HCl-doping of V/TiO_2-based catalysts reveals the promotion of NH_3-SCR and the rate limiting role of NO oxidative activation

Aldo Lanza[a], Lei Zheng[a,b], Roberto Matarrese[a], Luca Lietti[a], Jan-Dierk Grunwaldt[b], Silvia Alcove Clave[c], Jillian Collier[c], Alessandra Beretta[a,*]

[a] *Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy*

[b]*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany*

[c]*Johnson Matthey Technology Centre, Blounts Ct Rd, Sonning Common, Reading RG4 9NH, United Kingdom*

Key-words: NH_3-SCR, HCl, V_2O_5-MoO_3/TiO_2, NO activation, transient kinetic experiments, operando FT-IR

Abstract

NH_3-SCR is the best available technology for NO_x abatement from power plant, incinerators, gasifiers, and a well-established technology for on board NO_x emission control; in the last 40 years, the reaction mechanism and kinetics have been deeply investigated, but the understanding of the nature of surface intermediates and rate determining steps is still object of a lively discussion. A major factor, though, has been largely neglected in the scientific literature, that is the presence of HCl in the flue gases generated by coal, biomass and plastics. In this work, the effect of HCl on NH_3-SCR over V_2O_5 catalysts was investigated through combined kinetic analysis and operando FTIR. Unexpectedly, after HCl-doping, the catalyst intrinsic activity of a commercial catalyst increased by a factor of 5. Besides, it was found that while the NH_3 surface coverage is little affected by HCl-doping, the chemisorption capacity of $NO+O_2$ undergoes a remarkable promotion that scales with the promotion of the reaction rate. The HCl-effect provided thus an indirect but unambiguous piece of evidence that NO-activation by an O-species is a key rate controlling step of NH_3-SCR.

1. Introduction

NH_3-SCR (Selective Catalytic Reduction) is the best available technology for the abatement of nitrogen oxides emitted by power plants, stationary and marine diesel engines and other energy conversion systems based on the combustion or gasification of coal, biomass, organic waste and plastics [1-8]. The technology is now being deployed also in light and heavy-duty diesel vehicles.

Ternary V_2O_5-MoO_3(WO_3)/ TiO_2 formulations represent the catalysts of choice in stationary applications but their use in on-board deNO_x units is also widespread in Asian countries, such as China. Despite an over 40-years-long history of studies, the mechanism and kinetics of NH_3-SCR on V are still discussed and fertile soil of new findings [9-19]. Remarkably, a major factor, relevant in stationary applications, has been largely neglected (with very few exceptions [20-22, 26]) in the scientific literature, that is the presence of HCl in the flue gases. Novel studies from Perez-Ramirez's group and others have shown the tendency of several metal oxides, including TiO_2, and redox oxides like V_2O_5, to combine with HCl; which suggests possible implications for the SCR reaction [23-25]. Recently, the effect of HCl on the SCR activity of a MnCe catalyst was studied and a permanent deactivation was found due to volatilization of Mn [26]. However, commercial V-based SCR catalysts are designed to operate stably under HCl-containing flue gases.

The presence of HCl in the flue gases and its interaction with the V-based catalysts is unanimously recognized as the key behind the chemistry of the so-called mercury oxidation on SCR catalysts, a reaction of great interest because of the growing concern and emerging stringent regulations on Hg emissions from stationary power plants; across the SCR reactor, mercury is subject to combined oxidation and chlorination, highly desirable since the product $HgCl_2$ is more easily removed from the flue gases by means of conventional wet scrubbers downstream from the SCR unit. Recent DFT and kinetic studies have proposed the formation of chlorinated V-species [27-33]. Experience and theory thus confirm the ability of V-catalysts to bond and release Cl species from gas-phase HCl but what is the effect of V-HCl interaction on the chemistry and kinetics of NH_3-SCR is still unknown. Within a more extended kinetic investigation on Hg/HCl/O_2/NO/ NH_3 reacting

systems, we were driven into this long-overlooked aspect. Experiments were performed over a proprietary $V_2O_5/MoO_3/TiO_2$ catalyst and a model V/TiO_2 catalyst where HCl-doping was obtained by pre-impregnation. Transient activity tests and operando FT-IR experiments provided novel pieces of evidence on the kinetics of NH_3-SCR. In particular, the breakthrough evidence on the kinetic relevance of NO oxidative activation was clearly obtained.

The interaction of NO_X with V-sites has been discussed in the broad literature of standard and fast NH_3-SCR in close relation with the redox nature of the catalytic cycle; a debate is still open. Koebel et al. first showed that the powerful oxidizing property of NO_2 enhanced the kinetics of the oxidation step of the redox cycle ($V^{4+} \rightarrow V^{5+}$) and could explain the promoted kinetics of the fast SCR [34-37]. Similarly, surface nitrite/nitrate intermediates have been proposed to behave as enhancers of V^{4+} re-oxidation in the standard SCR by Arnarson et al. (based on DFT calculations) and by Beretta et al. (based on kinetic evidence) [38,9]. Concerning the reduction step, it is well known that the seminal studies by Ramis et al. [1,4,13] and Topsoe et al. [14,15,39] have proposed (based on spectroscopic results) the kinetic relevance of NH_3 partial oxidation to a surface N^{2-} species. Instead, Tronconi and co-workers have proposed the rate controlling role of NO adsorption over an oxidized site with formation of a surface N^{3+} species, able to rapidly react with adsorbed NH_3 and produce N_2, leaving a reduced site V^{4+} [40]. Recent studies investigated the promotion of low-temperature SCR by using Ce-modified V-based catalysts and have addressed the role of surface NO_X and nitrates (whose storage is largely promoted by CeO_2 sites) in the reaction mechanism [41- 48]. Brückner and coworkers [41] found that $Ce_{1-x}Ti_xO_2$ supports were as active in NH_3-SCR, as in the formation of nitrates from gaseous $NO+O_2$, however the involvement of adsorbed NO* intermediates was excluded when V was added (since no nitrate formation was observed over V-containing catalysts at 200°C). Instead, Li and coworkers [42, 43] confirmed the promoting effect of the VO_x-Ce interaction, associating it to the largely favored formation of surface NO_X species.

The present work aims at contributing to the presently open debate on the kinetics of NH_3-SCR on V-based catalysts, whose deep comprehension can lead to new formulations able to enhance the low-temperature NO_x conversion.

2. Materials and methods

2.1 Experimental

Catalyst samples - SCR experiments were performed over a proprietary Johnson Matthey $V_2O_5/MoO_3/TiO_2$ commercial catalyst developed for coal-fired power plants and combined biomass-coal-fired power plants; the same catalyst formulation was the object of previous studies [9, 33]. Prior to testing, the catalyst was pre-treated in flowing air at 450°C in a packed-bed reactor.

HCl-doping was obtained by impregnation with an aqueous solution of HCl (IWI method, details in Supplementary Material). After drying at 110°C, the concentration of HCl deposited by this methodology was estimated by ICP analysis at 35-40 $\mu mol/g_{cat}$.

Both doped and undoped catalysts were sieved (140-200 mesh) to obtain powders for the kinetic investigations in a lab-scale packed-bed reactor.

A 2%V/TiO_2 model catalyst was also used, as such and impregnated with HCl with ratio V/HCl=1.

Lab-scale apparatus for the kinetic investigations – The SCR activity and temperature programmed tests were performed in a micro fixed-bed reactor, consisting of a quartz tube (with 9 mm ID). The catalytic bed was diluted with quartz particles (140-200 mesh). Above the catalytic bed an additional bed of inert quartz granules (10-14 mesh) was loaded to obtain uniform flow distribution and preheating of the inlet stream. The reactor was placed in an electric-oven and the temperature was controlled by a type K thermocouple placed in the catalytic bed. A Pfeiffer Vacuum ThermoStar mass spectrometer was connected to the exhaust gases to continuously analyze the products.

NH_3-SCR activity tests were performed over the HCl-VMoTi catalyst by an initial adsorption/stabilization phase with flowing NH_3= 320 ppm, NO= 300 ppm and O_2= 3% in He at

150°C, followed by a temperature ramp from 150 to 400°C (5°C/min). After 3 hours of hold at 400°C, the reactor was cooled down and a second run was then repeated over the same sample with the same procedure.

The NO-TPSR were performed over HCl-VMoTi catalyst and the reference VMoTi catalyst after NH_3 pre-adsorption at 100°C (NH_3=500 ppm, 90 minutes). A ramp under NO=100 ppm+O_2=1000 ppm was then run from 100°C to 450°C (5°C/min). A second run was repeated on each sample.

The NO+O_2 adsorption/desorption tests were performed over HCl-VMoTi and over the reference VMoTi catalyst. After the initial storage phase under flowing NO=100 ppm and O_2=1000 ppm in He at 100 °C of 2 hours, a temperature ramp was then run from 100 to 400°C (5°C/min).

Steady state NH_3-SCR activity tests were performed over the HCl-doped and undoped VMoTi commercial sample and binary 2%V/TiO_2 model catalyst with flowing NH_3= 320 ppm, NO= 300 ppm and O_2= 3% in He.

Additional details on the procedure and operating conditions of each experiment (catalyst load, bed dilution, total flow rate) are given in the Supplementary Material.

Operando FT-IR tests– The NO_x and NH_3 storage capacity was investigated over the HCl treated 2%V/Ti catalyst and over the reference 2%V/Ti catalyst. The catalysts in the form of self-supported disks of ca. 15 mg were placed in a heated IR reactor cell (ISRI Infrared Reactor, Granger, IN, USA) working under flowing gases. NO and NH_3 adsorption were carried out at ambient temperature with NO (1000 ppm) in He + O_2 (3%, v/v) or 500 ppm of NH_3/He for 30 minutes, respectively. Additional details on the experimental apparatus and procedures are reported in the Supplementary Material and elsewhere [49].

2.2 Packed-bed reactor model

A steady state model of the plug flow micro-reactor has been reported elsewhere [9] and therein applied to the development of redox kinetics of NH_3-SCR, accounting for several compositional effects. The model consists of the differential mass balances of the reacting species

and accounts for the possible contribution of intra-porous mass transfer limitations. In this work, the same model was used as a simple tool for data analysis and estimation of the intrinsic activity. At this scope, the simplifying assumption of pseudo-first order kinetics was done, such that the model reduces to the mass balance of the species NO. All the details of the model and its use for the estimate of the kinetic constants are reported in the Supplementary Material.

3. Results

SCR activity tests - Figure 1 reports the results of two consecutive dynamic NH_3-SCR experiments over a HCl-impregnated sample.

[Figure 1]

In the first run, the reaction onset was observed at about 150°C; NO conversion grew with temperature with an activation energy of 92 kJ/mol (Figure S1) and turnover rates by far higher than those of the undoped catalyst. Above 275°C, NO conversion grew only moderately, then flattened at about 95% and finally decreased down to 83% during the 3-hours hold at 400°C. The high temperature loss of activity can be easily explained by the loss of HCl via desorption in the gas phase: this was indeed confirmed by a TPD experiment carried out over the HCl-doped VMoTi catalyst in flowing 0.5% O_2 in He (Figure S2), showing the release of HCl above 200°C.

