ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

NO adsorption and influence of the control of temperature over catalytic test results for NO oxidation

A. Serrano-Lotina[*], A.C. Bueno, C. Goberna-Selma, P. Ávila, M.A. Bañares

Instituto de Catálisis y Petroleoquímica, ICP (CSIC), Marie Curie 2, 28049 Cantoblanco, Madrid, Spain

ARTICLE INFO

Keywords:
NO oxidation
Adsorption
Unit refinement
Temperature control

ABSTRACT

A preliminary partial oxidation of NO to NO_2 is helpful for low-temperature SCR. Oxidation of NO was evaluated over a Pt-based catalyst. Prior to the study, which was focused on the influence of the control of temperature over the catalytic results, PID process parameters of the catalytic reaction system were optimized showing that the unit control refinement is crucial for a good performance of the catalytic tests. This is particularly important when a significant population of adsorbed species build on the surface of the catalyst, which is the present case; adsorption phenomena may lead to deceiving apparent conversion values. Temperature programmed desorption tests showed that O_2 is essential for the NO adsorption. Three modes of heating/cooling were checked. When ramp mode was used for controlling the temperature, adsorption/desorption phenomena led to deceptive results of catalytic conversion. However, when stepped mode was evaluated stationary state was reached, and then NO disappearance was only due to NO conversion to NO_2.

1. Introduction

Stationary state is a state in which every observable is independent of time. This state should be reached before measuring catalytic activity if the purpose is comparing between different systems. Otherwise, other phenomena such as adsorption/desorption or deactivation may interfere. For example, Tanabe et al. [1] studied supported Pt catalysts during NO reduction by hydrocarbons. Catalysts were evaluated in reaction using a 10 °C/min ramp. Since no stationary state was reached, adsorption/desorption phenomena appeared. At the beginning of their experiments there was no conversion but when the temperature increased apparently negative activity results were reported. This may be ascribed to the NO and C_3H_6 desorption as temperature increased. Then, that conversion was actually an "apparent conversion". Zhang et al. [2] studied MnOx-CeO_2/TiO_2 catalysts for selective catalytic reduction of NO_x with NH_3 at low temperature. The catalysts which contained Mn, Ce and K showed a surprising behavior below 180 °C: NO conversion remains almost constant with temperature. Authors did not explain how they took the measurements but it seems that stationary state was not reached and NO adsorption phenomena were taking place, leading to deceptive NO conversion values. Doronkin et al. [3] studied the "FastSCR"-like mechanism over Ag-based catalysts. Those catalysts were evaluated in reaction by decreasing the temperature using a 2 °C/min ramp. At temperatures below 130 °C, an increase in NOx conversion was reported again, probably due to NOx adsorption. Maldonado-Hódar [4] studied Pt-carbon aerogel as adsorbents and catalysts for VOCs removing. He wisely differentiated between total conversion as VOC disappearance and VOC conversion to CO_2. He related the difference between them to adsorption phenomena. In this case the comparison with other catalysts may be easier since real conversion was reported. Roldan-Cuenya and Behafarid [5] wrote a review focused on the role of the nanoparticle size and shape on chemisorption. They ascribed the hysteresis detected between heating and cooling measurements over Pt/Al_2O_3 to not having enough time to reach its equilibrium state.

There are different ways for evaluating catalytic activities at different temperatures. Single experiments for each temperature can be performed, although they are lengthier. If a unique experiment is carried, the catalyst can be evaluated by heating from room temperature or by cooling from an initial target temperature. In addition, heating and cooling can be accomplish using a ramp mode or a stepped mode, that is, maintaining each temperature until stationary state is reached. These options may be evaluated, together with a good optimization of the catalytic and analysis system. This will deliver the most accurate results.

A good optimization of the catalytic system comprises mass flow controller calibration and P,I,D. process parameters (PID) optimization. Mass flow controller optimization detects any drift from factory calibration and PID optimization allows a good regulation of temperature. The control is performed by algorithms which allow regulating the

---

[*] Corresponding author.
E-mail address: asl@icp.csic.es (A. Serrano-Lotina).

http://dx.doi.org/10.1016/j.cattod.2017.06.031
Received 10 April 2017; Received in revised form 1 June 2017; Accepted 24 June 2017

Please cite this article as: Serrano-Lotina, A., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.06.031

difference between the process value (PV) and the set point (SP) in order to correct this error. The best control is achieved when the right values to **P**, **I** and **D** (proportional, integral and derivative) parameters were selected [6]. **P** parameter is proportional to the error at the instant **t**, which is the "present" error. This element avoids the oscillating behavior defining a proportional band around the set point with control possibilities. Thus, the larger this digression is, the larger the signal from the control within the proportional band. Basically, high or low proportional bands are a compromise between speed to achieve the set point and the stability of the system trying to adequate the control output signal to the set point of the system. **I** element is proportional to the integral of the error up to the instant **t**, which can be interpreted as the accumulation of the "past" error. This parameter assesses the area between the value curve of the controlled variable and the straight line which represents the set value (SV), generating an additional response to the proportional control changing the output signal when there is any deviation. It is equivalent to the oscillating period of the system. A short integral value means a relatively fast response trying to correct the difference between SV and PV. On the contrary, a long integral action is more secure but it takes longer to reach target values. The correct value corresponds to the oscillating period of the system. **D** element is proportional to the derivation of the error at the instant **t**, which can be interpreted as the prediction of the "future" error. It manages to anticipate measuring the speed with which the error is produced and it evaluates the slope of the curve that represents the oscillation of the controlled variable improving the stability of the stationary state. It is measured in seconds. By choosing excessively short values, it will interfere before there is a scope for action. However, by choosing values in excess it will create a high instability in the system [7].The values of the proportional band (%), of the integral time (seconds) and of the derivative action time (seconds) must conveniently couple with the elements of control. There are several methods to tune the PID parameters such as Ziegler-Nichols [8], Harriot [9] or Chidambaram [10]. In this case, as the model of the process is unknown, they have been determined by estimation (trial-error-trial) until achieving an optimized process control. This general procedure is based on performing repetitive tests introducing disturbances by changing the set point and returning to its initial value. Therefore, the adjustment will be refined observing the output control signal and its response to the disturbance created (not too large, to avoid damage) [6].

