

# Synergistic effect between Pt and K in the catalytic reduction of NO and N<sub>2</sub>O

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## Abstract

The simultaneous reduction of NO + N<sub>2</sub>O was studied with carbon supported K/Pt catalysts. High conversion levels of both gases were achieved at relatively low temperatures (350 °C), and the catalyst stability was confirmed in long duration experiments. A synergistic effect between the two metals was observed under different reaction conditions, and for different metal load combinations, similarly to the effect previously reported for Ni and K. This synergy was analysed and explained in terms of different properties of the system, as well as by the simultaneous participation of K and Pt in the reaction mechanism.

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## 1. Introduction

Nitrogen oxides are involved in a series of environmental pollution processes that may lead to urban smog, rain acidification, global warming and the depletion of the stratospheric ozone layer. Hence, the control of the emissions of these pollutants is a major concern, and a vast amount of research work has been devoted to the development of techniques for their abatement [1–4].

The catalytic reduction of NO and N<sub>2</sub>O with carbon as reducing agent has been intensively investigated, using a variety of catalysts [5–25]. In this process, carbon will act both as a catalyst support and a reactant.

In the course of the reaction, the catalyst participates in a redox cycle involving oxygen transfer, i.e., the catalyst is oxidised by the nitrogen oxides and then reduced by the carbon support, leading to the formation of carbon–oxygen surface groups which decompose as CO and CO<sub>2</sub> [9–11,15,18,20–23,26]. Therefore, the performance of the catalyst depends on its oxidation state, on the efficiency of the active phases for NO and N<sub>2</sub>O dissociation, and on the

ease with which oxygen from the dissociation of the reactants is transferred from the metal to the carbon matrix and released as CO and CO<sub>2</sub>. It has been found that a reduced catalyst surface is required for NO and N<sub>2</sub>O dissociation [27–33].

Preliminary tests were carried out with catalytic systems of known activity in carbon gasification. Ni/K catalysts performed very well in the reduction of N<sub>2</sub>O, a considerable degree of synergy being observed between the two metals [34–36]. Illán Gómez et al. [22,37] and Carabineiro et al. [5,7] reported similar synergistic effects for other bimetallic systems. The synergy between Ni and K was ascribed to the ability of K to maintain Ni in the active (reduced) state, and to the higher resistance of the bimetallic formulation towards metal sintering and loss of contact between metal and support.

However, in the presence of NO, the Ni/K catalyst suffered significant deactivation, as a result of the oxidation of the active phase [35,36]. On the other hand, noble metal catalysts (Pd, Pt) were very active for the reduction of NO, but exhibited poor selectivity to N<sub>2</sub>, N<sub>2</sub>O being formed as a reaction by-product [35]. However, excellent performances were obtained with a bimetallic K/Pt system: it was possible to maintain stable levels of simultaneous conversion of

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NO + N<sub>2</sub>O above 95%, at relatively low temperatures (350 °C) [35].

In the present paper, we further investigate the synergistic effect observed with K/Pt catalysts. The influence of different catalyst pre-treatment procedures was analysed, as well as the performance of different catalyst bed configurations and corresponding reduction profiles. Some conclusions on the reaction mechanisms and the corresponding kinetics were derived from transient response experiments.

## 2. Experimental

### 2.1. Catalyst preparation

A NORIT activated carbon (ROX 0.8) was used as catalyst support. This material is supplied in the form of cylindrical pellets of 0.8 mm diameter and 5 mm length, and has the following properties: total pore volume 0.7 cm<sup>3</sup>/g; microporous volume and non microporous specific surface area, determined by the *t*-method, 0.36 cm<sup>3</sup>/g and 122 m<sup>2</sup>/g, respectively; BET specific surface area 950 m<sup>2</sup>/g; bulk density 399 g/dm<sup>3</sup>; ash content 2.6% (w/w); pH 8.3. The supported metal catalysts were prepared by the incipient wetness method using potassium nitrate and hexachloroplatinic acid as catalyst precursors. In the bimetallic catalysts Pt was introduced first; K was impregnated after the decomposition of the Pt precursor under inert atmosphere at 350 °C.

