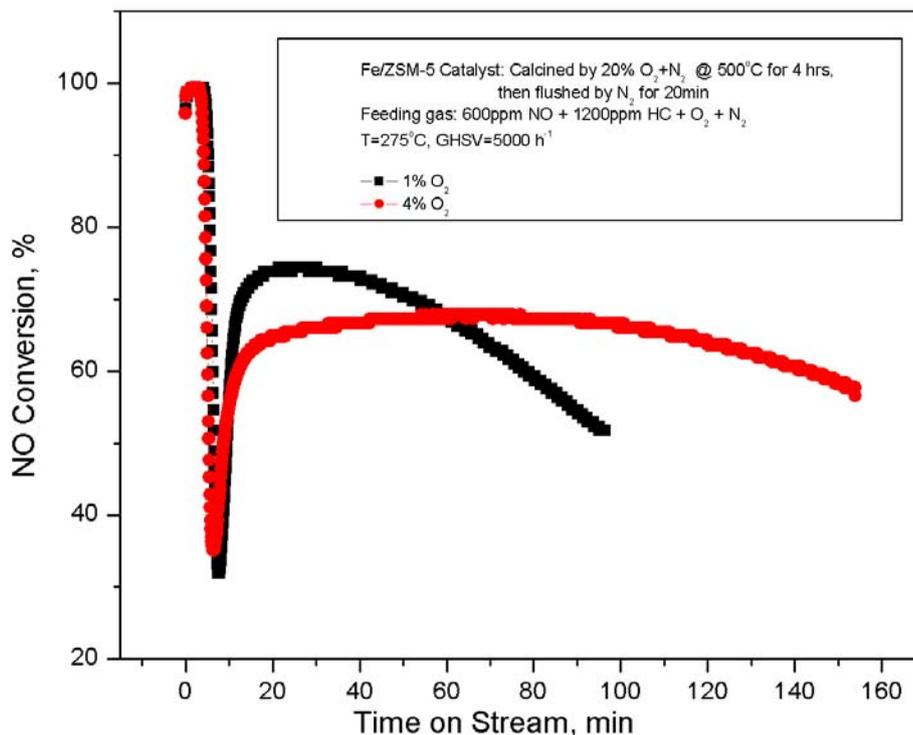
**Fig. 8 Effect of inlet O_2 concentration on the catalytic activity**

3.3 Effect of gas space velocity

The effect of gas space velocity on NO conversion at 350°C in the time-on-stream test is shown in Fig. 9. It is seen that the highest NO conversion was achieved when

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GHSV=5000h^{-1}, and the conversion remains stable over the tested time period. However, with the increase of GHSV, the peak NO conversion decreased. At the same time, at a higher GHSV, the NO conversion decreased more quickly with time in the test. That means that the GHSV has significant influence on the catalytic activity, and must be considered as a key factor when the dual zone reactor is designed and operated.
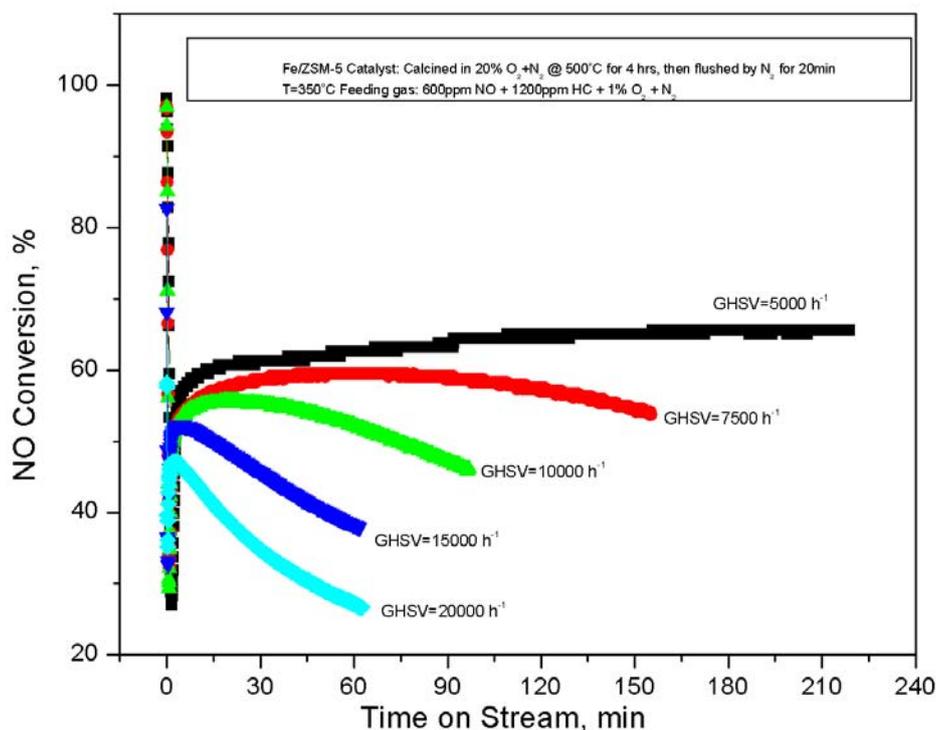

