Numerical Simulation of SCR of NOx with NH3 on Fe-based Catalyst

Dongdong Ren, Keting Gui*

Key Laboratory of Energy Thermal Conversion and Control of Ministy of Education, School of Energy and Environment, Southeast University, Nanjing 210096, China

Abstract

Selective catalytic reduction (SCR) of NOx with NH3 is an effective control technique for limiting nitrogen oxide emissions nowadays. However, commercial catalyst in SCR of NOx, V2O5/TiO2, has a higher active temperature window about 300 °C-380 °C and its main component vanadium will cause environmental pollution. Hence to develop new SCR denitration catalyst, which can make high efficiency under low temperature and no poison, has been paid more and more attention. In this paper, Fe-based catalyst which worked with low temperature was studied and a three-dimensional model was developed to describe the activity of an SCR reactor. We present herein a transient kinetic analysis based on some mathematical models include of the flow field in fixed bed, occurrence of adsorption phenomena, interface diffusion and interface chemical reaction. The distribution of reactants (NO, NH3, O₂) concentrations and products (N₂, H₂O) concentrations are demonstrated as well as the distribution of temperature field and velocity. Since the distribution of these physical quantities are calculated with the simulation, we could optimize the reactor with adjusting the velocity, temperature, NH3/NO ratio and O₂ concentration of reactant.

Keywords: SCR, Fe-based catalyst, low temperature, simulation

1. Introduction

As one of the main pollutant of atmosphere pollution, nitrogen does harm to human health and ecological environment. The catalyst is the core of the SCR technology which is already relatively mature and used widely to limit nitrogen oxide emissions. The stability, selectivity and catalytic activity of catalyst directly determine the performances on SCR process. Nowadays, researches have pay more attention to low-temperature denitration catalyst consider of energy saving, environmental protection and high industrial application value., Iron-based catalyst showed high denitration catalytic activity because of it's d orbital electron is in a state of underfilling. Fe is relatively abundant and cheap on earth, some scholars found that Fe₂O₃ have high thermal stability, besides, iron oxide [1], mixed iron oxide [2-4], and iron oxide sol catalyst [5, 6] showed good SCR denitration catalytic activity. Liu [7], has found that FeTiO_x catalyst which prepared using coprecipitation has good SCR denitration activity and thermal stability in the medium temperature. Studies have shown that [8] Fe₂O₃-TiO₂ catalyst denitration efficiency can reach 90%, and has high N₂ selectivity in the low temperature. Long [9] and other researches has shown that Fe/ZSM-5 catalyst has the high denitration efficiency under the 350-400°C.Yao [10] suggested that Fe₂O₃ as a catalyst had a high denitration efficiency at low temperature.

The numerical simulation of SCR process which use mathematical model to calculate the process of the denitration reactor is an effective way to research. Since the 90s, researchers have begun to carry on the numerical simulation on the condition of high temperature of SCR denitration reaction, and they have set up a variety of effective mathematical model of steady or unsteady [11-16] state. But because of the low temperature SCR denitration catalyst is still on the stage of research and development, there are few reports of the relevant numerical simulation [17].

^{*} Manuscript received March 1, 2018; revised August 5, 2018.

Corresponding author. Tel.: +86 130 6257 4737; E-mail address: ktgui@seu.edu.cn.

doi: 10.12720/sgce.8.5.550-555

The reaction process in the reactor is complex. It involves the fluid movement in the catalyst pore, the diffusion of the reactant, and the chemical reaction on the surface of the catalyst. The simulation of SCR process is simultaneously to solve the fluid flow and heat transfer equations, the composition transfer equations and the intrinsic kinetics equation and so on. With the development of computer technology, it is usually possible to use computer software to solve the problem. In this article, the commercial software Fluent is used to simulate the SCR denitration flow field and chemical reaction process. Iron-based catalyst reaction kinetics parameters is obtained by experiments, and import it into the calculation of the chemical reaction. Thus, we could simulate the flow and heat and mass transfer process coupled with chemical reaction, finally get the whole reaction process for flow field and concentration distribution of each composition.

2. Model

Fig. 1 shows the model and grid. The reactor is assumed to be a cylinder in order to simplify calculation. The flue gas containing nitric oxide, ammonia, oxygen flow in to the cylinder from the bottom, and nitrogen is a balance gas which accounts for large proportion. Fe-based catalyst is places on the underside of the reactor, in where the reactants is adsorbed on the surface of catalyst and produce chemical reaction. And then, the productions would flow out via the top. The model assumed an isothermal bed.

