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Chapter 10

Kinetic study of a simple chemical reaction

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1. Introduction

In this chapter the kinetic study of the oxidation of SO_2 to SO_3 as an example of a simple chemical reaction is illustrated with special emphasis on the following points: (i) identification of the experimental variable space; (ii) derivation of a rate expression for the chemical kinetics; (iii) experimental design for parameter estimation; (iii) statistical regression analysis.

The selective catalytic reduction (SCR) of nitrogen oxides with ammonia is widely used for the control of NO_x emission in flue gases from thermal power plants [1]. The process is based on the following reaction:

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

but in the case of S-containing fuels reaction (1) occurs simultaneously with the undesired SO_2 oxidation reaction:

$$SO_2 + 1/2O_2 \rightarrow SO_3 \qquad (2)$$

Commercial catalysts consist of homogeneous mixtures of anatase TiO_2 as a high surface area support, V_2O_5 and WO_3 as the active components, and of silico-aluminates as mechanical promoters. The catalysts are employed in the form of monoliths or plates and are required to exhibit high deNO_x activity, good stability and S-resistance, and low activity in the oxidation of SO_2. Typical industrial process specifications include NO_x reduction efficiencies ≥ 80% with ammonia slip of 1–5 ppm and SO_2 conversions lower than 1–2% [2]. The low admissible levels of NH_3 slip and SO_2 oxidation are due to the fact that SO_3, either produced through the oxidation of SO_2 or already present in the flue gases, is known to react with NH_3 to give ammonium sulfates [NH_4HSO_4 and $(NH_4)_2SO_4$] which may deposit on the cold equipment downstream of the reactor causing corrosion and pressure drop problems.

In the following I will discuss the results of a systematic study that was recently undertaken in our laboratories with the aim of clarifying, on qualitative and quantitative bases, the effects of operating conditions, feed composition and catalyst design parameters on the oxidation of SO_2 to SO_3 over honeycomb V_2O_5-WO_3/TiO_2 deNO_xing catalysts [3].

2. Identification of the experimental variable space

The variables of interest in a kinetic study are those of relevance for the reaction under investigation. If the kinetic equation is derived for reactor design and analysis the experimental space can be limited to the conditions of industrial interest; on the contrary if a fundamental approach is attempted a wider experimental variable space is usually considered. Catalyst design parameters can also be investigated if

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optimal catalyst design is addressed. In any case it is most desired that the kinetic investigation relies on a detailed knowledge of the physicochemical characteristics of the catalyst under study.

In the case of SO_2 oxidation, based on previous knowledge of the SCR process and of the catalysts performances, the following variables and associated experimental variable space have been considered:

Reactor temperature, from $\approx 300°C$ to $\approx 400°C$. This corresponds to the temperature range of the SCR process, the lower and upper temperature limits being due respectively to condensation of ammonium sulfates within the catalyst pores which causes reversible catalyst deactivation and to low process selectivity because of both direct oxidation of ammonia and high SO_3 production.

Pressure, atmospheric. The choice of honeycomb or plate type catalysts is essentially motivated by the very low pressure drop associated with their use.

Area velocity, from 4 to 33. The area velocity AV is defined as $AV = Q/(V_c a)$, where Q is the reactant flow rate in N m^3/h, V_c is the volume of the catalyst sample, and a is the catalyst geometric (outer) surface area per unit volume, in m^2/m^3. Notice that V_c includes both the volumes of the ceramic catalytic material and of the empty channels of the catalyst. AV $\times a$ can be regarded as the 'contact time' for the SCR process, considering that the $deNO_x$ reaction is confined to the external geometric surface of the catalyst because of strong intraparticle diffusional limitations [4]. In the case of SO_2 oxidation not only the outer surface but the entire volume of the ceramic catalytic material participates to the reaction and accordingly contact time must be evaluated with respect to the volume of the catalytic material and not to the catalyst geometric surface area.

SO_2 concentration, from 60 to 1750 ppm. The upper SO_2 concentration corresponds to $\approx 3\%$ by weight S content in the fuel.

O_2 concentration, from 0.125 to 6% v/v. The O_2 content in flue gas is typically of a few percents.

H_2O concentration, from 2.5 to 10% v/v. The water content in flue gas depends on the fuel and is higher in the case of natural gas because of the higher H/C ratio.

