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NO reduction by CH_4 over Pd/Co-sulfated zirconia catalysts

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Abstract

A series of sulfated zirconia supported Pd/Co catalysts was synthesized by the sol–gel method and examined for NO_x reduction by methane. The NO conversion increased up to a Co/S ratio of 0.43, and then decreased at a higher Co loading (Co/S = 0.95). Sulfate content was also essential for obtaining high selectivity to molecular nitrogen. A catalyst loaded with 0.06 wt.% Pd, 2.1 wt.% Co and 2.1 wt.% S (Pd/Co-SZ-2) exhibited remarkable performance under lean conditions and displayed stability in a long-term durability test using a synthetic reaction mixture containing 10% water vapor. This catalyst exhibited the highest sulfur retention most probably as cobalt sulfide. Besides, the catalytic oxidation of NO to NO_y groups was confirmed by FT-IR, in agreement with the general mechanism for the SCR of NO by hydrocarbons. In the absence of oxygen in the feed stream, the catalyst was highly active for NO reduction with methane. IR stretching bands assigned to N_2O and adsorbed nitro groups were identified upon adsorbing NO on Pd/Co-SZ-2. This indicates that under rich conditions disproportionation of NO to N_2O and NO_2 occurs and confirms that the formation of NO_2 species is an essential step for NO reduction by CH_4.

Keywords: Nitrogen oxides; Methane; SCR; Sulfated zirconia; Sol–gel Co-SZ; Pd/Co-SZ

1. Introduction

The SCR of NO_x by methane is a very attractive technology for diminishing NO_x emissions from stationary internal combustion engines because natural gas (mainly methane) is readily available. Effective CH_4-SCR has been reported over cobalt zeolites but, these catalysts are deactivated by water vapor [1,2]. More recently bimetallic cobalt and palladium loaded zeolites exhibited much more resistance to water vapor than monometallic Co-zeolites [3,4]. However, these catalysts also deactivate under long-term hydrothermal conditions. Alternative supports including sulfated zirconia (SZ) have been studied. Resasco and coworkers [5] examined the lean selective catalytic reduction of NO by methane over a series of Pd catalysts supported on SZ. This support was shown to be less sensitive to structural damage in comparison to zeolite carriers. Furthermore, they showed that SZ is able to promote the NO reduction activity similar to acid zeolites, by stabilizing Pd^{2+} ions which are selective sites for NO reduction by methane [5]. Recently, a cooperative effect between Pd and Pt supported on SZ has been reported for the lean NO_x reduction by methane [6]. NO_x conversions exceeding 50% even after 100 h TOS were found over a 0.38 wt.% Pd–0.12 wt.% Pt-Z(S) catalyst in the presence of 3 ppm SO_2 and using a CH_4/NO ratio of 20. In a subsequent paper [7] these authors suggested that Pd is an active site for NO_2 reduction with methane, while the role of Pt is to catalyze NO oxidation to NO_2. Ohtsuka [8] examined the activity of binary or physically mixed noble-metal supported on sulfated zirconias (Ru, Rh, Pd, Ag, Ir, Pt, and Au) for the lean NO_x reduction by methane. A Pd–Pt combination exhibited high activity. Similarly, Li et al. [9] studied a series of non-noble metal (Co, Mn, In, Ni) catalysts supported on SZ. NO_x conversions above 60% were obtained over a 4 wt.% Co/SZ catalyst. The catalyst was also stable during a long-term stability test (60 h). Additionally, the sulfation of the support was essential for the generation of active Co sites

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for the reduction of NO. Other studies [10] have also shown that sulfate prevents the formation of Co_3O_4 and isolated Co(II) on sulfated-ZrO_2 are the active sites for the lean selective reduction of NO with propene.

The mechanism of the selective catalytic reduction (SCR) of NO_x with hydrocarbons has been extensively studied by various authors [11–14]. It is widely accepted that oxygen greatly enhances SCR by interacting with NO. The catalytic oxidation of NO_2 into NO_y groups on the surface is an important step for NO_x reduction [15]. The NO_y groups interact with an impinging hydrocarbon to form a new adsorbed intermediate containing C, N and O atoms. In subsequent steps, this intermediate reacts with NO + O_2 or NO_2, and N_2 is formed [11].

The aim of the present work was to explore the possibility of using bimetallic Pd/Co supported on sol–gel sulfated zirconia catalysts for the SCR of NO by methane. Selected samples, fresh and after durability tests, were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and temperature programmed reduction (TPR). Several features of the synthesized catalysts are discussed in terms of sulfate and cobalt loadings. The potential structural effects of the coexistence of palladium and cobalt supported on SZ and stable species for the SCR reaction are also discussed.