The kinetics parameters of the Fe-based catalyst are obtained by experiments. The overall reaction may be represented as follows:

$$NO + NH_3 + \frac{1}{4}O_2 \xrightarrow{Fe} N_2 + \frac{3}{2}H_2O \quad (\Delta H = -407 \text{ kJ/mol})$$
(1)

In previous work, NO conversion rate can be expressed as the form of concentration of each reactant:

$$r_{NO} = -k_a C_{NH_3}^x C_{NO}^y C_{O_3}^z$$
(2)

$$k_a = A \exp(\frac{E_a}{RT}) \tag{3}$$

In the equation, r means surface reaction rate constant; C_{NH3} , C_{NO} , C_{O2} means the molarity of NH₃, NO, O₂; x, y, z means the order of reaction of NH₃, NO, O₂. Based on the experiments, we could evaluate the x, y, z is 0.8, 0.8, 0.1 respectively.



Fig. 1. The model and grid

Fig. 2. The device of SCR denitration reaction

On the reactor, the powdered sample of catalyst spread on the bottom evenly. And then, the mixed gas with NH_3 , NO, O_2 , N_2 feed to the reactor from the bottom. On the process, the catalyst particle would be influenced and the flow field would be affected by the particles. The governing equations of flow, heat and mass transfer process would be listed.

$$\frac{\partial}{\partial t} (\alpha_g \rho_g) + \nabla \cdot (\alpha_g \rho_g v_g) = S_{gm} \quad \frac{\partial}{\partial t} (\alpha_s \rho_s) + \nabla \cdot (\alpha_s \rho_s v_s) = S_{sm}$$
(4)

International Journal of Smart Grid and Clean Energy, vol. 8, no. 5, September 2019

$$\frac{\partial}{\partial t} \left(\alpha_g \rho_g \vec{v}_g \right) + \nabla \cdot \left(\alpha_g \rho_g \vec{v}_g \vec{v}_g \right) = -\alpha_g \nabla p + \alpha_g \rho_g \vec{g} + \nabla \cdot \tau_g - \beta \left(\vec{v}_g - \vec{v}_s \right) + S_{gv}$$
(5)

$$\frac{\partial}{\partial t} (\alpha_s \rho_s \vec{v}_s) + \nabla \cdot (\alpha_s \rho_s \vec{v}_s \vec{v}_s) = -\alpha_s \nabla p + \alpha_s \rho_s \vec{g} + \nabla \cdot \tau_s + \beta (\vec{v}_g - \vec{v}_s) + S_{sv}$$
(6)

The s, g means the solid and gas phase respectively; the β is drag coefficient between phases; S is the momentum transfer because of collision.

For the gas phase, we could apply the k- ϵ turbulence model to describe the flow field. Species mole fraction in the reactor are obtained as follows:

$$\frac{\partial}{\partial t} (\rho Y_i) + \nabla \bullet (\rho \vec{\nu} Y_i) = -\nabla \bullet \vec{J}_i + R_i$$
⁽⁷⁾

X 7 1

Yi is the mole fraction of i, and Ri is source generated on reaction.

Table 1. Parameters used in the simulation.

Parameter	value
Diameter of catalyst powder, m	10*-5
Concentration of NO in feed, ppm	500
Concentration of NH ₃ in feed, ppm	400, 450 ,500, 550, 600
Flue gas background	1%, 1.5%, 2%, 2.5%, 3% in N_2
Velocity of the gas feed, m/s	0.03, 0.04, 0.05
Reactor temperature, K	350, 400, 450, 500, 550
Activation energy of the reaction, kJ/mol	57.3

The process of simulation is proceeding based on the experiment result which is on the SCR denitration reaction while γ -Fe₂O₃ is catalyst. The parameters on the experiment is same with the Table 1. and the device is on Fig. 2. Experiments show that the γ -Fe₂O₃ particles have high denitration efficiency at low temperatures, and it even reach the highest denitration efficiency is 97.6% at 240 °C.

3. Results and Discussion







Fig 4. Phase distribution in the reaction

Fig. 3 shows the distribution of velocity vector in the reactor. As the figure shows, the flue gas which are reactants flow into the reactor from the bottom and products flow out via top. On this process, the reactant react on the surface of the catalyst powder which is solid phase in this simulation. The velocity are distributed uniformly in the reactor on the accounts of fully developed turbulence on the flue. Fig4

shows the phase distribution on the reactor. As we know, on this reaction, the catalyst powder is considered as continuous phase. On the figure, the catalyst phase as solid phase are mainly spread on the lower part of the reactor because the it's density is much higher than the gas phase.



