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Catalytic properties in deNO$_x$ and SO$_2$–SO$_3$ reactions

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Abstract

SCR-deNO$_x$ reaction and SO$_2$–SO$_3$ oxidation tests were carried out by different research groups over fresh and used EUROCAT oxide samples in order to characterize the reactivity of the catalysts and to compare data obtained in several laboratories (Politecnico of Milan, Università of Salerno, ENEL of Milan, Boreskov Insitute of Catalysis).

Data are presented which indicate that the used EUROCAT catalyst is slightly more active both in the deNO$_x$ reaction and SO$_2$–SO$_3$ oxidation than the fresh sample.

An analyses of data collected over honeycomb catalysts by means of a 2D, single-channel model of the SCR monolith reactor has been performed to evaluate the intrinsic kinetic constant of the deNO$_x$ reaction; a satisfactory comparison has been obtained between estimation of the intrinsic kinetic constant and estimation of the intrinsic catalyst activity from data collected over powdered catalysts. A good agreement has been found in the experimental results collected in the different labs, both for the deNO$_x$ reaction and SO$_2$–SO$_3$ oxidation.

Keywords: DeNO$_x$; SO$_2$–SO$_3$ reactions; Selective catalytic reduction

1. Introduction

The selective catalytic reduction (SCR) process is the most widely spread technology for the control of NO$_x$ emissions from stationary sources (including power-plants and incinerators), due to its efficiency and selectivity [1,2].

The deNO$_x$ process is based on the reaction between NO and ammonia to produce nitrogen and water according to the reaction

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

In the treatment of sulfur-containing flue gases, SO$_2$ is also fed to the SCR reactor; here it is partly oxidized to SO$_3$ which can react with water and unconverted ammonia to form sulfuric acid and ammonium sulfates. Accordingly, SO$_2$ oxidation represents a highly undesirable side reaction of the SCR process; catalyst formulation and operating variables have to be designed in order to minimize its extent and, as a consequence, to avoid the risk of deposition of ammonium-sulfates or corrosion in the cold sections of equipment of the plant downstream from the reactor.

Commercial SCR catalysts are a homogeneous mixture of vanadium pentoxide, tungsten (or molybdenum) trioxide, supported on a high-surface area anatase TiO$_2$ carrier. It is well accepted that tungsten (molybdenum) trioxide acts as a promoter of the

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deNO$_x$ reaction: it lowers the temperature threshold at which the reaction proceeds, and confers superior thermal stability and better mechanical properties to the catalyst [3–8]. V_2O_5 is the active component. In the case of the more traditional power-plant applications, the vanadium oxide content is generally kept low, in order to minimize SO_3 formation; when used in waste incineration plants, however, the catalyst V_2O_5 content may be higher, in order to accomplish the effective simultaneous abatement of dioxins and NO$_x$.

For this study of a commercial deNO$_x$ catalyst for the treatment of incinerator flue gases, the EUROCAT oxide supplied by Austrian Energy, has been the object of an international research project involving a large number of research and R & D labs from European Universities and Industries. In this working party reactivity tests in the deNO$_x$ and SO_2–SO_3 reactions have been undertaken simultaneously by different partners of the project.

Each laboratory received samples of the fresh and used EUROCAT catalyst; the used samples had been subject to 9000 h of operation in a full-scale SCR reactor.

This paper reports the results obtained by the research groups in charge with the characterization of EUROCAT oxide activity in the deNO$_x$ and SO_2–SO_3 reactions. Bal'zhinimaev and coworkers at the Boreskov Institute of Catalysis, Ciambelli and coworkers at Univertità di Salerno, Professor Forzatti and coworkers at Politecnico di Milano and Bregani and coworkers at the research laboratory of ENEL have independently performed deNO$_x$ and SO_2–SO_3 tests over both fresh and used EUROCAT samples. Most of the authors have tested the catalysts in the form of monoliths, as received by the supplier. Experiments from the Boreskov Institute of Catalysis were carried out in a continuously stirred tank reactor by using the catalysts in the form of powders. The results are collected herein and discussed with the twofold aim of fully characterizing the performance of the EUROCAT oxide and of verifying the match in the results from remote and independent laboratories where state-of-the-art procedures are in use.

In the following, a brief description of the testing units is given first. The results from activity data over fresh and used monoliths are then presented and compared. These have been analyzed by means of a 2D, single-channel model of the SCR monolith reactor developed previously [9,10]; the model analysis provided a better insight about the relative importance of intrinsic reactivity of the catalyst and mass transfer in EUROCAT oxide.

Finally, data from the Boreskov Institute of Catalysis are presented. As they were obtained under kinetic regime, and influences from inter-phase and intra-porous resistances were absent, these results were suitable to the direct estimation of the deNO$_x$ intrinsic activity of the catalyst.

