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NO_x storage and reduction over $Cu/K_2Ti_2O_5$ in a wide temperature range: Activity, characterization, and mechanism

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ABSTRACT

A novel NO_x storage-reduction catalyst $Cu/K_2Ti_2O_5$, which uses $K_2Ti_2O_5$ rather than Ba and Al_2O_3 as NO_x storage compound as well as support, has been synthesized and investigated. Activity tests including temperature-programmed ramping, isothermal storage, and lean-rich cycling reveal that $Cu/K_2Ti_2O_5$ adsorbs NO_x over a very wide temperature range (200–600 °C), with two peak temperatures at 280 and 550 °C, respectively. The NO_x storage and reduction mechanism over $Cu/K_2Ti_2O_5$ is studied in detail. We demonstrate that, at low temperature (200–400 °C), NO_x is adsorbed on the oxygen vacancy sites which are formed on $K_2Ti_2O_5$ support during the lean-period; whereas at high temperature (500–600 °C), the NO_x storage and reduction is explained by a structure switching between $K_2Ti_2O_5$ and $K_2Ti_6O_{13}$ caused by NO_2 adsorption and de-sorption. Our results also provide another option for synthesizing NSR catalysts with $K_2Ti_2O_5$ or even with other potassium containing compounds.

1. Introduction

NO_x abatement has been widely recognized as one of the most challenging problems for lean-burn engine emissions [1,2]. To achieve an efficient abatement of NO_x from these emission gases, several technologies including ammonia/urea selective catalytic reduction (ammonia/urea-SCR), hydrocarbon selective catalytic reduction (HC-SCR), and NO_x storage-reduction (NSR) have been developed during the last few decades [3–6]. However, each technology has its own inherent strengths and weaknesses [7]. For example, ammonia/urea-SCR is a more mature technology; however, its implementation for mobile applications will require the development of an ammonia/urea distribution network, with additional social disadvantages (NH_3 slip and odor) and enforcement difficulties [8]. HC-SCR is superior to ammonia/urea-SCR in terms of additional infrastructure construction, but the NO_x removal efficiency is low [9]. NSR operates alternatively under lean and rich conditions. NO_x is first stored on the catalyst under lean conditions and subsequently converted to nitrogen by unburned hydrocarbons under rich conditions. Its application is associated with a number of other complications, such as a fuel penalty for the rich events, sensitivity to fuel sulfur levels, and control under transient engine operation [10]. Despite these problems, NSR is still considered as the most promising technology, since it does not require new infrastructure and also provides superior high De-NO_x performance [9].

Typical NSR catalysts consist of a high-surface-area support (e.g., γ-Al_2O_3, TiO_2, ZrO_2, TiO_2–ZrO_2, etc.), a NO_x-storage component (an alkaline or alkaline earth metal oxide, e.g., Ba, K, Ca, Mg, etc.), and a noble metal (e.g., Pt, Rh, etc.) for both oxidation of NO and hydrocarbons, and the reduction of stored NO_x. During the lean burn stage, NO is oxidized by oxygen and stored in the form of nitrate or nitrite. Due to the presence of ample oxygen, HC, H_2, and CO can also be readily oxidized into water and carbon dioxide. When the engine is switched to operate with the normal air-fuel mixture, the resulting exhaust becomes comparatively oxygen-deficient. The remaining HC, H_2, and CO will react with the stored NO_x in the presence of noble or transition metals, and selectively reducing to N_2 [10–12].

The classical NSR catalyst is Pt–Ba/γ-Al_2O_3, which was developed by Toyota [6]. Although a large number of experimental investigations on Pt–Ba/γ-Al_2O_3 catalyst have been conducted and theoretical models for this reaction have been developed, problems still remain, mainly with respect to sulfur poisoning and thermal stability [13–15]. Deactivation caused by sulfur is the most difficult problem for NSR catalysts; this must be solved before commercial application. Sulfur dioxide is firstly oxidized on precious metals, and it then reacts with the support to form

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aluminum sulfate, which covers the surface of γ-Al_2O_3 or plugs the micro-pores of γ-Al_2O_3. SO_x may also react with the NO_x storage components to form barium sulfate, which is very difficult to decompose [16,17]. At high temperature, the support (γ-Al_2O_3) reacts with NO_x-storage component (Ba) to form $BaAl_2O_4$, leading to permanent activity loss [18–20].