Fig 5a, Fig 6a, Fig 7a, Distribution of NO $,O_2$, NH₃ mole fraction, Fig 5b, Fig 6b, Fig 7b, Variation of NO $,O_2$, NH₃ mole fraction with Z position.

Fig.5a shows the distribution of NO mole fraction on the reactor. Fig.5b shows the variation of NO mole fraction with Z position. It's could be seen from the diagram that NO can effectively participate in the reaction in the presence of iron-based catalyst. Because the reactants flow into reactor from the bottom and react on the condition of the presence of catalyst, the concentration of NO becomes lower and lower along the Z position which direction is the feed gas flow. Besides, the concentration of NO is minimum on the position of 0.05m where there is no catalyst, we could obtain that Fe-based catalyst could promote the reaction effectively.

Fig.6a, Fig.7a shows the distribution of the concentration of O_2 , NH₃ respectively. Fig.6b, Fig.7b, shows the variation of O_2 , NH₃ mole fraction with Z position respectively. On the reaction, NO, O_2 , NH₃ are reactants and N₂, H₂O are products. With the produce of the reaction, the concentration of O_2 , NH₃ are become lower. NH₃, which is the main gas to participate the reaction, reduce with the same proportion because of the same stoichiometric coefficient. And the O_2 is also the important reactant to react with NO.

In order to optimize the reactor, we also simulation the reaction on different operation condition. We analyze the reaction process with different O_2 concentration on the feed flow, reactor temperature, NH_3 concentration and inlet velocity.



Fig 8a. Variation of NO mole fraction with Z position in different reactor temperature; b Conversion rate in different reactor temperature

There is an important influence factor is the temperature of the reactor. Fig. 8a shows the variation of NO concentration with Z position in different reactor temperature and Fig. 8b shows the different conversion rate value on experiment and simulation respectively. In the Fig. 10a, the left part of the dash line means it is of the bed of catalyst and so as the Fig. 9a, Fig. 10a, Fig. 11a. On this condition, the concentration of O_2 , NH₃, NO is 3%, 500ppm and 500ppm, the inlet velocity is 0.03m/s, and the reactor temperature is 350K, 400K, 450K, 500K, 550K. It can be seen from the diagram that efficiency increased with the increase of temperature on the range of low temperature. And the result is consistent with the experimental value on the low temperature.



Fig 9a, 10a, 11a Variation of NO mole fraction with Z position, Fig9b, 10b, 11b Conversion rate, in different O₂ NH₃ concentration and velocity.

Fig. 9a shows the variation of NO concentration with Z position in different O_2 concentration on the feed flow and Fig. 9b shows the different conversion rate value on experiment and simulation respectively. On this condition, the reactor temperature is 500K, the inlet velocity is 0.03m/s, and the concentration of NO and NH₃ both are 500ppm. And the O_2 concentration is increasing from 1% to 3%. O_2 is an important reactant, so it's concentration play an important role on the reaction process. With the increase of the concentration, the conversion rate also increase. From the Fig. 8b, we could compare the conversion of NO between the simulation and experiment, the tendency of the conversion rate is accordant with the change of the O_2 concentration. Which means the O_2 is an important reactant and increasing its' concentration can partly promote the reaction.

Fig. 10a shows the variation of NO concentration with Z position in different NH_3 concentration and Fig10b shows the different conversion rate value on experiment and simulation respectively. On this condition, the reactor temperature is 500K, and the inlet velocity is 0.03m/s, the O_2 concentration of feed is 3%, the NO concentration is 500ppm, but the NH_3 concentration varies and the rate of NH_3 and NO is 0.8, 0.9, 1.0, 1.1, 1.2. Compared with the O_2 , NH_3 also is an vital reactant to participate the reaction, and NH3 has greater impact on the process. With the increase of ammonia concentration, conversion rate improved significantly. On the reaction, the NH_3 , which is the main gas to participate the reaction, changes proportionally with NO, and it has higher reactor order than O_2 . From the Fig. 9b and Fig. 10b, we could get that the result of the simulation is close to the real value which got from experiment, it could say that the model could describe the real SCR process partly.

Fig. 11a shows the variation of NO concentration with Z position in different inlet velocity and Fig. 11b shows the different conversion rate value on experiment and simulation respectively. On this condition, the concentration of NO, NH_3 , O_2 is 500ppm, 500ppm and 3%, the reactor temperature is 500K. The inlet velocity is 0.03m/s, 0.04m/s, 0.05m/s. On this model, the 0.03m/s means the GV is 5000/h. With the increase of velocity, conversion rate decreases. When the velocity is lower, the reactants could remain

more time in the reactor so that they could have enough time to react on the catalyst surface. We could also get the result from the experiments.