A comparison between kinetic results obtained over powders and estimation of the catalyst activity constant obtained from the model fit to the monolith-data was then performed.

2. Experimental

2.1. Apparatus for activity test

2.1.1. Monolith catalyst

Fig. 1 shows a schematic of the apparatus used for the measurements of NO$_x$ reduction with ammonia (configuration A) over honeycomb catalysts at Politecnico of Milano; the same apparatus was modified (configuration B) to perform activity tests of SO_2 oxidation. A detailed description of both configurations has been reported elsewhere [11,12].

The gas feed consisted of NO$_x$/N_2, O_2/N_2, H_2O and N_2. Mass flow-meters (F) were used to measure and control the single gaseous streams, while a metering micro-pump (P) was used to inject water.

The feed stream was preheated and premixed in the mixer (M); to avoid side reactions, ammonia was added to the gas mixture immediately before entering the reactor.

The reactor (R) consisted of a stainless steel tube heated with four electric resistors; the inner wall of the reactor was lined with a glass tube in order to prevent undesired oxidation reactions over the metallic parts upstream from the reaction zone. The temperature was measured and controlled by a thermocouple sliding inside a capillary tube inserted in the catalyst (C).

Before loading, the monolith was wrapped with quartz wool and a bandage of ceramic material that prevented the outer surface of the catalyst from catalyzing the reaction; it was then forced into the

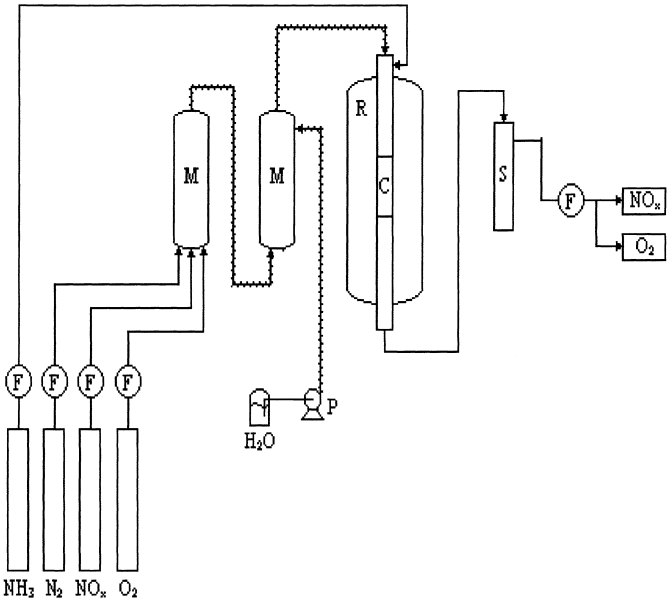

Fig. 1. Politecnico of Milan experimental apparatus for deNO_x activity tests.

reactor taking care that no gas could bypass the catalyst.

The gas exiting the reactor was scrubbed (S) with an aqueous solution of phosphoric acid to trap unconverted ammonia, then cooled in an *iso*-propylic alcohol cooler to condense water vapor.

In the configuration A the gases were analyzed by a chemiluminescence NO/NO_x analyzer and by a paramagnetic oxygen analyzer.

In the configuration B, used to study the oxidation of SO_2 to SO_3, the SO_3 concentration in the product gas was determined through condensation of sulfuric acid at 363 K in a glass spiral, followed by analysis with an Ionic Chromatograph.

Blank experiments had been performed to confirm that contributions of the apparatus to the deNO_x and SO_2–SO_3 reactions were absent.

The apparatuses developed at the University of Salerno and ENEL for the deNO_x experiments and for the SO_2–SO_3 oxidation tests had similar configurations; their description is thus omitted.

2.1.2. Powdered catalyst

The apparatus used at the Boreskov Institute of Catalysis consisted of a continuously stirred tank reactor (operated within temperature region 523–623 K), wherein gases were fed by stainless steel lines, and a specially designed membrane circulating pump used to recycle the gas stream. The pump had a capacity of 1000 l/h at 408 K and provided a recycle ratio equal to 200. All parts were heated at 408 K to avoid salts formation.

The glass reactor was placed inside an electrical furnace. To avoid internal diffusion, the catalyst was crushed and sieved to 0.009–0.016 cm particles. Prior to the reaction, the catalyst was calcined at 623 K for 2 h in a flow of 20 vol.% of O_2 in He. Then NO, NH_3 and O_2 in He were fed into the reactor. The inlet reactants concentrations were varied in each experiments in order to keep constant the composition of the outlet stream, which is detailed in the following.

