

Ambient Temperature Reduction of NO to N₂ in Ru-Tailored Carbon Subnanospace

Yoko Nishi, Takaomi Suzuki, and Katsumi Kaneko*

Department of Chemistry, Faculty of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263, Japan

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Ultrafine Ru particles were dispersed in micropores of activated carbon fiber (ACF). NO was efficiently and rapidly reduced to N₂ on the Ru particles through the disproportionation reaction of $3(\text{NO})_2 = 2\text{NO}_2 + 2\text{N}_2\text{O}$ in the micropore spaces at 303 K. The N₂ yield at 303 K was 0.8, and the half-life of the reduction reaction was 3 min. The amounts of the byproducts N₂O and NO₂ on Ru-tailored ACF at 303 K were less than 0.25%. The oxygen was not evolved at 303 K.

Introduction

Oxides of nitrogen NO_x are inevitable byproducts of high-temperature combustion and they are representative atmospheric pollutants. Increasing numbers of automobiles have emitted greater amounts of NO_x, giving rise to a serious atmospheric pollution problem in urban areas in particular. NO₂ can be easily absorbed in soils or dissolved in surface water. On the other hand, a diluted NO is kinetically stable, although N₂ and O₂ are thermodynamically more stable than NO at an ambient temperature. Consequently, an efficient catalyst for the reduction of NO to N₂ has been searched for since 1906.¹ Thus, active studies on catalytic reductions of NO to N₂ have been done all over the world;² their trials are not sufficiently accomplished. The most noticeable catalyst for the decomposition of NO to N₂ is Cu-ZSM-5 developed by Iwamoto et al.³ This Cu-ZSM-5 decomposes NO into N₂ and O₂ near 750 K, but coexistent SO₂ strongly poisons the catalytic activity. Recent efforts have been done for the development of the catalyst for selective catalytic reduction with N-free reductants.²

NO is quite important as not only the atmospheric pollutant but also a biological molecule; recently it was elucidated that NO included in biomolecular organisms of nanometer size plays an essential role in biofunctions.⁴ We must understand the state and properties of NO molecules confined in a model hydrophobic nanospace.

Micropores, of pore width less than 2 nm, 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 hydrophobic nanospaces. Recently unusual molecular behaviors in such graphitic micropores were reported on this journal.^{5–7}

Although supercritical gases cannot be sufficiently adsorbed even in micropores of ACF, supercritical NO can be noticeably adsorbed in the micropores of ACF modified with ultrafine iron oxide.⁸ NO molecules are dimerized in the micropore space at an ambient temperature,⁹ and the NO dimer brings about the disproportionation reaction ($3(\text{NO})_2 = 2\text{N}_2\text{O} + 2\text{NO}_2$) even at 303 K and a subatmospheric pressure,¹⁰ which occurs above 20 MPa in the case of the bulk gaseous reaction.¹¹ Further, NO over the iron oxide dispersed ACF is gradually reduced into N₂ above 423 K.¹² The high-pressure effects^{10,13} 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 N₂O from NO to N₂ at an ambient temperature.

Experimental Section

The cellulose-based ACF was immersed in the RuCl₃ solution and dried at 383 K in vacuo. The dispersed RuCl₃ 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 formation of metallic Ru particles was evidenced by XPS examinations. The Ru particle-tailored ACF is designated Ru-ACF in this Letter. The microporosity of Ru-ACF and ACF was determined by N₂ adsorption at 77 K. The dispersion of Ru fine particles on ACF did not seriously change the microporosity. The surface area and micropore volume are 1130 m² g^{−1} and 0.51 mL g^{−1} for Ru-ACF and 1100 m² g^{−1} and 0.52 mL g^{−1} for ACF, respectively. The average slit-pore widths of Ru-ACF and ACF were 0.94 and 0.90 nm, respectively. The decomposition reaction of NO of 10 kPa was examined at 303, 323, and 423 K for 3 h with the circulation reaction system after pre-evacuation of samples at 383 K and 10 mPa for 2 h. The reaction extent was determined by the compositional change of the gas phase with FT-IR and mass spectrometers.

Results and Discussion

Figure 1 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 NO₂ and N₂O appear at 1618 and 2224 cm^{−1}, respectively. As the molecular absorption coefficient of NO is noticeably weak compared with that of the NO₂ or N₂O band, the concentration of produced NO₂ or N₂O after 3 h corresponds to only less than 0.3% of the residual NO; evolution of CO₂ was negligibly small (<0.01 %). IR cannot detect N₂, so the whole gas after 3 h was analyzed by the mass spectroscopy. The mass analysis elucidated the formation of N₂ corresponding to the 77% yield. Hence, we can conclude that NO is rapidly changed into N₂ over Ru-ACF at 303 K. Almost all N₂ molecules are not adsorbed at 303 K. Figure 2 shows the change in the NO concentration ratio vs the initial concentration determined from the corrected IR absorption band intensity of NO at 1876 cm^{−1}. NO is rapidly reduced to N₂ at 303 K and 323 K, and then the NO decomposition almost finishes within 7 min. The first-order plot for the initial reaction gave a 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 NO₂ and N₂O but also CO₂. The N₂ yield at 423 K was 0.82, which is close to those at 303 and 323 K. However, the NO reduction proceeds

