Cu/ZrO$_2$ Catalysts for NO-CH$_4$ Reaction

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Cu(2wt%)/ZrO$_2$ shows a high activity for catalytic NO decomposition with CH$_4$ at 873 K. Cu K-edge XANES results show that Cu^{2+} ions were reduced to form Cu$^+$ after the reaction, and, metallic Cu^0 was scarcely seen. It is concluded that the redox of the Cu ions (Cu^{2+} $\rightleftarrows$ Cu$^+$) plays an important role for NO- CH$_4$ reaction.

Since the appearance of the reports on Cu/MFI,[1,2] many workers have reported the selective catalytic reduction (SCR) of NO$_x$ with hydrocarbons on copper-containing heterogeneous catalysts. In particular, SCR of NO with CH$_4$ is one of the noteworthy reactions because of the low reactivity of CH$_4$. In the presence of O$_2$, many Cu ion-exchanged zeolites such as Cu-MFI catalyze rather CH$_4$ combustion than SCR of NO.[3] In this reaction case, In/MFI-based catalysts[4] or Pd-based ones[5,6] are reported to exhibit high activity. In the absence of O$_2$, Cu-MFI[7] and Pd-MFI[6] catalysts have been reported as the active ones. For other catalyst systems except for zeolite-based ones, Cu/ZrO$_2$ has reported recently to exhibit the SCR activity with ammonia or hydrocarbons in the oxidizing atmosphere.[8,9] The reactivity of NO decomposition with CO and the details of the active species of Cu/ZrO$_2$ for NO decomposition were reported.[10,11] In this case, highly dispersed Cu metal species were formed during the reaction at above 473 K, and deactivation was brought about by aggregation of Cu metal species at high temperature of around 773 K. Since CO shows strong reducibility, Cu on ZrO$_2$ can be reduced easily. In this study, we employed the Cu/ ZrO$_2$ catalyst for NO decomposition with CH$_4$. It has been found that ZrO$_2$-supported Cu shows higher activity for this reaction than Cu catalysts on other supports. The relationship between the reactivity and the formation of the active Cu species was also discussed by using Cu K-edge XANES spectroscopy.

Supported Cu catalysts (2 wt% as Cu) were prepared by impregnation of each oxide support with an aqueous solution of Cu(NO$_3$)$_2$·3H$_2$O (Nacalai Tesque). The oxide supports used in this study were SiO$_2$ (Aerosil), γ-Al$_2$O$_3$, ZnO (Nacalai Tesque), TiO$_2$ (Wako; mixture of rutile and anatase), ZrO$_2$ (Nacalai Tesque; monoclinic), and SiO$_2$-Al$_2$O$_3$ (JRC-SAH-1; containing 28.6 wt% of Al$_2$O$_3$). These supports were calcined at 873 K for 3 h prior to the impregnation. The MgO support was obtained by calcination of Mg(OH)$_2$ (Kojundo-Kagaku) at 873 K for 6 h. The impregnating solution was stirred at room temperature, and then evaporated at 343 K for ca. 6 h to form a paste. The paste was then dried overnight and calcined at 773 K for 6 h. A reference compound, CuZrO$_3$ (Soekawa Rikagaku), was also employed for the reaction The NO decomposition with CH$_4$ was carried out using a fixed-bed flow reactor with an on-line gas chromatograph. The catalyst sample (0.25 g) was set in a ceramic tube reactor. Each catalyst sample was treated at 873 K for 1 h in a He atmosphere before the reaction. For the reaction, a gas mixture containing NO (5300ppm)/CH$_4$(2700ppm)/He was fed to the reactor. The total flow-rate was 33.5 cm^3 min^{-1} (SV = 8040 cm^3 g-cat^{-1} h^{-1}) in both the pretreatment and reaction. In the case of rising temperature reaction, the product gas was analyzed at 50 K intervals (kept on this temperature for 10 min) while the temperature was raised from 423 to 873 K at a rate of 5 K min^{-1}. In the steady state reaction case, the reaction was carried out at 773 K with the same composition and flow rate as in the non-steady state case. For each reaction mode, the product gas was analyzed periodically by means of a gas-chromatograph (Shimadzu GC-4B, TCD) with two columns packed with Porapak-Q and molecular-sieve 5A. After the reaction, the catalyst sample was treated with He for more than 5 min at the reaction temperature, and cooled to room temperature overnight in a He atmosphere. The catalyst sample was then collected and was subjected to the XANES measurement. The XANES spectra were measured at the BL-7C station of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF) with a Si(111) double crystal (d = 3.13551 /Å) monochromator. The spectra were measured in a transmission mode at room temperature. Data analysis of XANES was carried out by the method described elsewhere.[12]

Table 1. Reactivity of NO decomposition with CH$_4$ (temperature-rising reaction) over supported Cu (2 wt%) catalysts

Catalyst	At 773 K		At 873 K	
	CH$_4$ Conv./%	NO Conv. /%	CH$_4$ Conv./ %	NO Conv./ %
Cu/ZrO$_2$	11.5	6.7	36.1	100
Cu/ZnO	6.7	2.8	37.1	45.5
Cu/MgO	4.4	1.6	23.6	34.2
Cu/Al$_2$O$_3$	trace	trace	17.1	11.7
Cu/SiO$_2$-Al$_2$O$_3$	trace	trace	2.2	trace
Cu/TiO$_2$	0	0	9.6	8.0
Cu/SiO$_2$	0	0	0	trace
CuZrO$_3$	0	0	0	0
ZrO$_2$	0	0	0	0