The concentration of all the species exiting the reactor were determined using a three-column gas chromatograph with an automatic analysis system (Tsvet 500) combined with a combustion gas analysis computer “Ecom-omega”. A Cromosorb 104 column was used for NH_3 and H_2O separation. A Poropak QS column was used for the analysis of N_2O and NO_2. The sensitivity limit for N_2O was 3.0×10^{-3} vol.% NO_2 and NO concentrations were determined by Ecom-omega.

Table 1
Geometry of the EUROCAT monolith catalyst

Channel number	9
Pitch	3.6 mm
Wall thickness	0.6 mm
Length	15 cm
Geometrical surface area	194.400 cm^2

The gas mixture was diluted 17 times by nitrogen and after complete ammonia adsorption with concentrated H_3PO_4 it was directed to NO and NO_2 sensors, working within 0–2000 ppm.

2.2. Operating conditions

Table 1 lists the geometrical characteristics of the fresh and the used EUROCAT catalyst samples provided to the different project partners.

The standardized operating conditions adopted by the research groups for the deNO_x activity tests over monoliths were suggested by Austrian Energy and are representative of industrial application. They are listed in Table 2. In comparison with the operating conditions generally used to study SCR catalysts for power-plant applications [11,12], the present conditions are characterized by high oxygen concentration. Forzatti and coworkers performed additional experiments under experimental conditions (also listed in Table 2) traditionally used at Politecnico of Milano and common in the literature for the screening of commercial SCR catalysts.

Table 2
DeNO_x activity tests over fresh and used EUROCAT monoliths[a]

	Austrian Energy (conditions A)	Politecnico di Milano (conditions B)
Area velocity (N m/h)	12.8	33
α (=NH_3/NO_x)	1	1.1
NO (ppm)	300	500
NH_3 (ppm)	300	550
O_2 (vol.%)	11	2
H_2O (vol.%)	20	10
N_2	Balance	Balance
SO_2	Absent	Absent

[a] Operating conditions: Università di Salerno, Politecnico di Milano and ENEL have carried out experiments under conditions A. Politecnico di Milano and ENEL performed additional experiments under conditions B.

Table 3
SO_2 oxidation tests over fresh and used EUROCAT monoliths: operating conditions of the experiments performed by Università di Salerno and Politecnico di Milano

Area velocity (N m/h)	10
O_2 (vol.%)	2
H_2O (vol.%)	10
SO_2 (ppm)	300
N_2 (ppm)	Balance

In the case of the deNO_x activity tests over powders in CSTR reactor, a total flow rate of 75 cm^3/min (STP) was used. The outlet concentrations of NO, NH_3 and O_2 were kept constant at 0.17, 0.2 and 2 vol.%, respectively, in all the experiments.

SO_2–SO_3 oxidation tests over monoliths were performed by Università di Salerno and Politecnico di Milano under the experimental conditions listed in Table 3.

3. DeNO_x activity data

In this section a full report is given of the deNO_x activity tests performed by the four research groups, using both the fresh and the used EUROCAT samples.

3.1. Tests over monoliths

3.1.1. Comparison of data from different laboratories

Table 4 shows the results obtained over the fresh EUROCAT monolith by different laboratories under operating conditions A; these are compared with reference data provided by the same supplier. The results are presented in terms of NO_x conversion as a function of temperature within the range 420–560 K. The activity of the catalyst was remarkable, as about 30–40% NO conversion was accomplished already at 420–430 K; NO conversions higher than 90% were then observed at 500 K.

The results obtained at Politecnico of Milano and those obtained at the University of Salerno were in good agreement; both the sets of data also compare well with the result provided by Austrian Energy at 553 K.

The ENEL experimental results show a certain degree of deviation from the other data: ENEL observed higher NO conversions in the whole temperature range investigated.

Table 4
Results of deNO$_x$ tests over the fresh EUROCAT monolith with operating conditions A

Temperature (K)	NO$_x$ conversion (%)			
	Austrian Energy	Politecnico di Milano	ENEL	University of Salerno
429		25	45	32
443			64	
449		45		50
453			71	
463			82	
473			85	
479		73		75
483			89	
493			90	
503			96	
512		88		89
533		93		95
553	97	96		97

The same results are represented in Fig. 2 in terms of overall kinetic constant k (N m/h), estimated by the expression

$$k = \mathrm{AV} \ln\left(\frac{1-\chi}{100}\right) \quad (1)$$

wherein AV is the area velocity (N m/h) and χ the percentage NO conversion. This equation is derived on the assumption of plug-flow reactor, isothermal conditions, first order kinetics in NO concentration and zero order kinetics in ammonia concentration. An apparent activation energy as low as 20 kJ/mol can be estimated from the temperature dependence of k.

Again, it appears that the data from Politecnico of Milan and University of Salerno were in good agreement.