NO concentration, from 0 to 1000 ppm. The NO concentration depends on the fuel, the type of boiler and whether primary measures have been applied to reduce the formation of NO_x during combustion.

NH_3 concentration, from 0 to 75 ppm. Although NH_3/NO_x inlet molar ratios of 0.8 are typically employed in practice one must consider that ammonia is consumed according to the $deNO_x$-SCR reaction that is a very fast reaction, that steep ammonia gradients are present and confined to the outer surface of the catalyst, and that ammonia strongly inhibits the SO_2 oxidation so that an asymptotic behavior is already manifest at 75 ppm under the investigated experimental conditions.

Honeycomb catalysts with different V_2O_5 content and different thickness have been investigated to clarify the dependence of SO_2 conversion on these two characteristics of the catalyst.

3. Transient effects during SO_2 oxidation

To obtain significant and reproducible results in the oxidation of SO_2 to SO_3 the catalyst must be conditioned. The conditioning procedure implies operation at the reaction temperature with gaseous mixtures containing sulfur dioxide, oxygen, water and nitrogen as a balance. Fig. 1 shows the results of a typical conditioning experiment: the concentration of SO_3 at the reactor exit increases with time until a steady state level is approached. When the flow of sulfur dioxide is stopped the concentration of SO_3 decreases slowly, indicating that SO_3 is released from the catalyst. If the SO_2 supply is resumed the outlet concentration of SO_3 gradually recovers its original value.

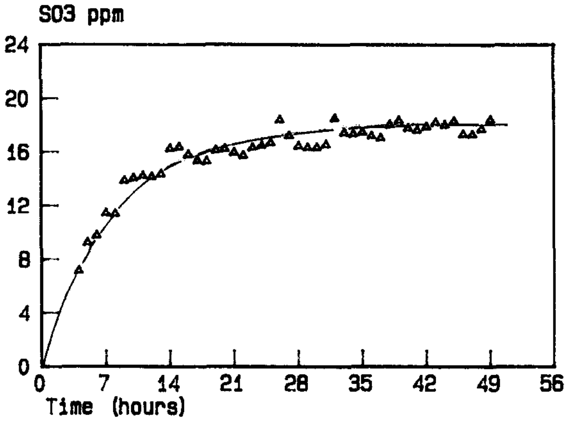

Fig. 1. Results of a typical conditioning experiment.

These data prove that the conditioning of the catalyst is associated with a slow process of build up of metal oxide sulfates onto the catalyst surface (it may last for several hours up to ≈ 70 hs depending on the experimental conditions and on catalysts) and proceeds until a steady state concentration of metal oxide sulfates is reached. The steady state concentration of sulfates appears to be limited by the formation–decomposition equilibrium of metal oxide sulfates via SO_3 adsorption–desorption processes.

Transient effects were also observed after changing the experimental conditions and particularly the reaction temperature and the SO_2 concentration: they can also be interpreted in terms of adsorption–desorption processes of SO_3 and typically lasted for several hours.

The transient effects observed in SO_2 oxidation can be explained by a progressive saturation of the catalyst surface by SO_3 with a virtually constant rate of SO_2 oxidation (i.e. a constant number of active sites) throughout during catalyst conditioning and upon modifying the experimental settings or alternatively by a change with time of the concentration of the active sites due to the reaction. The active sites, as discussed below and in line with the well consolidated picture of active sites in commercial sulfuric acid catalysts [5,6], are envisaged as oxidized sulfated binuclear vanadyl centers. Unfortunately, discrimination between the two above hypotheses was prevented by the impossibility of obtaining reliable direct measurements of the low SO_2 conversions (< 2–3%). SO_3 concentration in the product gas were determined through condensation of sulfuric acid at 90°C followed by analysis by ionic chromatography.

