Available online at www.sciencedirect.com

Catalysis Today 112 (2006) 174–179

www.elsevier.com/locate/cattod

Dynamics of SO_2 adsorption–oxidation in SO_x traps for the protection of NO_x adsorbers in diesel engine emissions☆

Gabriele Centi, Siglinda Perathoner *

Department of Industrial Chemistry and Engineering of Materials[1], University of Messina, Italy

Abstract

The SO_2 uptake behaviour at different temperature and SO_2 concentration of a reference SO_x trap is studied in a thermobalance apparatus and in a flow reactor under reaction conditions close to those in the emissions from a diesel engine. The data of the latter apparatus are also kinetically modelled to derive which controlling regime dominates the performances. The results evidence that at 200 °C the behaviour is largely controlled by the slow solid-state diffusion of the sulphate species, while above 300 °C there is an initial region controlled by the surface reaction, although for levels of SO_2 uptake above a weight increase of 4–5% (due to sulphation) the solid-state diffusion dominates the performances also at high temperature.

Keywords: SO_2 adsorption; Thermobalance apparatus; SO_x trap; SO_2 sorbents

1. Introduction

The lowering of sulphur content in diesel fuel has made attracting the possibility to eliminate the residual sulphur from the emissions prior the NO_x-adsorber (often indicated also as NO_x-storage reduction catalyst or NO_x trap) using a SO_x trap [1–5]. If the SO_x concentration in the emissions can be completely eliminated there is no need for this periodic regeneration which increase fuel consumption and creates problems in the engine management. But even if it is not possible to reach virtually S-free conditions in the emissions, there are still benefits, because the periodic regeneration can be made in less severe conditions (in terms of time and temperature, and λ value, e.g. air to fuel ratio). Decreasing the severity of regeneration and/or their frequency, decreases (i) the fuel consumption and (ii) the formation of side toxic products (H_2S and COS) and increases (iii) the durability of the NO_x-adsorber due both to a reduction in the fraction of noble metal irreversibly deactivated (due essentially to the formation of PtS like species) and to a lower sintering rate.

While for sulphur contents in the fuel of 50 ppm or above, it was not possible to consider the possibility of a SO_x trap (SO_x traps periodically regenerated in situ were necessary, but their management is too complex), with the new fuels commercially available with sulphur content of 10 ppm, it is possible to consider a SO_x trap disposable or ex situ regenerable which can operate for about 20,000 km. For e.g., a typical medium distance of 1 year for a car. The requested SO_x trapping capacity, of the order of 14 g sulphur (for a 10 ppm fuel) per monolithic trap, means that the SO_x trap should operate efficiently (e.g. remove over 80% of the SO_x) up to high levels of sulphation (corresponding to at least 20% of weight increase, considering an amount of trapping component of about 200 g per monolithic trap). Currently available state-of-the-art SO_x traps have still not sufficient performances. New materials should be developed which combine very active surface sites (able to adsorb and oxidize to SO_3 the SO_2 present in low concentrations) to a fast bulk transport of the sulphate in order to maintain the rate of SO_2 capture even at high storage levels. The design of novel materials requires to understand and kinetically model the dynamics of SO_2 adsorption–oxidation and SO_x storage and relate these aspects to the catalyst nature and texture at the nano-scale level.

☆ Work realized in the frame of the activities related to the Coordination Action CONCORDE (Coordination of Nanostructured Catalytic Oxides Research and Development in Europe) supported from the European Union (6FP).

* Corresponding author. Tel.: +39 090 6765609; fax: +39 090 391518.
E-mail address: perathon@unime.it (S. Perathoner).

[1] ELCASS (European Laboratory for Catalysis and Surface Science), and UdR of INSTM (Consortium for the Science and Engineering of Materials), Salita Sperone 31, 98166 Messina, Italy.

