



Enhanced NO_x conversion by coupling NO_x storage-reduction with CO adsorption-oxidation over the combined Pd–K/MgAlO and Pd/MgAlO catalysts



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ABSTRACT

NO_x conversion was enhanced by coupling NO_x storage-reduction (NSR) with CO adsorption-oxidation (CAO), which was observed in NSR lean-rich cycle tests with CO as a reductant on catalysts of Mg–Al mixed oxides supported Pd (Pd/MgAlO) and Pd–K (Pd–K/MgAlO). CO was adsorbed on Pd sites in the rich condition and then oxidized by gaseous NO_x via Eley–Rideal mechanism during the transition from the rich condition to the lean condition, which results in an enhanced NO_x conversion. This is confirmed by different configuration experiments of Pd–K/MgAlO and Pd/MgAlO, acting as NSR and CAO catalysts, respectively. The intimate mixture of Pd–K/MgAlO and Pd/MgAlO showed much higher activity due to the resultant coupling effect of NSR with CAO in comparison with a zone-arranged catalyst system no matter whether Pd–K/MgAlO or Pd/MgAlO was in the front. The coupling also worked in the presence of H₂O and CO₂ despite that the efficiency were spoiled. This strategy is ease to be implemented and thereby is potential for the practical after-treatment technology for lean-burn and diesel engines.

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1. Introduction

Automotive lean-burn engines running at an air to fuel ratio much higher than stoichiometric (≈ 14.7) take the advantages of higher fuel efficiency and lower CO₂ emission, which will become more popular than conventional gasoline engines. However, the toxic NO_x in exhaust cannot be efficiently removed since NO_x reduction is inefficient under lean operating conditions compared with the traditional three-way catalysts. In order to meet the increasingly stringent emission limits, three ways to remove NO_x in the lean-burn exhaust have been developed [1]: (i) direct decomposition of NO, which is still infeasible due to the poor activity of the present catalysts; (ii) selective catalytic reduction of NO_x (SCR), which is inherent to the problem of carrying reductant sources on

board; and (iii) NO_x storage and reduction (NSR), which overcomes the difficulty of reduction in an oxygen-rich environment by operating in lean-rich cycles and is a promising lean-NO_x abatement technology and the catalysis technology of choice.

The concept of NSR was brought up by Toyota laboratories [2,3], in which alternating lean-rich conditions are employed. NO_x is first stored in the catalyst under lean conditions and then reduced by introducing reductants such as H₂, CO and hydrocarbons under rich conditions. Thereby, a NSR catalyst should have both sites for NO_x storage (alkali metal or alkaline earth metal compounds) and those for NO_x oxidation/reduction (noble metals) [1]. A prototypical NSR catalyst is Pt–Ba/Al₂O₃, which consists of Pt and Ba dispersed on a high-surface-area alumina support [4]. The NSR process is accomplished by the cooperation between noble metal and alkali/alkaline earth metal. However, the cooperation is at the expense of detriment to the redox properties of noble metal. Olsson et al. [5] found that BaO is apt to suppress the rate of NO oxidation on the supported Pt catalyst. Both Frolaet et al. [6] and Castoldi et al. [7] reported that Ba can mask Pt particles. Pellegrini et al. [8] suggested that K as an alkaline dopant will lower the reducibility of PdO. The

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group of Meng [9,10] revealed that K species may cover a number of the Pt sites, in agreement with the finding of Luo et al. [11]. The presence of alkali/alkaline earth metal significantly limits the NO oxidation and reductant activation, leading to insufficient utilization of reductants in the NSR process. An efficient way to enhance the NSR strategy demands not only to keep the inherent redox properties of noble metal but also to achieve a high NO_x storage capacity of the alkali/alkaline earth metals.

Mg–Al hydrotalcite mixed oxide (MgAlO) NSR catalysts have been reported to behave low temperature activity [12] and high thermal stability [13]. Furthermore, MgAlO supported K (K/MgAlO) showed improved NSR performance at high temperatures [14]. In our previous work [15], Mg–Al mixed oxides supported Pd and K (Pd–K/MgAlO) were investigated and displayed an excellent NSR efficiency. The detriment of K to the redox property of Pd was observed. In this work, the NSR activities of Pd–K/MgAlO were further evaluated in cyclic lean-rich conditions with CO as the reduction agent. Apart from NSR process, a CO adsorption-oxidation (CAO) process was observed for the first time during lean-rich cycles, demonstrating a new NSR strategy by coupling with CAO process. The NO_x conversion was remarkably enhanced by a simple mixture of Pd–K/MgAlO (NSR catalyst) and K-free Pd/MgAlO (CAO catalyst), by which the negative effect of K on the activities of Pd was compensated to a great extent.

2. Experimental

2.1. Catalyst preparation

A mixed salt solution of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O was prepared with the Mg/Al mole ratio of 3:1 and with the total concentration of Mg and Al being 1.5 mol/L. Another solution of Na₂CO₃ and NaOH with the (CO₃²⁻)/(OH⁻) mole ratio of 1:2 was used as the precipitating agent. Both solutions were simultaneously dropped into 100 mL deionized water held at 65 °C with stirring at a pH value of 10.0 ± 0.1 by adjusting the dropping speeds. The resulting precipitate was aged in suspension at 65 °C for 30 min, stirred for 18 h at room temperature, filtered, thoroughly washed by the distilled water and dried overnight at 120 °C. The obtained hydrotalcite was calcined at 950 °C for 12 h to produce stable MgAlO mixed oxides [16].