NO oxidation reaction has been chosen as the target reaction due to its importance as previous step for fast-SCR reaction [11,12]. Nitrogen oxides (NO_x) commonly derived from the combustion of fossil fuels or solid wastes are considered primary atmospheric pollutants, being responsible for a wide range of environmental problems such as photochemical, smog, acid rain, tropospheric ozone and ozone layer depletion [13,14]. The most popular NO_x abatement technology is SCR with ammonia (NH_3), but this process has several drawbacks, such as high reaction temperatures (> 300 °C) and unreacted reducing agents that at low temperatures (< 200 °C) can generate ammonium salts that can be explosive. Besides, typical NOx emissions from combustion processes contain significantly more NO than NO_2, and the inclusion of NO oxidation step prior to the SCR process is useful for increasing SCR rates of reaction [15].

The aim of this work was to study the influence of **P**, **I** and **D** parameters over the heating of the reactor, to study adsorption/desorption phenomena over the Pt-based catalyst and to evaluate the influence of the control of temperature over the catalytic activity.

2. Materials and methods

2.1. Unit refinement

The reaction system consisted of a Microactivity-Efficient (MA-Effi, PID Eng & Tech) unit coupled to an online ThermoNicolet 6700 FT-IR spectrometer fitted with a thermostated (120 °C) multiple pass gas cell with 2 m optical path, Thermo Scientific. The reaction was run in the latter, while reaction activity data were monitored in the former.

Reliable catalytic test depend on accurate control of reaction conditions parameters. A study on the optimization of the reaction system and its consequences was firstly performed. The role of maximum power supplied to the oven was studied. For this purpose, the unit was operated in automatic mode, that is, without establishing a set point. This indicates the maximum temperature that the reactor can reach with a specific power supply (the oven control output signal). Then, depending on the reaction temperature, a limited control output signal was selected and an optimization of proportional-integral-differential (PID) parameters was carried to safely reach the set point with the minimum use of time and power.

Online activity measurement run by the infrared gas cell required appropriate calibration of the spectrometer to quantify NO (1905–1855 cm^{-1}). This calibration was done by feeding different known NO concentrations and integrating NO infrared band.

2.2. NO isothermal adsorption and temperature programmed desorption tests

Two types of experiments were performed over the Pt based catalyst. In the first one, the adsorption step was done at room temperature during two hours using 700 ppm of NO with a total flow of 1000 mLn·min^{-1} with N_2 as balance. Afterwards, 1000 mL·min^{-1} of N_2 was fed to the reactor and after 20 min, the temperature was increased from room temperature to 490 °C with a ramp of 3 °C·min^{-1}. The other TPD test was performed in the same conditions but using also a 5% of O_2 during the adsorption stage. The Microactivity-Efficient (MA-Effi, PID Eng & Tech) unit coupled to a ThermoNicolet 6700 FT-IR spectrometer equipped with a heated multiple pass gas cell (Thermo Scientific) described above were also employed for this study.

2.3. Catalytic tests

To evaluate the influence of the reaction conditions in the catalytic behavior, different modes were used: a ramp mode in which the temperature was linearly increased from room temperature to 400 °C at 3 °C·min^{-1}; a stepped mode, with common PID parameters for all temperatures (optimized for 400 °C) and a stepped mode where PID parameters were selected for each temperature. In the stepped modes temperature was held for 60 min. The role of all these modes was evaluated during heating and cooling cycles. During the cooling, the decrease of temperature happened due to the momentum of the reactor that will dissipate the heat cutting the power of the control signal.

The catalytic tests were performed in the following conditions: a total flow rate of 1000 mLn·min^{-1}, 700 ppm of NO, 5% O_2, in N_2 as balance; GHSV was 10,000 h^{-1}. A Pt-TiO_2 catalyst was used. The conversion was calculated using the equation:

$$\text{Conversion (\%)} = \frac{([\text{No}]_0 - [\text{No}])}{[\text{No}]_0} \times 100$$

where [NO] is the outlet NO concentration (ppm) and $[NO]_0$ is the inlet NO concentration (ppm).

The inlet concentration was measured prior to the experiment using the bypass mode (without going through the reactor). NO (1905–1855 cm^{-1}) and NO_2 infrared band were evaluated (1642–1605 cm^{-1}) during the reaction. It was only possible to calculate NO concentrations since it was not possible to calibrate the NO_2 infrared band (NO_2 readily dimerization hampers the availability of reliable calibrated cylinders).