Modeling the selective catalytic reduction of NO_x by ammonia over a Vanadia-Titania catalyst from exhaust gases

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Abstract
Nitrogen oxides,NO_x ($NO+NO_2$), emitted with exhaust gases during the gases during the combustion of fossil fuels or biofuelsare among the main sources of air pollution.NO_x are contributed to a variety of environmental problems including acid rain, ground level zone (smog) and visibility degradation. Selective catalytic reduction (SCR) of NO_x is one of the most efficient and economic technology for the removal of NO_x by using reducing agents such as CO, H_2, NH_3 and hydrocarbons. Ammonia was found to be a suitable reductant for NO in the presence of oxygen, because ammonia reacts selectively with NO to produce N_2.The present study discusses the testing of a mechanistic kinetic model for the SCR of NO_x to describe the kinetics of V_2O_5/TiO2 catalysis at atmospheric pressure and a temperature of in a plug flow reactor. A good agreement between experimental and model results has been obtained. A homogeneous model consisting of mass balance equations was solved. The results show that NO_x conversion increases with the increase in the operation temperature. However, NO/NH_3does not change the NO_x conversion

Keywords: Selective catalytic reduction **(**SCR), Modeling, V_2O_5/TiO_2**,**NO_x reduction

1.Introduction

In atmospheric chemistry the term NO_x is used to mean the total concentration of NO plus NO_2. The three primary sources of NO in combustion processes are thermal NO, fuel NO, and prompt NO. Thermal NO formation, which is highly temperature dependent, is recognized as the most relevant source when burning natural gas.Fuel NO tends to dominate during the combustion of fuels, such as coal, which have significant nitrogen content, particularly when burned in combustors designed to minimize thermal NO.Many studies have been conducted on numerous metal oxide catalysts, such as MoO_3/TiO_2, V2O5/TiO_2 and CuO/Al_2o_3, forNO elimination. However, the fact is that in order to avoid the deactivation by SO_2 and H_2O which takes place at low temperatures, these catalysts usually function at high temperatures (higher than 3500℃). Also, Fe zeolite SCR catalysts which are commercially available for stationary applications are shown to operate at temperature up to 6000℃. Fe zeolite SCR when exposed to high temperatures in the presence of H_2O, may be subjected to the problems of stability. When exposed to the temperatures higher than 6000℃, in a process flow with high concentration of H_2O, zeolites SCR has the tendency to be deactivated by de-alumination, while the Al^{3+}ions in the SiO_2-Al_2O_3framework start to migrate out of the structure, the Cu/zsm-5 plays an active role in NO_X reduction within the temperature window of about 200-4000℃, but its thermal durability is insufficient. It is evident that the V_2O_5catalyst shows quite high activity for NO elimination at low temperatures, and the presented SO_2 in the flue gas does not deactivate the V_2O_5 catalyst but even can enhance its activity in the absence of H_2O. Therefore, it seems that the V_2O_5 catalyst could be an excellent alternative for SCR of NO with NH_3. The vastly studied support for vanadium is TiO_2 as it is resistance to poisoning effects of sulfur and has the ability to effectively disperse the V_2O_5. But, Titania dose suffer from several limitations, such as it is expensive, sintering non-resistance, and has relatively low surface area.The overall reaction considered for development of thekinetic models for selective catalytic reduction of NO_x given in reaction (1) occurs swiftly on the catalyst at temperatures between 250 and 450◦C in the presence of excess oxygen. The“selective” term indicates that ammonia reacts directly with NOx rather than being oxidized by oxygen to form N2,N_2O,and NO.

$$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O \qquad (1)$$

The oxidation of ammonia is an undesired reaction duringNO_xdestruction. The presence of excess oxygen leads to thereaction(2)to form $N_2$by ammonia oxidation.

$$4NH_3+3O_2 \rightarrow 2N_2+6H_2O \ (2)$$

The present study addresses a kinetic analysis of the chemical reactions occurring in the catalytic filter material. A numerical model, based on available knowledge of SCR kinetics, is developed, validated with published plug flow reactor data.

2. Experimental database

The NO reduction activities of the prepared catalysts were examined out at atmospheric pressure in a fixed bed reactor. The glass tube reactor (1 cm inner diameter) was located inside in a furnace, which is electrically heated. The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm NH3,5%$O_2$and Ar as balance. In all the tests, catalyst was packed between plugs of glass wool; the total flow rate was fixed at 200 $cm^3 min^{-1}$. The NO reduction experiments were carried out at different temperature. A gas chromatography (SHIMADZU model 2010 plus) equipped with a molecular sieve (HP-Molesieve, 30 mlength, 0.53 mm diameter) column system and a thermal conductivity detector (TCD) was used for $N_2$and N_2O (as products of NO reduction) analysis.

