

Top Catal (2009) 52:1799–1802
DOI 10.1007/s11244-009-9334-x

ORIGINAL PAPER

Flame-Made Pt/K/Al₂O₃ for NO_x Storage–Reduction (NSR) Catalysts

Robert Büchel · Reto Strobel · Alfons Baiker ·
Sotiris E. Pratsinis

Published online: 10 July 2009
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Abstract High surface area Pt/K/Al₂O₃ catalysts were prepared with a 2-nozzle flame spray method resulting in Pt clusters on γ -Al₂O₃ and amorphous K storage material as evidenced by Raman spectroscopy. The powders had a high NO_x storage capacity and were regenerated fast in a model exhaust gas environment. From 300 to 400 °C no excess NO_x was detected in the off gas during transition from fuel lean to fuel rich conditions, resulting in a highly effective NO_x removal performance. Above 500 °C, the NSR activity was lost and not recovered at lower temperatures as K-compounds were partially crystallized on the catalyst.

Keywords NO_x storage–reduction · Potassium · Flame spray pyrolysis · Fast NO_x storage · Lean NO_x trap

1 Introduction

Stricter limits for exhaust emission motivate the development of new catalysts especially for NO_x removal under oxygen rich conditions as encountered in lean burn and

direct injection engines. NO_x storage–reduction (NSR) catalysts [1] can trap exhaust NO_x under fuel lean conditions on an alkali or alkaline-earth metal in the form of metal-nitrates. The alkalinity determines the NO_x trap performance in the order: K > Ba > Sr ≥ Na > Ca > Li [2]. Regeneration of the NO_x trap occurs under fuel rich conditions where metal-nitrates are decomposed and the released NO_x is reduced to nitrogen [3]. Potassium- and barium-containing compounds have been studied extensively for their NO_x storage capacity [4]. The best performance of K as storage material, especially at high temperatures, is attributed to its stable nitrates [5]. Furthermore K₂CO₃ is less toxic and cheaper than BaCO₃. The main drawback of K is its low resistance to sulfur poisoning whereby regeneration is possible at 700 °C [6]. Catalysts for NSR are typically operated around 400 °C, however, their performance at low temperature is also important. For example, during certification of light duty vehicles, the exhaust stream is most of the time at 200–250 °C [7].

Here novel flame-made catalysts are explored with high NO_x removal efficiency as they have inherent advantages compared to wet-prepared ones [8]. More specifically amorphous K/Pt/Al₂O₃ was made by a 2-nozzle FSP setup [9] which allowed simultaneous but separate synthesis of the Al₂O₃ support and K-storage component along with Pt clusters and even preferential Pt deposition on Al- or K-components [10].

2 Experimental

The Pt/K/Al₂O₃ catalysts were prepared by the 2-nozzle FSP having an inter-nozzle distance (d) of 6 cm and an angle φ of 160° [10]. The Al-precursor solution consisted

R. Büchel · R. Strobel · S. E. Pratsinis (✉)
Particle Technology Laboratory, Department of Mechanical
and Process Engineering, ETH Zurich, Sonneggstrasse 3,
8092 Zurich, Switzerland
e-mail: sotiris.pratsinis@ptl.mavt.ethz.ch

R. Büchel · A. Baiker
Department of Chemistry and Applied Biosciences,
Institute for Chemical and Bioengineering, ETH Zurich,
Wolfgang-Pauli-Strasse 10, 8093 Zurich, Switzerland

Present Address:
R. Strobel
Satisloh Photonics AG, 8812 Horgen, Switzerland

of aluminum-tri-*sec*-butoxide (Fluka, 95%) dissolved in a 2:1 vol. ratio mixture of diethylene glycol monobutyl ether (Fluka, 98%) and acetic anhydride (Riedel-de Haën, 99%). The aluminum concentration was kept constant at 0.5 mol/L. The K-precursor was potassium acetylacetonate hemihydrate (Fluka, 97%) dissolved in 1:1 vol. ratio toluene (Riedel-de Haën, 99%) and 2-ethyl hexanoic acid (Riedel-de Haën, 95%). Platinum(II) acetylacetonate (STREM, 98%) was added to the K-solutions. The concentration of the metals in the liquid was chosen to result in a nominal Pt:K:Al₂O₃ weight ratio of 1:5.8:100. The K-precursor was fed at 3 mL/min through the first nozzle and the Al-precursor was fed at 5 mL/min through the second nozzle. Each solution was dispersed with 5 L/min oxygen (Pan-Gas, 99.95%) forming a fine spray. Both sprays were ignited by premixed pilot flames having a CH₄/O₂ vol. ratio of 0.5 each [11].

