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Industrial NO_x control via H_2-SCR on a novel supported-Pt nanocatalyst

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ABSTRACT

We describe here the performance of a novel MgO–CeO_2-supported Pt nanocatalyst (~1.5 nm mean Pt particle size) towards the selective conversion of NO ($X_{NO} > 90\%$) into N_2 ($S_{N_2} > 80\%$) using H_2 (H_2-SCR) in the low-temperature range of 120–180 °C for a wide range of O_2, H_2 and CO_2 feed concentrations. This catalytic system showed remarkable performance under industrial process conditions of NO_x control [1–5]. Using a feed composition containing 150 ppm NO, 2 vol% O_2 and H_2 in the 0.2–0.8 vol% range (GHSV = 33,000 h^{-1}), the NO conversion, X_{NO} (%) and N_2-selectivity, S_{N_2} (%) were found to increase with increasing H_2 feed concentration in the 120–180 °C range, where NO conversions in the 97–100% range and N_2-selectivities in the 83–93% range were obtained. By increasing the O_2 feed concentration from zero to 5 vol%, both the X_{NO} (%) and the S_{N_2} (%) were found to decrease by an extent which was dependent of reaction temperature. The effect of CO_2 in the feed stream (0–12 vol%) was found to be slightly negative for the NO conversion, while an opposite behavior was found for the S_{N_2} (%), likely due to competitive adsorption of CO_2 and NO on the same non-selective NO_x adsorption sites. *In situ* DRIFTS studies have shown that the oxygen feed concentration largely influenced the surface concentration of inactive NO_x and only slightly that of active NO_x intermediates of H_2-SCR but not their chemical structure.

1. Introduction

Selective catalytic reduction (SCR) of NO_x with ammonia under strongly oxidizing conditions (NH_3-SCR) was first introduced in 1973 [6–8]. Since then, NH_3-SCR is a widely practiced industrial NO_x control technology with a total capacity of more than 70 GW in both Japan and Germany [8]. However, many problems are encountered in the use of NH_3-SCR technology, namely catalyst deterioration, NH_3-slip (emissions of unreacted toxic ammonia), ash odor, air heaters fouling, and a high running cost [8,9].

Selective catalytic reduction (SCR) of NO_x from an industrial flue gas stream at low-temperatures ($T < 200$ °C) has many advantageous over that operated at higher temperatures ($T > 300$ °C). For example, placement of the catalyst after the electrostatic solid precipitator unit implies that the partially cleaned flue gas from dust would require less soot blowing and catalyst cleaning, thus providing longer catalyst lifetime. Furthermore, low-temperature SCR process reduces both investment and running costs since the SCR unit can be located at the end of the stack gas train (low-temperature region), thus minimizing the need to run ducting from a high-temperature region and return the flue gas to the stack gas train. Also, much less reheating of the flue gas from the de-SO_x to the SCR unit would be required [6,8,10], and new low-temperature SCR catalysts would also be capable of retrofitting large industrial utility boilers and installations firing natural gas or refinery fuel gas.

Successful industrial low-temperature SCR catalysts must be active and stable in the presence of H_2O, CO_2 and SO_2 in the flue gas stream, the composition of which would be dependent of the fuel used. Low-temperature NH_3-SCR catalysts (180–240 °C) are currently used in some industrial applications [11,12]. However, besides the general problems associated with the NH_3-SCR NO_x control technology used in stationary applications [8,9], the main disadvantage of the low-temperature NH_3-SCR technology is its susceptibility to ammonium bisulphate precipitation when SO_x are present in the flue gas stream.

Apart from the problems faced by the current NH_3-SCR NO_x control technology previously mentioned, and which require the urgent development of new SCR catalysts, the use of green technologies that would lead to the simultaneous reduction of both CO_2 and NO_x emissions demand the finding of suitable non-carbon-containing reducing agents for the catalytic elimination of NO_x from industrial flue gas streams at low temperatures ($T < 200$ °C) with reduced running and investment costs.