4. Conclusions

In the article, our simulations show the SCR process and we can get list conclusions:

1, Iron-based catalysts have good catalytic activity, that could promote effectively the NH3 and NO response. In the process of reaction, the concentration of NO, NH_3 , O_2 which are reaction gases gradually reduce; on the contrary, the concentration of N_2 , H_2O as products increase gradually;

2, The efficiency would be different on the different condition of operation. Reducing the flow velocity, improving the ammonia nitrogen ratio, increasing the oxygen content would improve the conversion rate effectively.

Acknowledgements

Financial support for this project from the National Nature Science Foundation of China (51276039) are gratefully acknowledgment.

References

- Busca G, Lietti L, Ramis G. Chemical and mechanistic aspects of the selective catalytic reduction of NOx by ammonia over oxide catalysts: A review. Applied Catalysis B: Environmental, 1998; 18(1-2): 1-36.
- [2] Liu Z, Millington PJ, Bailie JE. A comparative study of the role of the support on the behaviour of iron based ammonia SCR catalysts. *Microporous & Mesoporous Materials*. 2007:104(1): 159-170.
- [3] Lin QC, Hao JM, Li JH. Fe promotion effect in Mn/USY for low-temperature selective catalytic reduction of NO with NH3. *Chinese Chemical Lett.* 2006;17(7): 991-994.
- [4] Lunin AF, Adzhie VAY, Fedorova RI. Catalytic reduction of nitrogen oxides by ammonia. *Chemical & Technology of Fuels & Oils*, 1993; 29(11):11-12.
- [5] Willey RJ, Lai H, Peri JB. Investigation of iron oxide-chromia-alumina aerogels for the selective catalytic reduction of nitric oxide by ammonia. cheminform, 1991: 22 (41).
- [6] Fabrizioli P, Urgi TB, Baiker A. Environmental catalysis on iron oxide–silica aerogels: Selective oxidation of NH3 and reduction of NO by NH3. *Journal of Catalysis*, 2002; 206(1):143-154.
- [7] Liu F, He H, Zhang C.et al. Mechanism of the selective catalytic reduction of NOx with NH3 over environmental-friendly iron catalyst. *Catalysis Today*, 2011; 175(1):18-25.
- [8] Kato A, Matsuda S, Kamo T, et al. Reduction between nitrogen oxide(NOx) and ammonia on iron oxide-titanium oxide catalyst. *The Journal of Physical Chemistry*, 1981; 85(26):4099-4102.
- [9] Long RQ, Chang MT, Yang RT. Enhancement of activities by sulfation on Fe-exchanged TiO-pillared clay for selective catalytic reduction of NO by ammonia. *Applied Catalysis B: Environmental*, 2001;33(2):97-107.
- [10] Yao GH, Gui KT, Wang F. Low-temperature De-NOx by selective catalytic reduction based on iron-based catalysts. *Chemical Engineering & Technology*, 2010; 33(7): 1093-1098.
- [11] Buzanowski, Yang. Simple design of monolith reactor for selective catalytic reduction of nitric oxide for power plant emission control. *Industrial and Engineering Chemistry Research*, 1990; 29(10): 2074-2078.
- [12] Borisova, Noskov AS, Borova LN. Effect of unsteady-state catalyst surface on the SCR-process. *Catalysis Today*, 1997; 38(1): 97–105.
- [13] Christin W, Peter F, Patil MD, et al. Modeling of SCR denoxcatalyst: Looking at the impact of substrate attributes. Society of Auto motive Engineers, 2003; 112(4): 691-699.
- [14] Roduit, Baiker, Bettoni, et al. 3-D modeling of SCR of NOx by NH3 on vanadia honeycomb catalysts. *AICHE Journal*, 1998; 44(12): 2731-2744.
- [15] Snyder JD, Subramanian B. Numerical simulation of a reverse-flow NOx-SCR reactor with side-stream ammonia addition. *Chemical Engineering Science*, 1998; 53(4):727-734.
- [16] Khodayari, Odenbrand. Selective catalytic reduction of NOx: a mathematical model for poison accumulation and conversion performance. *Chemical Engineering Science*, 1999;54 (12): 1775-1785.
- [17] Tronconia E, Novaa I, Ciardellia C, et al. Modelling of an SCR catalytic converter for diesel exhaust after treatment: Dynamic effects at low temperature. *Catalysis Today*, 2005; 105(3–4): 529-536.