Table 5 reports the results of the deNO$_x$ activity tests performed over the used EUROCAT catalyst

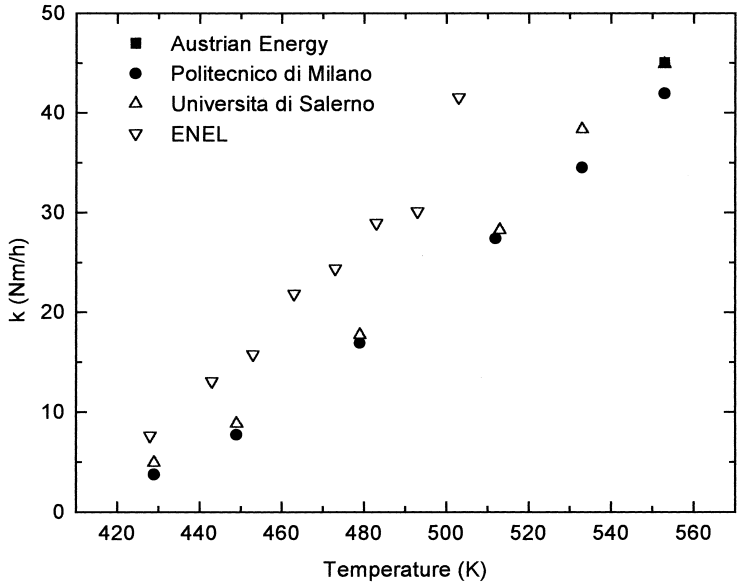

Fig. 2. Results obtained by the different partners under experimental conditions suggested by the supplier over the fresh EUROCAT sample.

Table 5
Results of the activity tests performed over the used EUROCAT catalyst under experimental conditions suggested by the supplier (conditions A)

Temperature (K)	NO_x conversion (%)		
	Politecnico di Milano	ENEL	University of Salerno
424		45	
429	43		43
443		67	
451	66		61
463		80	
473		88	
480	83	90	79
514	91		91
531	96		95
555	97		98

using the experimental conditions A. The same range of temperature was investigated as for the fresh sample (420–560 K), in order to facilitate a direct comparison of the performances of fresh and used catalysts. As previously, a satisfying agreement was found among the three sets of data of different centers; the match was especially good between the results from Università di Salerno and those from Politecnico di Milano, while NO measurements at ENEL were slightly higher.

As mentioned above, additional deNO_x activity tests were performed by some of the authors under operating conditions B. The results obtained over the fresh EUROCAT catalyst and used EUROCAT catalysts are reported in Tables 6 and 7, respectively. A wider temperature range was investigated under these conditions, from 420 to 650 K, due to the higher AV value (33 vs. 12.8 N m/h) and the consequent lowering of NO conversion at equal temperature with respect to conditions A. The NO_x conversions measured by ENEL were still higher than those observed at Politecnico di Milano.

3.1.2. Fresh EUROCAT catalyst vs. used EUROCAT catalyst

Under both operating conditions A and operating conditions B, the fresh EUROCAT sample showed a lower activity in the deNO_x reaction than the used EUROCAT catalyst. No deactivation seems to accompany the 9000 h operation under industrial condition of the present catalyst: this results in line with the fact that commercial catalysts are generally guaranteed for 16 000–24 000 h operation.

On the contrary, there is the possibility that modifications of the catalyst surface enhance the catalyst activity. It is known, for instance, that the formation of vanadium agglomerates leading to a loss of dispersion (e.g. sintering of the catalyst [13]) increases significantly both the deNO_x and the SO_2–SO_3 activity in SCR catalysts. This seems a possible explanation for the behavior observed over the EUROCAT catalyst, given its rather high vanadium content. However, only a focused surface characterization of the fresh and used samples (which is beyond the scope of this paper) could provide the relevant pieces of evidence.

Table 6
Results obtained under Politecnico standard experimental conditions (conditions B) over the fresh EUROCAT sample

Temperature (K)	NO_x conversion (%)	
	Politecnico of Milan	ENEL
424		15
431	4	
453		29
461	16	
483		48
490	30	
513		63
519	45	
543		72
548	55	
572		79
578	67	
604		85
609	76	
629	78	
633		88

Table 7
Results obtained under Politecnico standard experimental conditions (conditions B) over the used EUROCAT catalyst

Temperature (K)	NO_x conversion (%)	
	Politecnico of Milan	ENEL
424		20
443		27
453		32
464		36
473		42
493		54
513	56	61
533	63	
543		71
550	67	
565	71	
573		79
584	75	
602	78	84
627	81	
644	82	

3.1.3. Effect of operating conditions

Fig. 3 compares the overall intrinsic activity k of the fresh EUROCAT catalyst measured under operating conditions A (representative of the industrial application) and operating conditions B, at Politecnico di Milano. It was found that at equal reaction temperature conditions A were associated with a much better deNO_x performance of the catalyst with respect to conditions B. The same effect was observed over the used catalyst and was confirmed by the experiments performed by ENEL. The increase of catalyst activity can be most likely associated to the higher oxygen content which characterizes the operating conditions suggested by Austrian Energy with respect to conditions B. Such an increase has been quantified with the model analysis presented in the following section wherein this effect is further discussed.