2.1. Kinetic model and parameter values

A homegeneous catalytic model is developed using steady-state mass balance equations.The following rate equation taken from the literature on intrinsic SCR kinetics is used in the study (Lintz and Turek,1992).

$$r_1 = \frac{k_1 C_{NO} a C_{NH_3}}{1 + a C_{NH_3}} \qquad (3)$$

$$r_2 = k_2 C_{NH_3} (4)$$

$$k_j = k_{j_0} \exp\left(-\frac{E_j}{RT}\right) \qquad (5)$$

$$a = a_0\, exp\left(-\frac{A}{RT}\right) \qquad (6)$$

The plug flow reactor with continuity equations for NO and NH_3Eqs. (7)-(9), treated as isothermal, given the small temperature effects due to the small amounts of NO converted.Underlying assumptions include steady state, ideal plugflow inz-direction, axial dispersion slow compared with convective transport, uniform concentrations in radial direction.

$$0 = u_{eff}\frac{dc_i}{dz} + \sum_i v_{ij} r_j \qquad (7)$$

$$0 = u_{eff}\frac{dc_{NO}}{dz} + \frac{k_1 c_{NO} a c_{NH_3}}{1 + a c_{NH_3}} \qquad (8)$$

$$0 = u_{eff}\frac{dc_{NH_3}}{dz} + \frac{k_1 c_{NO} a c_{NH_3}}{1 + a c_{NH_3}} + k_2 c_{NH_3} \qquad (9)$$

2.2. Numerical solution and model validation

The continuity equations for NH_3 and NO Eqs. (8) and (9)are solved numerically with a MATLAB routine (ODE 23s, Runge-Kutta algorithm are). The results of the fitting procedure are shown in Fig. 1 and Table 2. Calculated values of NO conversion agree well with the experimental values.

Table 1 – Experimental data of plug flow reactor

Operating conditions	
NO	1000 ppm
NH_3	1000 ppm
O_2	5%
Total flow	200 ml/min
Length of reactor	20mm
Radius of reactor	4mm
Density	0.18 g/cm^3

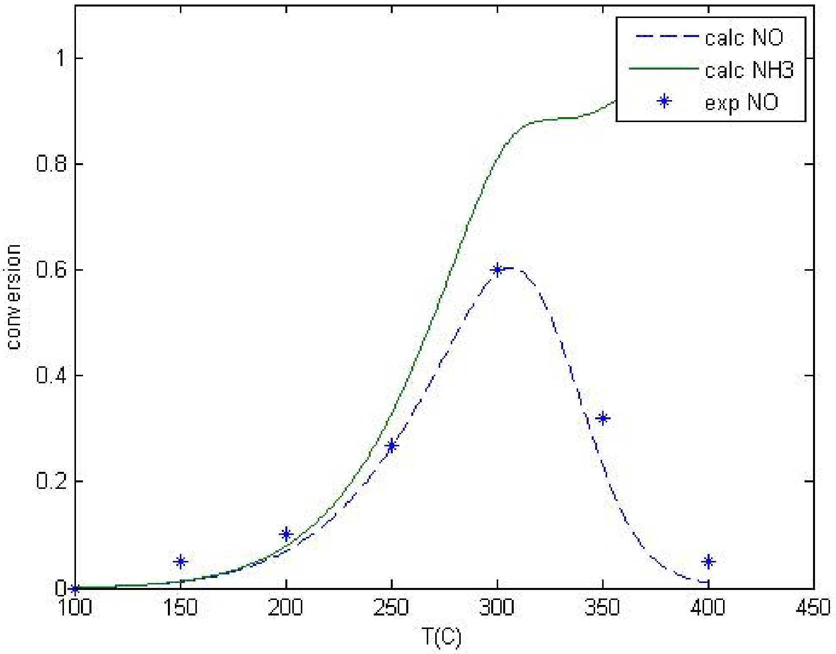


Fig. 1. Results of fitting procedure in modelvalidation, experimentaldata from plug flow reactor

Kinetic parameter	*Estimated value*	*Unit*
k_1	1×10^6	s^{-1}
k_2	6.8×10^7	s^{-1}
E_1	60	$kj\ mol^{-1}$
E_2	80	$kj\ mol^{-1}$
A	-243	$kj\ mol^{-1}$
a_0	2.68×10^{-17}	$m^3\ mol$

3. Results and discussion

Values for the reaction rates according to Eqs. (3) and (4), calculated for inlet concentration values, are shown in Fig. 3. The maximum in r_1 reflects the fact that above 380°C the NH_3 term (associated with adsorption of NH_3 on the catalyst surface) begins to decrease considerably.

