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Promotional role of H_2O in the selective catalytic reduction of NO with CO over $Ir/WO_3/SiO_2$ catalyst

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ABSTRACT

The catalytic activity of $Ir/WO_3/SiO_2$ for the selective reduction of NO with CO in the presence of excess O_2 was significantly increased by the presence of H_2O, whereas NO reduction hardly occurred in the absence of H_2O. Exposure of the reaction gas with H_2O to $Ir/WO_3/SiO_2$ at high temperature led to the stabilization and/or regeneration of reduced Ir sites, as suggested by X-ray diffraction and Raman spectroscopy. Temperature-programmed reduction by H_2 and a combination of scanning transmission electron microscopy and elemental analysis showed the presence of a strong Ir–W oxide interaction. Based on the activity and characterization results, we concluded that the promoting effect of coexisting H_2O is accounted for by the formation of the catalytically active reduced Ir sites, by H_2 produced *in situ* via water gas shift reaction, interacting strongly with W oxide dispersed on SiO_2 via migration of Ir to W oxide or vice versa.

1. Introduction

Catalytic reduction of NO in vehicle exhaust plays an important role in reducing NO_x. Although three-way catalysts for gasoline-fueled vehicles have been commercialized, this cannot be applied to oxygen-rich exhaust emissions such as those from diesel and lean burn engines. In this regard, a great number of studies have been made on the use of hydrocarbons as a reductant for the selective catalytic reduction of NO (HC-SCR) [1–3], since the first reports by Iwamoto et al. [4] and Held et al. [5] following the patents of Volkswagen [6] and Toyota Central R&D Labs [7]. Many kinds of catalysts based on zeolites [8], metal oxides [9], and noble metals [10] have been reported to show activity for HC-SCR. Nevertheless, practical application of HC-SCR has not been realized so far due to insufficient performance in real-life applications. In particular, catalyst deactivation and reaction inhibition by coexisting SO_2 and H_2O are major problems to be solved.

In addition to hydrocarbons, H_2 and CO have recently been proved to act as effective reductants for NO reduction under lean conditions. In 1997, Yokota et al. [11] reported the activity of Pt/mordenite for the selective catalytic reduction of NO with H_2 (H_2-SCR) in the presence of O_2 around 150 °C. They also found that the addition of Mo and Na widens the temperature window. Later, several researchers studied H_2-SCR over Pt- and Pd-based catalysts [12–17]. Although H_2-SCR is a promising approach to the efficient reduction of NO in the presence of O_2 at relatively low temperatures below 200 °C, the production and supply of H_2 is a difficult problem to solve from a practical point of view. On the other hand, CO is a more practical reductant than H_2, because a new type of internal combustion engine developed recently for the reduction of NO_x emission, the so-called homogeneous charge compression ignition (HCCI) engine, emits a relatively high concentration of CO [18], and CO can also be produced easily by engine operation when its amount is insufficient.

Various materials have been examined so far for catalytic performance in the selective catalytic reduction of NO with CO in the presence of O_2 (CO-SCR). To our knowledge, an article by Tauster and Murrell is the first report on the CO-SCR reaction, which takes place over Ir/Al_2O_3 [19]. Ogura et al. [20] found that NO can successfully be reduced to N_2 with CO over an Ir/silicalite catalyst and that the catalytic activity is not influenced by coexisting SO_2. Wang et al. [21] reported that Ir/ZSM-5 was effective for NO reduction with CO under lean conditions. Shimokawabe et al. [22–25] reported that Ir/WO_3 and Ir/ZnO show high activity for NO reduction with CO and that Ir/WO_3 is effective even in the presence of SO_2. Nanba et al. [26,27] found that the Ir/WO_3–SiO_2 catalyst shows high activity at a high space velocity (~50,000 h^{-1}). The CO-SCR reaction was also reported to take place catalytically over supported metal oxide catalysts such as Cu/Al_2O_3 [28] and Mn/TiO_2

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[29]. Although comparison of the activity of various supported metallic catalysts under the same reaction conditions is very difficult, iridium is a promising catalytically active species for NO reduction with CO.

We have also made extensive studies on CO-SCR over Ir/SiO_2-based catalysts since the first report in 2001 [30]. The most interesting feature we have found is that the coexistence of O_2 and SO_2 is essential for NO reduction to occur over Ir/SiO_2 catalysts [31]. By combining surface science techniques using a single-crystal model catalyst and a real catalyst [32], it was found that the coexisting SO_2 stabilizes the catalytically active reduced Ir site. Furthermore, we have found that the addition of Ba [33], WO_3 [34], Nb_2O_5 [35], and both Ba and WO_3 [36] to Ir/SiO_2 drastically enhances its NO reduction activity. In particular, WO_3 and Nb_2O_5 promoted Ir/SiO_2 are highly active catalysts for NO reduction with CO even in the absence of SO_2. This is quite a favorable characteristic for the treatment of diesel exhaust, because of the ever-decreasing sulfur content in diesel fuels.

In addition to small quantities of SO_2, diesel exhaust invariably has excess H_2O. The influence of H_2O on the HC-SCR reaction has been extensively studied, and for many catalysts the presence of H_2O was found to be detrimental to NO conversion. A few catalysts, on the other hand, show NO conversion enhancement due to the presence of H_2O [37–39]. The promotional effect of H_2O in HC-SCR is well understood and is correlated with the removal of carbonaceous materials deposited on the catalyst surface and also with the suppression of undesirable hydrocarbon oxidation reactions. However, the effect of H_2O on CO-SCR is not well understood from fundamental and practical application points of view. In the present work, we have investigated in detail the effect of coexisting H_2O on the catalytic activity of $Ir/WO_3/SiO_2$, which showed high activity for CO-SCR [34,40]. The role of coexisting H_2O in promoting NO conversion is discussed based on the reaction data as well as catalyst characterizations such as X-ray diffraction (XRD), Raman spectroscopy, temperature-programmed reduction by H_2 (H_2-TPR), transmission electron microscopy (TEM), and high-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) with energy dispersed X-ray spectroscopic (EDS) analyses.

