

Structural study of the effects of water and oxygen on the nitric oxide decomposition on $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalysts

Taketoshi Minato,¹ Yasuo Izumi,*¹ Ken-ichi Aika,¹ Atsushi Ishiguro,² Takayuki Nakajima,² Yasuo Wakatsuki²

¹Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259

Nagatsuta, Midori-ku, Yokohama 226-8502

²Institute of Physical and Chemical Research, 2-1, Hirosawa, Wako, Saitama 351-0198

Introduction

Various catalysts have been investigated to effectively decompose nitric oxide with reducing agent, such as ammonia, carbon monoxide, or hydrocarbons. In the practical applications of these catalysts, catalytic performance in the presence of moisture (water) and molecular oxygen is of primary importance. The presence of moisture and molecular oxygen has the possibility both to modulate the reaction mechanism and to modify the structure of catalyst active site. Due to this reason, in most cases it is not clear how these gases effect on the nitric oxide decomposition reactions. In this report, active site was defined by supporting ruthenium organometallic cluster $[(\text{PPh}_3)_2\text{N}]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$ (**1**) on TiO_2 . The active site structure was investigated by XAFS at Ru K-edge in the presence/absence of moisture/ O_2 . The effects of moisture and O_2 on catalytic nitric oxide decomposition with carbon monoxide are discussed.

Experimental Section

The cluster complex **1** was reacted at 290 K in tetrahydrofuran with TiO_2 (Aerosil P-25, BET surface area $60 \text{ m}^2\text{g}^{-1}$) previously heated in vacuum at 573 K. The solvent was evaporated. The Ru content was 1.5 wt%. The catalytic reaction was performed at 423 K in $\text{NO} + \text{CO}$ (1 : 1, 4.0 kPa). 1.7 – 3.1 kPa of water and/or 0.56 kPa of O_2 were added to the reaction gas mixture. Ru K-edge XAFS was measured at 10B in transmission mode. All the procedure of catalyst preparation and transfer was carried out in argon atmosphere.

Results and Discussion

The decomposition reaction of nitric oxide proceeded by 6.0 – 23 times faster on $[\text{Ru}_6\text{C}]/\text{TiO}_2$ than the case of conventional Ru/TiO_2 . As we reported in *Activity Report 2000B*, p.22, the active site structure was very similar to that of $[\text{Ru}_6\text{C}(\text{CO})_{12}(\text{NO})_3]^-$ crystal. The Ru_6 octahedral framework structure, stabilized by carbido carbon, was destroyed when the catalyst was heated above 523 K. The catalytic decomposition rate of nitric oxide once increased to 212% in the presence of 1.7 kPa of H_2O and then decreased to 31% in the presence of 3.1 kPa of H_2O in addition to the reaction gas of $\text{NO} + \text{CO}$. The change of Ru K-edge EXAFS (Fourier transform) is

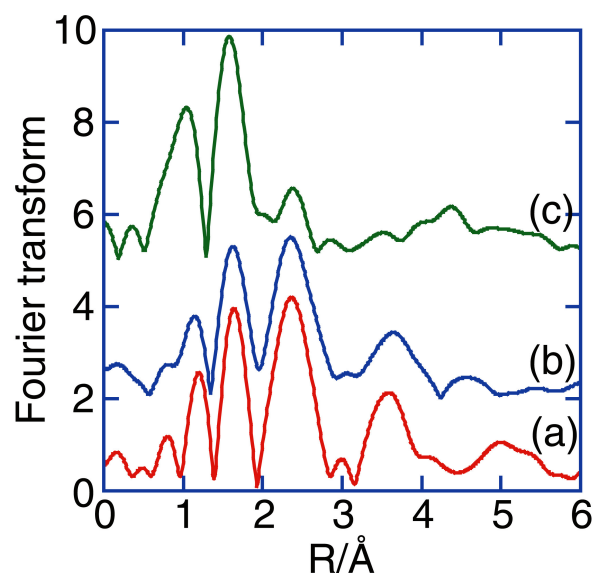


Figure 1. The Fourier transform of Ru K-edge EXAFS for $[\text{Ru}_6\text{C}]/\text{TiO}_2$ after the decomposition reaction of NO (2.0 kPa) with CO (2.0 kPa) was performed (a). 3.1 kPa of H_2O (b) or 0.56 kPa of O_2 (c) was added in addition to $\text{NO} + \text{CO}$.

shown in Figure 1b by the addition of 3.1 kPa of H_2O . The Fourier transform is essentially the same as the case in the absence of water (a). Therefore, water did not modify the active site structure. When the adequate amount of water is adsorbed (1.7 kPa) on catalyst surface, it should be incorporated in the reaction mechanism, possibly the promotion of the decomposition step of isocyanate intermediate. However, excess amount of water adsorbed (3.1 kPa) may predominantly cover the Ru active site and retard the catalysis.

The catalytic decomposition rate decreased to 51% in the presence of 0.56 kPa of O_2 in addition to $\text{NO} + \text{CO}$. The change of Ru K-edge EXAFS by the addition of O_2 is shown in Figure 1c. Compared to the case in the absence of O_2 (a), Ru-C-Ru peak at 3.7 Å (phase shift uncorrected) disappeared. The peak appeared at 1.6 Å was fitted well as the Ru-O bond at 2.02 Å ($N = 1.6$). Thus, the decomposition of $[\text{Ru}_6\text{C}]$ structure by O_2 is the reason of deactivation of the catalyst.

*izumi@chemenv.titech.ac.jp