Journal of Colloid and Interface Science 333 (2009) 423–430

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Feature Article

NO_x decomposition, storage and reduction over novel mixed oxide catalysts derived from hydrotalcite-like compounds

Jun Jie Yu [a], Jie Cheng [a], Chun Yan Ma [a], Hai Lin Wang [a], Lan Dong Li [a], Zheng Ping Hao [a,*], Zhi Ping Xu [b,*]

[a] *Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China*
[b] *Australian Research Council (ARC) Centre for Functional Nanomaterials, Australian Institute for Bioengineering and Nanotechnology and School of Engineering, The University of Queensland, Brisbane, QLD 4072, Australia*

ARTICLE INFO

Article history:
Received 25 December 2008
Accepted 7 February 2009
Available online 12 February 2009

Keywords:
NO_x abatement
NO_x decomposition
NO_x storage and reduction
Hydrotalcite-like compounds
Mixed oxide catalysts

ABSTRACT

Effective control and removal of nitrogen oxides (NO_x) emission from vehicles exhausts under lean-burn condition is one of the most important targets in scientific research of environmental protection. A comprehensive introduction of NO_x storage and reduction (NSR), the most promising lean-NO_x control technology, is given including the sum-up of NSR materials, catalytic activity and related reaction mechanisms. Emphasis is put on the novel multifunctional NSR catalysts, derived from hydrotalcite-like compounds, with characteristic of simultaneous NO_x strorage–decomposition–reduction. Finally, future research directions in the area of lean-NO_x control based on mixed oxide catalysts derived from hydrotalcite-like materials is also proposed.

1. Introduction

Nitrogen oxides (NO_x), generally refereed to NO and NO_2, are generated primarily from combustion processes in the power stations and various vehicles. The emission of NO_x into air are directly responsible to various environment problems, such as photochemical smog, formation of acid rain and resultant acidification of soils and waters, which has harmed some plants, animals and the human health [1]. For these reasons, NO_x emissions from the combustion processes are required to be severely controlled and regulated. Therefore, the abatement of NO_x emission, i.e. deNO_x, has attracted much attention and great efforts of worldwide researchers.

On the other hand, due to the limited resource of the raw oil in the world and more serious global warming, a fuel-efficient vehicle is more desirable. Most current gasoline-burning engines are run in a very narrow air to fuel ratio region near the stoichiometric value ($A/F = 14.7$, rich-burn) with little or no O_2 in the exhaust, but the lean-burn engines ($A/F = 20$–25) can more efficiently burn the fuel, saving 30–35% consumption and releasing less CO_2 [2,3]. However, under these conditions, the conventional three-way catalyst is no longer effective for NO_x abatement due to the oxidant environment. Therefore, NO_x removal from the lean-burn exhaust stream faces more challenges in the environmental sciences.

Current deNO_x technologies under the lean-burn conditions include direct catalytic decomposition of NO_x [4], catalytic NO_x storage/reduction (NSR) [2], selective catalytic reduction (SCR) of NO_x with NH_3 and hydrocarbons (HCs) [5–7]. The SCR has been intensively investigated and a number of reviews have been published elsewhere [5–8], so this review paper will focus on the recent advances of the catalysts that are made of the normal transition metal oxides derived from hydrotalcite-like compounds (HTlcs) yet are effective in NO_x direct decomposition, and NO_x storage under lean-burn conditions. We finally present our comments on rational design of the active catalysts for such applications in terms of spatial structure and coordination of the active components in the nanometer scale as the concluding remarks.

2. Direct decomposition

Direct decomposition of NO_x to N_2 and O_2 is the simplest way to abate the NO_x emissions because no additional reactive agents are required and the operation is simple. The catalysts have been studied since 1970, however, the recent research advances in the material preparation and nanotechnology make direct decomposition prospective in NO_x abatement [4,9].