Recent research works in our laboratory [1–5,13] have demonstrated that *industrial H_2-SCR of NO* at temperatures in the 120–180 °C range is possible over a novel catalyst, namely Pt nanoparticles (e.g., $d_{Pt} = 1.5$ nm) supported on a mixed metal oxide of MgO–CeO_2 and using only 0.1 wt% Pt loading. Until full transition to a hydrogen economy and zero emissions of greenhouse

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gases are achieved, H_2-SCR might be considered as a breakthrough NO_x control technology in favor of the present NH_3-SCR, especially applied at industrial sites where hydrogen gas is available (e.g., olefin plants, petrochemical plants, oil refineries, hydrogen plants, etc.).

In the present work for the first time the catalytic performance of the novel 0.1 wt% Pt/MgO–CeO_2 catalyst towards H_2-SCR in the low-temperature range of 120–180 °C and using a low (150 ppmv) NO composition in the feed stream is presented. Emphasis is given in the effect of H_2, O_2 and CO_2 feed composition on the NO conversion and N_2-selectivity of reaction. *In situ* DRIFTS studies have been performed in an attempt to gather fundamental knowledge on the intrinsic reason(s) of the large influence of oxygen feed gas composition on N_2-selectivity of H_2-SCR.

2. Materials and methods

2.1. Catalysts preparation and characterization

The supported 0.1 wt% Pt/50 wt% MgO–50 wt% CeO_2 catalyst was prepared by the wet impregnation method using $H_2Pt(IV)Cl_6$ (Aldrich) as precursor of platinum metal. Appropriate amounts of MgO (Aldrich, CAS no. 1309-48-4) and CeO_2 (Aldrich, CAS no. 1306-38-3) solids were placed in a beaker containing de-ionized water and mixed thoroughly by stirring at 35 °C. After water evaporation the resulting solid was dried at 120 °C and a ground portion of it was then impregnated at 60 °C with an appropriate amount of $H_2Pt(IV)Cl_6$ solution so as to yield the desired Pt loading. After water evaporation the resulting solid was dried at 120 °C overnight, and then ground and heated in air at 500 °C for 2 h, cooled down to room temperature and stored for further use.

High resolution transmission electron microscopy (HRTEM) studies (JEOL 1010 electron microscope operated at an acceleration voltage of 80 kV) were performed on the used solid catalyst (following 20 h of H_2-SCR studies), where the fresh catalyst was calcined in air at 600 °C for 2 h followed by H_2 reduction at 300 °C for 2 h. A 5-mg powder sample was dispersed in 1 mL of ethanol/water mixture (1:1) and kept in an ultrasonic bath for 5 h. The sample was then deposited on a carbon-covered Cu grid and dried at 25 °C. HRTEM measurements allowed direct estimation of the mean Pt particle size based on the size distribution derived after examining 100 individual Pt particles.

X-ray photoelectron spectroscopy measurements were performed using an Escalab 200R spectrometer equipped with a hemispherical electron analyzer and an Al Kα ($h\nu$ = 1486.6, 120 W) X-ray source. The area of a given peak was estimated by calculating the integral of it after smoothing and subtracting an S-shaped background, while fitting of the thus derived experimental spectrum was made using a mixture of Lorentzian and Gaussian lines of variable proportions. All binding energies (BE) were referenced to the C 1s signal at 284.6 eV based on carbon contamination of the sample. Quantification of the surface atomic composition was obtained after integration of the peaks and using appropriate corrections for sensitivity factors [14]. XPS analyses performed on the 0.1 wt% Pt/MgO–CeO_2 solid catalyst sample were conducted following first *in situ* oxidation (20 vol% O_2/He, 600 °C, 2 h), then reduction in H_2 (1 bar) at 300 °C for 2 h, and finally H_2-SCR reaction (150 ppm NO/0.8 vol% H_2/2.5 vol% O_2/He, 140 °C, 30 min) in the pre-treatment chamber of the XPS apparatus.

