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Formation of NO_x from N_2 and O_2 in catalyst-pellet filled dielectric barrier discharges at atmospheric pressure

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At temperatures above 350 °C, significant amounts of NO_x formed from N_2 and O_2 have been observed in Cu-ZSM-5 catalyst-pellet filled dielectric barrier discharges, indicating the necessity of using low-temperature performance in all plasma-catalytic processes for removal of air pollutants.

In recent years, plasma-catalytic processes to remove air pollutants, such as NO_x, SO_x and VOCs, from atmospheric exhaust gas streams have been widely studied.[1] The plasma-catalytic reaction rate can be enhanced *via* the interactions between plasma-generated active species in the gas phase (electrons, ions, radicals, excited species) and the adsorbed species on the catalyst surface. However, as with all plasma processes, some by-products or the pollutant itself might be produced in plasma-catalysis cleaning approaches. Taking NO_x removal as an example, Shimizu *et al.*[2] and this laboratory[3] found that the dielectric barrier discharge (DBD) plasma-catalytic removal efficiency of NO_x from $N_2/O_2/NO_x$-containing mixtures over Cu-ZSM-5 catalysts degrades significantly at temperatures above 300 °C. From the thermodynamic point of view, at temperatures below 500 °C only a small amount of NO_x (less than a few ppm) can be formed from N_2 and O_2. However, the active species generated in non-thermal plasmas are able to open new reaction channels in producing NO_x beyond the thermodynamic equilibrium between NO_x and the ground states of N_2 and O_2. Nahorny *et al.*[4] studied NO_x formation from N_2 and O_2 in low-pressure (2 Torr) glow discharges. Rehbein and Cooray[5] investigated the formation of NO_x from ambient air in corona discharges. Krishtopa and Krasnoperov[6] studied the competition between NO_x destruction and production in dielectric barrier corona discharges with varying input discharge energies at atmospheric pressure and room temperature. Hammer *et al.*[7] studied both NO_x destruction and production using isotopically-marked NO in a plasma assisted catalysis process at temperatures between 100 and 200 °C. This work reports an experimental study on NO_x production in catalyst-pellet filled atmospheric DBD plasmas from room temperature to 450 °C and discusses the possible heterogeneous reaction channels to form NO.

The plasma reactor used in this work consists of an outer alumina tube (id 15 mm), a stainless steel tube (ϕ 2.5 mm) placed along the axis of the outer tube as the high-voltage electrode and 10 ml of catalyst pellets (20–40 mesh) filled between the two tubes. A stainless steel wire mesh wound on the outside surface of the alumina tube was used as the ground electrode. The DBD power supply source is capable of supplying a bipolar sine wave output with 0–40 kV peak-to-peak voltage (U_p) at an a.c. frequency of 50 Hz. An electric oven was used to heat the plasma reactor up to 600 °C.[8] The same gas mixture (5.4% O_2 in N_2) was used in all the plasma-catalysis experiments at atmospheric pressure. The individual NO and NO_2 concentrations were monitored by a chemiluminescence analyzer (Monitor). Before introducing the discharge, Cu-ZSM-5 pellets in the plasma reactor were heated in a nitrogen stream at 600 °C for 3 h. The Cu-ZSM-5 catalysts were prepared *via* a similar method which has been described previously.[9] The copper ion exchange was carried out by using Na-ZSM-5 (Si/Al = 25, Nakai University, China) and aqueous copper acetate solutions. Two kinds of copper-exchanged zeolites [Cu(165)-ZSM-5 and Cu(88)-ZSM-5] were prepared and characterized in this work. Here the number in parentheses following Cu is the exchange percentage of Cu^{2+} with Na^+. The catalytic activity toward NO decomposition was measured by using an experimental set-up similar to that described in Ref. 9. Briefly, 0.2 g catalyst (40–60 mesh) was filled into an atmospheric micro-catalytic reactor made from a quartz tube (id 4 mm). A gas mixture of 2.0% NO, 0.5% N_2 in He was used as the feeding gas. Before reaction, the catalyst was pretreated in a He stream at 600 °C for 3 h. The O_2, N_2 and NO in the effluent gas were analyzed by a gas chromatograph. Due to the reaction between the residual NO and the produced O_2, the NO decomposition percentage was calculated from the amount of N_2 produced.