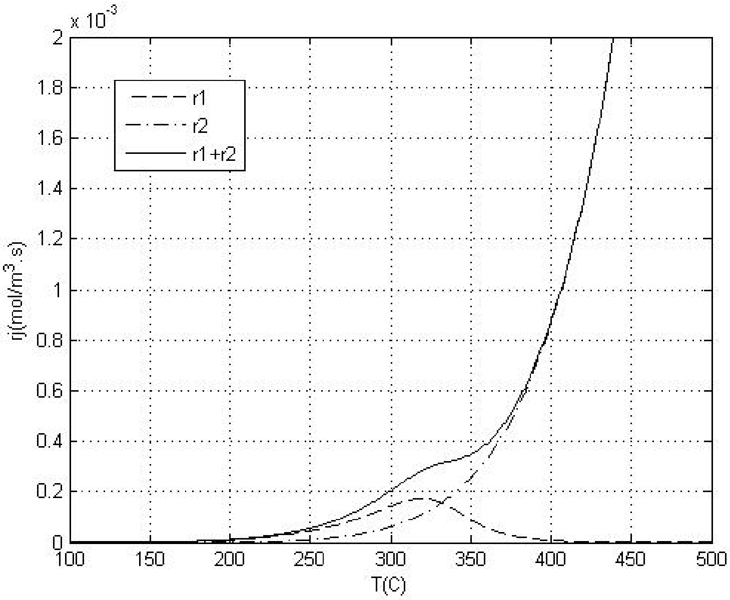
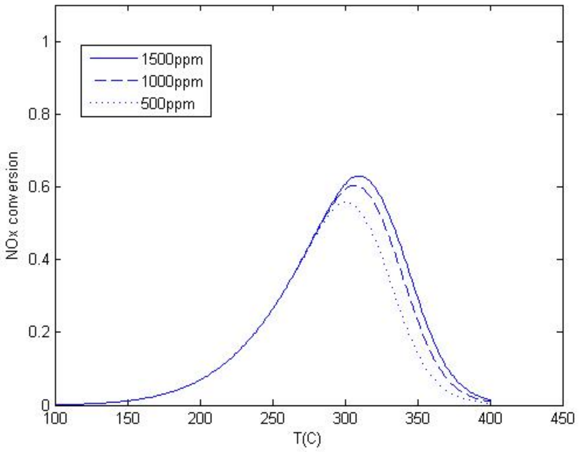


Fig.2. Calculated values of reaction rates r_1 and r_2 for inlet Concentrationvalues, conditions: seeFig. 1

An available mathematical model was used to calculate NO and NH_3 concentrationProfiles in the catalyst walls of a plug flow reactor structure and the efficiency factors in the catalyst, asvarying with temperature.



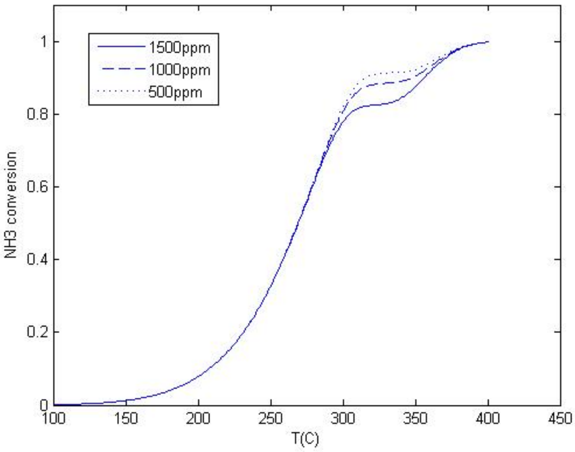


Fig. 4. Effect of inlet concentrations, conditions: seeFig. 1andTable 1

3. Conclusion

The present kinetic study based on experimental data with a plug flow reactor leads to the following conclusions: (a) according to the calculated results, NO conversion of 60-72% is possible on time scales of gas flow through the plug flow reactor for temperatures around 300°C, (b) A strongtemperature effect can be explained by means of a competition of two NH_3-consuming reactions, the desired SCR reaction and the undesired NH_3oxidationwith O_2, (c) The selectivity and concentration variation in the reactor have been studied. The NO_x conversion efficiency increases with increasing NO concentration and decreasing NH_3 concentration.(d) Also, the reaction rates in the reactor was studied. The obtained results indicated that reaction rate of NO increases from 290 to 330°C

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