The specific surface area (SSA) was determined by a 5-point nitrogen adsorption isotherm at 77 K using the BET method (Micrometrics Tristar). X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance instrument (40 kV, 40 mA, $\lambda = 1.54$ nm) and Raman spectroscopy was performed with a Renishaw InVia Reflex Raman system equipped with a 514-nm diode laser. The NSR measurements were made with 20 mg of catalyst in a fixed-bed reactor (inner tube diameter of 4 mm). The NO_x and NO concentrations in the effluent gas were monitored by a chemiluminescence detector (ECO Physics, CLD 822S). The NO_x conversion for a full cycle (one storage and one reduction) was derived from the corresponding NO_x outlet concentration according to:

$$\text{NO}_x \text{ conversion} = \frac{\text{NO}_{x,\text{in}} - \text{NO}_{x,\text{out}}}{\text{NO}_{x,\text{in}}} \times 100\%. \quad (1)$$

The NO_x conversion was measured at 250–600 °C while switching 50 times between oxidizing (3 min in 667 ppm NO and 3.3% O₂ in He) and reducing (1 min in 667 ppm NO and 1,333 ppm C₃H₆ in He) atmospheres. All catalysts were pretreated in 5% flowing H₂ for 10 min at the same temperature as the NO storage test was made. The total gas flow rate for all experiments was 60 mL/min corresponding to a space velocity of 72,000 h⁻¹.

3 Results and Discussion

3.1 Structural Properties

In XRD measurement only γ -Al₂O₃ was detected [12] as the as-prepared K₂CO₃ was amorphous and the Pt concentration was below the XRD detection limit. The Al₂O₃ support was essential to produce high surface area powders (SSA = 146 m²/g) because the high surface area of pure

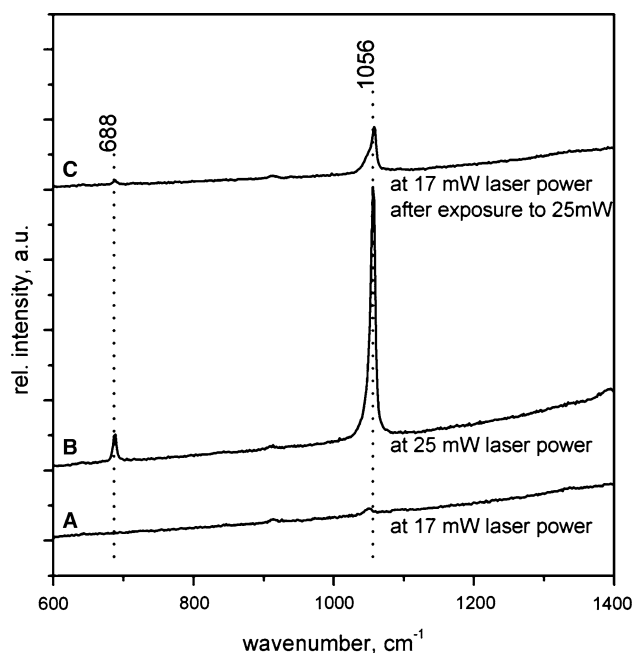


Fig. 1 Raman spectroscopy of as prepared amorphous potassium in Pt/K/Al₂O₃ catalysts exposed at the same position first to **A** 17 mW, then to **B** 25 mW, and again to **C** 17 mW. Crystalline K₂CO₃ was irreversibly formed at high laser power which later could be detected at low power

Al₂O₃ (SSA = 148 m²/g) keeps the K in a highly dispersed and amorphous state. Spraying only K precursor resulted in low surface, crystalline K₂CO₃ with a measured SSA of 7 m²/g. The amorphous nature of the 2-FSP-made Pt/K/Al₂O₃ was confirmed by Raman spectroscopy as shown in Fig. 1. When the amorphous power was exposed to the low laser power of 17 mW, no Raman signal was detected (Fig. 1A). When exposed to higher power (25 mW in Fig. 1B) the K crystallized and typical K₂CO₃ signals were detected at 1,056 and 688 cm⁻¹ [13]. This crystallization was irreversible (as shown in Fig. 1C), when measuring the transformed K₂CO₃ at low laser power (17 mW).

3.2 Dynamic NO Storage–Reduction

In Fig. 2, the NO_x conversion at different temperatures is shown for 50 fuel lean/rich cycles. The powder showed good catalytic behavior during cycling at 300 °C with a NO_x conversion above 80%. At 350 °C, the NO_x conversion was increased to 95% and at 400 °C almost no exhaust NO_x could be detected at any time. At 500 and 600 °C, the NO_x conversion decreased for both catalysts to around 60%. This sudden drop could be attributed to partial crystallization of K₂CO₃, though no difference in XRD could be observed. After the test at 600 °C, the same catalysts was examined at 300 °C and had lost 50% of its performance compared to the corresponding fresh powder. This indicates that the initial

structure of the Pt/K/Al₂O₃ was altered at 600 °C and probably crystalline K₂CO₃ was formed, similar as in the Raman investigation. Other catalysts were first cycled 50 times at 350 °C and subsequently cycled 50 times at 300 °C. The low-temperature aged catalysts showed similar, if not better, NO_x conversions compared to a fresh catalyst at 300 °C. To explain aging, further investigations are needed.

