NO REDUCTION OVER Ru -TAILORED ACTIVATED CARBON FIBERS AT AMBIENT TEMPERATURE

Y. Nishi, T. Suzuki, and K. Kaneko
Department of Chemistry, faculty of science, Chiba University, 1-33 Yayoi, Inage, Chiba 263, Japan

Introduction

Micropores, of which pore width is less than 2nm, have a deep molecular potential well due to overlapping of the molecule-surface interaction from opposite pore-walls. Activated carbon fiber(ACF) has abundant graphitic micropores of slit-shape and the micropores are available for good nanospace.

Oxides of nitrogen NO_x are inevitable byproducts of high temperature combustion and they are the representative atmospheric pollutants. Active studies on catalytic reductions of NO to N_2 have been done all over the world. Supercritical NO can be noticeably adsorbed in the micropores of ACF modified with ultrafine iron oxide. NO molecules are dimerized in the micropore space at an ambient temperature and the NO dimer brings about the disproportion reaction ($3(NO)_2 = 2N_2O + 2NO_2$) even at 303 K and a subatmospheric pressure[1]. Further, NO over the iron oxide dispersed ACF is gradually reduced into N_2 above 423 K[2]. The high pressure effects of the micropore can be expected to accelerate the chemical reaction. We prepared ultrafine Ru particle-tailored micropores of activated carbon fiber for decomposition of N_2O from NO to N_2 at an ambient temperature[3].

Experimental

The cellulose-based ACF was immersed in the $RuCl_3$ solution and dried at 383 K in vacuo. The dispersed $RuCl_3$ in the micropores was reduced to Ru fine metallic particles at 623 K for 10 h under a hydrogen atmosphere of 27 kPa and the treated ACF was cooled under the evacuating conditions. The Ru particle-tailored ACF is designated Ru-ACF. The microporosity of Ru-ACF and ACF was determined by N_2 adsorption at 77 K. The decomposition reaction of NO of 10 kPa was examined at 273, 303, 323, and 423 K for 3 h with the circulation reaction system. The reaction extent was determined by the compositional change of the gas phase with FT-IR and Mass spectrometers.

Results and Discussion

The dispersion of Ru fine particles on ACF did not seriously change the microporosity. The average slit-pore widths of Ru-ACF and ACF were 0.94 and 0.90 nm, respectively.

Figure1 shows the FT-IR spectral change of the gas phase over Ru-ACF at 303 K. The intensity of NO at 1876 cm^{-1} decreases rapidly; it becomes less than 10% of the initial intensity after 9 min. On the other hand, the bands of NO_2 and N_2O appear at 1618 cm^{-1} and 2224 cm^{-1}, respectively. As the molecular absorption coefficient of NO is noticeably weak compared with that of the NO_2 or N_2O band, the concentration of produced NO_2 or N_2O after 3h corresponds to only less than 0.3% of the residual NO; evolution of CO_2 was negligibly small (< 0.01 %). IR cannot detect N_2, then the whole gas after 3h was analyzed by the Mass spectroscopy. The Mass analysis elucidated the formation of N_2 corresponding to the 77% yield. Hence, we can conclude that NO is rapidly changed into N_2 over Ru-ACF at 303 K. Almost all N_2 molecules are not adsorbed at 303 K. Figure 2 shows the change in the NO concentration ratio against the initial concentration determined from the corrected IR absorption band intensity of NO at 1876 cm^{-1}. NO is rapidly reduced to N_2 at 303 K and 323 K, then the NO decomposition almost finishes within 10 min. The first order plot for the initial reaction gave the half-life of 3 min. The initial reaction rate of Ru-ACF was four times greater than that of ACF.

The NO reduction reaction at 323 K was almost similar to that at 303 K. As the amount of NO adsorption at 303 K was greater than that at 323 K, the removal ratio of NO at 323 K (0.92) is slightly smaller than that at 303 K (0.96). The NO reduction reaction at 423 K produces not only NO_2 and N_2O, but also CO_2. The N_2 yield at 423 K was 0.82, which is close to those at 303 K and 323 K. However, the NO reduction proceeds through the reaction route giving CO_2 in addition to the reaction route at 303 K.