2. Experimental

2.1. Catalyst preparation

Ir/SiO_2 was prepared by incipient wetness impregnation. An aqueous solution of $Ir(NO_3)_3$ (Ishifuku Metal Industry Co., Ltd.) was added to SiO_2 (Fuji Silysia Chemicals, Cariact G-10,300 $m^2\,g^{-1}$). The impregnated catalyst precursor was dried at 110 °C overnight and finally calcined at 600 °C for 6 h in air. The Ir loading was set to 0.5 wt.%.

WO_3/SiO_2 as a support was prepared by an impregnation method using an aqueous solution of $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ and citric acid. SiO_2 was added to the solution and water was evaporated; then the solution it was dried at 110 °C overnight and calcined in flowing air at 500 °C for 5 h. The WO_3:SiO_2 weight ratio was 1:9. The resulting WO_3/SiO_2 powder was then impregnated with a solution of $Ir(NO_3)_3$, followed by drying at 110 °C overnight and calcination at 600 °C for 6 h in air. The catalyst after calcination is abbreviated as "fresh". The loadings of Ir were 0.5, 1, and 5 wt.%.

2.2. Activity tests

Catalytic activity was evaluated using a fixed-bed continuous flow reactor. A catalyst sample (0.04 g) was held in a quartz tube (10-mm i.d.) by packing quartz wool at both ends of the catalyst bed. Prior to each reaction, the catalyst was pretreated *in situ* in a flow of helium at 600 °C for 1 h, unless otherwise specified. In some experiments, the catalyst was pretreated in a flow of either 10% H_2/He or 5% O_2/He at 600 °C for 1 h.

The standard reaction gas containing NO (500 ppm), CO (3000 ppm), O_2 (5%), SO_2 (1 ppm), and H_2O (6%) diluted in He as the balance gas was fed through the catalyst bed at a rate of 90 $cm^3\,min^{-1}$ (SV = ca. 75,000 h^{-1}). In some experiments, the concentration of H_2O was changed from 0% to 10%. The effluent gas was analyzed using two online gas chromatographs equipped, respectively, with a Molecular Sieve 5A column (for the analysis of N_2 and CO) and a Porapak Q column (for the analysis of CO_2 and N_2O). The reaction temperature was decreased from 600 to 200 °C in steps of 20–50 °C, and the steady-state catalytic activity was measured at each temperature. N_2 was mainly formed as the NO reduction products. The selectivity to N_2 ($N_2/(N_2 + N_2O)$) was more than 90% in most cases.

2.3. Catalyst characterization

The crystal structure was identified by XRD measurements using Cu Kα radiation at 40 kV and 150 mA (Mac Science M18XHF^{22}). The Raman spectra were measured with a JASCO NRS-3100 dispersive Raman spectrometer. The excitation was by a green laser (wavelength 532 nm) with a power of $\sim$10 mW measured at the analysis spot. H_2-TPR measurements were carried out to estimate the reducibility of catalysts pretreated under different conditions. The TPR profiles were obtained from room temperature to 600 °C in a 30-$cm^3\,min^{-1}$ flow of 10% H_2/Ar at a heating rate of 10 °C min^{-1}. The consumption of H_2 was monitored using a thermal conductivity detector (TCD). TEM and HAADF-STEM with EDS analyses were performed to examine the position of Ir on WO_3/SiO_2 support. TEM and HAADF-STEM images were obtained with a Tecnai G2 F20 (FEI, The Netherlands), operating at an acceleration voltage of 200 kV. The elemental analysis was performed by combining HAADF images with EDS (EDAX Inc.). The collection time of each EDS analysis was set at 100 s.

3. Results

3.1. Catalytic activity

3.1.1. Comparison of activity of Ir/SiO_2 and $Ir/WO_3/SiO_2$

Fig. 1 compares the activity of Ir/SiO_2 and $Ir/WO_3/SiO_2$ for NO reduction with CO in the presence of O_2 and SO_2 either without or with 6% H_2O, where the loading of Ir was 0.5 wt.%. In the absence of H_2O, Ir/SiO_2 showed slightly higher activity than $Ir/WO_3/SiO_2$. However, the activity of both catalysts was quite low. When 6% H_2O was introduced into the reaction gas, not only NO conversion but also CO conversion was enhanced for both catalysts. In particular, significant activity enhancement was observed for $Ir/WO_3/SiO_2$ catalysts, on which maximum NO conversion was increased from 4% to 79% at 280 °C. The presence of H_2O promotes NO reduction by CO over supported Ir catalysts, and this promotion is more pronounced when WO_3 is present in the catalyst. It is also of interest that a different shape of light-off curve was obtained for CO conversion over $Ir/WO_3/SiO_2$ in the presence of H_2O. Namely, a plateau region, where CO conversion was almost constant, was observed in the temperature range 400–280 °C.

Fig. 2 shows the activity of $Ir/WO_3/SiO_2$ with various Ir loadings for NO reduction with CO in the presence of H_2O. Their activity was compared on the basis of the reaction rate normalized by the total Ir content (mol s^{-1} g-Ir^{-1}). It is apparent that the activity normalized by the Ir content was increased with decreasing Ir loading. The maximum activity was obtained for 0.5 wt% $Ir/WO_3/SiO_2$ in