Then, after cooling the catalyst, a second run was started with the same flow conditions: the conversion curve appeared shifted by about 50°C, and is representative of the behavior of a HCl-free catalyst sample. In fact at 400°C the same conversion of 83% was observed during the second ramp.

The experiment revealed the formidable promotion of the reaction by HCl addition; at 225°C, the intrinsic rate constant increased by a factor of 5 as shown by the Arrhenius plot of pseudo-first order kinetic constants in Figure S1.

Additional experiments were performed to follow the loss in the catalyst activity at high temperature due to the loss of HCl. Starting from the HCl-doped VMoTi catalyst at 350°C, Figure S3 shows that the NO conversion decreases from over 90% down to about 70% in 4 hours on stream

(blue squares), eventually reaching the activity of the fresh catalyst (red squares). Then, upon decreasing the temperature of the HCl-doped VMoTi catalyst, the reactivity of the doped and undoped samples are superimposed.

$NO+O_2$-TPSR tests - $NO+O_2$-TPSR (Temperature Programmed Surface Reaction) with flowing NO and O_2 in He after NH_3 pre-adsorption at 100°C were also performed on both the HCl-doped catalyst and the undoped catalyst. The whole procedure is described in detail in the Supplementary Material. This kind of experiments allows to identify the onset of the reaction and quantify the amount of reacted NH_3 from the surface. Therefore, the comparison between the $NO+O_2$-TPSR tests on catalysts with and without HCl allows to measure simultaneously the effect of HCl on both the reaction rate and the NH_3-storage capacity. The results are reported in synthetic form in Figure 2 and in detailed form in Figure S4.

[Figure 2]

Both the undoped and the HCl-doped catalysts were subject to two consecutive experiments; Figure 2 reports for brevity the results of the first run over the undoped catalysts (the second ramp was identical), and the two consecutive runs over the HCl-doped catalyst. Over both doped and undoped catalysts, NH_3 desorption occurred as soon as the temperature ramp started, the concentration was maximum at about 250°C and then decreased rapidly with increasing temperature (Figure S4). Concerning NO consumption and N_2 formation (Figure S5), these started around 150°C in the first ramp over the HCl-doped catalyst: NO conversion grew rapidly, peaked at 70% at about 270°C, then extinguished as soon as the NH_3 coverage dropped. In the repeated experiment (second ramp in Figure 2, black curve), the onset of NO conversion was observed at 200°C with significantly lower initial rate; the overall consumption was also significantly lower. The comparison reported in Figure 2 (black line vs red line) reveals that these features are the same as those of the undoped catalyst, a further confirmation that the high temperature desorption of HCl leaves unchanged the surface of the catalyst and that the presence of HCl produced the important promotion of the reaction.

The integral consumption of NO amounted to 105 μmol/g_{cat} over the HCl-doped catalyst and 51 μmol/g_{cat} over the undoped catalyst; by considering also the overall desorption of NH_3 during the experiments, it was estimated that NH_3 coverage amounted to about 270 μmol/g_{cat} (at 100°C) on both HCl-doped and undoped catalyst. Which cannot explain the dramatic promotion of the reaction rate.

A simple quantitative analysis was performed over the low-temperature range of the TPSR curves (where the absence of any stoichiometric limitation by ammonia can be assumed). Pseudo-first order kinetic constants were estimated for the undoped and the HCl-doped catalyst, as detailed in the Supplementary Material (Figure S6); the analysis confirmed the estimate of an activation energy of 92 kJ/mol in the range 150-250°C and a promotion factor by over 550% after HCl doping.

The effect of HCl doping was investigated also on a binary model 2% V/TiO_2 catalyst. Reference steady-state NH_3-SCR experiments were first performed over the undoped catalyst under similar operating conditions as those used for the ternary commercial catalyst; a remarkable increase of the intrinsic activity was found (compared with the commercial catalyst), as expected for the large V-content. The temperature range of the experiments was thus limited to an upper value of 280°C. The binary catalyst was also impregnated with HCl and experiments were repeated over the HCl-doped catalyst; a remarkable increase of the activity was found, as documented in figure S7.

It was thus concluded that the interaction of HCl with the V-TiO_2 system is the key behind the observed performance of the ternary catalyst, despite the complex formulation of the commercial catalyst, that, together with the MoO_3 component typically includes several additives that convey structural and mechanical stability.

NO_x storage experiments - To further study the origin of the paramount effect on the DeNOx activity, pieces of evidence on the effect of HCl on the adsorption/activation of reactants were searched by dedicated experiments in the packed bed reactor (commercial catalyst) and in an operando FT-IR cell (model catalyst).

Figure 3 reports the results of experiments of $NO+O_2$ adsorption at 100°C over the ternary commercial catalyst, followed by temperature ramp (under flowing $NO + O_2$). The procedure is described in detail in the Supplementary Material.

[Figure 3]

Negligible adsorption and desorption of NO were observed over the undoped catalyst at 100°C (red line in Figure 3). Indeed, the negligible NO adsorption capacity of V-catalysts is well known and is the evidence behind the kinetic formalism of the Eley-Rideal rate expression, commonly adopted to describe the process [41, 50-52]. Instead, surprisingly, a significant NO peak was observed after the adsorption phase for the HCl-doped catalyst. NO desorption started at 150°C, peaked at about 200°C and extinguished at about 230°C. The temperature range involved in the desorption are the clear evidence of the existence of chemisorbed NO species and since the experiment was performed in the presence of O_2, we herein infer that the chemisorbing site was a surface O* or OH* species. The experiment thus reveals that more abundant adsorbed NO species were formed after the HCl-doping.

Further support was obtained by operando FT-IR experiments over a model 2% V/TiO_2 catalyst with and without HCl-doping. Experiments were performed over the binary catalyst in order to maximize the sensitivity. After a mild drying treatment in O_2/He flow, a $NO+O_2$ in He stream was admitted to the IR cell. Figure 4 shows the evolution of the spectra collected during 30 minutes from the reactant inlet.

[Figure 4]

Panel (a) refers to the undoped catalyst, while panel (b) refers to the HCl-doped $2\%V/TiO_2$ sample. In both cases the progressive accumulation of NO_x surface species occurred. According to the literature the main formation of different kind of surface nitrates (i.e. bridging, bidentate and monodentate nitrates) was observed in the 1650-1450 and 1300-1200 cm^{-1} regions [13,53,54]. Moreover, the presence of minor amounts of surface nitrites with both nitro and nitrito structures cannot be excluded because of their strong overlapping with nitrates. However, the intensity of signals

obtained over the HCl-doped sample was significantly higher than that of the undoped catalyst. The perturbation of the fundamental vanadyl (at about 1028 cm^{-1}) and of the overtone (about 2045 cm^{-1}, see insert in the Figure) were significantly more intense over the chlorinated catalyst, in line with the increased amounts of NO_x adsorbed [55,56].

NH_3 adsorption experiments were also performed in the FTIR apparatus; spectra were collected during the first 30 minutes after injection of the NH_3 containing stream. As reported in Figure S8, peaks representative of NH_3 adsorbed over Bronsted and Lewis acid sites were observed, but no appreciable difference between the undoped and HCl-doped samples were visible. This suggests that the surface acidity was not significantly modified by the presence of HCl.

4. Discussion

The bulk of data herein presented demonstrate a powerful promoting effect of HCl addition on the SCR reaction. The overall coverage and strength of adsorption of NH_3 did not change significantly after HCl doping; instead, an unexpected increase of the low temperature adsorption of NO in the form of nitrates was observed over the HCl-doped catalyst. The stored nitrates decompose upon heating, thus restoring gas-phase NO.

Notably, the same nitrate species are also formed over the undoped catalyst, but the storage is exalted in the presence of HCl. We thus speculate that the NO adsorption and activation has a role in the SCR reaction, and that the presence of HCl affects the NO interaction and reactivity with the active V sites. It is interesting to observe that the formation of nitrates from gas phase NO and O_2 and the reversible decomposition of nitrates to NO is the demonstration that nitrogen can travel through a reversible pattern between N^{2+} to N^{5+}. Within this pattern, the true reactive species is formed, i.e. an intermediate whose oxidation state suitably matches and balances the reduced state of nitrogen in the ammonia-derived adsorbed species (an amide species with state N^{2-} according to the conclusions of Topsoe [14,15,39] and Busca et al.[1,13] studies, or an adsorbed ammonia with state N^{3-} according

to Tronconi et al.[40]), although based on the present experiments we cannot speculate on the exact nature of such intermediate.

The redox nature of the reaction cycle has been recently confirmed in the literature, using operando characterization techniques, DFT, modeling and traditional experiments [9,38,52,57-60]. By means of dynamic experiments and time-resolved spectroscopic studies with isotopically labelled molecules, Wachs and coworkers have further proposed the kinetic relevance of NH_3 activation [2, 61]. The experiments herein reported show instead the kinetic relevance of NO activation, which conclusion is not necessarily contradictory with Wachs' proposal. In fact, also Wachs and coworkers confirmed that NH_3 alone cannot be the reducing agent in NH_3-SCR, while the combined NO/NH_3 mixture shows a synergistic reducing effect, as clearly demonstrated also by Ferri et al. [52].

We can speculate that adsorbed HCl interacts with V=O, giving rise to the formation of highly active Cl-V-OH sites as proposed by He et al. and Yang et al. [22,25]; such sites could favor the adsorption of NO and its transformation into an oxidized species that boosts the low temperature SCR activity. In the case of CeO_2-promoted VO_X catalysts, Hu et al. have identified such a species as HONO [62]

5. Conclusions

This work reports the results of a focused experimental campaign, which demonstrated the promoting effect of HCl doping on the $DeNO_X$ performance of a commercial V/Mo/Ti catalyst. Besides, it was found that HCl doping greatly enhances the adsorption of NO + O_2, while it increases only moderately the NH_3-storage. Thus, indirectly, the HCl effect (by perturbing the reacting system) also demonstrates that NO activation is truly kinetically limiting and passes through an oxidative adsorption.

The implications of the present results may be very important, spanning from the improvement of SCR catalysts formulations based on the concept that oxidative adsorption of NO is needed, to the development of catalysts and processes for NO_x adsorption and release. Further

research is needed to identify the nature of the NO-adsorption site and of V-HCl interaction by the combination of characterization, transient and steady state experiments.

Notation

$VMoTi$ = $V_2O_5/MoO_3/TiO_2$ commercial catalyst

$\mathrm{HCl} - \mathrm{VMoTi}$ = HCl-doped $V_2O_5/MoO_3/TiO_2$ commercial catalyst

$HCl - 2\%V/Ti$ = HCl-doped 2%V/TiO_2 binary model catalyst, nominal ratio V:HCl=1

IWI = incipient wetness impregnation

ID = internal diameter of the quartz tube reactor [mm]

Acknowledgements

A.L. acknowledges the financial contributions to his PhD scholarship from the Ministry of University and Research (MUR) and the Energy for Motion project of Department of Energy, Politecnico di Milano. L. Z. thanks the provision of a research travel grant by Karlsruhe House of Young Scientist (KHYS). LL and RM gratefully acknowledge the contribution of Fondazione Banca del Monte di Lombardia for the FTIR-operando set-up. The authors are thankful to the colleagues prof. Enrico Tronconi, prof. Elisabetta Finocchio and prof. Guido Busca for insightful discussion.

