ELSEVIER Catalysis Today 45 (1998) 103–108

CATALYSIS TODAY

Lean-DeNO$_x$ titania based monolithic catalysts

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Abstract

The activity of titania based copper and platinum monolithic catalysts in the reduction of nitrogen oxides was studied with exhaust gases from a Diesel engine injecting fuel as reductant. Combining both catalysts, a two-stage system was designed, studying the influence of the copper catalysts composition on its performance with synthetic gas mixtures. The influence of reactants concentration and operating conditions was also investigated. Taking into account these results, a double-bed system with a cell density of 33 cell cm^{-2} (210 c.p.s.i.) was prepared. Linear velocity had a strong influence on the performance of the Pt catalyst and of the double-bed. Two NO$_x$ conversion maxima were observed with Pt/TiO$_2$ at 225°C and 350°C operating at 6.6 m s^{-1}. Promising NO$_x$ conversions were achieved in the temperature range 200–450°C.

Keywords: NO$_x$ reduction; Monolith; Hydrocarbon; Diesel; Platinum; Copper oxide

1. Introduction

The reduction of nitrogen oxides (NO$_x$) in oxygen rich conditions, as in exhausts from Diesel and lean-burn gasoline engines, using hydrocarbons (HC) as reductant, has become of increasing interest in recent years, since the groups of Held et al. [1] and Iwamoto et al. [2] described the activity of the Cu/ZSM-5 catalyst in this reaction. Thus, this catalyst has been the most extensively studied [3], although its practical use is doubtful due to its poor hydrothermal stability [4]. Another relevant system has been Pt/Al$_2$O$_3$, and in general Pt supported on various metal oxides [5]. Other systems have been shown to be active, such as H/ZSM-5 [6], Ce-ZSM-5 [7], Pt/ZSM-5 [8], Co/ZSM-5 [9], Ga/ZSM-5 [10] and Cu/ZrO$_2$ [11]. The reduction of NO$_x$ with these catalysts has been generally found to take place over a fairly narrow temperature range. However, the temperature of Diesel exhaust varies from 200°C to 500°C. Thus, to obtain the needed reduction over a wide range of operating temperatures more than one catalyst has been used. The combinations of catalysts have been recently reviewed by Hamada [12], who distinguishes two main types of systems: bifunctional catalysis, in which there is a cooperation of two catalytic species, and staging of two or more catalysts in line.

Bifunctional catalysis has been pointed out in two types of cooperation. One is the additive effect of an oxidation catalyst or catalytic species. Yokoyama and Misono [13] showed that the NO$_x$ reduction activity by propene of Ce-ZSM-5 was improved in the lower temperature region by mechanical mixture with Mn$_2$O$_3$ or CeO$_2$. This effect was also found by Ueda et al. [14], following Misono's procedure, for Au/

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0920-5861/98/$ – see front matter
PII: S0920-5861(98)00255-7

Al_2O_3 mechanically mixed with Mn_2O_3, and by Kikuchi et al. [15] adding Pt to In-ZSM-5, due to the high NO oxidation activity of Pt in the presence of water vapor. The other is the combination of acidity and metallic species using methane as reductant, as reported by Misono et al. [16,17] for Pd/H-ZSM-5, showing the essential role of the protonic acidity in the reaction, and Loughran and Resasco [18] for Pd/SO_4–ZrO_2, amongst others.

Multi-stage systems are also effective to broaden the temperature window for the reduction of NO. In this case, the activity is normally the sum of that of the component catalysts. One of the first applications of a multi-stage system was developed by Oishi et al. [19], combining four Pt/TiO_2, Pt/CeO_2, Pt/ZrO_2 and Pt/Al_2O_3 phases washcoated on cordierite monoliths. A wider temperature range of activity was also observed by Obuchi et al. [20] with a Rh/Al_2O_3 catalyst, followed by Pt/Al_2O_3. Recently Iwamoto et al. [24] observed an increased activity of In-MFI zeolite by oxidizing NO to NO_2 on a Pt-MFI zeolite before adding the reductant, ethene. Several other examples are found in the patent literature. Amongst them, Montreuil et al. [21], from Ford Motor, have reported about a system with a first catalyst consisting in CuO supported on ZrO_2, TiO_2 or La_2O_3, or Cu-ZSM5, and a second Pt and/or Pd on Al_2O_3 catalyst. Recently Saito et al. [22,23], from Riken, described a three-stage system using Al_2O_3 as support, washcoated on cordierite monoliths and the active phase of the first catalyst is Ag, the second Ag or Cu/Ni, and the third Pt and/or W.