Figure 3 shows the N_2 yield and the ratio of CO_2 to N_2 for Ru-ACF and ACF as a function of the reaction temperature. The N_2 yield of Ru-ACF is almost constant regardless of the reaction temperature, being noticeably greater than that of ACF. The CO_2/N_2 ratio of Ru-ACF is almost zero below 323 K, but it becomes 0.095 at 423 K, although it is much smaller than that of ACF at the same temperature. It is clearly shown that both of CO_2/N_2 ratio and N_2 yield of ACF increase with the increase of the reaction temperature, nevertheless the CO_2/N_2 ratio is less than 0.5 even at maximum. The N_2 reduction over ACF accompanies the production of CO_2, but it is not predominant. As the CO_2 production should be attributed to the following Shah reaction of NO with carbon[4],

$$2NO+C \rightarrow N_2+CO_2 \quad (1)$$

the CO_2 evolution indicates the consumption of the microporous carbon. With Ru-ACF a slight part of the NO reduction produces CO_2 only at 423 K, and thereby NO reduction mechanism over Ru-ACF below 323 K is different from the Shah reaction. The NO reduction over Ru-ACF at the ambient temperature can be associated with the disproportionation reaction of the NO dimer.

NO molecules are dimerized to be adsorbed in micropores of ACF even at 423 K according to the previous study. The observation of NO_2 and N_2O in the gas phase for both systems at all reaction temperatures indicates that the N_2 formation is mainly attributed to the reaction path through the disproportionation reaction of the NO dimer. The dimerized NO is in an equilibrium with NO_2 and N_2O in the micropore of ACF at 303 K, as given by eq.2.

$$3(NO)_2 \rightarrow 2\,N_2O + 2\,NO_2 \quad (2)$$

The dispersed Ru particles accelerate the decomposition of N_2O into N_2 and a chemisorbed oxygen O_{chem} on the carbon wall, while NO_2 is chemisorbed on the carbon wall to produce NO and O_{chem}. The chemisorbed oxygen on carbon ,O_{chem}, can be released as CO_2 at higher temperature. If the chemisorbed oxygens are released as molecular O_2, the perfect decomposition of NO at ambient temperature will be accomplished. This excellent catalysis of the fine Ru particles in the carbon nanospace should show a new direction in the surface and environmental sciences.

References

[1] Imai, J., Souma, M., Ozeki, S., Suzuki, T. and Kaneko, K., *J. Phys. Chem.*, 1991, 95,9955.

[2] Imai, J. and Kaneko, K., *Cat. Lett.* 1993,20,133.

[3] Nishi, Y., Suzuki, T. and Kaneko, K., *J. Phys. Chem.*, in press.

[4] Shah, M.S., *J. Chem. Soc.*, 1929, 2661.

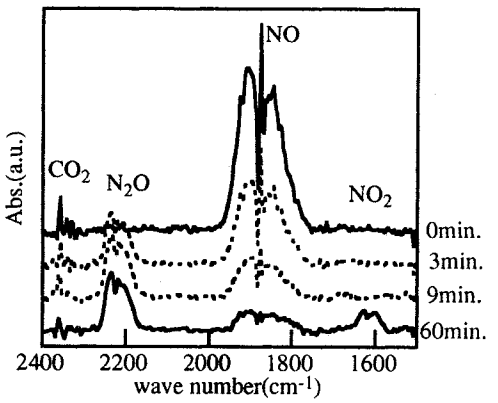

Figure 1 The FT-IR spectral change of NO over ultrafine Ru particle-tailored ACF with the reaction time at 303 K.

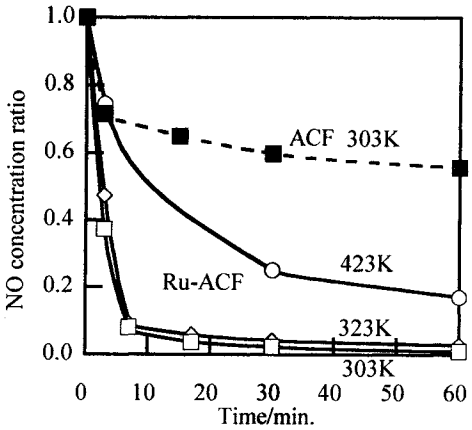

Figure 2 The changes of the NO concentration ratio with the reaction time for ultrafine Ru particle-tailored ACF and ACF at 303 K.

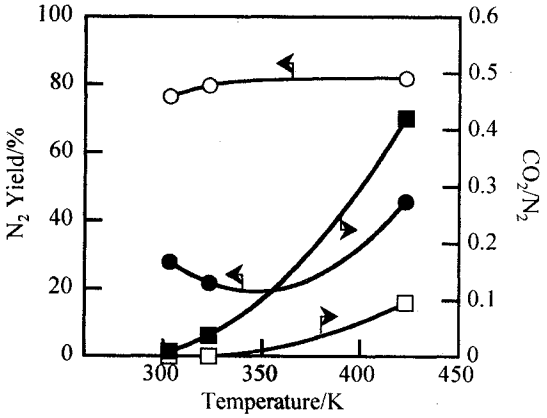

Figure 3 The N_2 yield and CO_2/NO ratio against the reaction temperature for ultrafine Ru particle-tailored ACF and ACF.