0920-5861/\$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.11.078

Limited studies has been reported in the literature on SO_x traps. Li and King [6] have studied SO_2 adsorbents based on manganese oxide octahedral molecular sieves. Limousy et al. [7] have analyzed the performances of commercial cordierite-type monoliths (the washcoat contains noble metals, Ba, Cr, Zr as the key component). Wang et al. [8] have investigated Mg–Fe–Al–O mixed oxide with spinel structure. Dathe et al. [9] have analyzed MCM-22, MCM-36 and ITQ-2, loaded with a SO_x storage component (Ba, Al, Mg) by impregnation or pillaring. Iretskaya et al. [10], Hao et al. [11] and Centi et al. [12,13] have investigated copper-on-alumina sorbents. In order to contribute to the understanding of this issue we have investigated a reference (state-of-the-art) SO_x trap using both a thermogravimetric method (often used to analyze the performance of SO_x traps) and flow reaction studies in reaction conditions close to application, using a suitable kinetic modelling of the latter data to obtain a better insight of the kinetically controlling regime.

2. Experimental

2.1. Materials

The reference SO_x trap used was supplied from Johnson Matthey (Royston, UK) and contains 2% Pt, besides alkaline and/or alkaline-earth metals as SO_x trapping agent and a mixed oxide as the support. The sample can be considered as a state-of-the-art SO_x trap. The surface area is about 115 m^2/g.

2.2. Reactivity tests: thermobalance

Screening of the performances of the SO_x traps was made in a thermobalance (TG) flow apparatus (TGA Q50 from TA Instruments) characterized by a tangential flow of the reactive gas just above the pan containing about 10 mg of the sample in the form of powder. The experiments were typically made under isothermal conditions, after pre-treatment of the sample at 600 °C to fully eliminate adsorbed substances. The catalyst is then cooled down up to the requested temperature in a flow of N_2, and after reaching a constant weight, the flow is switched from N_2 to air containing 0.1% SO_2, monitoring the change of weight as a function of the time on stream.

2.3. Reactivity tests: breakthrough curves

Breakthrough curves of SO_2 uptake were determined in a flow reactor apparatus formed by (i) a section of feed control, (ii) a quartz tubular reactor of internal diameter of about 10 mm in which the SO_x trap, in the form of about Ø 0.1 mm grains (40 mg), is put in the middle between two glass–wood layers; and (iii) a section of on-line continuous analysis by a FTIR apparatus with a gas cell having about 10 m of (multiple) path length (total volume of the cell is 0.7 l). The SO_2 bands at 1346 and 1369 cm^{-1} were monitored. The tests were made at a space-velocity of 150,000 h^{-1}. The feed composition was the following: 10 or 20 ppm SO_2, 11% CO_2, 5% O_2, remaining N_2.

3. Results and discussion

3.1. Thermogravimetric tests

In inset of Fig. 1 the SO_2 uptake curves determined at 150, 300 and 450 °C in the TG apparatus are reported, while in main Fig. 1 an elaboration of these data in terms of dependence of the rate of SO_2 uptake from the total SO_x uptake, e.g. the weight increase in the sample due to adsorption of SO_3, is presented. In fact, SO_2 is fast oxidized to SO_3 in this sample due to the presence of 2% Pt. The adsorption is irreversible, as shown from tests stopping the flow of SO_2, and thermodesorption curves after these SO_2 uptake tests indicate that clearly mainly sulphate species are present. This is confirmed also by FTIR characterization of the samples after sulphation.

Increasing the reaction temperature, an increase in the initial rate of SO_2 uptake is observed, while the rate progressively decreases on increasing the amount of adsorbed SO_3 (a weight increase of 10% corresponds to 1.25 mmoles of SO_3 adsorbed per gram of SO_x trap). Even for a reaction temperature of 450 °C, the rate of SO_2 uptake drops to very low values above a weight increase of about 10%. This amount does not corresponds to sorbent saturation, because, for example, in Cu–Al mixed oxides obtained from hydrotalcite precursors and having comparable surface area, the rapid drop in the rate of reactions occurs for a weight increase about four times higher. In addition, the complete $Al_2O_3 \rightarrow Al_2(SO_4)_3$ transformation corresponds to a weight change of 235 wt.%, therefore about 23 times higher than the limit observed in our SO_x trap. The change in the rate of weight increase above this 5–10 wt.% threshold (depending on the reaction temperature), thus derives from a change in the kinetic regime of SO_2 uptake, e.g from a surface adsorption control to a bulk diffusion control.