However, the above described systems were mainly based on alumina. This material is deactivated in the presence of sulfur oxide by sulfate formation, while titania, on the contrary, is hardly sulfatized [25]. Therefore, titania was used as support in the catalysts presented in this work. This oxide has been used as support for NO_x reduction in lean-burn conditions, as a powder [26], and as a washcoat on cordierite monoliths [21], but not as titania monoliths.

Additionally the lean-DeNO_x activity of Pt/TiO_2 has been previously compared with other Pt catalysts supported on various oxides such as alumina and zirconia by Burch and Millington [5] using propene as reductant, and by Van den Tillaart et al. [27] using *n*-hexadecane. The results are contradictory, as the former authors found Pt/TiO_2 less active than the other systems, while the latter found similar activities after aging of the catalysts. Our group showed in a recent study [28] the strong influence of the titania origin and nature on the activity of Pt/TiO_2 monolithic catalysts, which would take account of these different results, indicating that a high activity can be achieved with titania supported catalysts by a careful selection of the raw material.

The aim of the present work has been, firstly, to test the lean-DeNO_x activity of a CuO/TiO_2 and a Pt/TiO_2 monolithic catalyst in real Diesel conditions, using injected fuel as reductant. Secondly, to develop with these catalysts a monolithic two-stage system active in a wide range of operating temperatures, studying the influence of the catalysts composition, reactants concentration and operating conditions on the performance of the system.

2. Experimental

The catalysts used in this work were based on a monolithic support containing titania (Rhône-Poulenc) and natural silicates as binders. They were prepared by kneading the raw powders in water, extruding and subsequently drying and heat treating at 500°C, to obtain two monolithic shaped supports: with 10 and 33 cells cm^{-2} and geometric surface areas of 1040 and 1800 $m^2\,m^{-3}$, respectively. Both with a nitrogen BET surface area of 130 $m^2\,g^{-1}$, and a mercury intrusion porosimetry total pore volume of 0.76 ml g^{-1}, with a bimodal intrusion curve with main contribution from pore diameters of 7–40 and 60–120 nm.

Copper and nickel were deposited by impregnating the support in an aqueous solution containing copper nitrate and nickel nitrate (Panreac, Spain), respectively, and subsequent heat treating at 500°C in an air atmosphere. For the platinum catalysts an aqueous hexachloroplatinic acid (Sempsa, Spain) solution was used and the impregnated material was subsequently reduced with 5 vol% ammonia at 440°C.

Steady-state experiments with real Diesel exhaust were performed on a Volvo 7.3 l bus Diesel engine, with two 4 l reactors connected to the exhaust pipe fed with Swedish low sulfur content city-fuel, which was injected as reductant upstream of the catalyst with an air assisted spray nozzle. The gas sampled before and after the catalyst was led through heated pipes and passed through a JUM Engineering model 222 heated gas filter before entering the analyzing equipment. The NO_x content was determined with a TECAN CLD 700 EL ht chemiluminescence detector, the hydrocarbon content (C_1) with a JUM Engineering model VE5 FID detector, and N_2O content by non-dispersive IR spectrometry with a Siemens Ultramat 5E device.

