

Flame-made Pt–Ba/Al₂O₃ catalysts: Structural properties and behavior in lean-NO_x storage-reduction

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Abstract

A series of Pt–Ba/Al₂O₃ catalysts with Ba loadings in the range of 4.5–33 wt% was prepared using a two-nozzle flame spray pyrolysis method. The structural properties and activities of these catalysts in NO_x storage-reduction (NSR) were compared to corresponding standard Pt–Ba/Al₂O₃ catalysts prepared conventionally via wet impregnation. The catalysts were characterized by XRD, TEM, ESI, DRIFT, TG-MS, TPRD, and gas adsorption. Calcined flame-derived catalysts were composed of agglomerated spherical nanoparticles of alumina and Pt/barium carbonate of low thermal stability (LT-BaCO₃), whereas barium carbonate of high stability (HT-BaCO₃) was absent. In contrast, in the corresponding conventionally prepared catalysts, the Ba-containing phases were composed of BaO, LT-BaCO₃, and HT-BaCO₃. DRIFTS measurements of CO adsorption revealed distinct differences in the distribution of CO chemisorbing sites on Pt particles depending on the preparation method applied. The CO:Pt ratio varied between 0.8 and 0.7 depending on the Ba loading and the preparation method. Decreased Pt dispersion at higher Ba loadings was observed for the wet-impregnated catalysts, whereas Pt dispersion increased only slightly at higher Ba loadings for the flame-made catalysts. The structural differences of flame-made and conventionally prepared catalysts affected strongly their NO_x storage efficiency. Investigation of the behavior of the catalysts in NSR showed that the larger Ba/Al₂O₃ interface existing in conventionally prepared catalysts results in a higher NO_x storage efficiency of these catalysts at Ba loadings up to ca. 17 wt%, whereas the absence of the HT-BaCO₃ phase in flame-made catalysts lead to improved NO_x storage potential at higher Ba loadings.

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1. Introduction

NO_x pollution from combustion processes has been a challenging area of environmental chemistry ever since new, more efficient engines operating under lean conditions were introduced [1,2]. NO_x storage-reduction (NSR) catalysts proposed by Toyota in 1995 [3] seem to offer the most realistic solution in terms of dynamic NO_x control. Nitrogen oxides are stored under lean conditions over an alkaline or alkaline-earth component (i.e., BaCO₃ or BaO) in the form of nitrates, which are then reduced to nitrogen during a short fuel-rich period [4–7]. The standard NSR catalyst is Pt–Ba/Al₂O₃ generally prepared

by wet impregnation of an alumina support with aqueous solutions of barium and platinum precursors [8].

The classical NO_x storage mechanism assumes that either BaO or BaCO₃ species are the storage compounds [8]. Recently it has been shown that the distribution of different Ba-containing species over the support [9–14] is a crucial factor for storage efficiency [15,16], especially in the case of alumina-supported catalysts [17,18]. A detailed study of the influence of the Ba loading in standard Pt–Ba/Al₂O₃ revealed the presence of different Ba-containing phases in the conventional Pt–Ba/Al₂O₃ NSR catalyst. The existence of different Ba-containing phases was traced to varying interaction of the Ba species with the alumina support [15]. In a preceding study we described the activity of each of these Ba-containing phases in the NO_x storage process and proposed a direct relation be-

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tween thermal stability and storage potential of the diverse BaCO_3 phases [16]. BaCO_3 in intimate contact with the support (LT- BaCO_3), partially decomposing to BaO at low temperatures, was found to be the most active Ba-containing phase in the NO_x storage process, whereas bulk-like BaCO_3 decomposing at higher temperatures (HT- BaCO_3) represents a limiting factor for NO_x storage efficiency. Recently our findings were confirmed by Chen et al. [13], who identified two different Ba- NO_x species with different thermal stabilities, resulting from the thermal decomposition of alumina-supported $\text{Ba}(\text{NO}_3)_2$.

Intrigued by our earlier findings, we attempted to prepare Pt–Ba/ Al_2O_3 -based catalysts with limited formation of larger BaCO_3 clusters, accompanied by HT- BaCO_3 formation [15]. Among the various preparation methods, flame spray pyrolysis (FSP) was chosen, based on some of its unique features [19]. This method, based on dispersing and igniting combustible precursor solutions [20], gives access to all kinds of metal-containing nanoparticles [19]. Such flame-made (FM) materials are characterized by a relatively high surface areas [21] due to the external surface of the nanoparticles and the nonporous structure generally improving thermal stability [21,22].

The conventional single-nozzle FSP process has some inherent limitations in controlling the distribution of two or more components in the material, as in the case of mixed metal oxides, resulting in poor NSR catalysts [23]. Recently, we have shown that a two-nozzle flame process adds further flexibility in setting of flame parameters and provides better control of particle mixing at the nanolevel in the Pt–Ba–Al system [23].