In Fig. 3, the outlet NO_x concentration for the discussed temperatures are shown for the 46th cycle. During storage at 300 °C, the NO_x concentration continuously increases until the fuel rich cycle starts, where the NO_x concentration increases fast for a short time. This overshooting has been observed before and attributed to formation of large amounts of CO₂ promoting NO_x release [14]. Remarkable is here, that the maximal concentration of the NO_x overshooting is below that of the NO inlet concentration. This overshooting even decreased for 350 °C and nearly disappeared at 400 °C. This can be explained by the synergistic effect of Pt and K leading to fast storage and fast regeneration of the NSR catalysts [15].

The NO_x concentration at 300–400 °C returns to zero in the fuel rich phase within 30 s. This would allow shortening the fuel rich time, to further optimize fuel usage. At 600 °C, high overshooting signals are seen with peak concentrations up to 3,000 ppm NO_x, what is more than 4 times the inlet NO concentration. At 600 °C, the storage reaches 50% of the NO_x inlet concentration after 1 min, to reach the same outlet concentration the catalyst at 300 °C can store NO for 3 min. This is an indication that surface storage sites were lost during temperature treatment. Aged

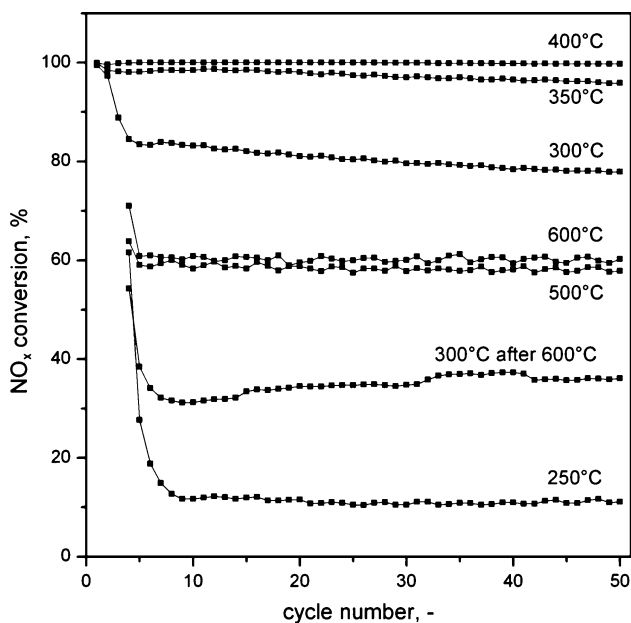


Fig. 2 NO_x conversion of Pt/K/Al₂O₃ for different temperatures

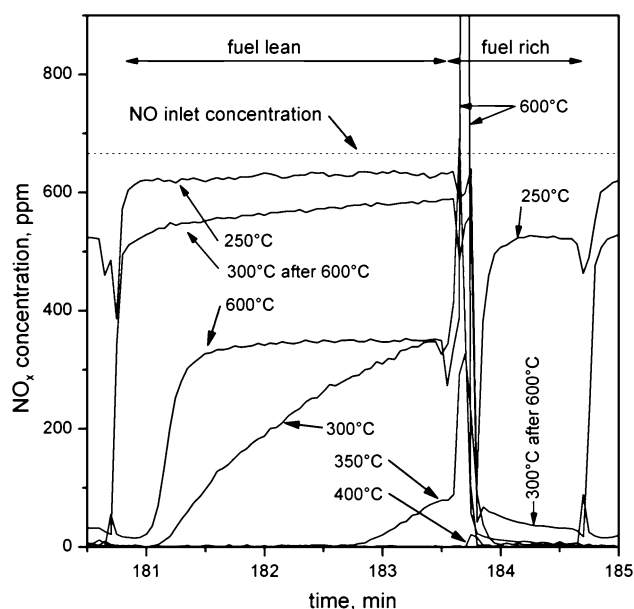


Fig. 3 NO_x exhaust concentration at steady state condition (46th cycle) in fuel lean and fuel rich environment for different temperatures (Pt/K/Al₂O₃ = 1/5.8/100)

catalysts are similar to fresh ones at 250 °C where the Pt activity is still too low to store NO_x efficiently. The catalysts shown here perform very well at 300–400 °C, and at elevated temperatures 60% NO_x conversion is attained, however, the initial storage activity is lost. This aging might limit the use of these catalysts at high peak temperatures that could ruin the Pt/K/Al₂O₃ structure, as in sulfur regeneration [6].

4 Conclusions

Flame synthesis of Pt/K/Al₂O₃ resulted in amorphous K₂CO₃ with NO_x conversion >80% in the optimal temperature range of 300–400 °C. This high performance could be reached by fast NO_x uptake during the fuel lean and fast regeneration during the fuel rich phase. Additionally, the typical overshooting of the NO_x signal during the switch from fuel lean to fuel rich gases was significantly decreased and never exceeded the inlet NO_x concentration. This superior performance was attributed to good K distribution in the catalysts and the amorphous nature of the K species. High temperatures, however, alter the catalyst structure which lowers the catalyst performance, an issue that requires further investigation.

Acknowledgements We thank for the financial support by ETH Zürich (TH-09 06-2) and the contribution of platinum chemicals by Johnson Matthey PLC is greatly appreciated.

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