Potassium is another key element that has shown potential as a storage component with significant benefit at higher temperatures; the K-based nitrate is more stable than the typical Ba-based nitrate [21,22]. Previous studies have demonstrated the good performance of K-based lean NO_x trap catalysts, even in the presence of CO_2 and H_2O in the feed [23–25]. Titanium oxide (TiO_2) has also been reported as the most promising candidate as support to overcome sulfur poisoning, since the stability of sulfates on TiO_2 surface is weaker than that on other oxides. SO_x deposit on the catalyst with TiO_2 support (3.2 μmol g^{-1}) is much lower than that on the catalyst with γ-Al_2O_3 support (7.2 μmol g^{-1}) [19]. Because of the solid reaction between K and TiO_2, however, researchers believe that these two materials cannot be used simultaneously for NSR catalysts [18,19]. Surprisingly, we found that the reaction product $K_2Ti_2O_5$, synthesized at 850 °C, exhibited a superior NO_x storage capacity at 500–600 °C. We therefore proposed metal-doped $K_2Ti_2O_5$ (M/$K_2Ti_2O_5$, M = Pt, Cu, Co, Ce, Ag, etc.) as NSR catalysts, for which the NO_x adsorption temperature could be significantly decreased. Among them, Cu/$K_2Ti_2O_5$ shows the most interesting performance and most promising applications.

Cu has received much attention due to its capability of simultaneous removal of SO_2 and NO_x from flue gases because: (i) Cu readily adsorbs SO_2 in the presence of O_2 to form $CuSO_4$ in low temperature range (200–400 °C); (ii) $CuSO_4$ is relatively easy to be regenerated under reducing conditions; (iii) copper compounds (Cu, CuO and $CuSO_4$) are active for SCR of NO_x to N_2 [26–31]. Eguchi et al. and Machida et al. [32,33] have also reported some Cu-based NO_x storage compounds, e.g., Ba–Cu mixed oxides and $La_{1.4}Ba_{0.6}SrCu_2O_6$. Therefore, Cu rather than other transition metals was selected and studied. In the present work, Cu/$K_2Ti_2O_5$ was synthesized and characterized by means of X-ray diffraction (XRD), BET surface area measurement, and field emission scanning electron microscopy (FE-SEM). Its NO_x storage-reduction performance was further studied by temperature-programmed ramping, isothermal storage, and lean-rich cycling tests. Finally, the mechanisms for NO_x storage and reduction over Cu/$K_2Ti_2O_5$ in both low and high temperature ranges were investigated.

2. Experimental

2.1. Catalyst synthesis

$K_2Ti_2O_5$ and $K_2Ti_6O_{13}$ were prepared by the well-established solid state reaction method [34,35]. Briefly, 13.82 g (for $K_2Ti_2O_5$) or 4.61 g (for $K_2Ti_6O_{13}$) K_2CO_3 (Yakuri Pure Chemical Co., Ltd.), 7.99 g TiO_2 (Hombikat UV 100), and a proper amount of water were perfectly mixed by ball milling for 24 h, followed by drying in oven over night. After crushing to fine powder, these two samples were, respectively, calcined at 850 and 1180 °C for 10 h in air to obtain $K_2Ti_2O_5$ and $K_2Ti_6O_{13}$. Then Cu/$K_2Ti_2O_5$ was synthesized by incipient wetness impregnation with $Cu(NO_3)_2{\cdot}3H_2O$ as precursor, followed by further calcination at 850 °C for 10 h in air. In this work, the Cu loading is 7.5 wt.%, except when noted otherwise. Cu–Pt/$K_2Ti_2O_5$ and Cu–Rh/$K_2Ti_2O_5$ were also prepared by successively impregnating Pt (or Rh) and Cu on $K_2Ti_2O_5$. $H_2PtCl_6{\cdot}5.7H_2O$ (Kojima Chemicals Co., Ltd) and $RhCl_3{\cdot}xH_2O$ (38–40% Rh, Sigma–Aldrich Co., Ltd.) were used as precursors and the obtained samples were further calcined at 850 °C for 10 h in air.