3.2. Data over powders

Table 8 reports the experimental results obtained at the Boreskov Institute of Catalysis over the powdered fresh and the used EUROCAT samples. NO_x conversion measurements were performed in the range 430–560 K.

In the following section these data are presented and compared to those obtained over monoliths.

3.3. Monolith reactor modeling and data analysis

Some of the authors have previously developed a 2D, single-channel model of the SCR monolith reactor [9,10,14]. The model relies upon some simplifying assumptions: same conditions inside the monolith

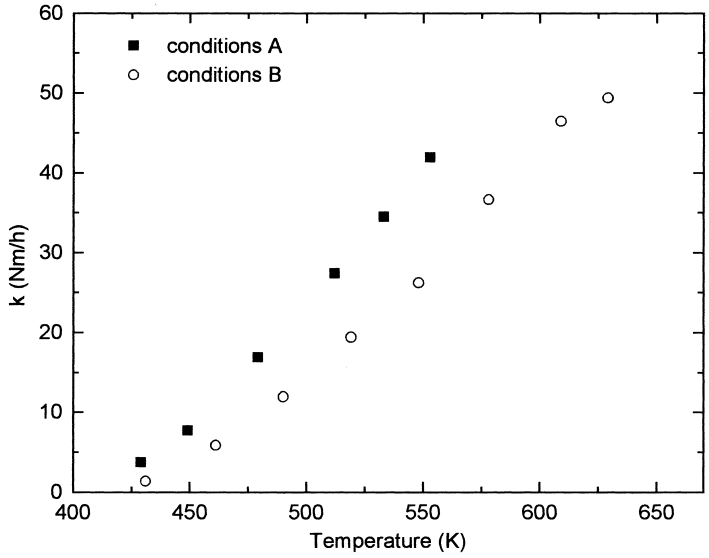

Fig. 3. Results obtained at Politecnico of Milan over fresh catalysts using different sets of operating conditions.

Table 8
Results obtained over the fresh and the used EUROCAT catalyst at the Boreskov Institute of Catalysis

Temperature (K)	NO_x conversion (%)	
	Fresh EUROCAT	Used EUROCAT
427	47	48
448	48	47
476	68	69
557	60	59

channels, isothermal reactor, negligible axial diffusion. It accounts for the single steps of inter-phase diffusion, intraporous diffusion and reaction on the catalyst surface which the deNO_x process kinetics involves. Gas–solid mass transfer is described on the basis of the analogy with the Graetz–Nusselt problem of heat transfer in square ducts with laminar flow and constant wall temperature [9]. An Eley–Ridel mechanism is assumed to govern the reaction between NO (gas phase) and ammonia (strongly adsorbed) with kinetic expression

$$r_{NO_x} = k_{NO_x} C_{NO_x} \frac{K_{NH_3} C_{NH_3}}{1 + K_{NH_3} C_{NH_3}} \tag{2}$$

Eq. (2) reduces to first order kinetics with respect to NO in the case of excess ammonia, i.e. $K_{NH_3} C_{NH_3} \gg 1$. Effective diffusivity coefficients for NO and NH_3 inside the monolith wall are evaluated with the "random-pore model" proposed by Wakao and Smith [15]. Also, the model includes an analytical approximate expression of the catalyst effectiveness factor; this is valid both for first order and for Eley–Rideal kinetics, under the assumption of large Thiele moduli (i.e. the concentration of the limiting reactant is zero at the centerline of the catalytic wall).

Model equations include the following dimensionless material balances for NO and NH_3 in the gas phase

$$\frac{dC^*_{NO}}{dz^*} = -4Sh_{NO}(C^*_{NO} - C^*_{NO,\,wall}),$$
$$z^* = 0,\ C^*_{NO} = 1 \tag{3}$$

$$\alpha - C^*_{NH_3} = 1 - C^*_{NO}, \quad z^* = 0,\ C^*_{NH_3} = \alpha \tag{4}$$

$$Sh_{NO} = 2.977 + 8.827(1000z^*)^{-0.545} \exp(-48.2z^*) \tag{5}$$

and in the solid-phase

Table 9
Geometrical data and morphological characteristics of the fresh EUROCAT catalyst as assumed for model analysis