Due to the different fluidodynamics and feed composition between those in the TG apparatus and those present under practical conditions of application (e.g. a monolith in contact

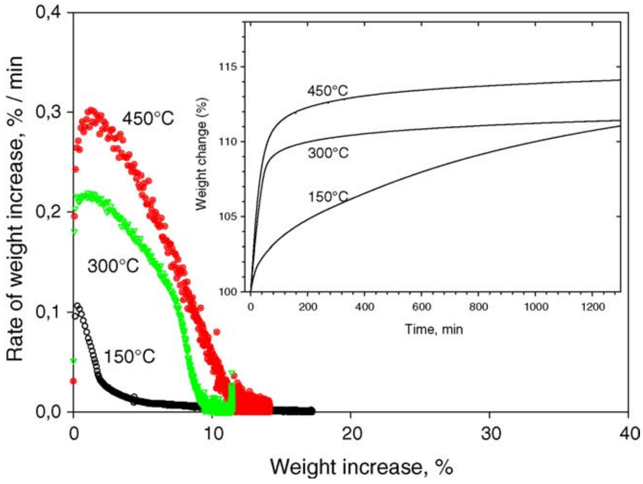

Fig. 1. Rate of weight increase vs. weight increase obtained by elaborating TG data shown in the inset (SO_2 isothermal uptake curve at different reaction temperature).

with the exhaust gases from a diesel engine), it is not possible to hypothesize the controlling kinetic regime in the latter case, and therefore determine which aspect should be primarily considered in the TG curves. In other words, if the first part of the TG curves at low degree of sulphation (mainly controlled from surface reaction) or the end part of the TG curves (at high sulphation degree, controlled by solid-state diffusion).

For the selection of new materials as SO_x traps, it is necessary to understand this aspect. For this reason, we determined experimentally the breakthrough curves of SO_2 uptake in conditions close to application (high SV, low SO_2 concentration, presence of 10% CO_2) and then these curves were analyzed with suitable kinetic models in order to obtain the indication about the dominant kinetic regime in these conditions.

3.2. Kinetic modelling of the breakthrough curves in SO_2 uptake

For proper interpretation or prediction of breakthrough curves it is necessary to (i) apply conservation equations to an element of the bed for fluid and solid phase, and (ii) establish the point kinetics and rate coefficients of the various rate processes and evaluate the equilibrium isotherm. The governing equations derive from the mass balance equation for the absorbable component (SO_2) in the flow direction

$$D_{\mathrm{af}}\frac{\partial^2 C}{\partial z^2} - u_0\frac{\partial C}{\partial z} - (1-\varepsilon)\rho_{\mathrm{P}}\frac{\partial q}{\partial t} = \varepsilon\frac{\partial C}{\partial t} \tag{1}$$

where C is the adsorbate concentration in the gas phase, ρ_{P} the density of the adsorbate, D_{af} the axial dispersion coefficient, u_0 the superficial fluid velocity, ε the bed void fraction and q the number of moles of adsorbate per unit weight of adsorbent.

The rate of adsorption is controlled by the step, which exerts the greatest resistance to transfer and is inherently the slowest. The mathematical solution is simplified by neglecting all resistances but the rate controlling one or by combining all the steps into one effective step with a single apparent rate. It is also necessary to know the relationship between the adsorbate (SO_2) in the adsorbed and free state (the adsorption isotherm). The following controlling mechanisms can be considered: (1) external transfer, (2) pore diffusion, (3) solid phase diffusion and (4) adsorption–desorption (surface reaction). However, due to the high linear gas flow velocity (high Reynold number), external transfer limitations are negligible. The distinction between pore diffusion and solid diffusion is important to predict breakthrough behaviour. SO_2 may enter a particle of adsorbent material directly from the exterior surface by movement in condensed form along the pore surfaces (solid diffusion), or it may diffuse through the fluid phase held in the pores and then be deposited in a stationary location on the pore surface. Whereas the concentration level will usually change abruptly at the fluid–solid interface because of the reaction or phase change that occurs there, the pores also exhibit a fluid-phase concentration that varies continuously from the exterior to the centre of the particle. In pore diffusion, the controlling mass-transfer process occurs before the phase change, but in solid diffusion it occurs afterward. At different operating conditions, the same particle can show either solid- or pore-diffusion behaviour, favouring the former if the pore-fluid concentration level is low and the latter if this level is high. Two distinct models have been used to describe the diffusional processes: the homogeneous solid diffusion model and the pore diffusion model.