Pd/MgAlO and K/MgAlO were synthesized via an incipient wetness impregnation method with an aqueous solution of Pd(NO₃)₂ and K₂CO₃, respectively. The Pd–K/MgAlO catalyst was prepared by incipient wetness impregnation of Pd/MgAlO with an aqueous solution of K₂CO₃. The above samples were dried overnight and then calcined at 850 °C for 2 h to stabilize the supported Pd [15]. The nominal Pd contents of the Pd-containing catalysts was fixed at 1 wt.%.

2.2. Catalyst characterization

The elemental compositions were measured by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) on the IRIS Intrepid IIXSP instrument from Thermo elemental. X-ray absorption fine structure (XAFS) spectra at Pd K-edge were obtained at the BL14W1 at Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics (SINAP), China. Surface areas and pore size distributions were determined by N₂ adsorption-desorption at 77 K using a Micromeritics ASAP 2020 instrument after outgassing at 300 °C for 5 h prior to analysis.

2.3. Cyclic NSR tests

The lean-rich cyclic tests for NSR were performed in a fixed-bed reactor under cyclic operation, in which a rapid self-motion

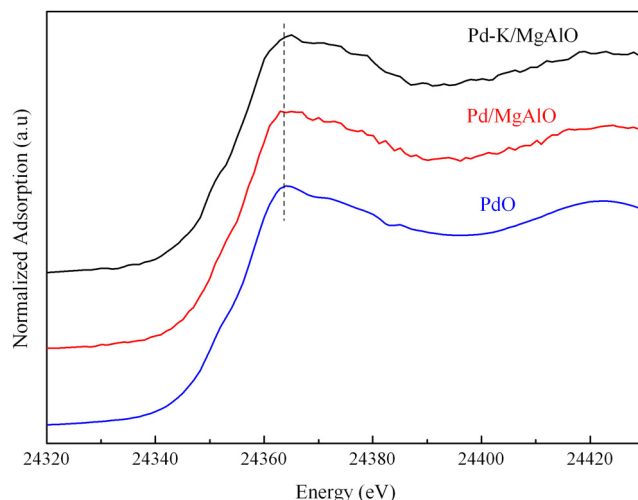


Fig. 1. Pd K-edge XANES spectra of PdO, Pd/MgAlO and Pd–K/MgAlO.

switching four-way valve system was used to alternate between the lean and rich gas mixtures. The catalyst (50 mg) was first pre-treated in situ for 30 min at 500 °C under He flow, and then cooled down to 200 °C in He flow. After that, the cycles consisting of 60 s lean periods and 10 s rich periods were conducted over the 200–500 °C temperature interval. During the lean period, the sample was exposed to 540 ppm NO and 7.5% O₂ with He as the balance (400 mL/min). During the rich period, the sample was exposed to 1% CO with He as the balance (400 mL/min). The concentrations of NO_x (NO + NO₂), N₂O, NH₃ and CO₂ in the effluent were measured by a FT-IR continuous gas analyzer (MKS MultiGas 2030, USA). These gases were simultaneously analyzed by a quadrupole mass spectrometer (MS, OmniStar 200, Switzerland), in which NO_x, CO and CO₂ were characterized by the signals at *m/z* 30, 28 and 44, respectively. The signal at *m/z* 28 for CO was corrected by removing the contribution of CO₂.

In order to obtain the NSR performance in simulated exhaust gas, 5% CO₂ and 5% H₂O were introduced into the feed. In addition, the NSR performance were tested with the space velocity varying from 110,000 to 1,100,000 h⁻¹.

The NO_x conversion was given by [17]

$$X_{\text{NO}_x} = \frac{\int [\text{NO}_x]_{\text{Fed}} - \int [\text{NO}_x]_{\text{Slipped}}}{\int [\text{NO}_x]_{\text{Fed}}} \times 100\% \quad (1)$$

The selectivity to N₂ was calculated by the mass balance with the selectivities to N₂O and NH₃ as given by [17]

$$S_{\text{N}_2\text{O}} = \frac{2 \times \int [\text{N}_2\text{O}]_{\text{Product}}}{\int [\text{NO}_x]_{\text{Fed}} - \int [\text{NO}_x]_{\text{Slipped}}} \times 100\% \quad (2)$$

$$S_{\text{NH}_3} = \frac{\int [\text{NH}_3]_{\text{Product}}}{\int [\text{NO}_x]_{\text{Fed}} - \int [\text{NO}_x]_{\text{Slipped}}} \times 100\% \quad (3)$$

$$S_{\text{N}_2} = 1 - S_{\text{N}_2\text{O}} - S_{\text{NH}_3} \quad (4)$$

3. Results and discussion

The elemental compositions of as-prepared catalysts were determined by ICP, as listed in Table 1. The K contents of K/MgAlO and Pd–K/MgAlO were determined as 5.55 and 6.36 wt.%, respectively, while the Pd contents of Pd/MgAlO and Pd–K/MgAlO were measured as 0.85 and 0.77 wt.%, respectively, being close to the nominal value (1 wt.%). The state of Pd element was characterized by XAFS (Fig. 1). The Pd K-edge X-ray absorption near edge structure (XANES) spectra of Pd/MgAlO and Pd–K/MgAlO were identical to

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