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Modeling and optimization of NH_3-SCR performance of MnO_x/γ-alumina nanocatalysts by response surface methodology

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ABSTRACT

To model and optimize the NH3-SCR performance of MnO_x/γ-alumina nanocatalysts, the response surface methodology (RSM) based on a central composite design (CCD) was employed. The MnO_x/γ-alumina nanocatalysts were prepared by homogeneous deposition precipitation and characterized by XRD, H2-TPR, N2 adsorption and TEM. The effect of process variables, including Mn loading, calcination temperature, concentration of O_2, NH_3/NO ratio and reaction temperature on NO_x conversion and N_2 selectivity was studied. Analysis of variance confirmed the accuracy and precision of generating quadratic models. The calcination temperature and reaction temperature had the most pronounced effects on NO_x conversion and N_2 selectivity, respectively. The maximum NH3-SCR performance (94.6% NO_x conversion and 93.7% N_2 selectivity) was predicted and experimentally validated at the optimum conditions: Mn loading 6.7 wt. %, calcination temperature 507.5 °C, concentration of O_2 4.5 (vol. %), NH3/NO ratio 0.94 and reaction temperature 269.8 °C.

1. Introduction

Nitrogen oxides (NO_x), emitted from combustion processes, are the main atmospheric pollutants [1]. In the last 2 decades, many approaches have been developed to control the emission of NO_x [2,3]. The selective catalytic reduction of NO_x using NH_3 (NH_3-SCR process) is a well-known low cost and highly efficient technology for NO_x emissions reduction of stationary sources [4,5]. Different groups of catalytic systems, including transition, noble and rare earth metal supported on different supports (zeolites, alumina, TiO_2 and activated carbons) have been reported to be active for NH_3-SCR of NO_x [6–9].

Alumina-based catalysts prompted by noble and transition metals (Mn, Cu, V, Pt and Pd) have shown an excellent catalytic performance in NH_3-SCR of NO [10,11]. Among the transition metal oxides, manganese oxides are the most studied due to their low volatility (various types of loosely bound oxygen species) [12,13]. This catalytic system presents high de-NO_x activity in the wide temperature range, significant resistance to poisons contained in car-exhausts, and a high thermal stability [12,14]. However, some operational variable could affect the NH_3-SCR performance (NO_x conversion and N_2 selectivity) of MnO_x/γ-alumina. In order to enhance the NH_3-SCR performance of MnO_x/γ-alumina, especially for practical applications, process variables must be optimized.

The individual effects of process variables on response can be studied by classical optimization methods, which change one variable at a time [15]. Such optimizing methodology often leads to the unreal optimal condition and is expensive as well as time consuming. However, these problems can be overcome by using an experimental design method [16,17]. The RSM is a collection of statistical and mathematical techniques useful for designing experiments, modeling, and optimizing of processes [18]. In the RSM, the main objective is fit for empirical models to the experimental data obtained in experimental design [15,19].

In recent years, the RSM is widely used for modeling and optimization of many fields of engineering studies [16,20,21]. Mousavi et al. [22] used RSM to model and optimize the preparation of Mn/active carbon nanocatalysts in NH_3-SCR of NO_x. Their developed RSM model gave coefficient of determination (R^2) of 0.972. They found the most significant effective parameter on efficiency of Mn/AC nanocatalyst by the Pareto analysis. Zarei et al. [23] employed the RSM to assess individual and interactive effects of the four main independent parameters on the decolorization efficiency of peroxi-coagulation process based on carbon nanotube-PTFE electrode as cathode. Their developed RSM model showed a high R^2 value and they also found the optimum conditions which had the highest decolorization (>95%).

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The aim of the present work is investigating the effect of five process variables, including Mn loading, calcination temperature, concentration of O_2, NH_3/NO ratio and reaction temperature as well as their interactions on NH_3-SCR performance of MnO_x/γ-alumina by RSM. The NO_x conversion and N_2 selectivity were selected as a response for optimization and tried to find the optimum conditions for maximum NH_3-SCR performance.

2. Material and methods

2.1. Catalysts preparation and characterization

Alumina powder (gamma phase, average particle size ≤ 10 μm) obtained from Sigma-Aldrich was used for preparation of the catalysts. The MnO_x/γ-alumina nanocatalysts with different Mn loadings (wt. %) were prepared by homogeneous deposition precipitation (HDP) using urea as the precursor for the precipitating agent. Typically, specified amount of $Mn(NO_3)_2.3H_2O$ (supplied by Merck) was dissolved in 100 mL deionized water and 1 g of γ-alumina was suspended in this solution with stirring. The temperature of this suspension gradually increased to 95 °C, after which excess amount of urea (supplied by Merck) was added. The suspension was kept at that temperature for 5 h, until hydroxide precipitate was completed. The resulting mixture was aged for 14 h at room temperature and then the loaded γ-alumina were thoroughly washed, dried at 110 °C for 12 h, and subsequently calcined at desired temperature for 4 h in air. The prepared catalysts were kept in desiccator until testing time for inhibition of water and contaminant adsorption.