References

[1] G. Busca, L. Lietti, G. Ramis, F. Berti, Chemical and Mechanistic Aspects of the Selective Catalytic Reduction of NO_x by Ammonia over Oxide Catalysts: A review. Appl. Catal. B Environ. 18 (1) (1998) 1-36.

[2] M. Zhu, J-K. Lai, M. E. Tumuluri, Z. Wu, I. E. Wachs, Reaction pathways and kinetics for selective catalytic reduction (SCR) of acidic NO_X emissions from power plants with NH_3, ACS Catal. 7 (12) (2017) 8358-8361.

[3] P. Forzatti, L. Lietti, E. Tronconi, Nitrogen Oxides Removal-Industrial, Encyclopedia of Catalysis, John Wiley & Sons Inc. (2012).

[4] L. Lietti, I. Nova, G. Ramis, L. Dall'acqua, G. Busca, E. Giamello, P. Forzatti, F. Bregani, Characterization and reactivity of V_2O_5-MoO_3/TiO_2 De-NO_x SCR Catalysts, J. Catal. 187 (1999) 419-435.

[5] L. J. Alemany, L. Lietti, N. Ferlazzo, P. Forzatti, G. Busca, E. Giamello, F. Bregani, Reactivity and Physicochemical Characterization of V_2O_5-WO_3/TiO_2 De-NO_x SCR Catalysts, J. Catal. 155 (1) (1995) 117-130.

[6] J.-K. Lai, I. E. Wachs, A Perspective on the Selective Catalytic Reduction (SCR) of NO with NH_3 by Supported V_2O_5-WO_3/TiO_2 Catalysts. ACS Catal. 8 (7) (2018) 6537-6551.

[7] P. Forzatti, I. Nova, E. Tronconi, New "Enhanced NH_3-SCR" Reaction for NO_X Emission Control, Ind. Eng. Chem. Res. 49 (21) (2010) 10386-10391.

[8] L. Zheng, M. Casapu, M. Stehle, O. Deutschmann, J.-D. Grunwaldt, Selective Catalytic Reduction of NO_x with Ammonia and Hydrocarbon Oxidation Over V_2O_5-MoO_3/TiO_2 and V_2O_5-WO_3/TiO_2 SCR Catalysts, Top. Catal. 62 (2019) 129-139

[9] A. Beretta, A. Lanza, L. Lietti, S. Alcove Clave, J. Collier, M. Nash, An investigation on the redox kinetics of NH_3-SCR over a V/Mo/Ti catalyst: Evidence of a direct role of NO in the re-oxidation step, Chem. Eng. J. 359 (2019) 88-98.

[10] C. Wang, C. Li, Y. Li, L. Huangfu, Z. Liu, S. Gao, J. Yu, Destructive Influence of Cement Dust on the Structure and DeNO_x Performance of V-Based SCR Catalyst, Ind. Eng. Chem. Res. 58 (43) (2019) 19847-19854.

[11] T. V. W. Janssens, H. Falsig, L. F. Lundegaard, P. N. R. Vennestrom, S. B. Rasmussen, P. G. Moses, F. Giordanino, E. Borfecchia, K. A. Lomachenko, C. Lamberti, S. Bordiga, A. Godiksen, S. Mossin, P. Beato, A Consistent Reaction Scheme for the Selective Catalytic Reduction of Nitrogen Oxides with Ammonia, ACS Catal. 5 (5) (2015) 2832-2845.

[12] I. Nova, A. Beretta, G. Groppi, L. Lietti, E. Tronconi, P. Forzatti, Monolithic catalysts for NO_x removal from Stationary Sources, Structured Catalysts and Reactors (2nd ed.), Taylor & Francis. (2006) 171-214.

[13] G. Ramis, G. Busca, F. Bregani, P. Forzatti, Fourier transform-infrared study of the adsorption and coadsorption of nitric oxide, nitrogen dioxide and ammonia on vanadia-titania and mechanism of selective catalytic reduction, Appl. Catal. 64 (1990) 259-278.

[14] N.-Y- Topsoe, H. Topsoe, J. A. Dumesic, Vanadia/titania catalysts for selective catalytic reduction (SCR) of nitric oxide by ammonia. I, J. Catal. 151 (1995) 226-240.

[15] J. A. Dumesic, N.-Y. Topsoe, H. Topsoe, Y. Chen, T. Slabiak, Kinetic of selective catalytic reduction of nitric oxide by ammonia over vanadia/titania, J. Catal. 163 (1996) 409-417.

[16] I. Nova, C. Ciardelli, E. Tronconi, NH_3-SCR of NO over a V-based catalyst: low-T redox kinetics with NH_3 inhibition, AIChE J. 52 (9) (2006) 3222-3233.

[17] L. Casagrande, L. Lietti, I. Nova, P. Forzatti, A. Baiker, SCR of NO by NH_3 over TiO_2-supported V_2O_5-MoO_3 catalysts: reactivity and redox behavior, Appl. Catal. B Environ. 22 (1) (1999) 69-77.

[18] T. Yan, Q. Liu, S. Wang, G. Xu, M. Wu, J. Chen, J. Li, Promoter rather than Inhibitor: Phosphorus Incorporation Accelerates the Activity of V_2O_5–WO_3/TiO_2 Catalyst for Selective Catalytic Reduction of NO_x by NH_3, ACS Catal. 10 (2020) 2747-2753.

[19] N.R. Jaegers, J.K. Lai, Y. He, E. Walter, D.A. Dixon, M. Vasiliu, Y. Chen, C. Wang, M.Y. Hu, K.T. Mueller, I.E. Wachs, Y. Wang, J.Z. Hu, Mechanism by which Tungsten Oxide Promotes the Activity of Supported V2O5/TiO2 Catalysts for NOX Abatement: Structural Effects Revealed by 51V MAS NMR Spectroscopy, Angew. Chemie - Int. Ed. 58 (2019) 12609–12616.

[20] L. Lisi, G. Lasorella, G. Russo, Single and combined deactivating effect of alkali metals and HCl on commercial SCR catalysts, Appl. Catal. B Environ. 50 (4) (2004) 251-258.

[21] Y. Hou, G. Cai, Z. Huang, X. Han, S. Guo, Effect of HCl on V_2O_5/AC catalyst for NO reduction by NH_3 at low temperatures, Chem. Eng. J. 247 (2014) 59-65.

[22] Y. Yang, W. Xu, J. Wang, T. Zhu, New insight into simultaneous removal of NO and Hg^0 on CeO_2-modified V_2O_5/TiO_2 catalyst: A new modification strategy, Fuel. 249 (2019) 178-187.

[23] M. A.G. Hevia, A. P. Amrute, T. Schmidt, J. Pérez-Ramirez, Transient mechanistic study of the gas-phase HCl oxidation to Cl_2 on bulk and supported RuO_2 catalysts, J. Catal. 276 (1) (2010) 141-151.

[24] R. Liu, W. Xu, L. Tong, T. Zhu, Mechanism of Hg^0 oxidation in the presence of HCl over a commercial V_2O_5-WO_3/TiO_2 SCR catalyst, J. Environ. Sci. 36 (2015) 78-83.

[25] H. Sheng, Z. Jinsong, Z. Yanqun, L. Zhongyang, N. Mingjiang, C. Kefa, Mercury oxidation over a vanadia-based selective catalytic reduction catalyst, Energy and Fuels. 23 (2009) 253–259.

[26] S. Xiong, J. Chen, N. Huang, T. Yam, Y. Peng, J. Li, The poisoning mechanism of gaseous HCl on low-temperature SCR catalysts: MnO_x-CeO_2 as an example, Appl. Catal. B Environ. 267 (2020) 118668.

[27] A. S. Negreira, J. Wilcox, DFT Study of Hg Oxidation across Vanadia-Titania SCR Catalyst under Flue Gas Conditions, J. Phys. Chem. C. 117 (2013) 1761-1772.

[28] K. Alexopoulos, P. Hejduk, M. Witko, M.-F. Reyniers, G. B. Marin, Theoretical Study of the Effect of (001) TiO_2 Anatase Support on V_2O_5, J. Phys. Chem. C. 114 (2010) 3115-3130.

[29] B. Zhang, J. Liu, G. Dai, M. Chang, C. Zheng, Insights into the mechanism of heterogeneous mercury oxidation by HCl over V2O5/TiO2 catalyst: Periodic density functional theory study, Proc. Combust. Inst. 35 (2015) 2855–2865.

[30] Y. Gao, Z. Li, A DFT study of the Hg^0 oxidation mechanism of the V_2O_5-TiO_2 (001) surface, Mol. Catal. 433 (2017) 372-382.

[31] L. Zhao, Y. Liu, Y. wen Wu, J. Han, S. lin Zhang, Q. Lu, Y. ping Yang, Mechanism of heterogeneous mercury oxidation by HCl on V2O5(001) surface, Curr. Appl. Phys. 18 (2018) 626–632.

[32] Y.-W. Wu, Z. Ali, Q. Lu, J. Liu, M.-X. Xu, L. Zhao, Y.-P. Yang, Effect of WO_3 doping on the mechanism of mercury oxidation by HCl over V_2O_5/TiO_2 (001) surface: Periodic density functional theory study, Appl. Surf. Sci. 487 (2019) 369-378.

[33] N. Usberti, S. Alcove Clave, M. Nash, A. Beretta, Kinetics of Hg° oxidation over a V_2O_5/MoO_3/TiO_2 catalyst: Experimental and modelling study under $DeNO_X$ inactive conditions, Appl. Catal. B: Environ. 193 (2016) 121-132.

[34] M. Koebel, M. Elsener, M. Kleemann, Urea-SCR: a promising technique to reduce NOx emissions from automotive diesel engines, Catal. Today. 59 (2000) 335–345.

[35] M. Koebel, M. Elsener, G. Madia, Reaction pathways in the selective catalytic reduction process with NO and NO2 AT low temperatures, Ind. Eng. Chem. Res. 40 (2001) 52–59.

[36] G. Madia, M. Koebel, M. Elsener, A. Wokaun, The effect of an oxidation on the NOx reduction by ammonia SCR, Ind. Eng. Chem. Res. 41 (2002) 3512–3517.

[37] M. Koebel, G. Madia, F. Raimondi, A. Wokaun, Enhanced reoxidation of Vanadia by NO2 in the fast SCR Reaction, J. Catal. 209 (2002) 159–165.

[38] L. Arnason, H. Falsig, S. B. Rasmussen, J. V. Lauritsen, P. G. Moses, A complete reaction mechanism for standard and fast selective catalytic reduction of nitrogen on low coverage VO_x/TiO_2(0 0 1) catalysts. J. Catal. 346 (2017) 188-197.