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The dependence of concentration and production yield[10] of NO_x formed in Cu(165)-ZSM-5, Cu(88)-ZSM-5 and Na-ZSM-5 pellet filled DBD plasmas on reaction temperature is shown in Fig. 1. The production yield of NO_x is defined as the number of NO_x molecules produced by one unit of input discharge energy (J). It is evident that from room temperature to 250 °C, there is a significant increase in NO_x formation over all the samples. The NO_x production yield for all of the three samples at U_p = 28.8 kV rises from about 0 to ~ 1.3×10^{14} molecules J^{-1} when reaction temperature increases from room temperature to 250 °C. At a reaction temperature above 350 °C, NO_x formation is enhanced along the order of the increasing NO catalytic decomposition activities shown in Fig. 2: Na-ZSM-5 << Cu(88)-ZSM-5 < Cu(165)-ZSM-5. The NO_x production yields at 350 °C over Cu(165)-ZSM-5, Cu(88)-ZSM-5 and Na-ZSM-5 in similar DBD plasmas are increased to 11.2×10^{14}, 6.5×10^{14} and 3.4×10^{14} molecules J^{-1}, respectively. The dramatic increase of NO_x production yields in Cu-ZSM-5 catalyst filled

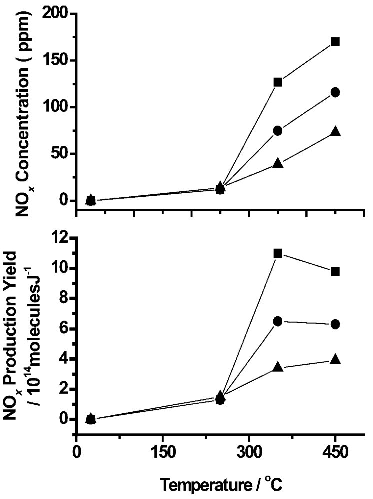

Fig. 1 Concentration and production yield of NO_x formed in Cu(165)-ZSM-5 (■), Cu(88)-ZSM-5 (●) and Na-ZSM-5 (▲) pellet filled DBD plasmas as a function of temperature (5.4% O_2 in N_2, GHSV = 2000 h^{-1}, U_p = 28.8 kV).

plasmas above 350 °C approximately coincides with the initiation temperature of NO catalytic decomposition over Cu-ZSM-5 zeolites (Fig. 2). About 90% of the NO_x products in all the plasma-catalysis experiments are NO implying that NO is the major plasma-induced or plasma-catalysis-induced reaction product while NO_2 is mainly generated *via* the reactions between NO and oxygen-containing species.

Table 1 lists the major investigated elementary reactions to form NO *via* $N/N^* + O_2/O_2^*$ and $O + N_2^*$ interactions in the gas phase [11] (M^* denotes the electronically excited state of M). From the kinetic data listed in this table, the reactions between N/N^* and O_2/O_2^* are the primary sources to produce NO in the gas phase. Penetrante *et al.*[12] calculated the N-atom production yield as a function of E/n (E = electrical field strength, n = total number density of the particles) in gas discharges, based on experimental studies of N_2–electron interactions. Besides the gas phase reactions, in the zeolite-pellet filled DBDs, the "heterogeneous" analog of gas phase reaction R1, *i.e.* the reaction between the N atom in the gas phase and the adsorbed O_2 on the catalyst (R6) may be strongly enhanced by the activation of the O–O bond due to its adsorption on active sites of the catalyst surface.[13]