The phase composition of the MnO_x/γ-alumina were determined by X-ray powder diffraction (XRD) using a Siemens D5000 dual goniometer diffractometer by a graphite monochromator CuKα radiation ($\lambda = 1.54$ nm) through the range of $2\theta = 5°$ to 75°. The reducibility of prepared catalysts was determined by temperature programmed reduction with H_2 (H_2-TPR) experiments in a Micromeritics 2910 apparatus, using 3 vol. % H_2 in Ar at a total flowrate of 15 cm^3/min. The textural properties of the catalysts were investigated by transmission electron microscopy (TEM) images (using a JEM-2010 microscope) and nitrogen adsorption–desorption isotherms (using a Micromeritics Asap 2000 Analyser). The specific surface area was calculated by BET method, whereas the pore size and volume were estimated using the *T*-plot method.

2.2. Catalytic activity test

The NH_3-SCR activity of catalysts was measured in a fixed bed quartz reactor (i.d. = 10 mm) at atmospheric pressure. In all the tests, 0.2 g catalyst was dispersed on quartz wool and the feed gas mixture containing NO, NH_3, O_2 and Ar as balance with a known composition was fed into the reactor at a total flow rate of 200 cm^3 min^{-1}. The concentration of NO was kept constant (1000 ppm) and different NH_3/NO were obtained by changing the NH_3 concentration. The NH_3-SCR experiments were carried out at desired reaction temperature. The concentrations of NO and NO_2 at the inlet and outlet of the reactor were monitored by a flue gas analyzer (Testo 350 M/XL). A gas Chromatograph (SHIMADZU model 2010 plus) equipped with a molecular sieve column (HP-Molesieve, 30 m length, 0.53 mm diameter) and a thermal conductivity detector was used to determine the concentration of N_2 and N_2O. According to the concentration of NO, NO_2, N_2 and N_2O in the inlet and outlet flow, the NO_x conversion and the N_2 selectivity were calculated using the following equations:

$$NO_x\text{conversion}\% = ([NO])_{in} - ([NO])_{out}/([NO])_{in} \times 100 \quad (1)$$

$$N_2\text{selectivity}\% = ([N_2])_{out}/([N_2] + [N_2O])_{out} \times 100 \quad (2)$$

Table 1
Independent variables and their corresponding values in the experimental design.

Independent variables		Ranges and levels				
		−2 (−α)	−1	0	+1	+2 (+α)
Mn loading (wt. %)	(X_1)	1	3	5	7	9
Calcination temperature (°C)	(X_2)	300	375	450	525	600
Concentration of O_2 (vol. %)	(X_3)	0	2.5	5	7.5	10
NH_3/NO ratio	(X_4)	0.5	0.75	1	1.25	1.5
Reaction temperature (°C)	(X_5)	200	235	270	305	340

The subscripts in and out indicate the inlet and outlet concentration at steady state, respectively.

2.3.. Design of experiments

The RSM usually contains four steps: (1) design a property experiment set; (2) developing a polynomial model through regression; (3) evaluating the model parameters efficiently; (4) optimizing the process. Here, RSM based on a full quadratic CCD including 2^5 factorial designs, ten axial points ($\alpha = \pm 2$) and eight replications at the center point, which lead to a total number of 50 experiments, was employed for modeling the NH_3-SCR performance of MnO_x/γ-alumina. The effective process variables such as Mn loading (wt. %), calcination temperature (°C), concentration of O_2 (vol. %), NH_3/NO ratio in the gas feed and NH_3-SCR reaction temperature (°C) were selected as the independent variables. The independent variables and their corresponding actual and coded values are shown in Table 1. It should be mentioned that preliminary experiments were conducted for determining the range of the process variables.

Design expert software (Ver. 9.0.5) was utilized to design the experiments and to analyze the data. The following second-order polynomial (Eq. (3)) was used to correlate the response and independent variables:

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum\sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where Y is the predicted responses (NO_x conversion and N_2 selectivity), $\beta_\circ$ is a constant, β_i is the ith linear coefficient, β_{ii} is the ith quadratic coefficient and β_{ij} is the interaction coefficient of the variables. The x_i is the independent variable, $x_i x_j$ represents the first order interaction between x_i and x_j ($i < j$), k is number of studied factors and ε is the associated error. The accuracy and precision of generated models was expressed by using the ANOVA. The interaction of the process variables was examined by constructing the surface and contour plots. With the aim of maximizing of NO_x conversion and N_2 selectivity of MnO_x/γ-alumina nanocatalysts, the optimum condition is (within the experimental range) obtained by using the response optimizer function of design expert software.

3. Results and discussion

3.1. Characterization of nanocatalysts

The XRD patterns of γ-alumina and MnO_x/γ-alumina with different Mn loadings (1, 5 and 9 wt. %) is shown in Fig. 1. The characteristic peaks corresponding to γ-alumina phase having spinel lattice (JCPDS file no. 29-63) have appeared in all XRD patterns. It corresponds that the original structure of γ-alumina is not destroyed during preparation of nanocatalysts. According to the XRD patterns, there is no diffraction peak related to MnO_x phases in the 1 wt. % and 5 wt. % MnO_x/γ-alumina samples (see Fig. 1b and c). It suggests that the well-dispersed nanosized MnO_x phases were

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