Steady-state activity measurements with synthetic gas mixtures were made in a monolithic reactor of 2.54 cm ID at 120 kPa. The composition of the inlet gas was: 1000 ppm NO, 3000 ppm (C_1) C_3H_6, 10 vol% oxygen, 3 vol% water, and nitrogen as balance. The NO_x concentration was determined by chemiluminescence with a Beckman analyzer model 951A, oxygen content by paramagnetic analysis in a Beckman 755 analyzer, and hydrocarbons by means of a Beckman flame ionization detector model 400A.

The linear velocity was 1.0 m s^{-1}, if not otherwise stated. Linear and gas hourly space velocities (GHSV) in this work are given in normal conditions.

3. Results and discussion

Two monolithic catalysts containing copper oxide (1.5 wt% CuO) and platinum (0.18 wt% Pt) supported on titania were tested in real conditions in a Volvo 7.3 l bus Diesel engine, injecting the engine fuel as reductant. The NO_x conversions achieved in these experiments are shown in Fig. 1. The platinum catalyst exhibited maximum conversion at a lower temperature, 250°C, than the copper catalyst, 360°C. The reduction selectivity to nitrogen was ca. 100% for the latter, and ca. 65% for the former catalyst. Although no deactivation of the platinum catalyst was detected after 50 h in operation, a slight decrease in the copper low temperature activity was observed.

Based on these results in real conditions, the copper and platinum catalysts were combined in a two-stage reactor to obtain the required reduction over a wide range of operating temperatures. Additionally, nickel was added to the copper catalyst to stabilize the active phase. The behavior of the double-bed system, with the copper catalyst situated up-stream of the platinum catalyst, and each catalyst operating at a GHSV of 10 000 h^{-1}, was studied with synthetic gas mixtures using propene as reductant. Thus, a NO_x conversion maximum was observed at 250°C and a shoulder at 330°C, corresponding to the platinum and copper contributions, respectively. However, keeping the platinum catalyst composition constant, the NO_x conversion of the system was strongly dependent on the copper oxide content of the copper catalyst.

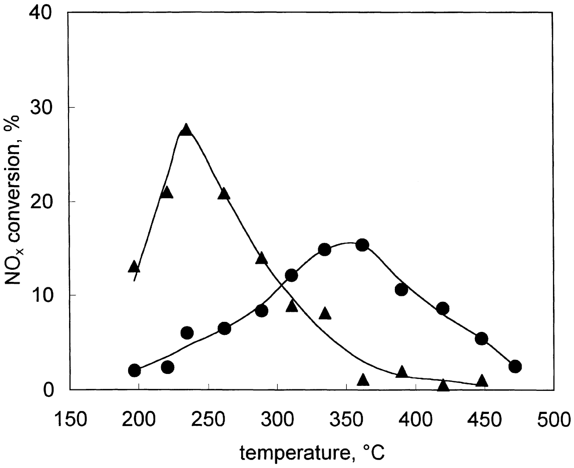

Fig. 1. NO_x conversion of a copper (●) and a platinum (▲) titania catalyst in a Volvo 7.3 l Diesel engine operating at 1200 rpm. GHSV=16 000 h^{-1}. [hydrocarbon]/[NO_x] =6 (ppm C_1/ppm). Pitch=0.32 cm.

In Fig. 2, the influence of the copper oxide content in the copper catalyst on the NO_x conversion of the double-bed is shown. The addition of copper, with CuO/NiO=10 (w/w), did not strongly affect the NO_x conversion at 250°C, but induced at 330°C, after a rapid increase until 0.3 wt%, a decrease. Thus, this effect should be related to the performance of the copper catalyst, for which the NO_x and HC conversions at the latter temperature are shown in Fig. 2. As can be observed, the NO_x and HC conversions increased with the copper content until 0.6 and 1.5 wt%, respectively. However, if the variation of the NO_x conversions of the double-bed (○) and the copper catalyst (●), both at 330°C, are compared, the effect of adding copper was much stronger on the former, than that observed on the latter. This would indicate a contribution of the Pt catalyst to the double-bed NO_x conversion at low copper contents and, thus, at a low HC oxidation capacity of the copper catalyst, which would allow higher amounts of unburned reductant to reach the Pt catalyst.