[39] N.-Y. Topsøe, Mechanism of the Selective Catalytic Reduction of Nitric Oxide by Ammonia Elucidated by in Situ On-Line Fourier Transform Infrared Spectroscopy. Science. 265 (5176) (1994) 1217.

[40] E. Tronconi, I. Nova, D. Ciardelli, M. Chatterjee, M. Weibel, Redox features in the catalytic mechanism of the "standard" and "fast" NH_3-SCR of NO_x over a V-based catalyst investigated by dynamic methods. J. Catal. 245 (2007) 1-10.

[41] T. H. Vuong, J. Radnik, J. Rabeah, U. Bentrup, M. Schneider, H. Atia, U. Armbruster, W. Grünert, A. Brückner, Efficient $VO_X/Ce_{1-X}Ti_XO_2$ Catalysts for Low-Temperature NH_3-SCR Reaction Mechanism and Active Sites Assessed by in Situ/Operando Spectroscopy, ACS Catal. 7 (2017) 1693-1705.

[42] Y. Peng, C. Wang, J. Li, Structure-activity relationship of VO_x/CeO_2 nanorod for NO removal with ammonia, Appl. Catal. B Environ. 144 (2014) 538-546.

[43] L. Chen, J. Li, M. Ge, Promotional Effect of Ce-doped V_2O_5-WO_3/TiO_2 with Low Vanadium Loadings for Selective Catalytic Reduction of NO_x by NH_3, J. Phys. Chem. C. 113 (2009), 21177-21184.

[44] Z. Liu, S. Zhang, J. Li, L. Ma, Promoting effect of MoO_3 on the NO_x reduction by NH_3 over CeO_2/TiO_2 catalyst studied with in situ DRIFTS, Appl. Catal. B Environ. 144 (2014) 90-95.

[45] A. Marberger, D. Ferri, M. Elsener, A. Sagar, C. Artner, K. Schermanz, O. Kröcher, Relationship between structures and activities of supported metal vanadates for the selective catalytic reduction of NO by NH_3, Appl. Catal. B Environ. 218 (2017) 731-742.

[46] P. A. Kumar, Y. E. Jeong, H. P. Ha, Low temperature NH_3-SCR activity enhancement of antimony promoted vanadia-ceria catalyst, Catal. Today. 293-294 (2017) 61-72.

[47] W. Hu, Y. Zhang, S. Liu, C. Zheng, X. Gao, I. Nova, E. Tronconi, Improvement in activity and alkali resistance of a novel V-Ce$(SO_4)_2$/Ti catalyst for selective catalytic reduction of NO with NH_3, Appl. Catal. B Environ. 206 (2017) 449-460.

[48] S. Gillot, G. Tricot, H. Vezin, J-P. Dacquin, C. Dujardin, P. Granger, Development of stable and efficient $CeVO_4$ system for the selective reduction of NO_x by ammonia: Structure-activity relationship, Appl. Catal. B Environ. 218 (2017) 338-348.

[49] A. Porta, T. Pellegrinelli, L. Castoldi, R. Matarrese, S. Morandi, S. Dzwigaj, L. Lietti, Low Temperature NO_x Adsorption Study on Pd-Promoted Zeolites, Top. Catal. 61 (2018) 2021-2034.

[50] R. Willi, B. Roduit, R.A. Koeppel, A. Wokaun, A. Baiker, Selective reduction of NO by NH_3 over vanadia-based commercial catalyst: Parametric sensitivity and kinetic modelling, Chem. Eng. Sci. 51 (11) (1996), 2897-2902.

[51] B. Roduit, A. Wokaun, A. Baiker, Global kinetic modeling of reactions occurring during selective catalytic reduction of NO by NH_3 over Vanadia/Titania-based catalysts, Ind. Eng. Chem. Res. 37 (12) (1998) 4577-4590.

[52] A. Marberger, D. Ferri, M. Elsener, O. Kröcher, The Significance of Lewis Acid Sites for the Selective Catalytic Reduction of Nitric Oxide on Vanadium-Based Catalysts, Angew. Chemie - Int. Ed. 55 (2016) 11989–11994.

[53] K. Hadjivanov, H. Knozinger, Species Formed after NO adsorption and NO+O_2 Co-adsorption on TiO_2: an FTIR Spectroscopic Study, Phys. Chem. Chem. Phys. 2 (2000) 2803-2806.

[54] M. A. Larrubia, G. Ramis, G. Busca, An FT-IR study of the adsorption of urea and ammonia over V_2O_5-MoO_3-TiO_2 SCR catalysts, Appl. Catal. B. Environ. 27 (3) (2000) L145-L151.

[55] T.J. Dines, C.H. Rochester, A.M. Ward, Infrared and Raman study of the adsorption of nitrogen oxides on titania-supported vanadia catalysts, J. Chem. Soc. Faraday Trans. 87 (1991) 1617–1622.

[56] R. Mikhaylov, A.A. Lisachenko, B.N. Shelimov, V.B. Kazansky, G. Martra, S. Coluccia, FTIR and TPD Study of the Room Temperature Interaction of a NO-Oxygen Mixture and of NO_2 with Titanium Dioxide, J. Phys. Chem. C. 117 (20) (2013) 10345-10352.

[57] D.E. Doronkin, F. Benzi, L. Zheng, D.I. Sharapa, L. Amidani, F. Studt, P.W. Roesky, M. Casapu, O. Deutschmann, J-D. Grunwaldt, NH_3-SCR over V-W/TiO_2 Investigated by Operando X-ray Absorption and Emission Spectroscopy. J. Phys. Chem. C. 123 (23) (2019) 14338-14349.

[58] R. Kuma, T. Kitano, T. Tsujiguchi, T. Tanaka, In Situ XANES Characterization of V_2O_5/TiO_2-SiO_2-MoO_3 Catalyst for Selective Catalytic Reduction of NO by NH_3, Ind. Eng. Chem. Res. 59 (30) (2020) 13467-13476.

[59] Y. Ganjkhanlou, T. V.W. Janssens, P. N.R. Vennestrøm, L. Mino, M. C. Paganini, M. Signorile, S. Bordiga, G. Berlier, Location and activity of VO_x species on TiO_2 particles for NH_3-SCR catalysis, Appl. Catal. B: Environ. 278 (2020) 119337.

[60] R. J. G. Niguid, D. Ferri, A. Marberger, M. Nachtegaal, O. Kroecher, Modulated Excitation Raman Spectroscopy of V_2O_5/TiO_2: Mechanistic Insights into the Selective Catalytic Reduction of NO with NH_3. ACS Catal. 9 (2019) 6814-6820.

[61] M. M. Mason, Z. R. Lee, M. Vasiliu, I. E. Wachs, D. A. Dixon, Initial Steps in the Selective Catalytic Reduction of NO with NH_3 by TiO_2-Supported Vanadium Oxides, ACS Catal. 10 (2020) 13918-13931.

[62] W. Hu, R. Zou, Y. Dong, S. Zhang, H. Song, S. Liu, C. Zheng, I. Nova, E. Tronconi, X. Gao, Synergy of vanadia and ceria in the reaction mechanism of low-temperature selective catalytic reduction of NOx by NH_3. J. Catal. 391 (2020) 145-154.

Captions

Figure 1 – NO conversion in NH_3-SCR activity tests over HCl-doped catalyst (120 mg). Total flow rate = 236 Nml/min. Composition: 300 ppm NO, 320 ppm NH_3, 3% O_2, balance He. Temperature ramp = 5°C/min up to 400°C; 3.5 h hold at 400°C.

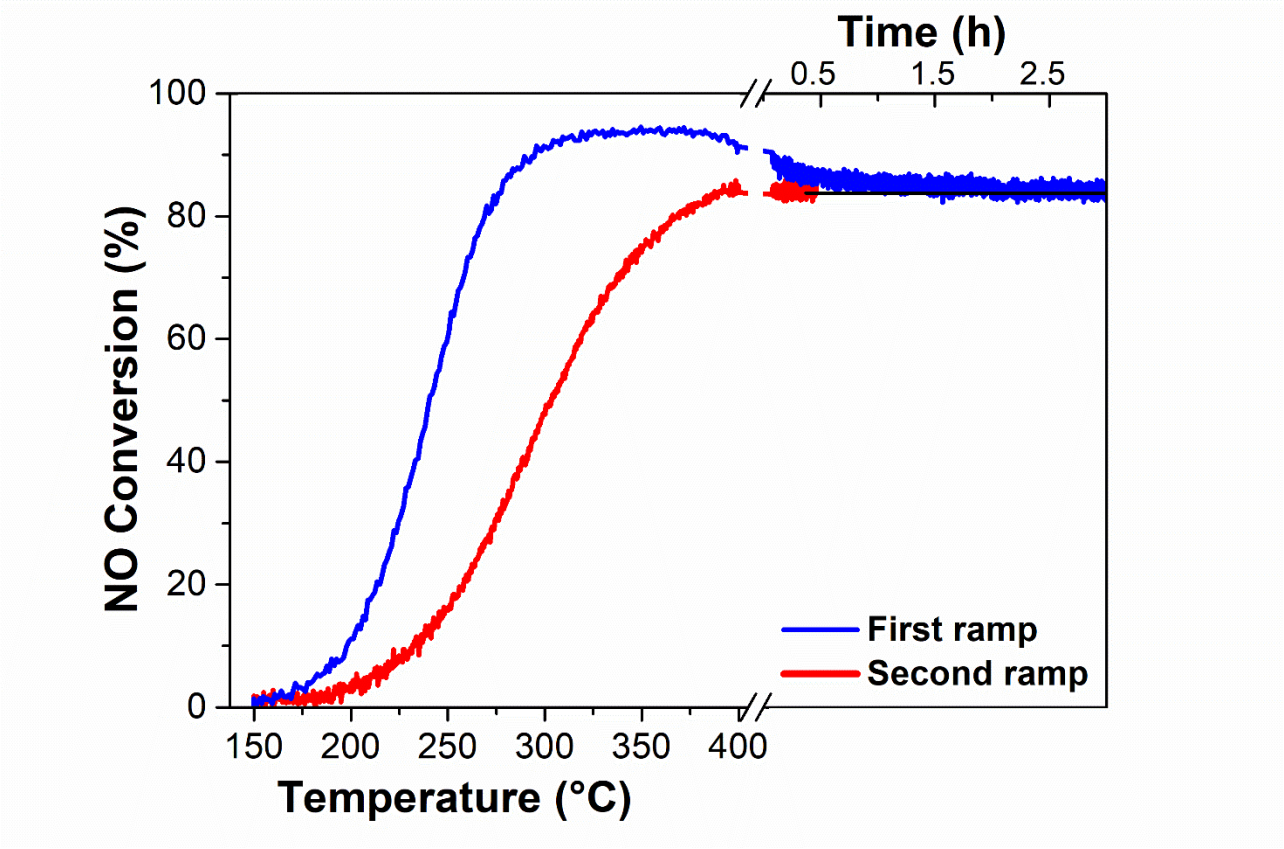
Figure 2 – NO conversion during NO+O_2-TPSR after NH_3 saturation on HCl-doped V/Mo/Ti catalyst (two consecutive experiments) and undoped catalyst. Catalyst = 80 mg. Total flow rate = 200 Nml/min. Composition: 100 ppm NO, 1000 ppm O_2 in He. T-ramp = 5°C/min.