In the homogeneous solid diffusion model the adsorption process occurrs at the outer surface of the pellet, followed by the diffusion of the SO_2 in the adsorbed state. Although the particle is assumed to be homogeneous, this does not preclude the use of this model for particles actually possessing substantial porosity. The main point is that no attempt is made to relate the transport processes to the structure in terms of such properties as surface area and pore size distribution. The diffusion equation is the following:

$$\frac{\partial q}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) \tag{2}$$

where D is the effective diffusion coefficient. In the pore diffusion model the particles consists of a solid phase interspersed with very small pores. There is a threeway division of the bed volume: the external void fraction, the internal void fraction and the internal solid. Diffusion occurs in the internal void fraction. The diffusion equation is the following:

$$\begin{aligned}&\left(\rho_{\mathrm{f}} + \frac{\rho_{\mathrm{s}}}{(1)}\frac{\partial q}{\partial c_{\mathrm{pore}}}\right)\frac{\mathrm{d}c_{\mathrm{pore}}}{\mathrm{d}t}\\ &\quad = \left[\frac{\rho_{\mathrm{f}}D_{\mathrm{p}}}{1c_{\mathrm{pore}}} + \frac{\rho_{\mathrm{s}}D_{\mathrm{solid}}}{(1)}\frac{\mathrm{d}q}{\mathrm{d}c_{\mathrm{pore}}}\right]\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{\mathrm{pore}}}{\partial r}\right)\end{aligned} \tag{3}$$

This equation assumes that the adsorption process itself is instantaneous (no surface reaction effects). On the left hand side, the first term is the accumulation of adsorbate in the fluid phase and the second is that in the adsorbed state. On the right hand side, the first term is the diffusion of SO_2 in the fluid phase and the second is surface diffusion of the adsorbed SO_2 species. The SO_2 loading, q, refers to the actual moles adsorbed per gram of dry adsorbent and does not include the moles of SO_2 held in the fluid phase in the pores. In the measurement of an adsorption isotherm, the direct result is a determination of the SO_2 in the adsorbed state plus that held in the pores of the sorbent. The loading, q, can then be calculated by subtracting out the quantity of SO_2 in the pores if the porosity of the sorbent is known.

From a physical standpoint, the two diffusion models are quite different. In the homogeneous model, even though the pellets may be porous, there are no sinks for the SO_2 since it diffuses into them in the adsorbed state. The entire process may be pictured as an adsorption at the outer surface of the sorbent followed by a sponge-like absorption of the SO_2 into the pellets. On the other hand, for the pore diffusion model, an absorption of the SO_2 occurs into the pores with concurrent distributed adsorption all along the pore walls. In spite of these very different physical pictures, the two models can result in identical breakthrough curves under certain conditions.

If the adsorption isotherm of SO_2 on the SO_x trap is nearly linear in the region of interest, the derivative dq/dc_{pore} is constant. As a consequence the entire coefficient on the right hand side of Eq. (3) is a constant and the diffusion can be described in terms of a single pseudo diffusivity. Additionally, if the voidage of the bed is about 0.5 and the concentration of SO_2 small as in our case, the pore diffusion model and the homogeneous model become equivalent. The fact that the homogeneous model and the pore diffusion model can be approximated by the same equation has two advantages: (i) both pore and solid phase diffusion can be treated with a single equation in the form of an effective diffusion coefficient. (ii) The mathematical solution of the homogeneous model equation is relatively straightforward; an analytical solution exists [14–16], which represents the fraction of the sorbent particle saturated by SO_2

$$\frac{q}{q_\infty} = 1 - \frac{6}{\pi^2}\sum\frac{1}{n^2}\exp\left[-\frac{4D\Delta t n^2}{d_p^2}\right] \tag{4}$$

where q is the concentration of SO_2 on the sorbent in moles per unit weight of dry adsorbent at time Δt and q_∞ is the concentration of SO_2 on the solid that would be in equilibrium with the gas phase SO_2 concentration.