Wall half-thickness = 0.03 cm
Channel opening = 0.3 cm
Pore volume, range: $r_p \le 100$ Å = 0.14 cm^3/g from N_2 adsorption–desorption
Pore volume, range $100 \le r_p \le 500$ Å = 0.24 cm^3/g from Hg intrusion
Mean pore radius = 150 Å
Catalyst bulk density = 1.75 g/cm^3

$$Sh_{NO}(C^*_{NO} - C^*_{NO,\,wall}) = Sh_{NH_3}(C^*_{NH_3} - C^*_{NH_3,\,wall}) \frac{D_{e,\,NH_3}}{D_{e,\,NO}} \tag{6}$$

$$Sh_{NO}(C^*_{NO} - C^*_{NO,\,wall}) = Da \left[C^{*2}_{NO} - Y_0^2 + 2(S_1 - S_2) \left(C^*_{NO} - Y_0 - S_2 \ln \frac{C^*_{NO} + S_2}{Y_0 + S_2} \right) \right]^{1/2} \tag{7}$$

$$S_1 = \frac{D_{e,\,NH_3}}{D_{e,\,NO}} C^*_{NH_3} - C^*_{NO},$$
$$S_2 = S_1 + \frac{D_{e,\,NH_3}}{D_{e,\,NO}} \frac{1}{K^*_{NH_3}} \tag{8}$$

$$\text{if } S_1 \ge 0,\ Y_0 = 0,\ \text{else } Y_0 = -S_1 \tag{9}$$

In Eqs. (3)–(9), concentrations of NO and NH_3 are normalized with respect to the inlet NO concentration C^0_{NO}, the dimensionless axial coordinate is $z^* = (z/d_h)/Re\,Sc$ (d_h being the hydraulic channel diameter), $Da = (k_{NO} D_{e,\,NO})^{1/2} d_h / D_{NO}$ is a modified Damköhler number, $K^*_{NH_3} = K_{NH_3} C^0_{NO}$ is the dimensionless NH_3 adsorption constant, D_i (cm^2/s) the molecular diffusivity of species i, and $D_{e,i}$ the effective intraporous diffusivity of species i.

This model was successfully compared with laboratory data of NO conversion over commercial honeycomb SCR catalysts. It was also applied to the analysis of deNO_x activity data obtained over plate-type monoliths.

The same model has been used to analyze the data collected over the EUROCAT catalyst in the shape of monoliths. The analysis has been circumscribed to the performance of the fresh catalyst and, for simplicity, the deNO_x activity data obtained by Politecnico of

Milano were used for model fit, only. Such data were taken as fully representative of the experiments performed by the other partners of the project.

The geometrical and morphological characteristics assumed as input parameters are summarized in Table 9.

It has been observed above that the tests over monolith showed quite different activity depending on the operating conditions adopted. Namely, the reference Austrian Energy operating conditions (characterized by high oxygen concentration, 11 vol.%) resulted in higher deNO$_x$ activity than the conditions B (with low oxygen concentration, 2 vol.%). Notably, low O_2 feed content (3.5 vol.%) was also adopted by the research group at the Boreskov Institute of Catalysis for the activity tests over powders. Accordingly both situations were analyzed by the model.

The catalyst intrinsic activity and effectiveness factor were estimated by model fit to the data listed in Table 4 (conditions A), in order to characterize the EUROCAT oxide performance under industrial conditions. Model fit to the data listed in Table 6 (conditions B) provided elements for a more homogeneous comparison between estimated activity of the monolith and measured activity of powders.

Since experiments were performed at NH_3/NO feed ratios $\geq$1, first order kinetics were assumed. The results of model fit are shown in Fig. 4. In both the cases of high and low O_2 concentration, a good match between experimental and calculated *T*-dependence of NO conversion was obtained based on the estimated intrinsic activation energy of 66.99 kJ/mol. This value is more than three times higher than the apparent activation energy estimated in a previous section.

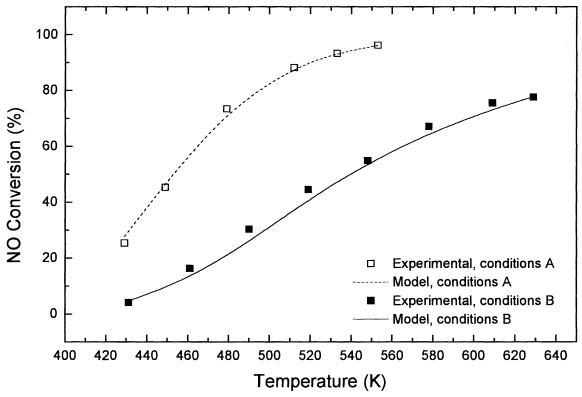

Fig. 4. Model fit (solid line) to activity data obtained under Austrian Energy conditions (solid symbols) and model fit (dashed line) to activity data obtained under conditions B.