2.2. Catalytic performance studies

The flow system used for performing catalytic studies for the H_2-SCR of NO at 1 atm total pressure consisted of a flow measuring and control system (mass flow controllers, MKS Instruments, Model 247C), mixing chambers, and a quartz fixed-bed microreactor (2 mL nominal volume) [1,15]. Analysis of the dry effluent gas stream from the reactor was performed using: (a) mass spectrometer (Balzers, model Omnistar, amu = 1–300) for H_2 ($m/z = 2$), and O_2 ($m/z = 32$), (b) NO_x chemiluminesence analyzer (Thermo Electron Corporation, model 42C) for NO and NO_2, (c) N_2O infrared gas analyzer (Teledyne Analytical Instruments, model IR 7000), and (d) CO and CO_2 infrared gas analyzer (Horiba, model VA-3000). Using a mass of catalyst (powder, $d < 0.2$ mm) of 0.3 g and a total volume flow rate, Q of 200 mL/min, a gas hourly space velocity: GHSV = $Q/V_{\text{cat. bed}}$ of 33,000 h^{-1} ($L/L_{\text{cat. bed}}$/h) was estimated. The fresh (as synthesized) catalyst sample was first pre-treated in 20%O_2/He gas mixture (50 mL/min) at 600 °C for 3 h and then in pure H_2 (50 mL/min) at 300 °C for 2 h.

Integral N_2 or N_2O production and NO consumption rates were calculated based on the product analyses using the following relationships:

$$\text{Rate}_i(\text{mol/g s}) = F_T \cdot y_i / W \quad (1)$$

$$\text{Rate}_{NO}(\text{mol/gs}) = F_T \cdot y_{NO}^{f} \frac{X_{NO}}{W} \quad (2)$$

where F_T is the total molar flow rate (mol/s), y_i is the molar fraction of component i (e.g., N_2, N_2O) expressed in ppm × 10^{-6}, X_{NO} is the conversion of NO, y_{NO}^{f} is the molar fraction of NO in the feed, and W is the weight of catalyst (g). The N_2 and N_2O reaction selectivities were then calculated based on the following relationships:

$$S_{N_2O}(\%) = \left[\frac{2\ \text{Rate}_{N_2O}}{\text{Rate}_{NO}}\right] \times 100 \quad (3)$$

$$S_{N_2}(\%) = \left[\frac{2\text{Rate}_{N_2}}{\text{Rate}_{NO}}\right] \times 100 \quad (4)$$

For the NO/H_2/O_2/He reaction feed stream, the only N-containing product species formed were found to be N_2 and N_2O. It was also reported [16] that for the present 0.1 wt% Pt/MgO–CeO_2 catalyst formation of N_2O does not involve gas-phase oxygen. Thus, the following reaction network must be considered:

$$2NO + 4H_2 + O_2 \rightarrow N_2 + 4H_2O \quad (\Delta H^\circ = -573.7\ \text{kJ/molNO}) \quad (5)$$

$$2NO + H_2 \rightarrow N_2O + H_2O \quad (\Delta H^\circ = -170.2\ \text{kJ/molNO}) \quad (6)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \quad (\Delta H^\circ = -241.7\ \text{kJ/molH}_2) \quad (7)$$

The conversion of NO (X_{NO}, %) of the H_2-SCR was estimated based on the following relationship:

$$X_{NO}(\%) = \frac{(F_T \cdot y_{NO}^{f} - F_T \cdot y_{NO})}{F_T \cdot y_{NO}^{f}} \quad (8)$$

In the case of use of water in the reaction feed stream, some ammonia formation was noticed in the condensate after passing the effluent stream from the reactor to a condenser (Peltier Gas Cooler, model ECP1000, M&C TechGroup). Quantification of ammonia in the condensate was performed using UV spectroscopy (Thermo Scientific, Model Helios-Beta) and available commercial kits (Merck, Product Number 100683). Based on a material balance at steady-state reaction conditions, and accounting for the water removal efficiency of condenser used, the concentration of ammonia in the effluent stream (wet-basis) and the corresponding reaction selectivity to ammonia, S_{NH_3} (%) can be estimated.

The reaction temperature reported in the present work refers to that at the inlet of the catalyst bed. It was estimated that the adiabatic temperature rise in the catalyst bed (0.3 g) for 95% conversion of NO, 90% N_2-selectivity, and 85% H_2-conversion obtained at 155 °C (150 ppm NO, 5% O_2, 0.8% H_2, He as balance gas), and considering the network of reactions (5)–(7) was about 7 °C.