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Effects of potassium loading and thermal aging on $K/Pt/Al_2O_3$ high-temperature lean NO_x trap catalysts

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ABSTRACT

The effects of K loading and thermal aging on the structural properties and high temperature performance of $Pt/K/Al_2O_3$ lean NO_x trap (LNT) catalysts were investigated using in situ X-ray diffraction (XRD), temperature-programmed decomposition/desorption of NO_x (NO_x-TPD), transmission electron microscopy (TEM), NO oxidation, and NO_x storage tests. In situ XRD results demonstrate that KNO_3 becomes extremely mobile on the Al_2O_3 surface, and experiences complex transformations between orthorhombic and rhombohedral structures, accompanied by sintering, melting and thermal decomposition upon heating. NO_x storage results show an optimum K loading around 10% for the best performance at high temperatures. At lower K loadings where the majority of KNO_3 stays as a surface layer, the strong interaction between KNO_3 and Al_2O_3 promotes KNO_3 decomposition and deteriorates high-temperature performance. At K loadings higher than 10%, the performance drop is not caused by NO_x diffusion limitations as for the case of barium-based LNTs, but rather from the blocking of Pt sites by K species, which adversely affects NO oxidation. Thermal aging at 800 °C severely deactivates the $Pt/K/Al_2O_3$ catalysts due to Pt sintering. However, in the presence of potassium, some Pt remains in a dispersed and oxidized form. These Pt species interact strongly with K and, therefore, do not sinter. After a reduction treatment, these Pt species remain finely dispersed, contributing to a partial recovery of NO_x storage performance.

1. Introduction

The removal of NO_x from lean burn engine exhaust, especially in a highly efficient way in order to implement more stringent regulations, remains a significant challenge in the field of emission control catalysis, since current commercial three-way catalysts lack efficient NO_x reduction capability under a net oxidizing environment. Therefore, two after-treatment techniques have been developed for reduction of NO_x from lean burn engines; namely, lean NO_x traps (LNT; also known as NO_x storage/reduction (NSR) catalysts) and selective catalytic reduction (SCR) [1,2]. Commercialized LNTs mainly consist of noble metals Pt (Pd, Rh) and Ba supported on Al_2O_3 or $CeZrO_x$, which show excellent NO_x reduction activity, especially in the temperature range from 350 to 400 °C [3–7]. However, their efficiency becomes unsatisfactory for certain applications, such as for lean burn gasoline engines (GDI, gasoline direct injection) with exhaust temperatures as high as 400–500 °C [8]. At these temperatures, the stored NO_x phase, in the form of $Ba(NO_3)_2$, becomes unstable and tends to decompose. In this regard, developing lean NO_x trap catalysts with enhanced high temperature performance is very necessary. Researchers from Toyota Motor Company previously pointed out that barium and potassium are the two most suitable elements of LNT catalysts in NO_x storage and HC conversion [6]. K-based LNTs show much higher NO_x storage capacities in the high temperature range (400 °C and above) than Ba-based ones, due to the stronger basicity of K. Recently, potassium has begun to play a larger role in emission control catalysis; traditionally K has primarily been considered a "promoter" in the long history of catalysis [9,10]. One example is its recent application in simultaneous NO_x reduction and soot combustion because of its high NO_x storage capacity, and especially because of K's mobility which enables intimate contact with soot

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particles [11–15]. Meanwhile, K-based LNTs have been the subject of considerable study that has included preparation methods, support effects, and storage/reduction mechanisms [16–21]. For example, by utilizing a two-nozzle flame spray method, high surface area $Pt/K/Al_2O_3$ catalysts were successfully prepared, which exhibit effective NO_x removal performance [16]. Besides Al_2O_3, the support materials were also examined in detail, aiming at improving NO_x storage capacity, thermal stability and sulfur durability. Studied support materials include La_2O_3, CeO_2, CeO_2/Al_2O_3, TiO_2–ZrO_2, Al_2O_3–ZrO_2–TiO_2, K-titanate ($K_2Ti_2O_5$, $K_2Ti_8O_x$), and $MgAlO_x$ [8,22–26]. For the most commonly studied $Pt/K/Al_2O_3$ material, the storage/reduction mechanisms have been investigated by means of FT-IR spectroscopy, generally by comparison with barium-based LNTs, and focusing on their similarities and differences [27–29]. In addition, for $Pt/K/Al_2O_3$ catalysts, aspects such as the effects of CO_2 and H_2O on NO_x sorption, sulfation/desulfation, and spatially resolving the regeneration of a monolith sample have also been studied by researchers from Oak Ridge National Laboratory [30–32].

As is well-known, the morphology of the storage phase plays a key role in NO_x storage. For Ba/Al_2O_3 catalysts, two types of barium species exist: a BaO monolayer on the Al_2O_3 surface, and small particles of bulk-like BaO (~5 nm) on top of the monolayer at BaO loadings >8 wt.% [33–35]. Upon NO_2 exposure at room temperature, the BaO monolayer converts to surface nitrate and the bulk-like BaO converts to small nanosized bulk $Ba(NO_3)_2$. These two types of nitrate species have different thermal stabilities. The surface nitrate decomposes and desorbs NO_2 at lower temperatures, while the bulk-like nitrate decomposes and releases $NO + O_2$ at higher temperatures. Similarly, on a $BaCO_3$-based LNT, three types of Ba species have been identified, i.e., a BaO monolayer, a low-temperature $BaCO_3$ (LT-$BaCO_3$) phase, and a high-temperature $BaCO_3$ (HT-$BaCO_3$) phase, according to their stability difference [36,37]. Among which, the LT-$BaCO_3$ phase serves as the most active species for NO_x storage; while the efficiency of the HT-$BaCO_3$ phase is limited by NO_x diffusion, due to the formation of a dense $Ba(NO_3)_2$ shell. It is worth pointing out that the relative population of the three phases depends strongly on the barium loading. Similarly, we expect that such a loading effect would also significantly affect the performance of the K-based catalysts for high temperature NO_x storage, especially when there exists dramatic stability differences for the different stored NO_x phases. To the best of our knowledge, only few reports have addressed the K loading effect.