Considering the case of a deep bed, and assuming constant pattern conditions (i.e. when the ratio between the concentration of SO_2 on the sorbent divided that on the solid in equilibrium with the gas phase SO_2 concentration, q/q_∞ is equal to the ratio between the SO_2 outlet concentration at any time t divided the inlet SO_2 concentration, c/c_0) the following analytical equation approximates the breakthrough curves:

$$\frac{c}{c_0} = (1 - \exp(-\theta - 0.614 + \Sigma))^{0.5} \tag{5}$$

where the solution capacity parameter, θ, and the column capacity parameter, Σ (equivalent to the number of transfer units in differentially continuous separation) have the following definition:

$$\theta = \frac{4D\pi^2}{d_p^2}\left(t - \frac{V\varepsilon}{F}\right), \qquad \Sigma = \frac{4D\pi^2}{d_p^2}\Lambda\tau,$$
$$\Lambda = \frac{q_\infty(1-\varepsilon)\rho_p}{c_0}, \qquad \tau = \frac{V}{F} \tag{6}$$

$V\varepsilon/F$ is the time required to fill a column of void volume $V\varepsilon$, at a volumetric flow rate F. t is the time on stream. For reaction controlled adsorption kinetics, similarly for deep bed approximation, it may be derived the following analytical equation which approximates the breakthrough curves:

$$\frac{c}{c_0} = \frac{1}{\exp[-k(t - \varepsilon\tau - \Lambda\tau)] + 1} \tag{7}$$

where k is the pseudo-kinetic constant.

3.3. SO_2 breakthrough curves

Determination of the breakthrough curves for SO_2 capture was made in a flow reactor apparatus, with a small catalyst loading (40 mg), using a high space-velocity (150,000 h^{-1}), and a feed containing a low SO_2 concentration (10 ppm), 11% CO_2 and about 5% O_2. Kinetic analysis of the breakthrough curves was made using two models, the first based on considering the rate of SO_2 capture determined from the surface reaction (Eq. (7)) and the second from the bulk diffusion of SO_2 in the solid (Eq. (5)), as discussed in the previous section.

The results at 200 °C for the reference SO_x trap are reported in Fig. 2. The diffusion limited equation was calculated based on Eq. (5), while the kinetic limited eq. on the basis of Eq. (7). The following parameters were used for the simulation: $k = 0.484787$, $\varepsilon = 0.45$, $\tau = 0.0004$, $\Lambda = 21{,}100$, $D = 0.0000127$, $d_p = 0.083$, $\Sigma = 0.61426$. It is well evident that experimental results show that the SO_2 capture under conditions close to application is controlled by bulk diffusion in the solid. It may be thus concluded that the performances of these reference SO_x traps are mainly determined from the bulk diffusion of the sulphate. There is a fast initial adsorption/oxidation of SO_2, but the phase transformation from oxide to sulphate (with consequent large increase in the cell volume) determines a quick blocking of the reaction (possibly also to the occlusion of the smaller pores). Therefore, shortly after the start of the sulphation process, the reaction becomes controlled by the solid-state diffusion.

The effect of SO_2 inlet concentration is reported in the inset of Fig. 2. There is a shift to lower times on stream due to the quicker saturation of sorption capacity on increasing SO_2 concentration in the feed, but the shape of the curve remains the same and could be described by a solid-state diffusion model.

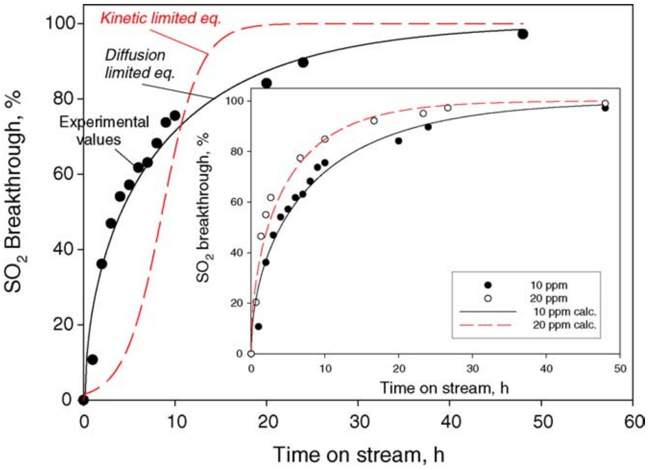

Fig. 2. Experimental data in the SO_2 breakthrough curve for reference SO_x trap at 200 °C and their kinetic modelling based on a kinetic limited equation (surface reaction as rate limiting step) and on a diffusion limited eq. (bulk diffusion in the SO_x trap as the rate limiting step). In the inset: experimental data in the SO_2 breakthrough curve for reference SO_x trap at 200 °C for an SO_2 concentration in the feed of 10 and 20 ppm and the kinetic modelling and on a diffusion limited equation.