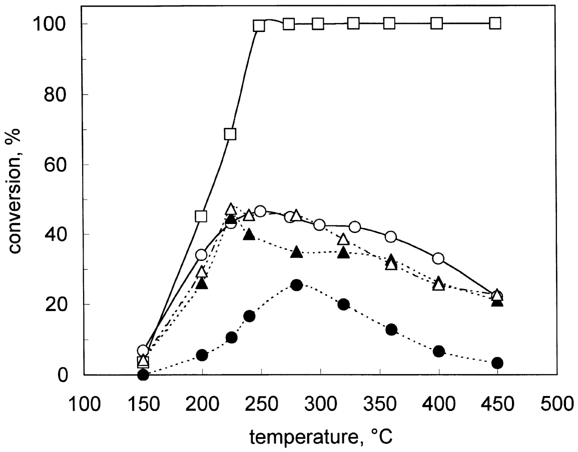

Fig. 2. Conversions of the Cu catalyst at 330°C: HC (■) and NO_x (●) at GHSV=10 000 h^{-1}, and NO_x conversions of the double-bed: at 250°C (△) and 330°C (○), each bed at GHSV=10 000 h^{-1}, vs. copper oxide content in the catalyst. Pitch=0.32 cm.

From these results a 0.6 wt% CuO (CuO/NiO=10, w/w) was selected as the more convenient copper content for the first catalyst in the double-bed system, obtaining the NO_x and propene conversions that are shown in Fig. 3. Conversions higher than 30% in a temperature range 200–400°C, and total HC conversion above 250°C were observed.

In the figure, this is compared to the NO_x conversion estimated as addition of the catalysts conversions, operating under the same conditions. For this estimation, the composition of gas at the outlet of the copper catalyst operating alone, as well as the NO_x conversion of the platinum catalyst operating alone, was measured. Then, the latter conversion was corrected taking into account the concentration of reductant present in the gas mixture at the outlet of the copper catalyst. From these data the NO_x conversion of the double-bed was estimated, and is shown in Fig. 3. The NO_x conversion obtained was close to that estimated at low temperatures, 200–250°C, but greater in the range 300–400°C. Thus, the wide shoulder at high temperatures would not only be due to the addition of the catalysts conversions. In certain copper [29] and ceria [13] catalysts, the formation of oxygen and nitrogen containing by-products in the gas phase has been detected using propene as reductant. The formation of by-products on the copper catalyst in the present work could be responsible for the observed higher activity and is currently under investigation.

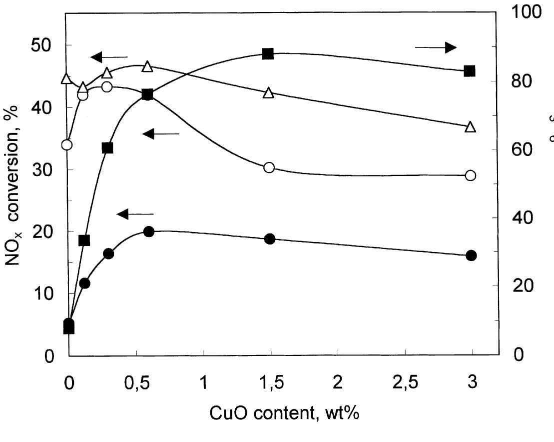

Fig. 3. NO_x conversions of the Cu (●) and Pt (▲) catalysts at GHSV=10 000 h^{-1}, and conversions of the double-bed: NO_x measured (○) and estimated (△), and C_3H_6 (□), each bed at GHSV=10 000 h^{-1}, vs. temperature. Pitch=0.32 cm.

The influence of oxygen, hydrocarbon and water concentration on the $DeNO_x$ performance of the system at 250°C and 330°C was also studied. The results shown in Fig. 4 indicated that oxygen is \displaystyle ecessary for the reaction, reaching a maximum with 1 vol% O_2.