Another important issue worth investigating is the thermal stability of the catalysts. As is known, LNTs are susceptible to sulfur poisoning, such that periodic desulfations at high temperatures are required; e.g., typical desulfations are carried out between 600 and 750 °C for barium-based LNTs [4,38]. For these LNTs, such high-temperature treatments may result in irreversible Pt sintering and $BaAl_2O_4$ phase formation [39,40]. For the potassium-based LNTs, desulfation may require even higher temperatures to decompose the even more stable potassium sulfates. Preliminary results indicated that a desulfation temperature around 800 °C may be required [8,31]. Therefore, it is important to investigate thermal aging effects of $Pt/K/Al_2O_3$ catalysts at such high temperatures.

To address these issues, in this paper we systematically investigate the effects of K loading and thermal aging on the structure and performance of the $K/Pt/Al_2O_3$ catalysts as high temperature LNTs. Besides similarities found between K- and Ba-based LNTs, such as the decreased stability of surface nitrates due to stronger interaction with Al_2O_3, we also observe new features unique for K-based LNTs including the extreme mobility of the storage phase, novel mechanisms for decreased performance at high K loadings, and the formation of different Pt species during thermal aging.

2. Experimental

2.1. Catalyst preparation and treatment

Pt/Al_2O_3 was prepared via wetness impregnation. The γ-Al_2O_3 support (Alfa Aesar, 150 $m^2\,g^{-1}$) was first added into a dilute $Pt(NH_3)_4(NO_3)_2$ (Alfa Aesar) solution at room temperature, followed by drying at room temperature and calcining at 500 °C for 4 h in air. Next, K was loaded onto Pt/Al_2O_3, also by impregnation, using K_2CO_3 (Alfa Aesar) as the K source. Five catalysts were prepared at different K loadings (2, 5, 10, 15, and 20%, weight basis). The resultant catalysts were dried and calcined at 600 °C for 4 h in air. Thermal aging of the catalysts was performed by calcination at 800 °C for 4 h in air. Reduction of the aged catalysts was done in 4% H_2/He at 800 °C for 1 h.

Three KNO_3/Al_2O_3 samples with different K loadings (5, 10, and 20%, weight basis) were prepared via impregnation (at 80 °C to improve KNO_3 solubility) using KNO_3 (Alfa Aesar) as the precursor. These samples were used as models of the storage phase for characterization purposes.

2.2. LNT performance testing

NO_x storage capacity (NSC) at different temperatures, from 550 to 250 °C at 50 °C per step, was measured in a quartz tube reactor (O.D. ≡ 1/2 in.). First, 120 mg of sample was loaded into the reactor and exposed to 20 lean/rich cycles (L/R ≡ 50/10 s) to reach steady-state cycle-to-cycle performance. Subsequently, the catalyst was continuously exposed to the lean environment for measurement of NO_x uptake. NO_x storage capacity was measured by integrating the amount of NO_x adsorbed until the outlet NO_x concentration reached 60 ppm. The lean and rich gas mixtures were prepared from cylinder gases and metered by mass flow controllers (Brooks), and H_2O was introduced via a syringe pump. The lean gas consisted of 150 ppm NO, 5% O_2, 5% CO_2, 5% H_2O balanced by He; and the rich gas consisted of 4% H_2, 5% CO_2, 5% H_2O balanced by He. The total flow rate was 400 ml/min, corresponding to a weight hourly space velocity of 200,000 ml/g h^{-1}. The L/R switching was achieved using a 4-port valve controlled with an electric actuator (Valco Instruments). Outlet NO_x concentrations were measured with a chemiluminescence NO_x analyzer (Thermo Electron, 42 C). Some NO_x storage experiments were also conducted using NO_2 as the NO_x source.

2.3. Catalyst characterization

KNO_3 temperature-programmed decomposition (KNO_3-TPD) was performed by heating 50 mg of the KNO_3/Al_2O_3 samples in He (400 ml/min) from 100 to 800 °C at a rate of 5 °C/min, in the same reaction system described above. Outlet NO and NO_2 concentrations were analyzed by the same chemiluminescence NO_x analyzer (Thermo Electron, 42 C).

NO_x temperature-programmed desorption (NO_x-TPD) of the $K/Pt/Al_2O_3$ samples was carried out as follows: First, 50 mg samples were exposed to 0.5% NO_2/He (99.999% Purity, Matheson) at room temperature for 1 h to ensure saturation, then the sample was purged with pure He (200 ml/min) for 2 h. Subsequently, the sample was heated from room temperature to 800 °C at a rate of 5 °C/min. Outlet NO and NO_2 concentrations were analyzed using the same NO_x analyzer described above.

NO oxidation was tested by flowing a gas mixture of 150 ppm NO, 5% O_2, 5% CO_2, 5% H_2O balanced by He (400 ml/min) through 30 mg $K/Pt/Al_2O_3$ catalysts. Reaction was carried out from 250 to 550 °C in increments of 50 °C per step. At each temperature, the reaction was held for 30 min to reach steady state. Note that the determination of NO oxidation reaction rates were made after the