Applied Catalysis A: General 365 (2009) 187–193

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

NOx abatement for lean-burn engines under lean–rich atmosphere over mixed NSR-SCR catalysts: Influences of the addition of a SCR catalyst and of the operational conditions

E.C. Corbos [a,*], M. Haneda [a], X. Courtois [b], P. Marecot [b], D. Duprez [b], H. Hamada [a]

[a] *Research Centre for New Fuels and Vehicle Technology, National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

[b] *Laboratoire de Catalyse en Chimie Organique (LACCO), LACCO - UMR 6503, Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

ARTICLE INFO

Article history:
Received 10 April 2009
Received in revised form 4 June 2009
Accepted 5 June 2009
Available online 16 June 2009

Keywords:
NOx storage and reduction
Selective catalytic reduction
Ammonia
Pt–Rh
Ba
Ag
Cu
Co
Alumina
Reduction time
NCO

ABSTRACT

Mixtures of equal amounts of a Pt–Rh/Ba/Al_2O_3 NOx storage reduction (NSR) model catalyst and Ag/Al_2O_3, Co/Al_2O_3 or Cu/ZSM-5 selective catalytic reduction (SCR) model catalyst were evaluated for the NOx removal activity under lean–rich atmosphere. NOx removal activity was increased by adding Co/Al_2O_3 or Cu/ZSM-5 to Pt–Rh/Ba/Al_2O_3 while adding Ag/Al_2O_3 had no significant influence. Experiments performed by using two catalytic beds (upstream Pt–Rh/Ba/Al_2O_3 and downstream Co/Al_2O_3 or Cu/ZSM-5) suggested that both SCR catalysts are able to reduce NOx with the NH_3 produced during the rich step on Pt–Rh/Ba/Al_2O_3. Among the studied catalysts, the Pt–RhBa/Al_2O_3 + Cu/ZSM-5 physically mixed one showed the highest activity. This catalyst mixture presented an improved performance, as compared to the NSR catalyst, regardless of the reductant used (CO and/or H_2) or of the reduction time (10, 5 or 2.5 s). The highest activity was obtained by using both CO and H_2 as reductant during the rich pulse. The addition of water in the inlet gas led to a decrease of the NOx removal activity of the catalyst mixture. Nevertheless, the NOx removal activity of the mixed Pt–RhBa/Al_2O_3 + Cu/ZSM-5 catalyst was still significantly higher than that of Pt–RhBa/Al_2O_3.

1. Introduction

Diesel and lean-burn gasoline engines are a promising way to decrease the fuel consumption for automotive use, thus decreasing the CO_2 emissions. However, the NOx abatement from lean-burn engines is difficult to achieve since they work mainly under excess volumes of O_2. To overcome this problem, researchers have explored two main approaches toward NOx reduction in lean conditions: NOx storage reduction (NSR) and selective catalytic reduction (SCR).

The NSR catalysts operate alternatively under lean and rich conditions. During the lean conditions, NO is oxidized to NO_2 on precious metals (i.e. Pt) and then stored as nitrites/nitrates on a basic component (alkaline and/or alkaline earth oxides). Before too high an amount of NOx slips through the catalyst, the engine switches to rich conditions (excess of hydrocarbons) for a short period where the stored NOx are released and reduced into N_2 over the precious metal (i.e. Rh) [1]. These systems were extensively studied during the last years and a few mechanisms are proposed in the literature [2].

The NOx removal efficiency depends on both NOx storage and NOx reduction activities of the NSR catalyst. Generally, it is admitted that NOx removal is limited by both NOx storage and reduction at low temperature and mainly by the storage function at high temperature. The NOx storage depends on the NO oxidation activity (mainly at low temperature), on the Pt–Ba proximity and on the nitrates' stability (mainly at high temperature) [2–4]. Concerning the reduction step, it was shown that the reduction of nitrates strongly depends on the nature of the reductant (H_2, CO, hydrocarbons) and the length of the reduction pulse [5–8]. In real conditions the reduction step must be very short (few seconds) and should be highly selective towards N_2 production without emitting CO and HC in the process. If the reductant pulse is too short, the regeneration of storage sites is incomplete and the activity of NOx trapping decreases, but if the pulse is too long undesirable products, like ammonia (if H_2 is used as a reductant), are produced.