Interestingly, at high oxygen concentrations only a slight conversion decrease, which was greater at 330°C, was observed. The linear dependence of the NO_x conversion on the HC concentration is shown in Fig. 5. However, this behavior was larger at 250°C, achieving a 61% NO_x conversion at a $[C_3H_6]/[NO_x]$ (ppm C_1/ppm) ratio of 6, each catalyst operating at a GHSV of 10 000 h^{-1}. The addition of a 3% water induced a slight decrease of the NO_x conversion from 52% to 46%, at 250°C, and from 50% to 43%, at 330°C.

In order to decrease the volume of catalyst, monoliths with a smaller cell size of 0.14 cm, and a wall thickness of 0.04 cm, were prepared, increasing the cell density to 33 cell cm^{-2} (210 c.p.s.i.). Using the platinum catalyst prepared in this way, the influence of linear velocity on the NO_x and HC conversion was studied. As shown in Fig. 6, both conversions increased with increasing linear velocity. At a low linear velocity, no HC total conversion was achieved, indicating a control by interphase mass transfer phenomena. At high linear velocities, additionally to

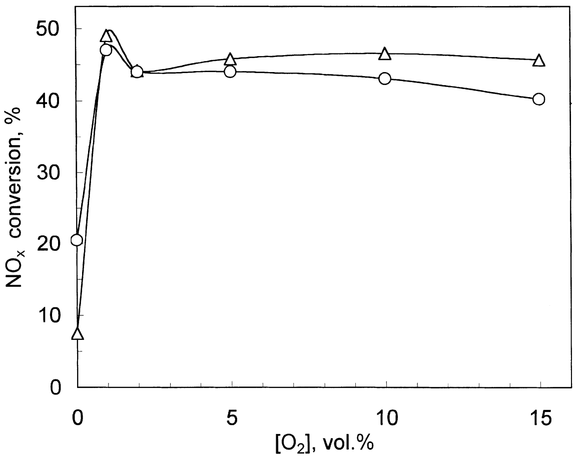

Fig. 4. NO$_x$ conversion of the double-bed, each bed at GHSV=10 000 h^{-1}, at 250°C (△) and 330°C (○) vs. oxygen concentration. Pitch=0.32 cm.

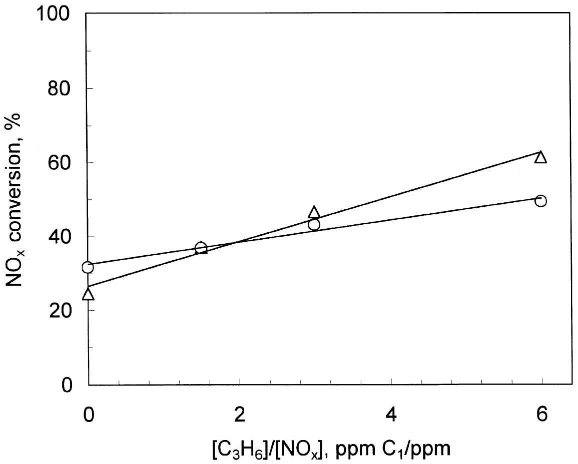

Fig. 5. NO$_x$ conversion of the double-bed, each bed at GHSV=10 000 h^{-1}, at 250°C (△) and 330°C (○) vs. propene concentration. Pitch=0.32 cm.

observing total HC conversion, a second new NO$_x$ conversion maximum at 350°C appeared.

The linear velocity influenced also the temperature and intensity of the NO$_x$ conversion maxima of the double-bed, as the three curves shown in Fig. 7 indicate. First, the linear velocity of the copper catalyst was decreased from 4.4 to 2.2 m s^{-1}, producing a conversion increase, specially above 300°C, and a shift to higher temperatures. Then, the platinum linear velocity was decreased, observing another temperature shift and a conversion decrease, in accordance with the influence of linear velocity on the performance of this catalyst (see Fig. 6). As the mass transfer control increases by decreasing the linear velocity, the oxidation capacity of both catalysts is lowered. This is beneficial in the case of the copper catalyst operating in the double-bed, probably because