4. Relevance of interphase and intraparticle resistances

Diagnostic calculations performed by invoking the analogy with the Graetz–Nusselt heat transfer problem to compute interphase mass transfer coefficients for SO_2 [7,8] showed that negligible SO_2 concentration gradients are present at the gas–solid interface; likewise, also intraporous limitations can be neglected on the basis of the Weisz–Prater criterion [9], since the SO_2 oxidation reaction is considerably slower than SO_2 diffusion in the catalyst pores. The absence of intraporous effects has also been proved experimentally by operating over a catalyst ground to 8–14 mesh. Comparable SO_2 rates of reaction have been measured over the ground catalyst and over the honeycomb catalyst. The data have been analyzed considering a first order kinetic dependence of SO_2 (see below) to account for the higher pressure (pressure drop > 1 atm) experienced when operating over ground catalyst.

It can be concluded that the process is controlled by the chemical reaction, which is indeed in line with the very low measured SO_2 conversions. Accordingly kinetic data in a chemical regime can be collected by operating directly over honeycomb catalysts.

5. Design of kinetic experiments

Statistical techniques in the design and analysis of experiments have been proposed in the literature [10] to cope with the problems of: (i) the selection of the best model among a set of plausible models; (ii) the efficient estimation of the parameters in the selected model.

Basically these techniques result in factorial designs, fractional factorial designs, sequential factorial designs as well as more sophisticated designs [11]. It is worth noting that the above designs are intended to provide a uniform exploration of the variable space and, in the case of linear models, they also result in straightforward analytical estimates of the parameters. The first point is certainly of relevance to guarantee the representativity of the model. The second point is no longer critical nowadays since efficient regression programs are available; besides the use of linear models is not appropriate for kinetic purposes.

The alternative classical approach is based on the study of the effects of one variable at a time. This approach provides a less uniform exploration of the variable space but it makes possible the direct comparison and analysis of the data, that can lead to the identification of unreliable results and of the physico-chemical implications associated with the effects of the investigated variables.

An important point, common to any approach in the design of experiments, is to make replicate genuine experiments that allow to obtain an estimate of the experimental error variance which is independent of the assumed mathematical model.

In the kinetic study of SO_2 oxidation the parameters were varied one at a time to study separately the effects of the variables.

The results show that:

(1) A first order dependence on SO_2 provides a reasonable approximation in the range 0–1000 ppm SO_2, in line with several technical reports [12]. Still an apparent kinetic order in SO_2 slightly higher than 1 for low SO_2 concentrations (< 200 ppm) and a inhibiting effect of SO_2 at high SO_2 concentration are apparent.

(2) The rate of reaction is almost independent of oxygen concentration above 0.5–1% v/v oxygen levels, due to the excess of oxygen. A dependence becomes manifest only for O_2 concentrations comparable to those of SO_2 (≈ 1000 ppm $= 0.1\%$ v/v), as expected.

(3) SO_2 conversion is depressed upon addition of water: the inhibiting effect of water is apparent at low water concentrations and levels off above 5% v/v water content. The inhibition of water is likely explained in terms of reversible blockage of vanadyl sulfate active sites.

(4) The oxidation of SO_2 is slightly enhanced by NO_x. This is possibly related to the contribution of the gas phase oxidation of SO_2 by NO_x, which is known to take place in the chamber process for the production of sulfuric acid. Alternatively NO_x might favor a more oxidized steady state level of the catalyst, which would imply a greater activity in SO_2 oxidation.

(5) The addition of ammonia to the reaction mixture strongly inhibits the oxidation of SO_2: in the presence of 75 ppm NH_3 the activity is markedly reduced and an asymptotic behavior is already manifest. When the flow of ammonia is stopped the original activity is almost completely restored within few hours. This eventually indicates that the active sites for the oxidation of SO_2 are deactivated but not destroyed upon adsorption of ammonia. The presence of a residual activity level at 75 ppm NH_3 suggests that the oxidation of SO_2, although to a more limited extent, occurs over sites that are not deactivated in the presence of ammonia as well; these sites could be possibly envisaged as W surface sites that are known to be less active in SO_2 oxidation and that show a lower tendency to sulfation.

(6) The data collected by varying AV obey the following equation:

$$k_{SO_2} = -\frac{Q}{V_c^*}\frac{T}{273^*}\ln(1 - x_{SO_2}) \qquad (3)$$

Eq. (3) assumes a simplified plug-flow reactor model, and a rate equation first order in SO_2 and zero order in O_2 in line with the results previously discussed. In Eq. (3) k_{SO_2} represents the pseudo-first order rate constant of SO_2 oxidation and x_{SO_2} is the conversion of SO_2. Eq. (3) implies that the inhibiting effect of water vapor is incorporated into the kinetic rate constant k_{SO_2}, and that the whole volume of the ceramic catalytic material participates effectively in the reaction due to the absence of intraparticle diffusional limitations.