NO decomposition over various catalysts, such as single-crystal metals, oxides, oxide-supported metals, has been reviewed in detail by Garin [4], including the various decomposition mechanisms and kinetics. The reports suggested that oxide-supported Pd catalysts [10] and Cu-ZSM-5 [11] appeared as the potential catalysts which catalytically convert 50–95% NO in the temperature range of 400–700 °C. Very recently, Fe–Mn/H-beta catalysts were reported to effectively decompose NO_x in 300–400 °C in the presence of O_2 and CO_2 with the conversion of 25–45% [12]. It is worth mention-

---

* Corresponding authors. Faxes: +86 10 62923564, +61 7 33463973.
E-mail addresses: zpinghao@rcees.ac.cn (Z.P. Hao), gordonxu@uq.edu.au (Z.P. Xu).

0021-9797/$ – see front matter
doi:10.1016/j.jcis.2009.02.022

ing that $BaMnO_3$-based dopant perovskite oxides can efficiently convert NO to N_2, O_2 and NO_2, while the temperature required is high, usually 600–800 °C [13,14], and the decomposition is severely affected by the presence of CO_2, H_2O or O_2 [15,16]. There was only one paper reporting that a particular mixed oxide catalyst derived from CoNiAl-HTlc is very active for NO direct decomposition, with ca. 50% NO decomposition at 300 °C with the space velocity of 7000 h^{-1} [17].

It is known that the decomposition is thermodynamically favorable at below 900 °C and the search for the catalysts for NO_x direct decomposition has been investigated for 40 years [4], there has been only a limited success. In our opinion, the major reason is the low selectivity of NO decomposition to N_2 and O_2. For example, during direct decomposition of NO to N_2 and O_2, NO_2 and N_2O are always the byproducts, and sometimes are the main components [4,13,14]. The second reason is the high decomposition temperature (600–900 °C) for high NO_x conversion (>80%), so that the practical application of the catalysts for the car exhaust treatment becomes impossible. The third factor is the low stability of catalysts in the catalytic activity under practical conditions. In general, the presence of water vapor, O_2 and CO_2 will reduce the activity to some to high degree [16]. More severely, the trace amount of SO_2 in the stream severely deactivates the catalytic activity. In this regard, the rational design of new types of active catalysts for NO_x direct decomposition has to take these factors into account.

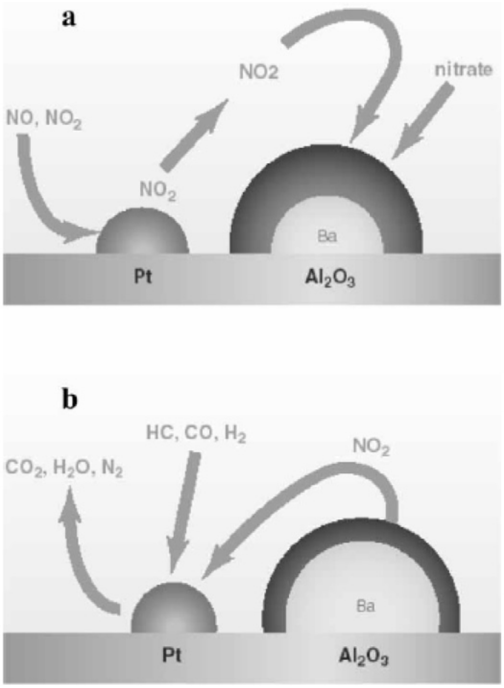

Fig. 1. Schematic of NO_x storage and reduction mechanism over $Pt/Ba/Al_2O_3$ under (a) lean-condition; (b) rich-condition [7].

3. NO_x storage/reduction technology

The NO_x storage/reduction method (NSR) developed by Toyato researchers is generally regarded as one of the leading technologies for the control of NO_x emission under lean-burn conditions [18–20]. The NO_x storage/reduction technology can be used in an engine that alternately operates under lean-burn and rich-burn conditions. Under lean-burn conditions, NO is oxidized and stored on the catalyst. When the engine is switched to the condition with a stoichiometric air-to-fuel ratio, i.e. the rich-burn condition, the stored NO_x are released and subsequently reduced by hydrocarbons (HCs) and CO. Therefore, NO_x storage/reduction (NSR) is a promising method to remove NO_x in the O_2-rich condition.