Figure 3 – NO concentration during the temperature ramp, after 2 hours adsorption at 100°C. Catalyst = 200 mg, total flow = 200 Nml/min. Composition: 100 ppm NO, 1000 ppm O_2. Temperature ramp = 5°C/min.

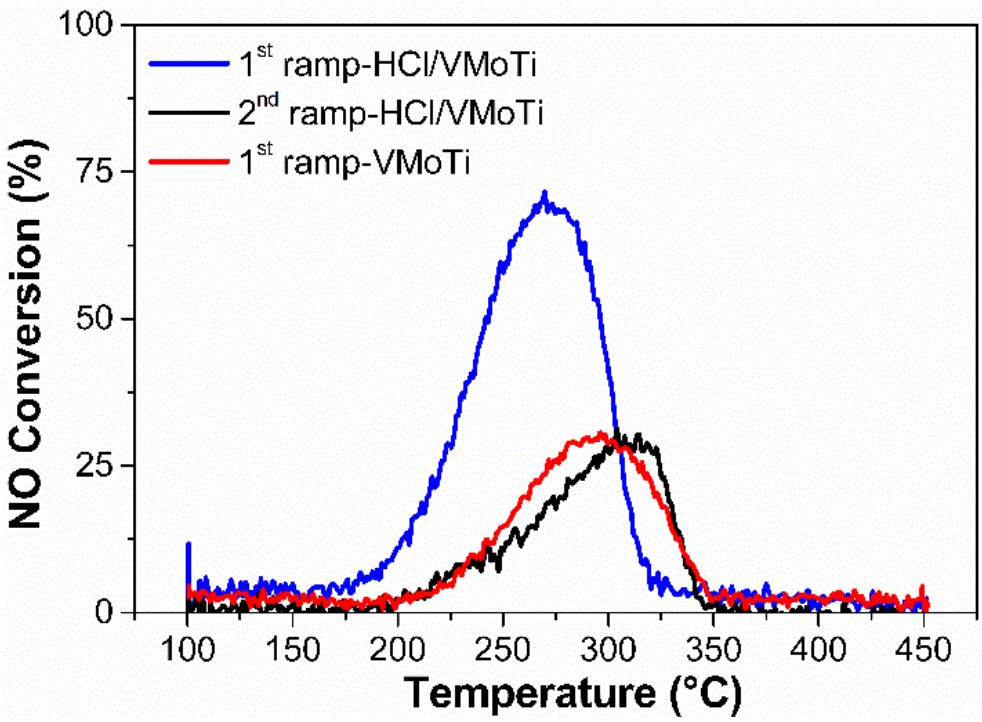
Figure 4 – Differential FTIR spectra collected under flowing NO+O_2 at 25°C. (a) undoped catalyst, 2%V/TiO_2; (b) HCl-doped catalyst, 2%V/TiO_2. Composition: 1000 ppm NO, 3% O_2 in He. The insert shows the 2000-2100 cm^{-1} wavenumber range.

Figures

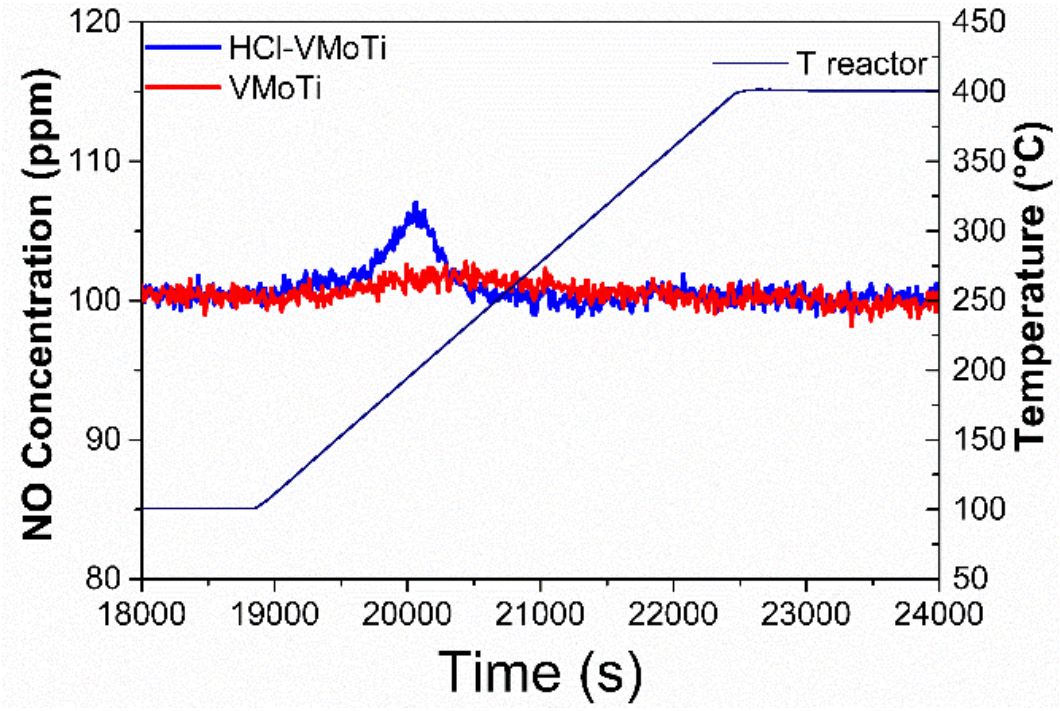
[Figure 1]



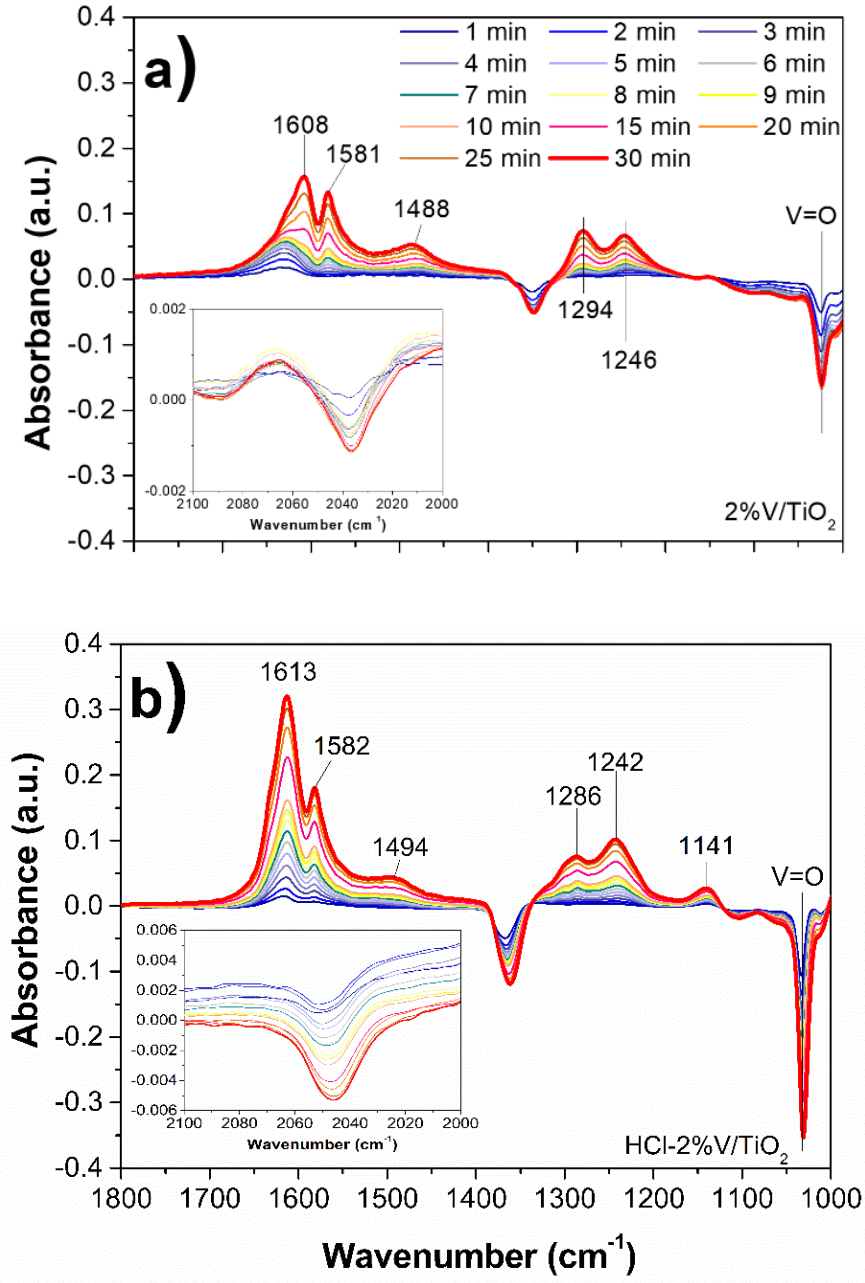
[Figure 2]


1st ramp-HCl/VMoTi
2nd ramp-HCl/VMoTi
1st ramp-VMoTi
NO Conversion (%)
Temperature (°C)
0
25
50
75
100
100
150
200
250
300
350
400
450

[Figure 3]


HCl-VMoTi
VMoTi
T reactor
NO Concentration (ppm)
Temperature (°C)
Time (s)
120
110
100
90
80
450
400
350
300
250
200
150
100
50
18000
19000
20000
21000
22000
23000
24000

[Figure 4]


a)
1 min
2 min
3 min
4 min
5 min
6 min
7 min
8 min
9 min
10 min
15 min
20 min
25 min
30 min
1608
1581
1488
1294
1246
V=O
2%V/TiO2
Absorbance (a.u.)
Wavenumber (cm-1)
b)
1613
1582
1494
1242
1286
1141
V=O
HCl-2%V/TiO2
Absorbance (a.u.)
Wavenumber (cm-1)

Supplementary Material

HCl-doping of V/TiO_2-based catalysts reveals the promotion of NH_3-SCR and the rate limiting role of NO oxidative activation

Aldo Lanza[a], Lei Zheng[a,b], Roberto Matarrese[a], Luca Lietti[a], Jan-Dierk Grunwaldt[b], Silvia Alcove Clave[c], Jillian Collier[c], Alessandra Beretta[a,*]

[a] *Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy*

[b]*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany*

[c]*Johnson Matthey Technology Centre, Blounts Ct Rd, Sonning Common, Reading RG4 9NH, United Kingdom*

Key-words: NH_3-SCR, HCl, V_2O_5-MoO_3/TiO_2, NO activation, transient kinetic experiments, operando FT-IR

Catalyst samples

The commercial V_2O_5-MoO_3/TiO_2 is a JM proprietary catalyst used in several long-term applications including coal-fired power plants, and combined biomass-coal power plants (with typically more than 10% of water, 1-50 ppm of HCl).