(7) The SO_2 conversion increases linearly with wall thickness in catalysts with comparable medium vanadia content, in line with the conclusion that the overall process is controlled by the chemical reaction.

(8) The conversion of SO_2 to SO_3 increases more than linearly with the Vanadia loading. This indicates that the oxidation of SO_2 depends primarily on the Vanadia content and that it can be properly controlled by using catalysts with low Vanadia loading. As a matter of fact the V_2O_5 content in commercial DeNO$_x$-SCR catalysts is typically lower than 1.5–2% w/w and is selected in view of the S content in the fuel. It is worth mentioning that in the case of commercial sulfuric acid catalysts it has been proposed that the active sites are constituted by dimeric vanadyl species [5,6], which would imply a second order dependence of the SO_2 oxidation rate constant k_{SO_2} on the V content.

(9) Apparent activation energies in the range 15–25 Kcal/mol have been calculated that are consistent with an overall process controlled by the chemical reaction, in contrast with deNO$_x$ reaction where apparent activation energies as low as ≈ 5 Kcal/mol were typically measured [13].

6. Derivation of the kinetic equation

The reported effects of the different operating and design variables can be reconciled on qualitative and quantitative bases according to a comprehensive kinetic equation as detailed below.

The active sites for the oxidation of SO_2 to SO_3 are identified with dimeric vanadyl sulfates and their surface concentration can be modelled assuming adsorption equilibrium:

$$[V_2 - SO_3]_{ox} = K_{SO3}C_{SO3}[V_2]_{ox} \tag{4}$$

where $[V_2\text{-}SO_3]_{ox}$, $[V_2]_{ox}$ and K_{SO3} represent the steady state concentrations of sulfated and not sulfated oxidized dimeric vanadyl sites and the equilibrium constant for SO_3 adsorption, respectively.

The inhibition of water and ammonia is accounted for by assuming adsorption equilibria at the vanadyl sulfates:

$$[V_2 - SO_3 - H_2O]_{ox} = K_{H_2O}C_{H_2O}[V_2 - SO_3]_{ox} \tag{5}$$

$$[V_2 - SO_3 - NH_3]_{ox} = K_{NH_3}C_{NH_3}[V_2 - SO_3]_{ox} \tag{6}$$

$[V_2\text{-}SO_3\text{-}H_2O]_{ox}$ and $[V_2\text{-}SO_3\text{-}NH_3]_{ox}$ represent the steady state concentrations of the sites poisoned through adsorption of water and of ammonia, and K_{H_2O} and K_{NH_3} stand for adsorption equilibrium constants.

Under the experimental conditions typical of the SCR process the rate of SO_2 oxidation appears to be independent of oxygen partial pressure and first order in SO_2 (at low SO_2 concentrations a kinetic order slightly higher than 1 is apparent however). Accordingly it can be assumed that the reaction proceeds through a redox mechanism, where SO_2 is first adsorbed at a sulfated dimeric Vanadium site. Assuming adsorption equilibrium we obtain:

$$[V_2 - SO_3 - SO_2]_{ox} = K_{SO_2}C_{SO_2}[V_2 - SO_3]_{ox} \tag{7}$$

The adsorption of SO_2 is followed by a slow step involving reduction of the vanadium site accompanied by the evolution of SO_3:

$$[V_2 - SO_3 - SO_2]_{ox} \rightarrow [V_2 - SO_3]_{red} + SO_3 \tag{8}$$

Finally reoxidation of the catalytic site results in the regeneration of the active sites:

$$[V_2 - SO_3]_{red} + 1/2O_2 \rightarrow [V_2 - SO_3]_{ox} \tag{9}$$

By requiring that the rate of catalyst reduction equals the rate of reoxidation, we obtain a relation between the steady state concentration of oxidized and reduced dimeric vanadyl sites:

$$[V_2-SO_3]_{red} = k_{red}[V_2-SO_3-SO_2]_{ox} k_{ox} C_{O_2} 1/2 \qquad (10)$$

k_{red} and k_{ox} in Eq. (10) stand for the rate constants of the reduction and reoxidation steps.