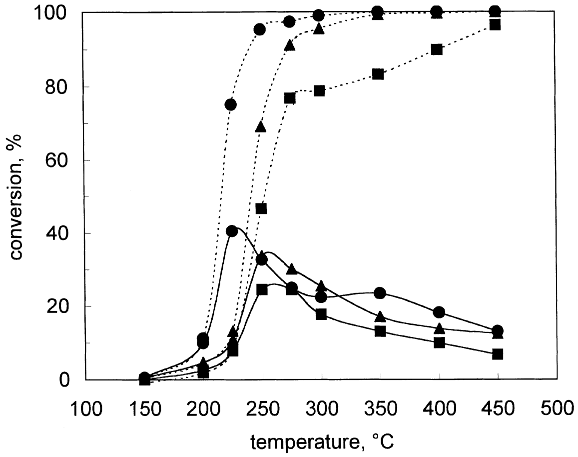

Fig. 6. Conversions of the Pt catalyst: NO$_x$ (——) and C$_3$H$_6$ (- - -) at GHSV=26 100 h^{-1} and different linear velocities (m s^{-1}): 1.5 (■), 3.3 (▲), and 6.6 (●) vs. temperature. [C$_3$H$_6$]/[NO$_x$]=4 (ppm C_1/ppm). Pitch=0.18 cm.

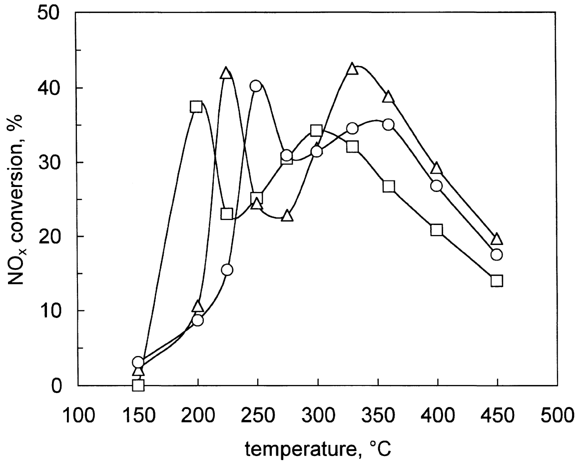

Fig. 7. NO$_x$ conversions of the double-bed each bed at GHSV=22 000 h^{-1} and different linear velocities (m s^{-1}): both beds 4.4 (□); Cu bed 2.2+Pt bed 4.4 (△) and both beds 2.2 (○) vs. temperature. [C$_3$H$_6$]/[NO$_x$]=4 (ppm C_1/ppm). Pitch=0.18 cm.

higher, and possibly better activated, HC amounts are available for the platinum catalyst.

4. Conclusions

Copper oxide and platinum catalysts based on sulfur resistant TiO_2 monolithic supports have been shown to be active in the NO_x reduction, using injected fuel as reductant, in real Diesel conditions.

With these catalysts a double-bed system, active from 200°C to 450°C, has been developed. The copper content of the first catalyst affected the performance of the double-bed, specially above 300°C. The $DeNO_x$ activity of this system exhibited a low oxygen and water dependence, and a linear relation with the hydrocarbon concentration.

Titania monoliths based catalysts were prepared with a cell density of 33 cell cm^{-2} (210 c.p.s.i.).

Linear velocity has been shown to have a critical influence on the performance of the platinum catalyst and of the double-bed system. In the latter opposite effects were observed, depending on the catalyst on which linear velocity was varied. Its increase led to the observation of a new maximum of conversion at 350°C of the Pt/TiO_2 system.

Acknowledgements

The authors are grateful for the financial aid from the NUTEK (Sweden); CICYT (Spain), Project AMB93-0244, and the "Comunidad Autónoma de Madrid" (Spain), Projects 0057/94 and 06M/077/96. We thank also B. Cyrén, J.E. Everett and M. Bruszt for technical assistance, and C. Künkel and Dr. M. Yates for valuable discussions.

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