2. Experimental

2.1. Catalyst preparation

Sulfated zirconia was prepared by modifying the procedure reported by Bedilo and Klabunde [16]: 6.5 ml of zirconium butoxide was added to 22.5 ml of ciclohexane at 60 °C. The solution was stirred for 1 h and then cooled at 3 °C. Subsequently, distilled water (4 mol/mol Zr) and sulfuric acid (0.48 mol/mol Zr) was added dropwise with constant stirring, until the mixture became hard to stir. The resultant gel was aged for 24 h at room temperature. Then, it was dried at 70 °C and calcined in air at 600 °C during 4 h. Co-SZ samples were obtained by the above procedure but, different amounts of cobalt acetate were added to cyclohexane before mixing with zirconium butoxide. Pd loaded samples were obtained by impregnation of SZ and Co-SZ samples with an aqueous solution containing the required amount of $Pd(NH_3)_4Cl_2{\cdot}H_2O$ to obtain a Pd loading of about 0.06 wt.%. After drying at 60 °C, pelletizing, crushing and sieving into 30–40 mesh (Tyler), catalyst samples were heated at 500 °C during 4 h in flowing helium. The elemental composition of selected materials is listed in Table 1.

2.2. Catalytic activity measurements

Catalytic experiments were carried out in a tubular reactor containing 150 mg of powder catalyst. The reactor was a Pyrex tube 3/8 in. o.d. containing a quartz frit to hold the catalyst. The typical volumetric composition of the reaction mixture was: 0.1% NO, 0.3% CH_4, 5% O_2, 10% H_2O and balance helium. The feed was introduced using electronic mass flow controllers (Brooks 5850E). The total flow was 100 $cm^3\ min^{-1}$. Taking a catalyst density of about 1.5 g/cm^3, the gas hourly space velocity (GHSV) was 45000 h^{-1}. Water was introduced using a peristaltic pump. Experiments were carried out in an ascending temperature mode, allowing enough time at each temperature to achieve steady-state conversion. Prior to each experimental run, catalysts were pretreated in situ by heating in helium at 500 °C for 2 h. The feed and effluent gases were analyzed using a gas chromatograph (Varian Star 3400) equipped with a TCD detector. A molecular sieve 5A column was used to separate O_2, N_2, CO, and CH_4, and a Porapak Q column to analyze N_2O and CO_2. In some runs, a FT-IR multicomponent gas analyzer (Temet, model Gasmet DX 4000, cell length 2.4 m, cell volume 1.0 l, cell temperature 120 °C) was used to follow NO, NO_2, N_2O, NH_3, CO, CO_2 and H_2O concentrations. To avoid condensation of water vapor, the tubing between reactor and gas analyzer was electrically heated and controlled at 120 °C. The NO_x and CH_4 conversions were calculated from the measured values of the formed nitrogen and reacted methane, respectively.

Table 1
Elemental composition of selected synthesized catalysts

Catalyst	wt.%			Atomic ratios		
	S	Co	Pd	Zr/S	S/Co	Co/Pd
SZ	4.1	0.0	0.0	5.0	–	–
Pd/SZ	1.1	0.0	0.06	21.6	–	–
Co-SZ	4.9	2.2	0.0	3.9	4.0	–
Pd/Co-SZ-1	2.3	0.9	0.05	6.3	4.5	32.8
Pd/Co-SZ-2	2.7	2.1	0.06	7.7	2.4	61.4
Pd/Co-SZ-3	2.0	3.6	0.08	10.4	1.0	81.9
Pd/Co-SZ-2 (aged)	2.7	2.1	0.06	–	1.6	61.4

2.3. Catalyst characterization

Selected fresh and aged catalysts were characterized by XRD, TPR and FT-IR. Fresh samples were used as prepared and aged samples were obtained by exposing fresh catalyst samples to a gas stream whose volumetric composition was: 0.1% NO, 0.3% CH_4, 5% O_2, 10% H_2O and balance helium at 550 °C, GHSV = 18,000 h^{-1} for 65 h.

The elemental composition of powder catalysts as determined by ICP is listed in Table 1.

X-ray diffraction (XRD) was performed with a Rigaku DMAX diffractometer, using Ni filtered Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 20 mA. Scanning was conducted from $2\theta = 20^\circ$ to 80° at a scan step of 0.1°.

H_2-TPR experiments: samples were loaded inside a quartz reactor, calcined in flowing O_2 at 500 °C for 1 h and cooled to room temperature. Then, gas composition was switched from oxygen to argon for 1 h before admitting the reducing mixture (5% H_2/Ar, 40 ml/min). Reduction was carried out by heating