$Pt/BaO/Al_2O_3$ has been intensively investigated worldwide as a model system to catalytically store NO_x since the last decade, and the storage mechanism has been well understood. In principle, this model NO_x storage/reduction catalyst comprises three major components: a high surface area support material (e.g., γ-Al_2O_3), a NO_x storage component containing alkali or alkaline earth metals (e.g., Ca, Sr, Ba, K and Na), and noble metal (e.g., Pt, Rh, and Pd) as the catalytic redox component. Regarding the storage mechanism, as illustrated in Fig. 1a, NO is first oxidized to NO_2 over Pt particle surface under the lean-burn condition. The freshly formed NO_2 is either adsorbed on the Pt surface or released back into the gas phase. The gaseous NO_2 can be disproportionated into nitrate and gaseous NO over the 'BaO' surface, and stored in the form of nitrate. The adsorbed NO_2 can be further oxidized to nitrate (NO_3^-) that can be then spilt over to the neighboring 'BaO' particle and stored in the form of nitrate. After switching to the rich-burn condition, the stored nitrate is decomposed to NO_2 that is reduced to N_2 by HCs, CO, and/or H_2 over noble metal particle surface (Fig. 1b), completing the removal of NO_x and resulting in regeneration of the catalyst.

In line with the understanding of NSR mechanism over $Pt/BaO/Al_2O_3$, a few similar systems have been also investigated as NSR catalysts. For example, as summarized in Table 1, Toops et al. examined the adsorption and oxidation of NO over $Pt/K_2O/Al_2O_3$ [21,22]. They reported that such a catalyst Pt(1.0 wt%)/K_2O(4.5 wt%)/Al_2O_3 can store up to 0.797 mmol (NO_x)/g at 250 °C within 1 h (300 ppm NO, 12% O_2 and bal. N_2). Yang et al. investigated the adsorption behaviors of NO on $Pd/CaO/Al_2O_3$, $Pt/CaO/Al_2O_3$ and $Rh/CaO/Al_2O_3$ with the storage amount of NO_x of 0.097 to 0.28 mmol/g at 300 °C within 7.5 min (1000 ppm NO, 7% O_2 and bal. He, Table 1) [23]. Vaccari et al. modified the storage component (BaO) into a composite (MgO–BaO) which shows a good

Table 1
Summary of NO_x storage catalysts that are known to have good performance.

Catalyst	Temp. (°C)/time	NO_x (bal. He or N_2)	NO_x storage (mmol/g)	Evaluation method	Ref.
PtRh/Ba/washcoat	300 (saturation)	500 ppm NO + 7% O_2	0.530	Adsorption	[51]
$Pt/BaO/Al_2O_3$	300 (saturation)	1000 ppm NO + 3% O_2	0.581	Adsorption	[52]
$Pt/K_2O/Al_2O_3$	250 (60 min)	300 ppm NO + 12% O_2	0.797	DRIFTS	[21]
$Pt/K_2O/Al_2O_3$	250 (saturation)	300 ppm NO + 12% O_2	0.936	DRIFTS	[21]
$Rh/CaO/Al_2O_3$	300 (7.5 min)	1000 ppm NO + 3% O_2	0.28	Adsorption	[23]
$Rh/CaO/Al_2O_3$	300 (7.5 min)	1000 ppm NO + 3% O_2	0.18	Adsorption	[23]
$BaAl_2O_4$	80–350 (~70 min)	500 ppm NO + 500 ppm NO_2 +	0.52	Dynamic	[53]
BaSnO3	100 (~70 min)	10% O_2 + 5% CO_2 + 5% H_2O	0.56	Dynamic	[29]
BaSnO3	300 (~70 min)		0.20	Dynamic	[29]
Ca_2CoAl-oxide	300 (60 min)	800 ppm NO + 8% O_2	0.602	Desorption	This work
$Ca_2CoLaAl$-oxide	300 (60 min)	800 ppm NO + 8% O_2	0.634	Desorption	This work
Ca_2CoAl-oxide	250 (60 min)	800 ppm NO + 8% O_2	0.622	Desorption	This work
$Ca_2CoLaAl$-oxide	250 (60 min)	800 ppm NO + 8% O_2	0.651	Desorption	This work