The site balance equation

$$[V_2]_{ox} + [V_2-SO_3]_{ox} + [V_2-SO_3]_{red} + [V_2-SO_3-SO_2]_{ox} + [V_2-SO_3-H_2O]_{ox} + [V_2-SO_3-NH_3]_{ox} = C_{tot} \qquad (11)$$

upon substitution from Eqs. (4)–(7) and (10) yields:

$$[V_2]_{ox} = C_{tot}/\left\{1 + K_{SO_3}C_{SO_3}\left[1 + K_{SO_2}C_{SO_2} \times \left(1 + k_{red}/\left(k_{ox}C_{O_2}1/2\right)\right) + K_{H_2O}C_{H_2O} + K_{NH_3}C_{NH_3}\right]\right\} \qquad (12)$$

C_{tot} represents the concentration of total active sites. Notice that C_{tot} is proportional to the square of the vanadia content in the catalyst since active sites involve dimeric vanadyl species.

Upon imposing that the rate of reaction equals the rate of catalyst reduction (8)

$$r_{SO_2} = r_{red} = k_{red}[V_2-SO_3-SO_2]_{ox} \qquad (13)$$

substituting for $[V_2\text{-}SO_3\text{-}SO_2]_{ox}$, introducing an empirical term $(1 + bC_{NO_x})$ in the numerator to account for the promoting effect of NO_x, and adding an empirical term $k_{SO_2}C_{SO_2}$ to account for the residual activity observed at 75 ppm NH_3 we eventually obtain:

$$r_{SO_2} = \left[\left(k_{red}K_{SO_2}K_{SO_3}C_{tot}\right)C_{SO_2}C_{SO_3} \times \left(1 + bC_{NO_x}\right)\right]/\left\{1 + K_{SO_3}C_{SO_3} \times \left[1 + K_{SO_2}C_{SO_2}\left(1 + k_{red}/\left(k_{ox}C_{O_2}1/2\right)\right) + K_{H_2O}C_{H_2O} + K_{NH_3}C_{NH_3}\right]\right\} + k_{SO_2}C_{SO_2} \qquad (14)$$

Eq. (14) has been used to analyze the experimental data collected at $T = 380°C$ by varying AV and the concentrations of SO_2, H_2O, O_2, NH_3 and NO_x.

It is worth stressing that a more simple rate equation can be used if the variable space of interest is more limited as it occurs in industrial practice. Accordingly a simple rate equation with a first order dependence in SO_2 and zero order dependence in O_2 is typically employed for technical purposes. Indeed the effects of H_2O and O_2 vanish for $C_{H_2O} > 5\%$ and $C_{O_2} >$ 1–2% whereas most of the catalyst volume in the SCR reactor does not experience the inhibiting effect of NH_3 because of the consumption of NH_3 according to the deNO$_x$ reaction and of the excess of NO_x.

7. Parameter estimation

The data were analysed according to the following plug flow reactor model:

$$Q dC_{SO_2}/d[(1-\epsilon)V_c] = -r_{SO_2} \qquad (15)$$

where ϵ is the catalyst void fraction. Integration of Eq. (15) provides the concentration of SO_2 at the reactor outlet. In spite of the very low conversion of SO_2 this integral approach is required to account for the variable SO_3 concentration along the axial coordinate.

The parameter estimation was performed by using the non-linear regression routine BURENL [14] which minimizes the residual sum of squares of the deviations between the experimental response C_{SO_2} at the exit of the reactor and the model prediction C'_{SO_2}:

$$SSE = \sum_{1\ i}^{N} \left(C_{SO_2,i} - C'_{SO_2,i}\right)^2 \qquad (16)$$

where N is the total number of experiments ($N = 30$). To favor convergence of the minimization procedure Eq. (14) has been subjected to reparameterization as follows:

$$r_{SO_2} = \left[k_1 C_{SO_2} C_{SO_3}(1 + k_2 C_{NO_x})\right] \Big/ \left[1 + k_3 C_{SO_3} + k_4 C_{SO_3} C_{SO_2} + k_5 C_{SO_3} C_{H_2O} + k_6 C_{SO_3} C_{NH_3} + k_7 C_{SO_3} C_{SO_2} / C_{O_2} 1/2\right] + k_8 C_{SO_2} \quad (17)$$