---

* Corresponding author. Tel.: +81 29 861 4646; fax: +81 29 861 4647.
E-mail addresses: crina-corbos@aist.go.jp, corbos@aist.go.jp (E.C. Corbos).

0926-860X/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2009.06.008

In realistic exhaust gas compositions H_2 is always present due to the Water Gas Shift (WGS) reaction on the catalyst [9]. Nevertheless, the ammonia production depends on the temperature and the amount of H_2 [6,10,11].

Another alternative for NOx abatement is the use of SCR technologies. A lot of works [12–18] focus on the SCR systems with NH_3; the use of NH_3-SCR is nowadays a well-established technique for DeNOx in stationary and non-stationary applications. The most studied catalysts for NH_3-SCR are V_2O_5/TiO_2 modified or not with WO_3 [12,13] and non noble metals like Cu, Fe and Ce supported on zeolite [14–18]. High NOx conversions can be achieved by using zeolite-supported catalysts, but at high temperatures these systems are less efficient due to the NH_3 oxidation into NOx. Other studies focused also on hydrocarbon SCR [19–21], which is considered as a promising technique since it eliminates the use of ammonia, considered as a toxic product. The catalysts studied for this application typically contain Pt, Cu, Fe, Co or Ag supported on different alumina or zeolite based materials [21,22].

Recently, a few papers focused on combining the NSR systems with NH_3-SCR ones [23–25]. The NH_3 formed on NSR catalyst during the rich pulses can be used to increase the NOx removal efficiency of the NSR system if a NH_3-SCR catalyst is put downstream. Thus, the ammonia is stored during the rich phase on the SCR catalyst and then used for NH_3-SCR reaction in the next lean cycle. We showed that the NOx removal efficiency can be greatly improved under lean–rich atmosphere if a NSR model catalyst is physically mixed with CuZSM-5 [25]; this effect was ascribed to an increase in the formation of NCO species, their formation being promoted by Cu/ZSM-5 catalysts.

The present study has two aims. The first one is to determine if the NOx removal efficiency under lean–rich atmosphere can be improved by using different NSR-SCR systems, with SCR catalysts reported as active either for NH_3-SCR or HC-SCR. The second aim is to study the influence of the operating conditions on the NOx reduction activity of mixed NSR-SCR catalysts. To achieve these goals, we used three different catalysts: CuZSM-5, which is known to be active for NH_3-SCR [17,26] and HC-SCR [27,28]; Co/Al_2O_3, mainly active for HC-SCR [20,29,30]; and Ag/Al_2O_3, found active for HC-SCR [20,21]. The NOx removal activity was measured by periodically switching between lean (100 s) and rich (10, 5 or 2.5 s) atmospheres. In addition to NOx and O_2, the lean gas also contained C_3H_6 and CO/H_2, while the rich gas contained NOx and CO and/or H_2. To give a more realistic picture about the catalyst behavior in realistic conditions, all the measurements were carried out in the presence of CO_2. Tests were also performed in the presence of water.