Fig. 9 Influence of gas space velocity on NO conversion

3.4 Influence of gas composition

The influence of O_2 and HC concentration on the catalytic activity at various temperatures is shown in Fig.10. In all cases, the increase of HC concentration enhanced NO conversion significantly. The NO conversion remained at a very low level (around 20~30%) when HC:NO was 0.5 at any temperature and O_2 concentrations. With the increase of HC:NO to 2:1, the catalytic activity increased very quickly, especially for the low O_2 concentrations (≤2%). However, further increase of HC:NO to 4:1 had less influence on the catalytic activity at low temperatures (≤300°C) compared to at high temperatures (≥325°C).

For HC:NO=0.5, the increase of O_2 concentration had less impact in the investigated temperature window. At a given HC:NO, the increase of O_2 concentration showed more negative impact on NO conversion when HC(ppm):NO(ppm)≥1, especially at high temperatures (≥325°C). The exceptional cases were shown at lower temperatures (≤300°C) where the NO conversion remained at a very close level when O_2 concentration ≤2%.
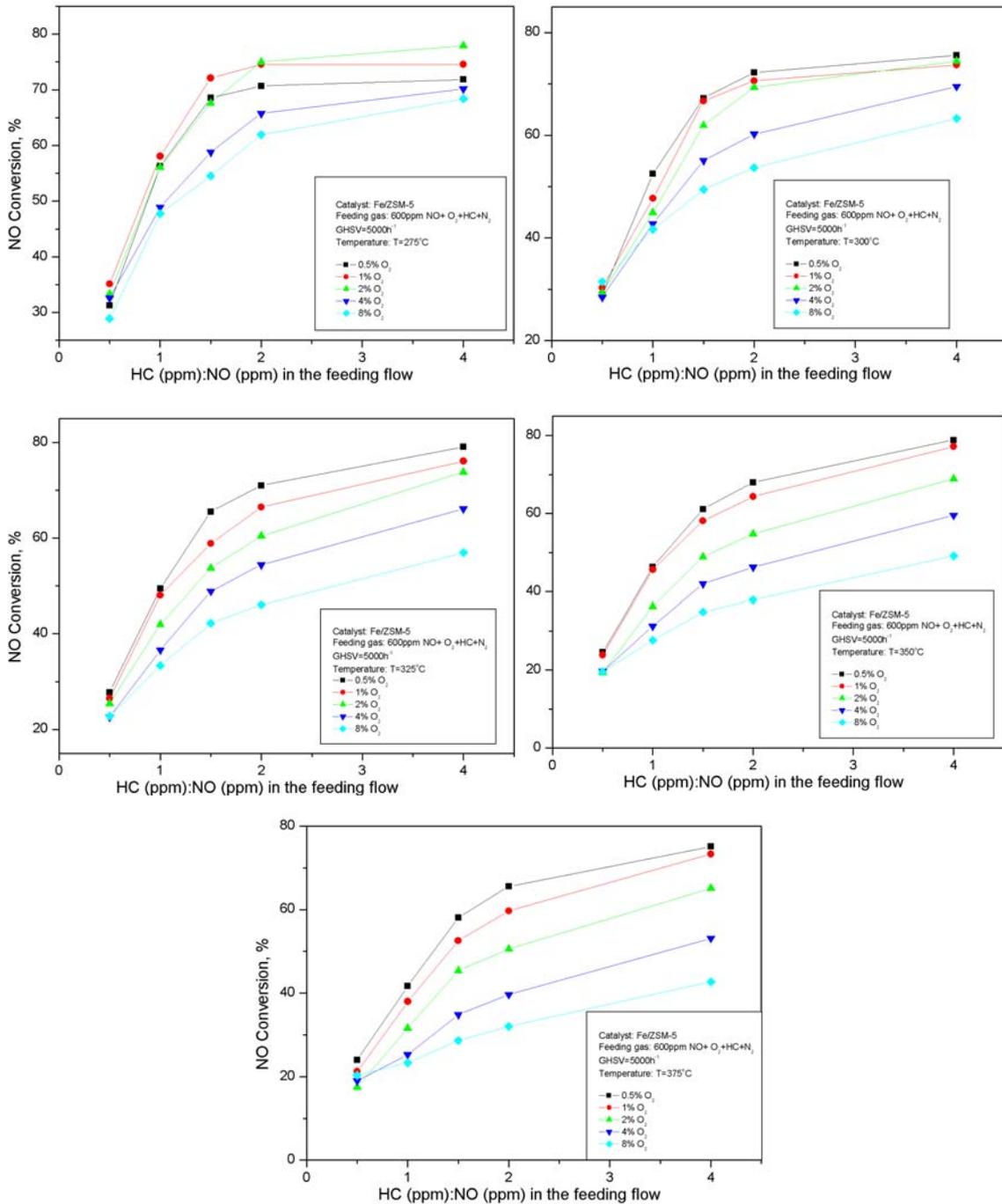
Fig. 10 Influence of gas composition on NO conversion

Generally speaking, high ratio of HC:NO can result in a high NO conversion, at a cost of high hydrocarbon consumption which will not be economical for the practical applications. From this point of view, a HC(ppm) to NO(ppm) ratio of 2:1 appears to be a good choice. O_2 played an important role in HC-SCR under lean-burn conditions, which agrees well

with the results from other researchers [3, 7, 8, 9]. This characteristic proved that a dual zone reactor design is a plausible choice for the abatement of NO in order to eliminate the negative influence of excess O_2 in the flue gas.

4. Conclusions

Fe/ZSM-5 catalysts showed reasonable NO adsorption capacity. The adsorption capacity and breakthrough time of Fe/ZSM-5 catalyst, which will be used for the design of the novel dual zone reactor system, can be predicted by the Freudlich equation at a given temperature and inlet NO concentration. However, the predicted breakthrough time must be corrected by a factor of 0.8 to account for the influence of the system dispersion.

The catalytic activity of Fe/ZSM-5 catalysts was sensitive to the reaction temperature and space velocity. To keep a long-term stable catalytic activity, the reaction temperature must be kept at T=350°C or higher, while the space velocity GHSV≤5000h^{-1}. To reach a high NO conversion, a high HC to NO ratio was needed. Considering both the economic aspect and the reduction efficiency of NO, a HC to NO molar ratio of 2 is recommended. O_2 concentration played an important role in the SCR of NO with propylene as the reducing agent. The catalyst exhibited acceptable activity when O_2 concentration was controlled at some low level (≤1% at 350°C).

Acknowledgements

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