The effect of the reaction temperature is analyzed in Fig. 3, which reports for comparison also the calculated values of expected breakthrough curves in the case of solid-state diffusion (diffusion limited equation, solid line) and surface reaction (kinetic limited equation, dotted line), while symbols are the experimental points. At 200 °C, as pointed before, the data can be correctly described with a solid-state diffusion equation (solid line), while at higher temperature (400 °C) the first part of the breakthrough curve (up to about 50–60% of SO_2 removal from the inlet feed) can be described with a surface reaction control equation (dotted line), while deviation is present for higher levels of SO_2 removal (e.g. for higher levels of sulphation of the SO_x trap) where the data can be again described from a solid-state diffusion equation (solid line).

A better understanding of these data derives from their elaboration in the form of SO_x trap productivity (moles SO_2 removed per hour and per gram of trap) as a function of the amount of SO_2 uptake reported as wt.% of weight increase of the SO_x trap (inset of Fig. 3), in order to have a result directly comparable with those in the TG apparatus (Fig. 1). This graph clarifies various interesting aspects of the behavior of the studied reference SO_x trap. It is evident that two regions of kinetic control can be evidenced, the first at low levels of sulphation, and the second at high levels of sulphation. The transition is a function of the reaction temperature. It occurs at 200 °C for an amount of SO_2 adsorbed in the range 0.5–1.0% of weight increase of the SO_x trap due to sulphation, in the 3–4% range for a temperature of 300 °C and in the 4–5% range for the temperature of 400 °C. A good agreement with the TG data (Fig. 1) is found. Above this threshold, a linear decrease in the productivity of the SO_x trap with the SO_x loading is evident. Again there is a good consistency in the trend of this limiting saturation value in these flow reactor experiments and those determined in the TG apparatus, taking into accout the higher SO_2 concentration of the latter tests.

4. Conclusions

The development of high-performance SO_x traps to protect the NO_x trap from sulphur deactivation in diesel engine emissions requires to understand the dynamics of SO_2 oxidation–adsorption of current state-of-the-art SO_x traps, in order to determine which properties should be optimized. The results presented in this work contribute to clarify some aspects of this problem. The first regards the kinetic controlling step. Data evidence that at low temperature (200 °C) the process is controlled by solid-state diffusion of the sulphate species. Therefore, the performances should be improved by increasing the rate of this process more than the rate of SO_2 to SO_3 oxidation. Present data indicate that probably noble metals are not necessary. In agreement, we will show elsewhere that noble-metal-free SO_x traps, based on Cu–Al mixed oxides derived from hydrotalcite precursors, have comparable and even better performances [17].

Data also evidence (Fig. 3) an initial region, especially above 300 °C, where the productivity of the trap is mainly dominated by the surface reaction, and therefore a dependence with the surface area is expected. The presence of macroporosity is beneficial, because enhances effective diffusivity of SO_2 within the particles, but data also evidence that these parameters are not enough and it is necessary to develop SO_x traps based on a solid-state structure flexible to accommodate the change from oxide to sulphate without inhibition of the reaction progress. For example, the presence of channels in the structure, which allow the diffusion of SO_x would facilitate the reaching of high sulphation levels.

A final comment regards the possibility to obtain reliable indications on the performances of SO_x traps using a TG apparatus. The results discussed here show that there is a good agreement between results found in a flow reactor and those in the TG apparatus. TG tests may be thus a valid equipment at least in a screening phase, but true indications about the