2. Experimental

2.1. Catalyst preparation

The $Pt–Rh/Ba/Al_2O_3$ catalyst was prepared by a successive wet impregnation method. First barium (20 wt% BaO) was impregnated from a $Ba(NO_3)_2$ solution to commercial Al_2O_3 (Mizusawa Chemical, GB-45, 190 $m^2 g^{-1}$). The resulting material was dried at 110 °C overnight and further calcined at 700 °C for 4 h in air. Platinum (1 wt%) was impregnated by using a $Pt(NH_3)_4(NO_3)_2$ solution and the catalyst was first treated at 700 °C for 4 h under N_2 before Rh impregnation (0.013 wt%) with a $RhCl_3$ solution. Eventually, the $Pt–Rh/Ba/Al_2O_3$ catalyst was treated at 700 °C under N_2 and then aged at the same temperature with wet air (5% H_2O/air) for 4 h [4]. A 4 wt% Ag/Al_2O_3 catalyst and a 2 wt% Co/Al_2O_3 catalyst were prepared by wet impregnation of the same commercial alumina with an aqueous solution of $AgNO_3$ or $Co(NO_3)_2$. After drying overnight at 110 °C, the catalysts were calcined at 500 °C for 5 h. A 5 wt% CuZSM-5, catalyst was prepared by wet impregnation of H-ZSM-5 (Tosoh, HSZ-830NHA, $SiO_2/Al_2O_3 = 28$) with an aqueous solution of $Cu(NO_3)_2{\cdot}2H_2O$. After drying overnight the catalyst was calcined in air at 500 °C for 5 h. The catalysts prepared as described above, $Pt–Rh/Ba/Al_2O_3$, Ag/Al_2O_3, Co/Al_2O_3 and CuZSM-5, are denoted as Pt–Rh/Ba, AgAl, CoAl and CuZSM-5, respectively.

2.2. Activity test

The catalytic tests were performed on physical mixtures of SCR and NSR catalysts using equal amounts of each (30 mg). When the individual activity of the Pt–RhBa or SCR catalysts was measured, 30 mg of each catalyst was diluted with 30 mg of inert α-alumina. The NOx removal activity was determined by alternatively switching between lean and rich conditions. The total gas flow was 90 $cm^3 min^{-1}$ which corresponds to a space velocity of ca. 55,000 h^{-1}. The gas composition is described in Table 1. The lean and rich periods were of 100 s and 10, 5 or 2.5 s, respectively. The activity of the catalysts was followed until stabilization. The NO, NO_2, N_2O, NH_3, CO and C_3H_6 concentrations were measured using a GASMET DX-4000 FT-IR apparatus. Before measurement, the catalysts were treated at 550 °C following the procedure reported in Fig. 1. This pretreatment normalized the state of the catalysts before each test and allowed one to have a standardized surface.

Fig. 2 shows an example of experimental curves obtained for NOx (where NOx stands for $NO + NO_2$), CO, NH_3 and N_2O evolution with time. The length of the lean cycles was 100 s and the rich pulse length was 10 s. The NOx removal efficiency (NOx removal) was calculated after stabilization for at least 5 rich/lean cycles as the NOx average at the inlet and outlet (where NOx stands for $NO + NO_2$) of the reactor. N_2, NH_3 and N_2O were considered as reduction products.

$$\text{NOx removal} = \left[1 - \frac{\text{Average NOx}_{\text{out}}}{\text{NOx}_{\text{in}}}\right] \cdot 100$$

The NOx storage capacity is calculated by integrating the area above the NOx curve for the first 100 s in lean conditions. The NOx storage is expressed in $\mu mol\ g^{-1}$ of Pt–RhBa catalyst. Additionally, the NOx conversion into N_2 was also estimated as follows:

$$\text{NOx conversion into N}_2 = \left[1 - \frac{\text{Average}(\text{NOx}_{\text{out}} + 2 \cdot [\text{N}_2\text{O}] + [\text{NH}_3])}{\text{NOx}_{\text{in}}}\right] \cdot 100$$

$[N_2O]$ and $[NH_3]$ were deduced from corresponding peak area (Fig. 2). The CO removal efficiency was calculated as: $(1 - CO_{out}/CO_{in}){\cdot}100$.

3. Results and discussion

3.1. NOx removal activity

Fig. 3 shows the NOx removal efficiency during the lean–rich cycles for the different catalyst mixtures (Pt–RhBa and SCR catalysts).

Table 1
Gas composition for the lean and rich mixtures.

Gas	NO	O_2	CO–H_2 (75%/25%)	CO_2	C_3H_6	He	Total flow
Lean (100 s)	500 ppm	10%	0.13%	1%	167 ppm	Balance	90 $cm^3 min^{-1}$
Rich (10 s)	100 ppm	–	8.53%	1%	–	Balance	