The regression routine provides the following results:

the parameter estimates along with their 95% confidence limits;

the variance–covariance and the correlation matrix of the parameter estimates. Values of the correlation index close to 1 indicate a strong correlation between the parameter estimates;

the minimized value of SSE. The number of degrees of freedom associated with SSE is $N - p = 23$, where p is the number of parameters in the model. In our case $p = 7$, considering that the value of k_3 has been fixed since it was found to be strongly correlated to the other parameters;

the sum of squares due to experimental error evaluated from 6 replicated experiments:

$$\mathrm{SSEE} = \sum_{1\ i}^{6} \left[C_{SO_2,i} - \left(C_{SO_2,i}\right)_{av}\right]^2 \quad (18)$$

where $(C_{SO_2,i})_{av}$ is the average value of C_{SO_2} in the 6 replicated experiments. Accordingly MSEE = SSEE/5 provides an estimate of the experimental error variance with 5 degrees of freedom;

the sum of squares due to lack of fit:

$$\mathrm{SSLF} = \sum_{1\ i}^{N-5} \left[\left(C_{SO_2,i}\right)_{av} - C'_{SO_2,i}\right]^2 \quad (19)$$

where $N - 5$ is the number of distinct experimental points in the variable space. Under the null hypothesis that the model is locally correct (expected value of $(C_{SO_2,i})_{av}$ = expected value of $C'_{SO_2,i}$ = value of the correct model at point i) MSLF = SSLF/$(N - 5 - p)$ represents an independent estimate of the experimental error variance with $N - 5 - p = 18$ degrees of freedom;

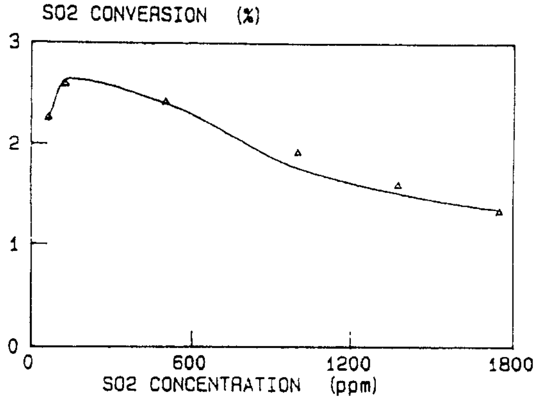

Fig. 2. Effect of SO_2 concentration.

the realisation of t = MSLF/MSEE = 1.39. This value can be used to perform the model adequacy test considering that t is distributed as $F(18,5)$ under the null hypothesis that the model is locally correct. The comparison between the realization of t and $F(18,5,0.95) = 4.53$ leads to accept the null hypothesis. It is worth stressing in this respect that statistical tests never prove the correctness of the null hypothesis; rather they provide evidence that there is no statistically significant indication against the null hypothesis. Accordingly statistics can provide rigorous mathematical methods for the estimation of the model parameters and for comparing experimental results and model predictions but still a careful and deep physico-chemical investigation of the reaction under study is needed to

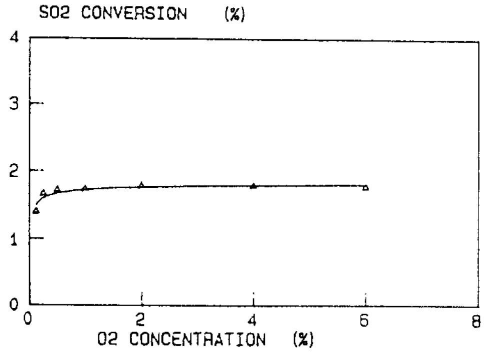

Fig. 3. Effect of O_2 concentration.

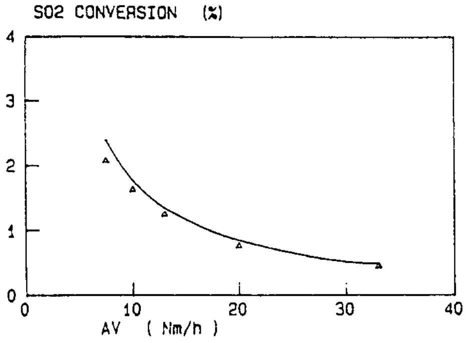

Fig. 4. Effect of AV.

arrive at a reliable and representative kinetic model;

the experimental response, the calculated model response, the percent error, the absolute error, the mean percent error and the mean absolute error. In our case the mean percent error was 3.79.

