

Plasma-catalytic Selective Reduction of NO with C₂H₄ in the Presence of Excess Oxygen

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Abstract: This paper reports observations of significant synergistic effects between dielectric barrier discharge (DBD) plasmas and Cu-ZSM-5 catalysts for C₂H₄ selective reduction of NO_x at 250 °C in the presence of excess oxygen by using a one-stage plasma-over-catalyst (POC) reactor. With the reactant gas mixture of 530 ppm NO, 650 ppm C₂H₄, 5.8% O₂ in N₂ and GHSV = 12000 h⁻¹, the pure catalytic, pure plasma-induced (discharges over fused silica pellets) and plasma-catalytic (in the POC reactor) NO_x conversion are 39%, 1.5% and 79%, respectively. The *in-situ* optical emission spectra of the reactive systems imply some short-lived active species formed from plasma-induced and plasma-catalytic processes may be responsible to the observed synergistic effects in this one-stage POC system.

Keyword: NO_x removal, selective catalytic reduction, non-thermal plasma, CuZSM-5, ethene, optical emission spectroscopy.

The selective catalytic reduction (SCR) of NO_x using the addition of reductants such as NH₃, urea, hydrocarbons, alcohols, has been studied intensively as a potential method to remove NO_x from exhaust gases with excess oxygen^{1,2}. For availability reasons, the use of hydrocarbons as reducing agent (HC-SCR) has been of special interest in last 15 years. But the effective temperature window of those catalysts is relatively narrow, and should be broadened to lower temperatures for practical applications. One of the attempts to improve the catalyst property, especially at low temperatures, is of using non-thermal plasma and combined catalyst systems^{3,4}. Under certain conditions, a better performance can be achieved by a catalytic post-treatment of the non-thermal plasmas effluent in the two-stage plasma-followed-by-catalyst (PFC) hybrid system³. However, for many cases, this solution is not very effective. Roland *et al.*⁵ considered that real synergy effects between non-thermal-plasmas and catalysis can be expected by introducing the catalyst into the discharge zone, *i.e.* the one-stage plasma-over-catalyst (POC) system. To our knowledge, there are very few examples of reporting synergistic effects between plasma and catalysts in one-stage POC systems in literatures. Very recently, our laboratory⁶ has pointed out that significant amounts of NO_x can be generated

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from N₂ and O₂ in a one-stage POC reactor at temperatures higher than 300°C very likely *via* reactions between the plasma-produced N atoms and the catalyst-activated O₂ molecules. This article reports observations of an unambiguous synergistic effect between DBD plasmas and Cu-ZSM-5 catalysts in a one-stage POC reactor for C₂H₄-selective-reduction of NO_x in the presence of excess oxygen around 250 °C.

Experimental

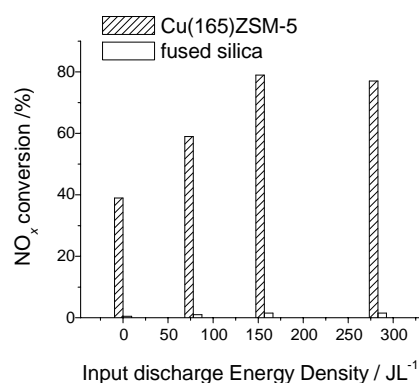
The one-stage POC reactor used in this work consists of a fused silica tube (*id* 10 mm), a stainless steel tube (*od* 2 mm) placed along the axis of the outer tube as the high-voltage electrode and 2 mL of catalyst pellets (20-40 mesh) filled between the two tubes. A stainless steel wire mesh wound on the outside surface of the outer 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. The input electric discharge power at a certain experimental condition was measured *via* the area of the voltage-charge Lissajous figures⁸. The input discharge energy density in JL⁻¹, E_{in} , can be controlled by adjusting U_p . An electric oven was used to heat the plasma-catalytic reactor. 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. The average of T_c and T_{out} was taken as the reaction temperature, T_{reac} . The Cu-ZSM-5 catalysts were prepared *via* a ion exchange method, which was described previously⁹. The individual NO and NO₂ concentrations were monitored by a chemiluminescence analyzer (Monitor, ML9841AS). The concentrations of N₂O in the outflow gas were determined by an infrared absorption spectrometer (SICK- MAIHAK -S710). The optical emission spectra (200-900 nm) from the center of the catalyst bed of the one-stage POC reactor during discharges were measured by a monochromator (Acton-SP-300i). A quartz focal lens, placed near a quartz window on the wall of the heated oven, was used to collect the emission light into the entrance slit of the monochromator through an optical fiber.

Results and Discussion

Figure 1 shows the NO_x conversion over Cu(165)-ZSM-5 and fused silica pellets in the one-stage POC reactor at $T_{reac} = 250$ °C as a function of input discharge energy density, E_{in} . Under this temperature, the pure NO_x SCR activity over fused silica pellets ($E_{in} = 0$) are low (< 1%) and the plasma-induced enhancements over fused silica are also small for the whole input discharge energy density range investigated (78-283 JL⁻¹). In contrast to this, over Cu(165)-ZSM-5, the significant plasma-enhanced effects for C₂H₄-SCR of NO_x have been observed and the rising E_{in} from 78 to 283 JL⁻¹ causes a monotonic increase of the NO_x conversion. The slight decrease of NO_x conversion after $E_{in} > 155$ JL⁻¹ may reflect that an optimum electron energy range is probably needed for the plasma-assisted NO_x catalytic conversion.