In the case of O_2-rich feed stream (conditions A), the following optimal estimation of EUROCAT intrinsic activity was obtained

$$k_{\mathrm{deNO}_x} = 199.817 \exp\left(-8052.34\left(\frac{1}{T} - \frac{1}{523}\right)\right) \quad (\mathrm{s}^{-1}) \tag{10}$$

As part of the model analysis results, it was found that the fresh EUROCAT guarantees good intraporous diffusion of reactants; the catalyst is in fact characterized by a high pore volume fraction in the range 100–500 Å, and, from application of Wakao–Smith formula, it has been estimated that NO effective diffusivity at the reaction temperature of 533 K amounts to 2.6 cm^2/s. This value is comparable with the highest values of effective diffusion coefficients reported in the literature for optimized SCR catalyst morphologies [16,17]. As a consequence, it was estimated by the model that the effectiveness factor of the EUROCAT catalyst was as high as 30% at 533 K. The catalyst effectiveness increased significantly with decreasing reaction temperature, so that the activity data collected below 473 K were associated to monolith wall effectiveness higher than 50%.

Concerning the catalyst behavior in the presence of 2% oxygen (conditions B), the following intrinsic activity constant was estimated within the *T*-range 431–629 K:

$$k_{\mathrm{deNO}_x} = 65.565 \exp\left(-8052.34\left(\frac{1}{T} - \frac{1}{523}\right)\right) \quad (\mathrm{s}^{-1}) \tag{11}$$

At the reference temperature of 533 K, it was thus found that by changing the operating conditions from A to B, the catalyst activity was reduced to almost one third. As already mentioned, this effect was likely associated to the decrease of oxygen concentration. It is usually reported in the literature that SCR reaction rate is affected by oxygen only at low O_2 concentrations, while it reaches an asymptotic trend for O_2 concentrations greater than 2–5 vol.% [2,12]. Apparently, this does not apply to the present EUROCAT catalyst at least in the range of relatively low temperatures at which it has been tested. Indeed, low temperatures and

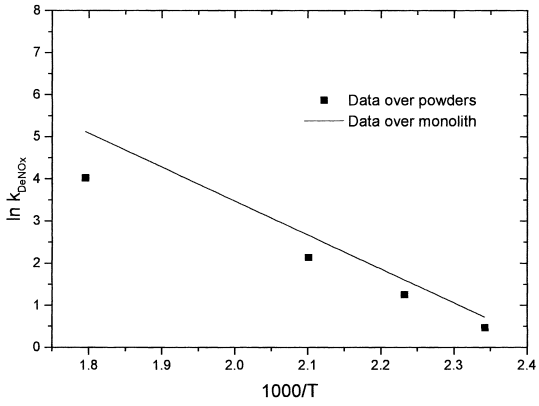

Fig. 5. Comparison between the estimation of the intrinsic activity constant k_{deNO_x} (s^{-1}) obtained from experiments over powders by Boreskov Institute of Catalysis (symbols) and that obtained through model fit to data obtained over monolith under conditions B by Politecnico of Milan.

high vanadium concentrations are expected to emphasize the kinetic effect of oxygen, which is intrinsically related to the redox reaction mechanism governing the deNO_x process [18].

As already noted, Bal'zhinimaev and coworkers also operated at lower oxygen concentration; as their data were obtained over powders (absence of intraporous diffusion resistances) and in a perfectly mixed reactor (concentration of reacting species inside the reactor equal to outlet concentrations), an estimation of the intrinsic activity can be derived directly from the conversion measurements, according to the equation:

$$F_{\mathrm{NO}}^{\mathrm{inlet}}\,\mathrm{conversion} = k_{\mathrm{deNO}_x} C_{\mathrm{NO}}^{\mathrm{outlet}} V_{\mathrm{cat}} \qquad (12)$$

wherein first order kinetics are assumed.

Fig. 5 shows the comparison between (i) estimation of EUROCAT intrinsic activity obtained from model fit to activity data over monolith under conditions B (Eq. (11)) and (ii) estimation of the catalyst intrinsic activity from application of Eq. (12) to the activity data over powders. The match is really satisfactory, given: (1) the completely independent nature of the sets of data, (2) the different reactor configurations used by the two research groups, (3) the possible inaccuracies of estimation of k_{deNO_x} related to the description of the catalyst morphology (in the case of data obtained over monolith) and to the simplifying character of Eq. (12) (in the case of data obtained over powders), (4) differences in operating conditions (e.g. water content). Such agreement further supports the evidence of a pronounced O_2-effect over the EUROCAT catalyst with a significant decrease of activity in the presence of lower oxygen concentrations.

4. SO_2–SO_3 activity data

Table 10 shows the values of SO_2 conversion to SO_3 measured by Politecnico of Milano and University of Salerno over the fresh and used EUROCAT samples.