Table 1 shows the reactivity of the supported Cu catalysts for NO decomposition with CH$_4$. The products on all the catalysts were N$_2$, H$_2$O, and CO$_2$ only, and N$_2$O or CO could not detected, indicating that the reaction, 4 NO + CH$_4$ $\rightarrow$ 2 N$_2$ + 2 H$_2$O + CO$_2$, proceeds predominantly. As the composition ratio of NO/CH$_4$ in the reactant gas is about 2, more than 60 % of CH$_4$ remained when NO decomposed completely. The reactivity at 873 K is summarized as follows; Cu/ZrO$_2$ > Cu/ZnO > Cu/MgO > Cu/Al$_2$O$_3$ > Cu/TiO$_2$ > others. In addition, copper-zirconate (CuZrO$_3$) and ZrO$_2$ showed no reactivity. ZrO$_2$-supported Cu catalyst exhibits the highest activity for supported catalysts, and this result is in accordance with the case of NO-CO reaction.[10] However, the reactive temperature ranges are different between NO-CO and NO-CH_4 reactions. NO reduction to produce N_2O and N_2 at low temperature of around 453 K took place in the case of NO-CO reaction,[10] although it does not proceed at this temperature in the NO-CH_4 reaction case. It is likely that the difference in the reactivity between these two reactions possibly relates to the reducibility of the reductants (CO and CH_4). From the result of successive (steady-state) reaction at 873 K, CH_4 conversion was 37.1 and 37.2 % for 30 and 180 min, respectively, and NO conversion is 100 % during the whole reaction time. It indicates that the NO decomposition takes place catalytically without deactivation of Cu/ZrO_2. The relationship between the Cu content in Cu/ZrO_2 and the activity (temperature-rising reaction) is shown in Table 2. In all the samples, NO decomposed completely at 873 K. The reactivities of 1–4 wt% Cu/ZrO_2 samples are almost the same, although 2 wt% Cu/ZrO_2 exhibits the slightly higher conversion of NO at 773 K. For 2 wt% Cu/ZrO_2 catalyst, the molar ratio of converted NO/CH_4 (at 873 K) was 5.3. In the case of steady-state reaction at 873 K, the ratio was 5.4 for 30 and 180 min. If the NO-CH_4 reaction proceeds stoichiometrically ($4\ NO + CH_4 \rightarrow 2\ N_2 + 2\ H_2O + CO_2$), the ratio should be 4. These results may suggest that non-stoichiometric ($2\ NO \rightarrow N_2 + O_2$ and/or $4\ NO \rightarrow N_2 + 2\ NO_2$) reaction independent on CH_4 proceeds partly.

Table 2. Reactivity of NO decomposition over Cu/ZrO_2 with various Cu contents

Cu content / wt%	NO conversion / % At 773 K	NO conversion / % At 873 K
1	6.0	100
2	6.7	100
4	5.4	100
8	1.1	100

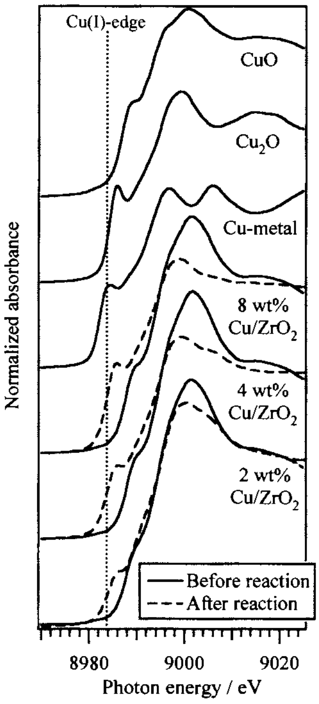

Figure 1. Cu K-edge XANES of Cu/ZrO_2 with various Cu contents and reference Cu samples.

Cu K-edge XANES was applied in order to reveal the state of active Cu species, because the XANES spectrum reflects the valence of Cu ions and their structure sensitively.[13,14] The XANES spectra of Cu/ZrO_2 with various Cu contents are shown in Figure 1. For the Cu/ZrO_2 samples before the reaction, the spectra almost resemble one another, and they can be reproduced roughly by the summation of XANES spectra of CuO and $Cu(OH)_2$. After the reaction at 873 K, the spectra of all the samples are changed; the edge energy of XANES becomes low, indicating that Cu^{2+} ions were partly reduced during the reaction. From the value of edge energy, the reduced Cu ions in the reacted Cu/ZrO_2 samples can not be assigned as Cu metal but can be interpreted as Cu^+. Thus, coexistence of Cu^{2+} and Cu^+ ions on ZrO_2 are suggested about after the NO-CH_4 reaction. In the case of NO-CO reaction, highly dispersed Cu^0 species are formed in Cu/ZrO_2 during the reaction at less than 773 K, and they may be the catalytically active species.[11] On the other hand, Cu^+ ion is formed in the NO-CH_4 reaction. These results show that Cu on ZrO_2 can be reduced easily during the NO decomposition with the reductant (CO or CH_4), and the reduction level of Cu ions strongly relates to the reducibility of the reductant. Since CH_4 has weak reducibility, Cu^{2+} is reduced partly to form Cu^+ when the decomposition of NO and CH_4 proceeds. Thus, the Cu^+ ions on ZrO_2 act as the active species, and redox of the Cu ions ($Cu^{2+} \rightleftarrows Cu^+$) plays an important role for NO-CH_4 reaction. For the NO-CO reaction, Cu^{2+} species on ZrO_2 are reduced stepwise to Cu^+, dispersed Cu^0, and finally to metal particles, and the formation of the metal particle causes the deactivation.[15] On the other hand, the metallic species is not formed for NO-CH_4 reaction, and therefore, the catalytically active Cu^+ species on ZrO_2 is stable for NO-CH_4 reaction at 873 K.

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