The catalyst was received in the form of slabs cut from the commercial plates. The catalyst layer was removed from the metal net, crushed and calcined in situ at 450°C under air flow of 200 Nml/min. The catalyst was impregnated with HCl by Incipient Wetness Impregnation method with a solution of 2.31mol/l prepared from a commercial concentrated HCl solution (37% solution in water, Acros Organics) and the resulting powders were dried overnight at 110°C in oven. ICP analysis showed a content of Cl of 0.12-0.13% (w/w). The catalyst with HCl is indicated in this work as "HCl-VMoTi", while the reference catalyst as "VMoTi".

A binary model catalyst 2%V/TiO_2 was prepared by IWI of TiO_2 (Tronox DT-51 anatase) with a solution of ammonium metavanadate (NH_4VO_3), oxalic acid and water (stirred at 80°C to ensure the complete dissolution of the salt). Impregnated powders were dried overnight at 100°C and calcined at 500°C for 2 h in air. The HCl impregnation was obtained by applying the same procedure as the VMoTi catalyst. The binary catalyst with HCl is indicated in this work as "HCl-2VTi", while the reference catalyst as "2VTi".

SCR-Temperature-Programmed Reaction

The reactivity of the HCl-VMoTi was tested by SCR-Temperature Programmed Reaction. The results are reported in Figure 1. A fixed-bed quartz tubular reactor was prepared with 120 mg of HCl-VMoTi catalyst (140-200 mesh) mixed with 180 mg quartz particles (same mesh).

The catalytic bed was dried for 60 min at 150°C under 3%O_2/He flow (236 Nml/min); afterwards, the feed mixture (300 ppm NO, 320 ppm NH_3 3% O_2 in He) was fed (236 Nml/min) for 60 min at 150°C. A temperature ramp was then started from 150 to 400°C (5°C/min), with final hold of 3 h at 400°C. The reactor was then cooled down to 150 °C under 3%O_2/He flow (236 Nml/min). A second ramp was finally started with the same conditions as the first ramp.

The experimental set-up is equipped with an Online QMS Mass Spectrometer (Thermostar Pfeiffer Vacuum) where signals of each reactant of interest are detected. Data are processed and elaborated to eliminate drifts and cross-influences of the signals due to mass fragmentations, and to quantify the concentrations; to

this scope, calibration of the instrument is periodically repeated by means of calibration mixtures and development of deconvolution algorithms.

$NO+O_2$-Temperature-Programmed Surface Reaction over HCl-VMoTi and VMoTi

For the $NO+O_2$-TPSR experiments, fixed-bed reactors were prepared with 80 mg of catalyst and 120 mg of quartz particles (140-200 mesh). The catalytic bed was initially dried under He flow (200 Nml/min) at 150°C. After drying, a flow of 500 ppm of NH_3/He was fed for NH_3 pre-adsorption for 90 min at 100°C; the treatment was followed by a purge in He for 2h at 100°C.

A feed flow of NO=100 ppm and O_2=0.1% was then fed for 60 min at 100°C and a first ramp was set from 100 to 450°C (5°C/min heating rate). The reactor was then cooled down to 100 °C under 0.1%O_2/He flow (200 Nml/min) and the same procedure was repeated for a second experiment.

$NO+O_2$ adsorption over HCl-VMoTi and VMoTi

A fixed-bed quartz tubular reactor was prepared with 200 mg of catalyst mixed with 200 mg of quartz powders (140-200 mesh) and was initially dried under He flow (200 Ncc/min) at 150°C. Then the catalyst was cooled down to 100°C and NO=100 ppm + O_2=1000 ppm were fed with He as balance at the total flowrate of 200 Nml/min at 100°C for 2h. The temperature ramp was then started up to 400°C (5°C/min of heating rate), keeping the $NO+O_2$ in He flow.

SCR activity tests over HCl-VMoTi and VMoTi

A fixed-bed quartz tubular reactor was prepared with 60 mg of catalyst mixed with 120 mg of quartz powders (140-200 mesh). SCR activity tests were performed with a flowrate of 236 Nml/min by feeding NH_3=320 ppm, NO=300 ppm, O_2=3% in He.

SCR activity experiments over HCl-2%V/TiO_2 and 2%V/TiO_2

A fixed-bed quartz tubular reactor was prepared with 33 mg of catalyst mixed with 300 mg of quartz powders (140-200 mesh). SCR activity tests were performed with a flowrate of 325 Nml/min by feeding NH_3=320 ppm, NO=300 ppm, O_2=3% in He.

NO+O_2 and NH_3 adsorption over HCl-2%V/TiO_2 and 2%V/TiO_2 on Operando FT-IR

For the Operando FT-IR analysis the catalysts in form of self-supported wafers (ca. 15 mg, diameter = 13 mm) were placed into an IR reactor cell (ISRI Infrared Reactor, Granger, IN, USA) connected to gas lines with gas mixing devices and mass flow controllers. All the experiments were performed under a total flow of 50 Nml/min. The spectra were collected on a FT-IR Vertex 70 (Bruker, Billerica, MA, USA) with a spectral resolution of 4 cm^{-1} and accumulating 64 scans using a MCT detector. The samples were pre-oxidized at 350°C (O_2=3% v/v in He) for 90 minutes and then cooled down to 25°C. The NO_x storage experiments were performed with gas inlet stream of NO=1000 ppm + O_2=3% v/v in He, for 30 minutes. For ammonia adsorption, the same pre-oxidation treatment was performed, then the catalyst was exposed to a He flow with NH_3=500 ppm for 30 minutes. All the spectra are reported as difference spectra: the spectrum subtracted is always that recorded at ambient temperature after the pre-oxidation treatment.

Packed bed reactor model

$NO\ mass\ balance$:

$$\frac{dc_{NO}}{dw_{cat}} = -\eta_{DeNOx} \cdot R_{DeNOx} \cdot \frac{1}{\dot{Q}} \qquad (S1)$$

$$with\ the\ initial\ condition:\ c_{NO}|_{w_{cat}=0} = c_{NO,in} \qquad (S2)$$

With the rate expression:

$$R_{DeNOx} = k\, c_{NO} = \left[\frac{cm^3}{s\, g_{cat}}\right] \left[\frac{mol}{cm^3}\right] \qquad (S3)$$

The effectiveness factor is defined as follows:

$$\eta_{DeNOx} = \frac{1}{3 \cdot \Phi^{\ 2}} \cdot (3 \cdot \Phi \cdot \coth(3 \cdot \Phi) - 1) \qquad (S4)$$

The Thiele modulus is calculated with a pseudo first order kinetic:

$$\Phi_{DeNOx} = \frac{d_p[cm]}{6} \cdot \sqrt{\frac{k\ \rho}{D_{eff,NO}}} \qquad (S5)$$

In Eq. (S1-S5), $\dot{Q}\left[\frac{cm^3}{s}\right]$ is total flow rate under actual T, P conditions, $k\left[\frac{cm^3}{s\, g_{cat}}\right]$ is the pseudo-first order activity constant, $C_{NO}\left[\frac{mol}{cm^3}\right]$ is the concentration of NO, $W_{cat}\ [g]$ is the catalyst weight, $D_{eff,NO}\ \left[\frac{cm^2}{s}\right]$ is the effective intraporous diffusivity of NO, calculated as in reference [S2].

In this work, the model was applied to the estimates of the intrinsic rate constants of the catalyst samples (with and without HCl). The model fit involved the data reported in Figure 1 (flow of NO, NH_3 and O_2 in He with temperature ramp) and Figure 2 ($NO+O_2$ – TPSR) in the low temperature range. Although the model is steady state, it can be suitably applied also to dynamic data when obtained under quasi-stationary conditions as in the present case (temperature ramp of 5°C/min). The effectiveness factor was unitary under the conditions analyzed.

The model fit has been herein reported in the form of Arrhenius plots, a conventional form of representation of the measured and estimated intrinsic rate constant k (obtained by integration of Eq. S1)

$$k = -ln(1-\chi_{NO})\frac{Q(T)}{W} \qquad \text{(S6)}$$

in a ln (k) vs 1/T plot that highlights the temperature sensitivity:

$$\ln(k) = \ln(k_0) - \frac{E_{act}}{R}\cdot\frac{1}{T} \qquad \textit{(S7)}$$

We note that the use of this methodology becomes improper when the behavior of the reactor is influenced (possibly limited) by the input/output dynamics; in particular the Arrhenius plots of dynamic data obtained at high heating ramping rate can be highly misleading.

Additionally, the model was used to extrapolate the low-temperature quasi steady state behavior to high temperature conditions, which better emphasizes where the deviations of the reactor behavior from the stationary conditions prevailed.

The model application is exemplified in Figure S6b, where dashed lines are the calculated results (extrapolated also to the higher temperature) and symbols are the experimental results.

The verifications confirmed that both for the HCl-doped and the undoped catalyst, the effectiveness factor was equal to 1 within the experimental rage, being 0.98 at 325°C for the very active HCl-doped catalyst.

Supplementary Figures

[Figure S1]

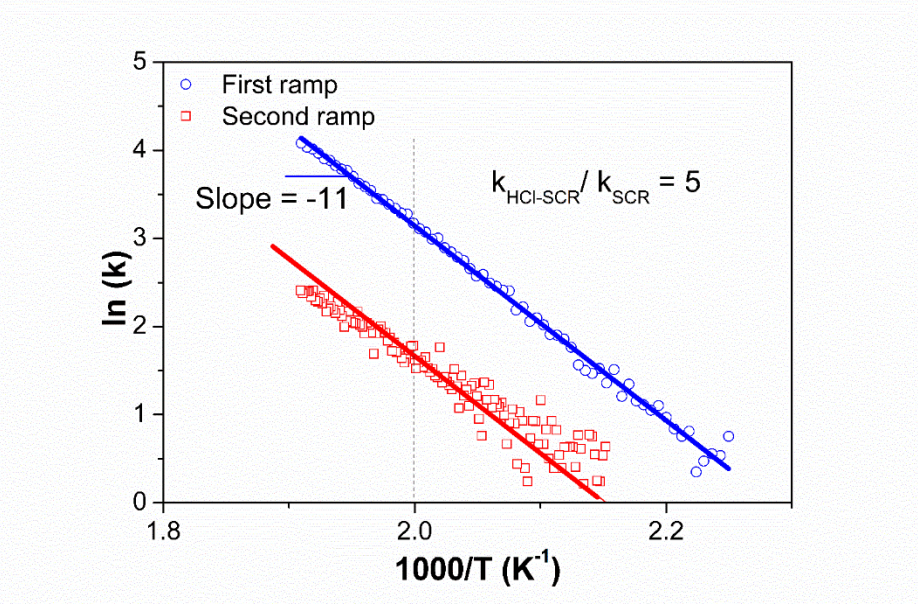


Figure S1 - Arrhenius plot of SCR-Temperature-programmed Reaction of Figure 1.