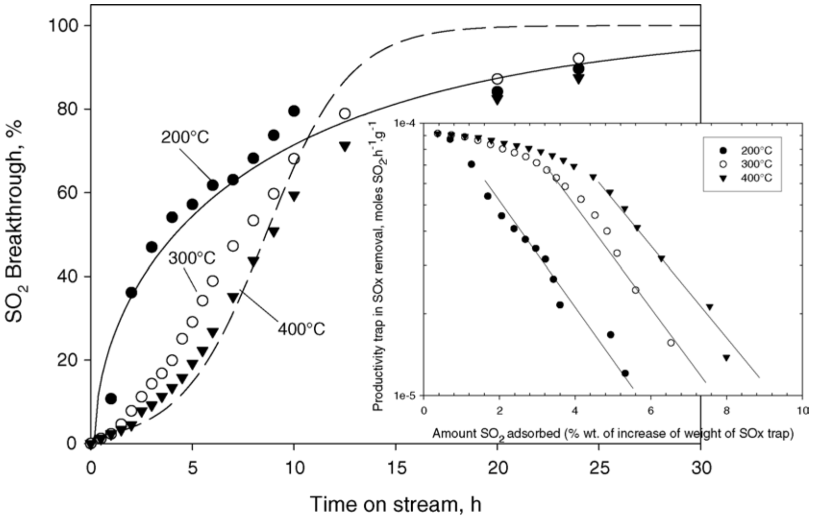

Fig. 3. SO_2 breakthrough curve for reference SO_x trap at 200, 300 and 400 °C and their kinetic modelling based on a kinetic limited equation (surface reaction as rate limiting step) and on a diffusion limited equation (bulk diffusion in the SO_x trap as the rate limiting step). In the inset: productivity of the trap in SO_x removal (moles SO_2 per hour per gram SO_x trap) as a function of the amount of SO_2 adsorbed and of the reaction temperature.

effective sorption capacity of the SO_x traps and their dynamics of SO_2 uptake require to make tests in a flow reactor apparatus and reaction conditions close to those of application. However, a modelling of the data is also necessary to analyze more correctly the results.

Acknowledgements

The financial support of EU (contract G3RD-CT2002-00793 NANOSTRAP) is gratefully acknowledged. We would also thanks Drs. Dennis Webster and Bob Brisley (Johnson Matthey) to have given the SO_x trap and for the useful discussion.

References

[1] A.N. Chigapov, A.A. Dubkov, B.P. Carberry, C.N. Montreuil, G.W. Graham, R.W. McCabe,W. Chun, Eur. Patent Appl. EP1374978 (2004), assigned to Ford Global Tech.
[2] Z. Hu, P.L. Burk, S.F. Chen, US Patent Appl. Publ. US2,003,175,192 (2003), assigned to Engelhard Co.
[3] M. Deeba, J.K. Hochmuth, U. Dahle, S. Brandt, US Patent Appl. Publ. US2,003,039,597 (2003), assigned to Engelhard Co.
[4] D. Dou, M. Molinier, O. Bailey, PCT Int. Appl. WO2001056686 (2001), assigned to Delphi Technologies.
[5] H.L. Fang, J.C. Wang, R.C. Yu, C.Z. Wan, K. Howden, Society of Automotive Engineers (SAE Papers), SP-1801 (Emissions: Advanced Catalyst and Substrates, Measurement and Testing, and Diesel Gaseous Emissions), 2003 pp. 185–194.
[6] L. Li, D.L. King, Ind. Eng. Chem. Res. 44 (2005) 168–177.
[7] L. Limousy, H. Mahzoul, J.F. Brilhac, P. Gilot, F. Garin, G. Maire, Appl. Catal., B: Env. 42 (2003) 237–249.
[8] J. Wang, Z. Zhu, C. Li, J. Molec. Catal. A: Chem. 139 (1999) 31–41.
[9] H. Dathe, C. Sedlmaier, A. Jentys, J.A. Lercher, Stud. Surf. Sci. Catal. 154 (2004) 3003–3009.
[10] S. Iretskaya, M.B. Mitchell, J. Phys. Chem. B 107 (2003) 4955–4962.
[11] Y.G. Hao, B.R. Cooper, Surf. Sci. 312 (1994) 250–258.
[12] G. Centi, N. Passarini, S. Perathoner, A. Riva, Ind. Eng. Chem. Res. 31 (1992) 1947–1955.
[13] G. Centi, N. Passarini, S. Perathoner, A. Riva, Ind. Eng. Chem. Res. 31 (1992) 1956–1963.
[14] D.M. Ruthven, Principles of Adsorption and Adsorption Processes, Wiley and Sons, New York, 1984.
[15] G.E. Boyd, A.W. Adamson, L.S. Meyer, JACS 69 (1947) 2836–2848; G.E. Boyd, A.W. Adamson, L.S. Meyer, JACS 69 (1947) 2849–2859.
[16] N.K. Lazaridis, T.D. Karapantsios, D. Georgantas, Water Res. 37 (2003) 3023–3033.
[17] G.E. Arena, L. Capitò, G. Centi, S. Perathoner, Appl. Catal. B: Env., in press.