2.2. Catalyst characterization

The XRD patterns were obtained using an X-ray analyzer (M18XHF, Mac Science Co., Ltd., Yokohama, Japan). Ni-filtered Cu Ka radiation (λ = 1.5415 Å) was used with an X-ray gun operated at 40 kV and 200 mA. Diffraction patterns were obtained within the range of 2θ = 5–80° with a step size of 0.02°. BET surface areas were measured with a Micromeritics ASAP 2010 sorption analyzer using a static volumetric technique, based on the amount of N_2 adsorbed at liquid N_2 temperature. The samples were degassed at 200 °C in vacuum for 5 h before the adsorption measurements. The catalyst morphology was investigated by FE-SEM (Hitachi, S-4200). Fourier transform infrared spectroscopy (FT-IR) experiments were performed using a PerkinElmer 2000 FT-IR spectrophotometer. A self-supporting thin disc of 13 mm in diameter was prepared by pressing 1 mg catalyst powder and 14 mg KBr (Aldrich, FT-IR grade) using a manual hydraulic press. All spectra were measured with 4 cm^{-1} resolution.

2.3. Catalytic activity test

NO_x storage and reduction over Cu/$K_2Ti_2O_5$ was investigated by temperature-programmed reaction, isothermal storage at a certain temperature, and lean-rich cycling tests, from which the optimum NO_x storage temperature, the maximum NO_x storage capacity, and the reduction activity of adsorbed NO_x were determined. Before these experiments, fresh Cu/$K_2Ti_2O_5$ was first pretreated with 3.5% H_2 at 400 °C for 30 min to remove nitrate residue from the precursor, and the obtained sample was referred to reduced Cu/$K_2Ti_2O_5$. The sample referred to oxidized Cu/$K_2Ti_2O_5$ in the present work was obtained by re-oxidizing the reduced Cu/$K_2Ti_2O_5$ with 10% O_2 at 400 °C for 30 min.

All these catalytic activity tests were performed in a flow-reactor, consisting of a packed-bed made of quartz tube (10 mm internal diameter). The reactor was controlled by a proportional-integral-derivative (PID) temperature controller/programmer (Han Kook Electronic Co.), and the temperature was measured by a K-type thermocouple (0.5 mm outer diameter). The reaction gases at the reactor outlet were continuously analyzed by means of a NO_x analyzer (Chemiluminescence NO–NO_2–NO*x* analyzer, Model 42C, high level, Thermo environmental instruments, Inc.) and an on-line quadrupole mass spectrometer (Balzers Pfeiffer, USA). The stability of adsorbed NO_x on Cu/$K_2Ti_2O_5$ was evaluated by temperature-programmed de-sorption with He. The NO_x evolution as a function of temperature from 25 to 700 °C (10 °C min^{-1}) was recorded by an on-line quadrupole mass spectrometer (Balzers Pfeiffer, USA).

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of $K_2Ti_2O_5$, reduced Cu/$K_2Ti_2O_5$, and oxidized Cu/$K_2Ti_2O_5$. As we expected, the reduced Cu/$K_2Ti_2O_5$ was composed of pure Cu doped on $K_2Ti_2O_5$, with the characteristic peaks of Cu at 41.5° and 50.5°, suggesting that CuO was completely reduced to metallic Cu by H_2 at 400 °C. The characteristic peaks of CuO (35.68°, 38.86°) for the oxidized Cu/$K_2Ti_2O_5$ indicated that metallic Cu was re-oxidized to CuO by O_2 at 400 °C. During all these processes, the structure of the $K_2Ti_2O_5$ support remained unchanged. Except for the characteristic peaks of Cu and CuO, all other XRD peaks of the reduced and oxidized Cu/$K_2Ti_2O_5$ matched well with those of synthesized $K_2Ti_2O_5$. A relatively low BET surface area of oxidized Cu/$K_2Ti_2O_5$ (0.5 m^2 g^{-1}) was also observed, further confirming that the catalyst was well crystallized.