$$N + O_2(ads) \rightarrow NO + O(ads) \qquad (R6)$$

For the dissociated adsorption of oxygen on the surface, the reaction R7 also can happen to increase the NO production:

$$N + O(ads) \rightarrow NO + \text{site (for adsorption)} \qquad (R7)$$

Recently, Teraoka *et al.*[14] studied the TPD spectra of O_2 on Cu(n)-ZSM-5 and Na-ZSM-5 after pretreatment of the samples at 500 °C and subsequent cooling to room temperature in an oxygen flow. From their measurements, the amount of oxygen desorbed from Na-ZSM-5 was a trace. The desorbed oxygen from Cu(n)-ZSM-5 was mainly observed between 250 and 750 °C and its amount increased with the Cu content n, indicating that Cu ions are responsible for the emergence of oxygen desorption. Based on this observation, the adsorption of oxygen over Cu-ZSM-5 at higher temperatures very possibly leads to the activation of the O–O bond or production of atomic oxygen adsorbed on Cu active sites and causes the increase of NO formation *via* reactions R6 and R7. Regarding the increase of NO_x production over Na-ZSM-5 in discharges with rising temperatures, due to the small amount of adsorbed oxygen on it, this increase should reflect the temperature dependence of gas phase reactions listed in Table 1.

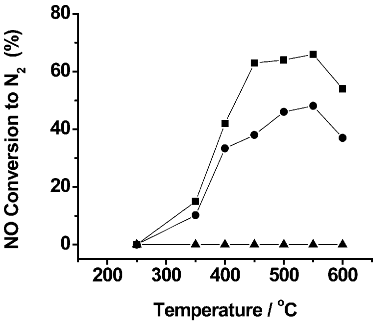

Fig. 2 Dependence of catalytic decomposition percentage of NO to N_2 on reaction temperature over Cu(165)-ZSM-5 (■), Cu(88)-ZSM-5 (●), and Na-ZSM-5 (▲) (2.0% NO and 0.5% N_2 in He, GHSV = 2000 h^{-1}).

Table 1 The primary elementary reaction channels to form NO from $N/N^* + O_2/O_2^*$ and $O + N_2^*$ in the gas phase[11]

		Rate constant/ cm^3 molecule^{-1} s^{-1}	
No.	Reaction	at 25 °C	at 450 °C
R1	$N + O_2 \rightarrow NO + O$	7.7×10^{-17}	1.1×10^{-13}
R2	$N + O_2(a^1\Delta) \rightarrow NO + O$	$< 9.0 \times 10^{-17}$	—
R3	$N(^2D) + O_2 \rightarrow NO + O(^3P, ^1D)$	6.0×10^{-12}	—
R4	$N(^2P) + O_2 \rightarrow NO + O(^1D, ^1S)$	2.0×10^{-12}	—
R5	$N_2(A\ ^3\Sigma_u^+) + O \rightarrow NO + N$	$< 6 \times 10^{-13}$	—

In conclusion, this communication reports an experimental study on NO_x production from N_2 and O_2 in Cu-ZSM-5 and Na-ZSM-5 pellet filled DBD plasmas for the first time. At temperatures above 350 °C, significantly higher NO_x plasma-catalytic production yields have been observed over Cu-ZSM-5 than over Na-ZSM-5, coinciding with their very different activities toward NO catalytic decomposition. This study provides a unique example showing the importance of heterogeneous reactions in plasma-catalytic processes. The results also indicate the necessity of using low-temperature performance in all plasma-catalytic processes for removal of air pollutants.

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Notes and references

1 (*a*) H. Miessner, R. Rudolph and K. Francke, *Chem. Commun.*, 1998, 2725; (*b*) F. Holzer, U. Roland and F. Kopinke, *Appl. Catal., B: Environ.*, 2002, **38**, 163 and references cited therein.