[Figure S2]

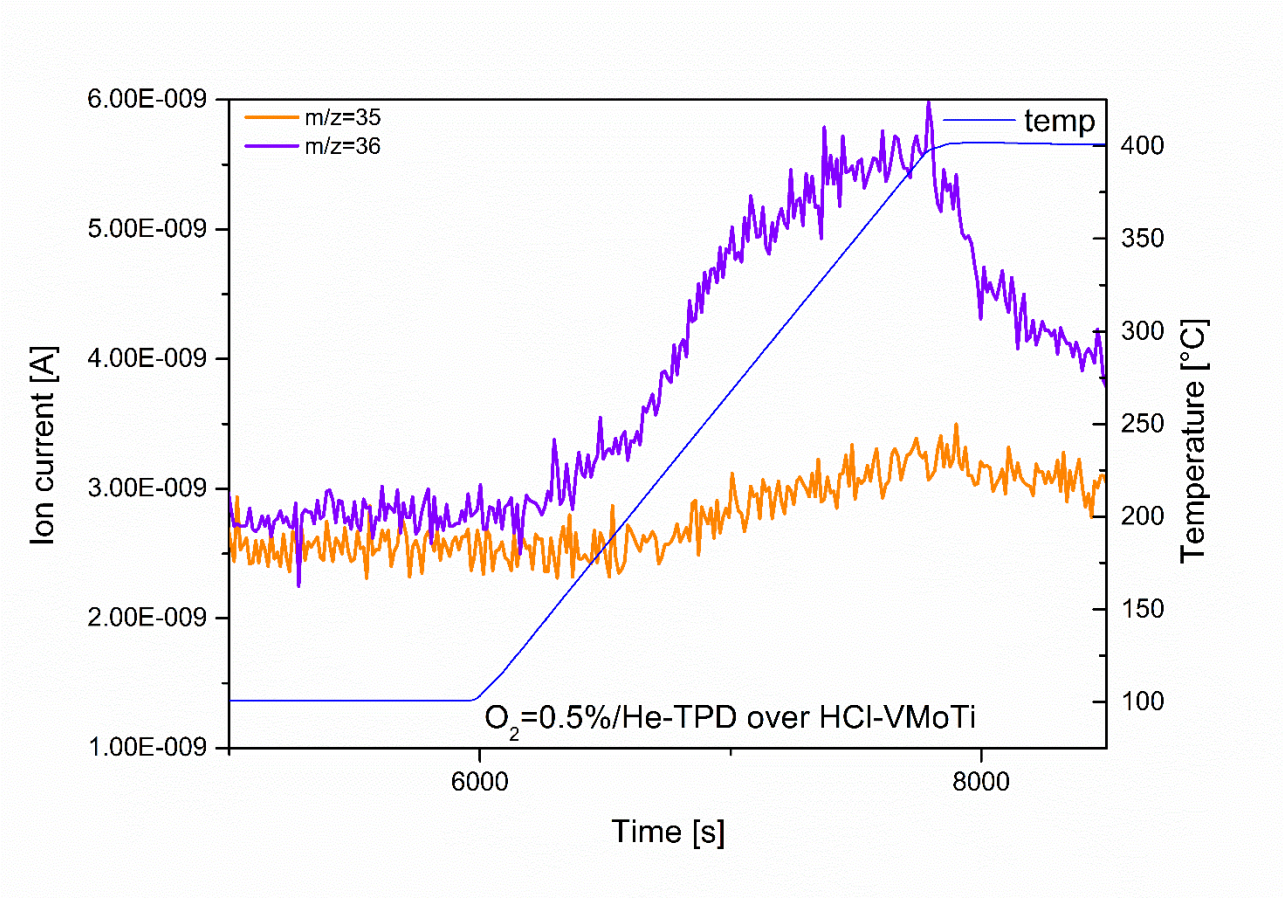


Figure S2 – TPD over HCl-VMoTi catalyst (200 mg). Stabilization at 100°C, then ramp from 100 to 400°C (5°C/min). Total flow rate = 200 Nml/min. Composition: 0.5% O_2, balance He.

[Figure S3]

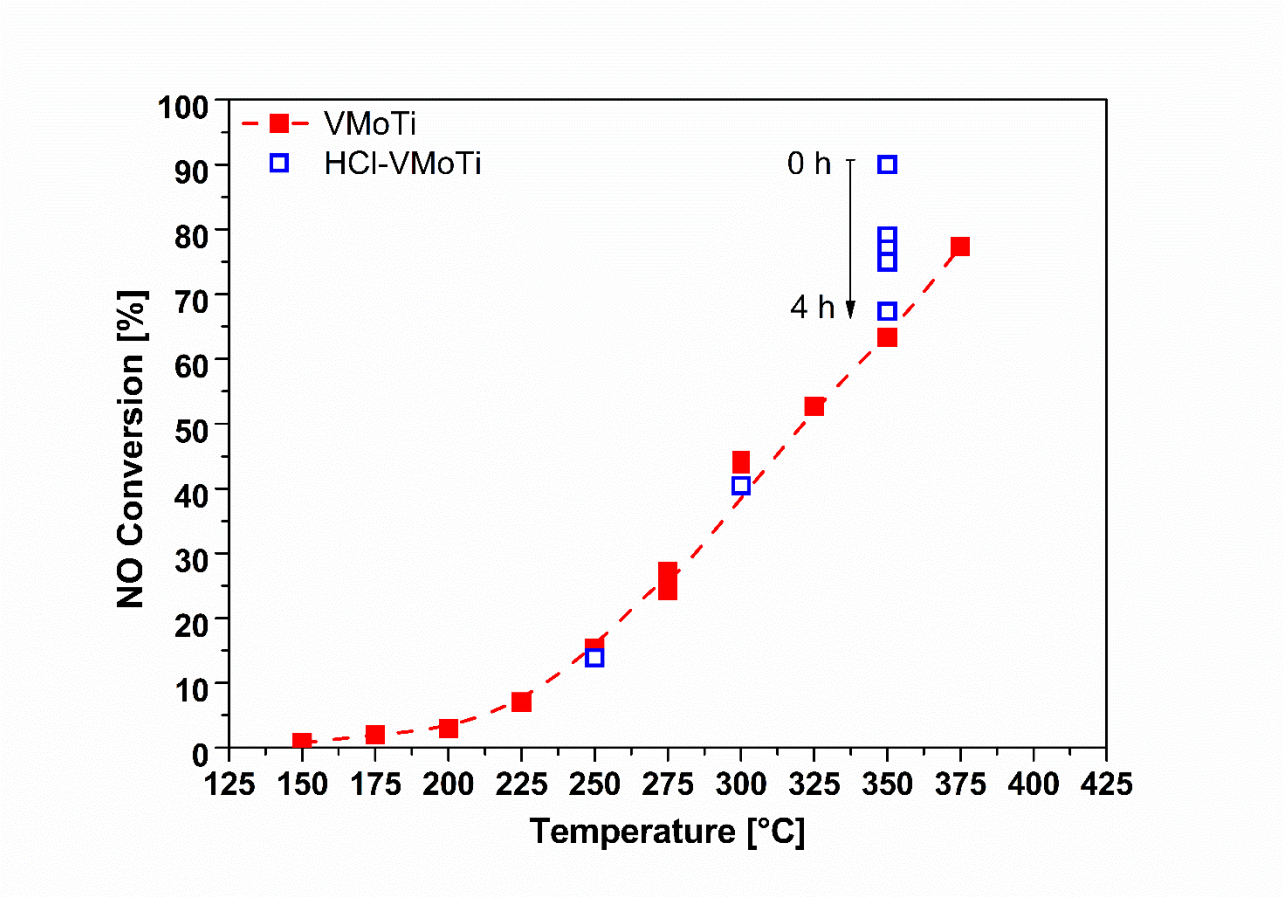
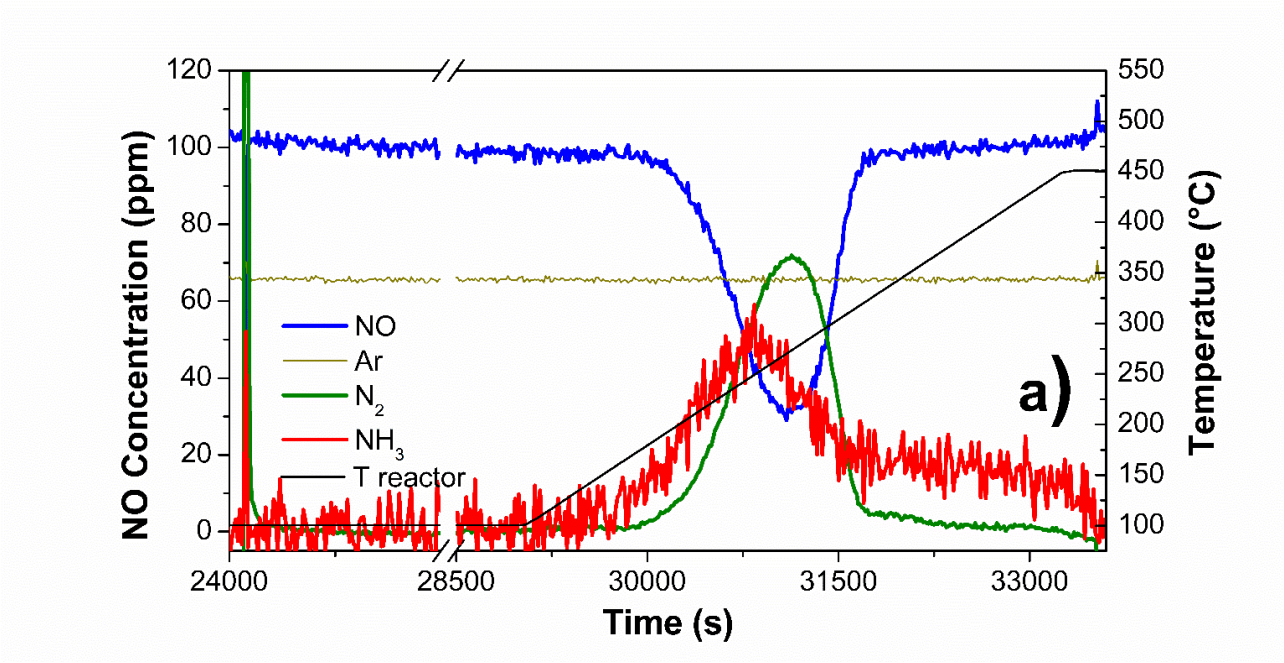


Figure S3 – NO conversion in NH_3-SCR steady state activity tests over HCl-doped catalyst (blue void squares, 60 mg) and over undoped catalyst (red squares, 60 mg). Total flow rate = 236 Nml/min. Composition: 300 ppm NO, 320 ppm NH_3, 3% O_2, balance He.