At $E_{in} = 155$ JL⁻¹, the DBD plasma generates a maximal enhancement for the NO_x conversion over Cu(165)-ZSM5. The NO_x SCR conversion over Cu(165)-ZSM-5 With-

Figure 1 NO_x conversion over Cu(165)ZSM-5 or fused silica pellets in the one-stage POC reactor with or without discharge as a function of input discharge energy density.



Reaction conditions: 250°C, 530 ppm NO, 650 ppm C₂H₄, 5.8% O₂ in N₂

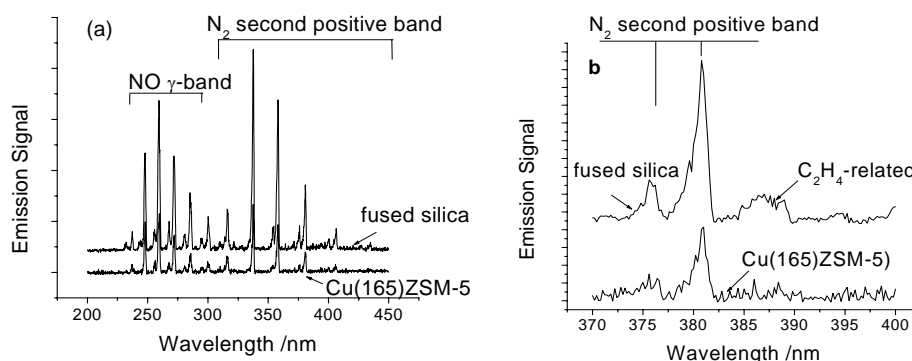
out discharges ($E_{in} = 0$), 39%, and over fused silica pellets with discharges, 1.5%, were taken as the “pure catalytic” and “pure plasma-induced” conversion, respectively. The corresponding plasma-catalytic NO_x conversion over Cu(165)-ZSM5 in the one-stage POC reactor, 79%, reflects an unambiguous synergistic effect between the plasma and the catalyst. At the experimental conditions, the N₂O content in the outflow gas of the POC reactor was less than 8 ppm. And the input electric discharge power was determined *via* the area of voltage-charge Lissajous figures to be 0.94 W, which corresponds to an energy assumption of 84 eV per converted NO molecule.

Below $T_{reac} = 200^\circ\text{C}$ the pure (without discharges) catalytic activity of Cu(165)-ZSM5 for C₂H₄-SCR of NO_x is very low and the enhancement from the DBD plasma is also insignificant. At $T_{reac} = 300^\circ\text{C}$, the pure SCR activity reaches a maximum and the plasma exhibits a negative effect to the NO_x conversion. As we pointed out previously, this is very likely related to the plasma-catalytic production of NO_x from N₂ and O₂ at higher temperatures⁶.

The plasma-enhanced C₂H₄-SCR of NO over Cu(165)-ZSM5 in the one-stage POC reactor as a function of O₂ concentration has been investigated at $T_{reac} = 250^\circ\text{C}$ and $E_{in} = 155\text{ JL}^{-1}$. Similar to all the pure HC-SCR of NO cases, addition of certain amount of oxygen, promoting the oxidation of NO to NO₂, or hydrocarbons to some oxidative derivatives, may play positive roles for NO_x reduction. When O₂ concentration is higher than 10%, the NO_x conversion is decreased probably due to the increased prohibition of oxygen to the adsorption of NO_x and C₂H₄ on the catalyst.

To determine gas phase active species in the one-stage POC system, *in-situ* optical emission spectra (200-900 nm) have been investigated under $E_{in} = 155\text{ JL}^{-1}$ over fused silica and Cu-ZSM-5 pellets at 250°C with gas mixtures: (a) 530 ppm NO in N₂, (b) 650 ppm C₂H₄ in N₂ (**Figure 2 a,b**). In both of cases, stronger emissions from discharge over fused silica pellets were observed than that from over CuZSM-5, very likely because of the higher optical reflectivity of fused silica and its much lower surface area, the excited species may be quenched through their collisions with the solid surface.

Figure 2 *In-situ* optical emission spectra under $E_{in} = 155 \text{ JL}^{-1}$ at 250 °C over Cu(165)ZSM-5 and fused silica pellets with different reacting gas mixtures: (a) 530 ppm NO in N_2 , (b) 650 ppm C_2H_4 in N_2



The observations of N_2 second positive band ($\text{C}^3\Pi \rightarrow \text{B}^3\Sigma$), $\text{NO}\gamma$ -band ($\text{A}^2\Sigma \rightarrow \text{X}^2\Pi$) and a C_2H_4 -related band with different gas mixtures imply that some short-lived active species formed from plasma-induced or plasma-over-catalyst-induced processes, such as C_2H_4 fragments, partially oxidized hydrocarbons, electronically excited NO_x species in the gas phase or vibrationally excited NO_x species on the catalyst surface may be partially responsible to the observed synergistic effects between plasmas and catalysts in the one-stage POC system. Since O_2 molecule is a very efficient quencher for some electronically excited species, $\text{NO}\gamma$ -band and the small C_2H_4 -related peak disappeared when 5.8% O_2 was added into the gas mixture.

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