2 K. Shimizu, T. Hirano and T. Oda, *IEEE Trans. Ind. Appl.*, 2001, **37**, 464.

3 Q. Sun, J. Niu, A. Zhu, Z. Song, Y. Xu and X. Yang, *Proceedings of the 13th National (Chinese) Conference on Catalysis, Hangzhou, 13–18 October 2002*, Hangzhou, Zhejiang University Press, p. 813.

4 J. Nahorny, C. Ferreira, B. Gordiets, D. Pagnon, M. Touzeau and M. Vialle, *J. Phys. D: Appl. Phys.*, 1995, **28**, 738.

5 N. Rehbein and V. Cooray, *J. Electrost.*, 2001, **51–52**, 333.

6 L. Krishtopa and L. Krasnoperov, *SAE (Tech. Pap.)*, 982510.

7 T. Hammer, T. Kishimoto, H. Miessner and R. Rudolph, *SAE (Tech. Pap.)*, 1999-01-3632.

8 The reaction zone temperatures were measured by two thermocouples placed on the outside tube wall and in the central tube of the plasma reactor at the height of the middle of the catalyst bed, respectively. The gas flow makes the outside temperature T_{out} higher than the central one T_c without discharges. When the discharge is applied, T_c increases somehow. For example, at GHSV = 2000 h^{-1} and a reaction temperature of 350 °C, T_c is 5 °C higher than T_{out} at U_p = 28.8 kV.

9 C. Shi, M. Cheng, Z. Qu, X. Yang and X. Bao, *Appl. Catal., B: Environ.*, 2002, **36**, 173.

10 In order to calculate the production yield of NO_x, the input electric discharge power (P_{in}) at a certain experimental condition was measured from the difference of two products of the corresponding primary voltages and currents of the discharge power source with and without discharges. At temperatures below 250 °C with all the studied U_p values and at temperatures above 350 °C but with $U_p \leq 22.4$ kV, P_{in} was also measured *via* the area of the voltage–charge Lissajous figures (L. Rosenthal and D. Davis, *IEEE Trans. Ind. Appl.*, 1975, **11**, 328). The P_{in} values measured using the latter technique are usually ~ 30% lower than those from the former method. The same P_{in} values were obtained from three zeolite-pellet filled DBD's at the same reaction temperature, gas flow rate and discharge voltage.

11 (*a*) D. Baulch, C. Cobos, R. Cox, P. Franck, G. Hayman, T. Just, J. Kerr, T. Murrells, M. Pilling, J. Troe, R. Walker and J. Warnatz, *J. Phys. Chem. Ref. Data*, 1994, **23**, 847; (*b*) W. DeMore, S. Sander, D. Golden, R. Hampson, M. Kurylo, C. Howard, A. Ravishankava, C. Kolb and M. Molina, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation number 12*, JPL Publication 97-4, 1997, p. 1:00–266; (*c*) H. Maetzing, in I. Prigogine, S. Rice (Eds.), *Advances in Chemical Physics*, **Vol. LXXX**, Wiley, New York, 1991, p. 315 and references cited therein.

12 B. Penetrante, M. Hsiao, B. Merritt, G. Vogtlin, P. Wallman, N. Neiger, O. Wolf, T. Hammer and S. Broer, *Appl. Phys. Lett.*, 1996, **68**, 3719.

13 No direct experiment regarding O–O bond activation of adsorbed oxygen on Cu-ZSM-5 has been found, but some groups investigated the O–O bond activation on other metal or metal oxide catalysts (*e.g.*, K. Tanaka, *Shokubai*, 1975, **17**, 141; K. Prabhakaran and C. Rao, *Surf. Sci.*, 1987, **186**, L575; C. Li, K. Domen, K. Maruya and T. Onishi, *J. Am. Chem. Soc.*, 1989, **111**, 7683).

14 Y. Teraoka, C. Tai, H. Ogawa, H. Furukawa and S. Kagawa, *Appl. Catal., A: Gen.*, 2000, **200**, 167.