SO_3 conversion values obtained over both the catalysts are quite higher than those measured over other SCR catalysts: this fact can be attributed to the higher vanadia loading present in the EUROCAT catalyst.

It is also clear that the SO_2–SO_3 activity tests results for the Politecnico of Milan and University of Salerno data are in good agreement.

The table also shows that the SO_2–SO_3 oxidation reaction over the used EUROCAT sample gives a slightly higher conversion than the fresh EUROCAT catalyst. As mentioned above, this effect may be attributed to modifications of the catalyst surface occurred under industrial operations (e.g. formation of vanadium agglomerates).

Table 10
SO_3 conversion values obtained over the fresh and the used EUROCAT sample

Temperature (K)	Fresh EUROCAT		Used EUROCAT	
	Politecnico of Milano	University of Salerno	Politecnico of Milano	University of Salerno
653	>3.7	3.5		
643			–	3.8
623	2.5	2.0	2.7	2.8
610	1.8	1.7	2.3	1.9
593	1.3	0.9	1.6	1.5
578	0.9	0.7	1.0	1.1

5. Conclusions

The following conclusions can be drawn from the results obtained over the EUROCAT oxide catalyst by different research groups and presented in this study:

- deNO$_x$ data collected at Politecnico of Milan and University of Salerno over both the fresh and used monolith samples are in good agreement, and compare well with the results provided by the catalyst supplier; the ENEL experimental results are slightly higher.
- Under both sets of experimental conditions under which the deNO$_x$ tests have been carried out, the used EUROCAT catalyst showed a higher reactivity than the fresh sample. This confirms that 9000 h of operation did not deactivate the EUROCAT catalyst.
- A 2D, single-channel model of the SCR monolith reactor was used to analyze data collected at Politecnico of Milano over monolith samples and an estimation of the intrinsic kinetic constant and of the effectiveness factor was made; these intrinsic activity data well compare with those obtained over powdered catalyst by the Boreskov Institute.
- SO_2–SO_3 activity tests were also performed: activity tests carried out by Politecnico of Milan and University of Salerno are in good agreement. The used EUROCAT sample presented a slightly higher conversion than the fresh EUROCAT catalyst.

References

[1] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.
[2] L. Lietti, P. Forzatti, Heter. Chem. Rev. 3 (1996) 33.
[3] J.P. Chen, R.T. Yang, Appl. Catal. A: Gen. 80 (1992) 135.
[4] L. Lietti, P. Forzatti, F. Bregani, Ind. Eng. Chem. Res. 35 (11) (1996) 3884.
[5] G.W. Spitznagel, K. Huttenhofer, J.K. Beer, in: J.N. Armor (Ed.), Enviromental Catalysis, ACS Symp. Ser. 552, American Chemical Society, Washington, DC, 1994, p. 172.
[6] E. Hums, G.W. Spitznagel, Preprints, Div. Pet. Chem., Vol. 39, American Chemical Society, 1994, p. 130.
[7] G. Busca, L. Marchetti, J. Chem. Res. (S) (1986) 174.
[8] H. Matralis, S. Theret, Ph. Sebastians, M. Ruwet, P. Grange, Appl. Catal. B: Environ. 5 (1995) 271.
[9] E. Tronconi, P. Forzatti, AIChE J. 38 (1992) 201.
[10] E. Tronconi, A. Beretta, A.S. Elmi, P. Forzatti, S. Malloggi, A. Baldacci, Chem. Eng. Sci. 49 (1994) 4277.
[11] J. Svachula, L. Alemany, N. Ferlazzo, P. Forzatti, E. Tronconi, F. Bregani, Ind. Eng. Chem. Res. 32 (1993) 826.
[12] J. Svachula, N. Ferlazzo, P. Forzatti, E. Tronconi, F. Bregani, Ind. Eng. Chem. Res. 32 (1993) 1053.
[13] Unpublished results from Politecnico of Milan.
[14] A. Beretta, E. Tronconi, G. Groppi, P. Forzatti, in: J. Mouljin, A. Cybulski (Eds.), Structured Catalysts and Reactors, 1998 (Chapter 5).
[15] N. Wakao, J.M. Smith, Chem. Eng. Sci. 17 (1962) 825.
[16] J.W. Beeckman, L.L. Hegedus, Ind. Eng. Chem. Res. 30 (1991) 969.
[17] A. Beretta, E. Tronconi, L.J. Alemany, J. Svachula, P. Forzatti, in: V. Cotés Corberan, S. Vic Bellon (Eds.), New Developments in Selective Oxidation, Vol. II, Elsevier, Amsterdam, 1994, p. 869.
[18] L. Lietti, P. Forzatti, F. Berti, Catal. Lett. 41 (1996) 35.