[Figure S4]



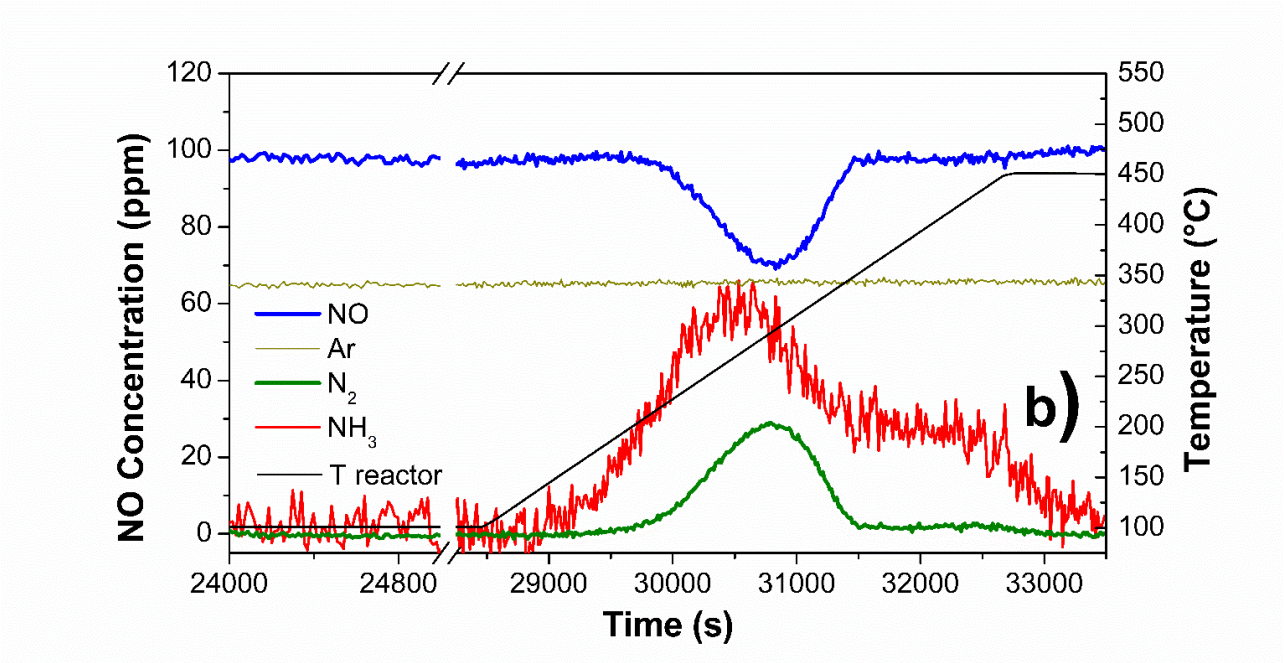


Figure S4 - First run of NO+O_2-TPSR over a) HCl-VMoTi; first run of NO+O_2-TPSR over b) undoped VMoTi.

[Figure S5]

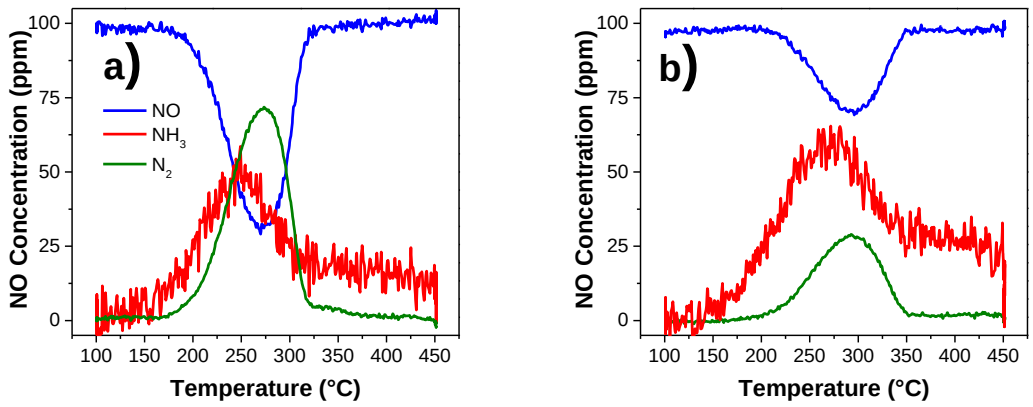


Figure S5 - NO+O_2-TPSR versus temperature of the a) first run over HCl-VMoTi; b) First run over undoped VMoTi

[Figure S6]

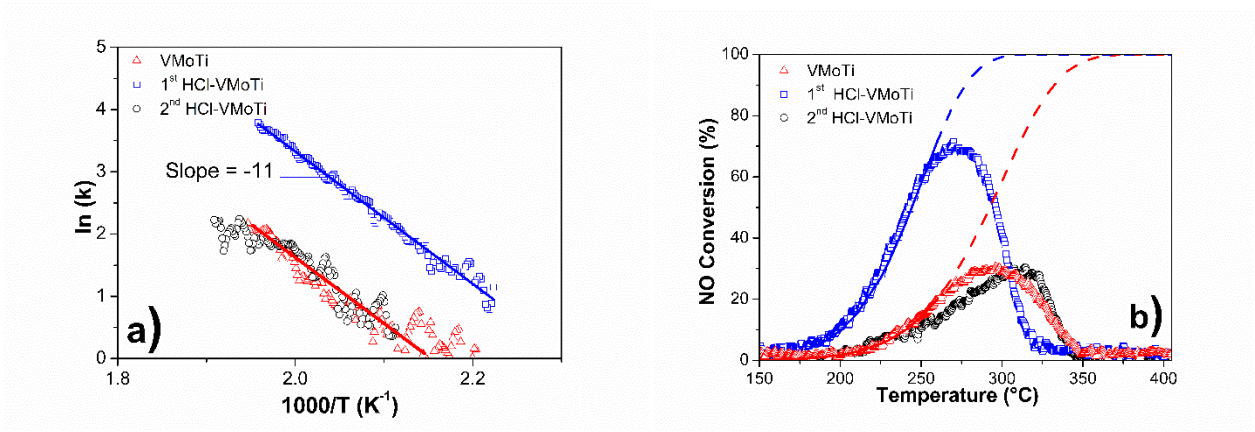


Figure S6 - a) Arrhenius plot of NO+O_2-TPSR; b) Comparison between the prediction of a steady-state reactor model with the results of the NO+O_2-TPSR. The model incorporates the intrinsic rate constants obtained for both HCl-VMoTi and VMoTi within the range of temperature of 150-250°C: k_{VMoTi} = 12 exp (-22000/RT (1/T-1/523.15)) and $k_{HCl\text{-}VMoTi}$ = 68 exp (-22000/RT (1/T-1/523.15))

[Figure S7]

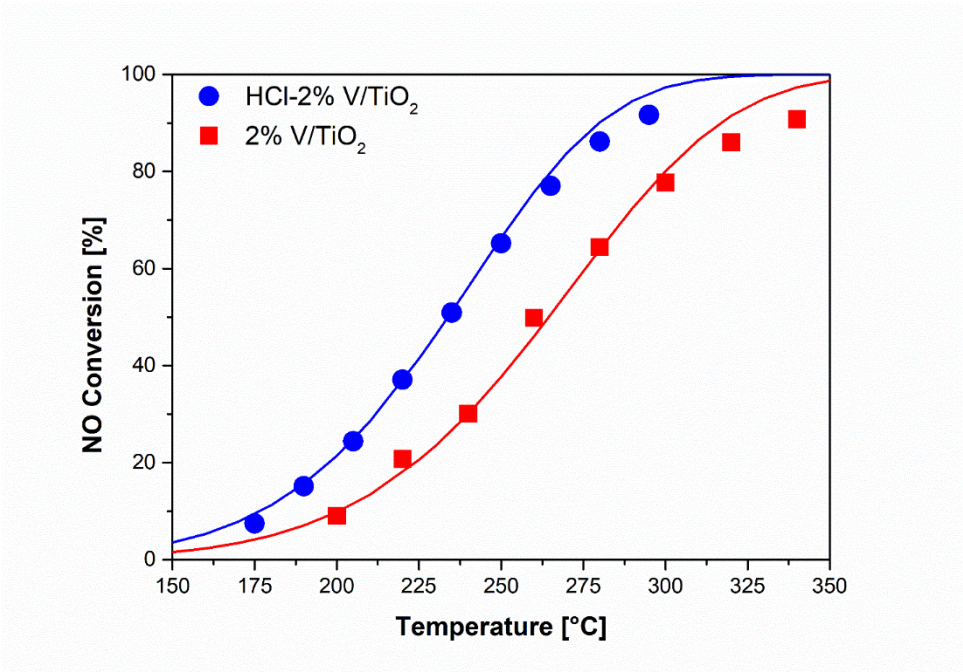


Figure S7 – NO conversion in NH_3-SCR activity tests over 2%V/TiO_2 and impregnated HCl-2%V/TiO_2 (33 mg). Total flow rate = 325 Nml/min. Composition: 300 ppm NO, 320 ppm NH_3, 3% O_2, balance He.

The interpolating lines represent the result of a modelling analysis which allowed to evaluate the intrinsic rate constants of the 2%VTi and the HCl-2%VTi catalysts: k_{VTi} = 150 exp (-16000/RT (1/T-1/523.15)) and $k_{HCl\text{-}VTi}$ = 350 exp (-16000/RT (1/T-1/523.15)).

[Figure S8]

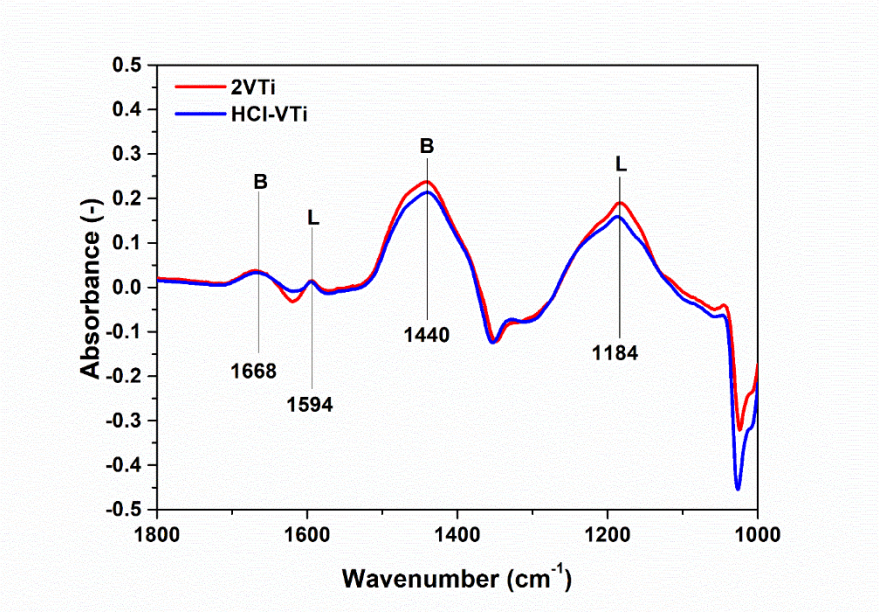


Figure S8 – Operando FT-IR spectra collected after 30 min at 25°C under NH_3=500 ppm/He over 2%V/TiO_2 and impregnated HCl-2%V/TiO_2. Total flowrate of 50 Nml/min.