The statistical analysis of the regression results can be completed with the analysis of the residuals that are expected to show a random distribution under the null hypothesis. This has been verified in the present case.

Figs. 2–4 illustrate the effects of SO_2 and O_2 concentrations and of AV. They demonstrate the good agreement obtained between model predictions and experimental results.

Based on the values of the parameters and considering the typical concentrations of the reagents the following order was derived for the concentration of the different surface species:

$$
\begin{aligned}
&[V_2-SO_3-H_2O]_{ox}\\
&\quad\approx[V_2-SO_3-NH_3]_{ox}\\
&\quad>[V_2-SO_3-SO_2]_{ox}\\
&\quad\approx[V_2-SO_3]_{ox}\approx[V_2-SO_3]_{red}
\end{aligned}
$$

8. Conclusions

The kinetic study on the oxidation of SO_2 to SO_3 over honeycomb $deNO_x$-SCR catalysts provides a representative example of the stages that can be encountered during a kinetic investigation of a simple chemical reaction. The oxidation of SO_2 represents a simple case since the reacting system is constituted by a single reaction occurring in a chemical regime. The main steps of the kinetic study are:

(i) the identification of the variables of interest and of their experimental space that depend heavily on the motivation of the study;

(ii) the investigation on the presence and relevance of diffusional limitations. Kinetic data must always be collected if possible under conditions free from diffusion limitations;

(iii) the design of the kinetic experiments. Again the motivation of the study can result in the preference for a specific design strategy (e.g. sequential factorial designs against conventional designs);

(iv) the derivation of the rate expression of the chemical kinetics. It is most desired that the derivation of the rate equation relies on a detailed knowledge of the physico-chemical characteristics of the catalyst and of its catalytic performances;

(v) the parameter estimation with the associated statistical analysis of the regression results.

Acknowledgements

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References

[1] H. Bosch and F. Janssen, Catal. Today, 2 (1988) 369.
[2] EPA/EPRI 1989 Joint Symposium on Stationary Combustion NO_x Control, San Francisco, 6–9 March, EPA Research, Triangle Park, NC, 1989.
[3] J. Svachula, L.J. Alemany, N. Ferlazzo, P. Forzatti, E. Tronconi and F. Bregani, Ind. Eng. Chem. Res., 32 (1993) 826.
[4] E. Tronconi, P. Forzatti, J.P. Gomez Martin and S. Malloggi, Chem. Eng. Sci., 47 (1992) 2401.

[5] B.S. Balzhimaev, V.E. Ponomarev, N.P. Belyaeva, A.A. Ivanov and G.K. Boreskov, React. Kinet. Catal. Lett., 30 (1986) 23.

[6] A.R. Glueck and C.N. Kenney, Chem. Eng. Sci., 23 (1968) 1257.

[7] R.D. Hawthorn, AIChE Symp. Ser., 137 (1974) 428.

[8] E. Tronconi and P. Forzatti, AIChE. J., 38 (1992) 201.

[9] G.F. Froment and K.B. Bishoff, Chemical Reactor Analysis and Design, Wiley, New York, 1979.

[10] D.M. Himmelblau, Process Analysis by Statistical Methods, Wiley, New York, 1970.

[11] P. Forzatti and E. Tronconi, Programmazione della Sperimentazione Industriale Chimica, CLUP, Milano, 1989.

[12] EPA/EPRI 1991 Joint Symposium on Stationary Combustion NO_x Control, Washington, DC, 25–28 March, EPA Research, Triangle Park, NC, 1991.

[13] J. Svachula, N. Ferlazzo, E. Tronconi, P. Forzatti and F. Bregani, Ind. Eng. Chem. Res., 32 (1993) 1053.

[14] G. Buzzi-Ferraris, Proceedings of the Congress on the Use of Computers in the Studies Preceding the Design of Chemical Plants, Florence, 1970.