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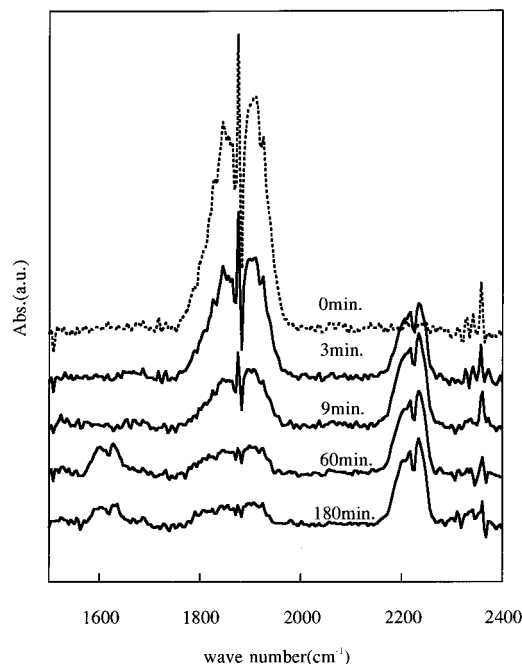


Figure 1. FT-IR spectral change of NO over ultrafine Ru particle-tailored ACF with the reaction time at 303 K.

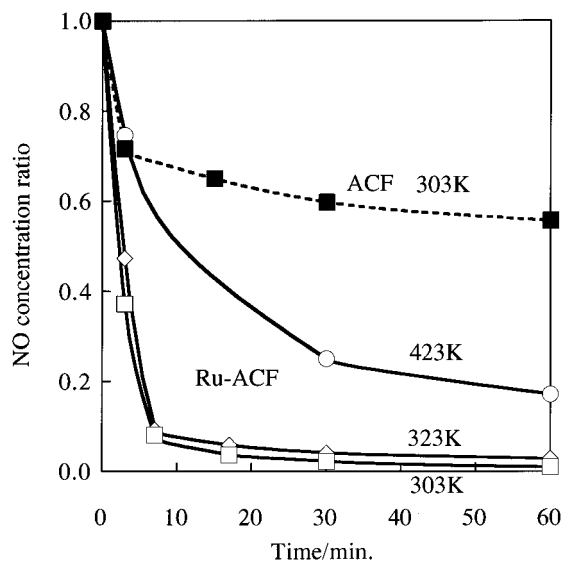


Figure 2. Changes of the NO concentration ratio with the reaction time for ultrafine Ru particle-tailored ACF and ACF at 303 K. The open and solid symbols denote Ru-ACF and ACF, respectively.

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 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 carbon¹⁴



the CO_2 evolution indicates the consumption of the microporous carbon. With Ru-ACF a slight part of the NO reduction

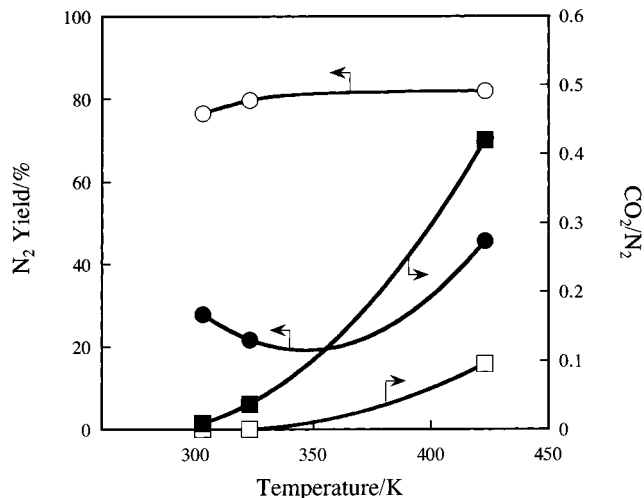
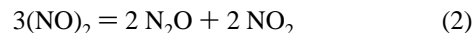


Figure 3. N_2 yield and CO_2/NO ratio vs the reaction temperature for ultrafine Ru particle-tailored ACF and ACF. The open and solid symbols denote Ru-ACF and ACF, respectively.

produces CO_2 only at 423 K, and thereby the 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.⁹ 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. 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 reproduced NO can be available for this NO reduction cycle repeatedly. The N_2 formation from N_2O is $2/3$ mol of NO, and that from the single NO_2 cycle is $2/9$ mol. Hence the total is equal to $8/9$ mol, which is close to the observed value of 0.77 at 303 K. The limiting value of this mechanism is 1. 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 surface and environmental sciences.

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