### 2.2. Catalytic tests

The catalytic tests were carried out at atmospheric pressure in a fixed bed reactor (diameter 1.7 cm). Two types of experiments were performed: temperature programmed reaction (TPRea), in which the sample was heated at 2.5 °C/min to 500 °C; isothermal reaction at different temperatures.

The feed gas containing either 1000 ppmv of NO and/or 500 ppmv of N<sub>2</sub>O diluted in He was adjusted by mass flow controllers and the amount of catalyst (~350–450 mg, i.e., 0.6 cm<sup>3</sup>) used in each run was calculated to obtain a ratio of catalyst volume to volumetric flow rate (determined at the conditions prevailing at the reactors inlet) of 15,000 h<sup>-1</sup>.

The gaseous products were analysed *on line* by gas chromatography (GC) using a thermal conductivity detector. In the TPRea experiments and in some isothermal experiments, NO and CO were followed by means of a chemiluminescence NO<sub>x</sub> analyser (Thermo Environmental 42C) and an infrared analyser (Thermo Environmental 48C), respectively.

Prior to the catalytic tests, each sample was reduced *in situ* with 5% H<sub>2</sub> in He at 400 °C for 1 h and then held at 400 °C under a flow of He for 30 min.

### 2.3. Transient response curves

Experiments involving step variations in the concentration of NO were carried out in the reaction setup previously

described. In order to reduce the length of the analysis program, each test was duplicated: N<sub>2</sub>, NO and CO were followed in the first sequence (with the GC column at 35 °C), while N<sub>2</sub>O and CO<sub>2</sub> were monitored in the duplicate test (with the GC column at 250 °C). The reaction conditions employed were the same as in the isothermal and TPRea experiments, namely GHSV = 15,000 h<sup>-1</sup> and NO concentration of 1000 ppm.

### 2.4. Temperature programmed reduction

Temperature programmed reduction experiments (TPRed) were carried out in a system composed of a U-shaped tubular micro-reactor placed inside a temperature controlled oven, the temperature near the sample being monitored by a K-type thermocouple. A 150 mg sample was heated under a flow of 5% H<sub>2</sub> diluted in He (gas flow rate of 25 cm<sup>3</sup>/min) from room temperature up to 400 °C at 5 °C/min and kept at the final temperature for 1 h. The effluent of the reactor was continuously analysed by a quadrupole mass spectrometer (Spectramass DXM). The H<sub>2</sub> consumption was followed by the signal *m/z* = 2; CO and CO<sub>2</sub> by signals *m/z* = 28 and 44, respectively.

### 2.5. Catalyst dispersion

The Pt dispersion was determined by H<sub>2</sub> chemisorption at room temperature in a Coulter Omnisorp unit, using the static method which involves the determination of two adsorption isotherms. The total amount of H<sub>2</sub> adsorbed was calculated from the first isotherm, by extrapolation of the linear segment of the isotherm back to zero pressure. A second isotherm was obtained after *in situ* degassing at room temperature, from which the amount of H<sub>2</sub> reversibly adsorbed was calculated. The amount of H<sub>2</sub> irreversibly adsorbed was determined by difference between the total and reversible adsorption amounts. No correction was made for the support, as it was confirmed that irreversible adsorption of H<sub>2</sub> on carbon at room temperature was negligible.

The metal dispersion was calculated assuming a stoichiometric ratio of H/Pt<sub>S</sub> = 1, where Pt<sub>S</sub> represents a surface Pt atom.

Prior to the chemisorption measurements, all samples were reduced following the standard procedure previously described.

The K dispersion was measured by CO<sub>2</sub> chemisorption at 250 °C assuming a stoichiometric ratio of CO<sub>2</sub>/(K<sub>2</sub>O)<sub>S</sub> = 1 where (K<sub>2</sub>O)<sub>S</sub> represents a surface K species [9,20]. These measurements were performed by the dynamic method in the same setup used for the TPRed experiments. Small volumes of CO<sub>2</sub> (25 μL) were injected in the carrier gas and the signal of CO<sub>2</sub> (*m/z* = 44) was followed *on line* by mass spectrometry at the outlet of the catalyst bed. The amount of CO<sub>2</sub> adsorbed was calculated by integration of the areas of the CO<sub>2</sub> peaks for each injection.

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