Consequently, intrigued by the obvious advantages of the two-nozzle flame process, we prepared a series of FM Pt–Ba/ Al_2O_3 catalysts with Ba loadings in the range of 4.5–33 wt% and compared their structural properties and behavior in NO_x storage reduction to those of corresponding standard Pt–Ba/ Al_2O_3 catalysts prepared by wet impregnation (WI).

2. Experimental

2.1. Catalyst preparation

Two sets of NO_x storage-reduction catalysts, with the standard formulation Pt–Ba/ Al_2O_3 , were prepared by means of two different methods: the incipient wetness technique (denoted as WI catalysts) and the flame spray pyrolysis (denoted as FM catalysts). The WI samples were prepared using $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ and $\text{Ba}(\text{CH}_3\text{COO})_2$ as precursors, and commercial γ - Al_2O_3 (BET surface area = $210 \text{ m}^2 \text{ g}^{-1}$) as a support. The detailed preparation procedure has been described previously [15]. As-prepared samples with a Pt content of 1 wt% were dried for 12 h at 80°C and then calcined at 500°C for 2 h, all in air. After calcination, the samples were impregnated with $\text{Ba}(\text{CH}_3\text{COO})_2$ solutions affording nominal Ba loadings of 4.5, 9, 16.7, 22, and 28 wt%, and then dried for 12 h in air at 80°C . Before each experiment, the samples were calcined in situ with a temperature ramp of $10^\circ\text{C min}^{-1}$ up to 500°C .

The setup for flame synthesis of Pt–Ba/ Al_2O_3 , described in detail previously [23], consisted of two separate FSP nozzles, with the angle between them fixed at 120° and the internoz-

Table 1
Nominal composition of WI and FM Pt–Ba/ Al_2O_3 catalysts: Ba and Pt loading in wt%

WI Pt–Ba/ Al_2O_3		FM Pt–Ba/ Al_2O_3	
Ba (wt%)	Pt (wt%)	Ba (wt%)	Pt (wt%)
4.5	0.94	4.5	0.94
9	0.91	9	0.91
16.7	0.83	16.7	0.83
22	0.77		
		23	0.76
28	0.71		
		33	0.66

zle distance between the angle tip and each nozzle center fixed symmetrically at 6 cm. The Al- and Pt/Ba-containing precursor solutions were fed separately through the two nozzles. The Al precursor consisted of aluminum(III) tri-*sec*-butoxide (Alfa Aesar, 95%) dissolved in a 2:1 vol% mixture of diethylene glycol monobutyl ether (Fluka, 98%) and acetic anhydride (Riedel de-Haën, 99%). For the Pt/Ba precursor mixture, barium(II) 2-ethylhexanoate (75% in 2-ethylhexanoic acid; Alfa Aesar, 99.8%) and platinum(II) acetylacetonate (Strem, 98%) were dissolved in ethanol (Alcosuisse, 98%). The Al concentration was maintained at 0.5 mol L^{-1} for all experiments. The platinum and barium concentrations were adjusted to afford a Pt content of 1 wt% and nominal Ba loadings of 4.5, 9, 16.7, 23, and 33 wt%. The flames were operated in open air environment, reaching maximum flame temperatures of up to 2500°C [20]. Liquid and gas flow rates were as described previously [23].

For comparison, Pt–Ba/ Al_2O_3 powder (with a relative formulation of 1:20:100) was also produced by one-nozzle FSP with a precursor feed rate of 5 ml min^{-1} and an oxygen dispersion gas flow rate of 5 L min^{-1} . In that precursor, the solutions of aluminum(III) tri-*sec*-butoxide, barium(II) 2-ethylhexanoate (Aldrich, 98%), and platinum(II) acetylacetonate were dissolved in toluene ($\text{Al} = 0.5 \text{ mol L}^{-1}$).

Both the WI and FM samples are designated as Pt–Ba(x), where x denotes the nominal wt% of Ba in the sample, for example, Pt–Ba(22.0). The relative loading of Pt was kept constant (i.e., Pt(1)–Ba(x)– Al_2O_3 (100)); therefore, the absolute Pt content decreases with increasing Ba loading to a minimal value of ca. 0.7 wt% for WI Pt–Ba(28) and 0.6 wt% for FM Pt–Ba(33) [15]. Table 1 lists the composition of the catalysts used in this study.

2.2. Catalyst characterization and NO_x storage-reduction tests

Specific surface areas (S_{BET}), specific pore volumes (V_p), and average pore diameters ($\langle d \rangle = 4V_p/S_{\text{BET}}$) of the calcined supports and supported Pt–Ba samples with different Ba loadings were determined by nitrogen adsorption–desorption measurements at 77 K using a Micromeritics Tristar 3000 instrument. Pore size distributions (not shown) were calculated using the Barrer–Joyner–Halenda method [24]. The assessment of microporosity was made using t -plot constructions [25].

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