Low temperature SCR on supported MnO_x catalysts for marine exhaust gas cleaning: effect of KCl poisoning

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Abstract

MnO_x-based catalysts supported at different loadings on TiO_2 (2-10 wt%) and H-ZM5 (2-20wt%) were tested for the NH_3-SCR of NO in the temperature range 50–250°C. All catalysts showed enhanced activity at low temperature compared to conventional SCR catalyst. A detailed characterization of catalysts (BET, H_2-TPR, NH_3- and O_2-TPD) revealed the predominance of MnO_2, with an enhanced dispersion when supported on TiO_2. SCR activity at low temperature correlated with lattice oxygen availability which in turn increased for highly dispersed MnO_x. The poisoning effects deriving from a hypothetical Sea Water Scrubber Desulphurization unit placed upstream of the SCR unit were investigated by ex-situ addition of KCl to the catalysts. KCl affected the acidic properties and particularly the oxygen mobility of the catalysts, lowering, as a consequence, their SCR activity. The strong acidic character of ZSM5 enhanced the tolerance to such poisoning effect.

KEYWORDS: Alkali poisoning; SCR; marine diesel; TPD; NH_3

1. Introduction

The Selective catalytic Reduction (SCR) of NO_x by NH_3 has been widely used to treat stationary exhausts [1-3] and, more recently, also for removing NO_x from diesel engine exhaust to meet the last emission regulations, including EURO VI and SULEV [4,5]. The SCR technology applied to automotive diesel engine requires catalyst to be active in a low temperature region, the normal exhaust gas temperature from a diesel engine ranging from 150 to 250 °C for light duty to 200–350°C for heavy duty engines [4-7].

Recently, also NO_x emissions standards for international shipping have been regulated. The International Maritime Organisation (IMO) strengthened the NO_x requirements worldwide for all new ships built after January 2011 [8]. Moreover, new emission standards must be introduced depending on speed for engines installed after 2016 thus requiring exhaust after- treatment [8]. Typically, SCR systems are applied to four-stroke medium speed engines,

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which have exhaust temperatures well above 300°C at normal load. Slow speed crosshead engines have lower exhaust temperatures and a small number, equipped with SCR, have the catalytic reactor placed upstream of the turbocharger to expose the catalyst to the highest temperature exhaust [9]. In this configuration the catalyst can be quickly deactivated due to the relatively low operating temperatures coupled to the exposure to high concentrations of SO_2 and particulates, particularly for those marine diesel engines burning low quality fuels [10]. Therefore, in recent years attention has been paid to the development of low temperature SCR catalysts to be used in a tail-end configuration after a flue gas desulphurization unit [11], such as a Dry or Sea Water Scrubber [9]. For the low temperature SCR reaction (50–250°C), supported transition metal oxide catalysts have been investigated [6, 12-22]. In particular MnO_x based catalysts supported on TiO_2 [6, 10, 12, 13, 15-18, 21, 22], zeolites [14] or even activated carbon [20] were reported as active and stable at low temperature. The good oxygen lability of manganese oxides, associated to the various oxidation states of manganese (i.e., MnO_2, Mn_2O_3, Mn_3O_4 and MnO), is the reason for the high activity at low temperature in SCR which is a typical redox reaction. TiO_2 anatase was found as one of the best support materials [10] promoting a high dispersion of manganese oxide when approaching the monolayer coverage. Highly dispersed MnO_x provided very good performance also in the presence of significant amounts of water vapour. Also zeolites as supports appeared to induce a good activity of MnO_x, providing in addition a high surface acidity [14].

SCR technique in marine applications, especially in tail-end configuration, requires a high resistance to catalyst poisoning by alkali metals, related to the use of sea water in the scrubber located upstream of the SCR unit. The adverse effect of alkali represents a great concern for both mobile and stationary applications (particularly biomass fired power plants). Those impurities decrease the deNO_x activity of the traditional SCR catalyst due to their deposition onto the acidic reaction sites [23-26, 29]. The main approach to design alkali-resistant catalysts is increasing the acidity of the substrate. Accordingly, zeolites as well as sulfated zirconia were proposed due to their very strong surface acidity [7, 23, 29]. Addition of CeO_2 to MnO_x was also reported to preserve to some extent the catalyst from K poisoning providing new Lewis acid sites for NH_3 adsorption [12].

In this work we set out to investigate the low temperature NH_3-SCR activity of MnO_x based catalysts supported on TiO_2 and H-ZSM5 at different loadings (lower, equal or exceeding the nominal monolayer value). KCl-poisoning was studied to evaluate the catalyst resistance when the SCR unit is located downstream of a sea-water scrubber unit in a marine diesel application. In fact potassium is commonly considered the strongest poison for acid

sites of SCR catalysts [24], whereas chlorine represents the most aboundant anion in sea-water. Finally, an extensive NH_3- and O_2-TPD analysis was performed to correlate acid and oxidation properties of supported MnO_x catalysts to their SCR performance.

2. Experimental

2.1 Catalysts preparation

Catalysts with various loadings of Mn (Table 1) were prepared by incipient wetness impregnation of pure anatase TiO_2 (Tioxide-Eurotitania) or H-ZSM5 (Zeolyst) powders, using aqueous solutions of $Mn(NO_3)_2 \cdot 4H_2O$ (Aldrich). After the impregnation step the samples were first dried in a stove at 120°C and then calcined in air 4h at 250°C. A bulk MnO_x sample was prepared for reference following the same steps. The most active catalysts for each type of support (namely 6Mn/T and 14Mn/Z) were poisoned ex-situ with KCl (1, 2, 3 %wt.) by incipient wetness impregnation (followed by calcination at 250°C).

2.2 Catalysts characterization

The BET surface area measurements were performed with a Quantachrome Autosorb 1-C by N_2 adsorption at 77 K after degassing samples for 2h at 150°C.

Temperature Programmed Reduction (TPR) tests with H_2 were carried out with a Micromeritics Autochem II TPD/TPR analyzer equipped with a TCD on the catalyst pre-treated 30 min at 250°C under He flow. The sample (200mg) was reduced by heating at 10°C/min up to 700°C under a 2% H_2/Ar flow.

NH_3- Temperature Programmed Desorption (TPD) tests were carried out in the same apparatus after standard pretreatment of catalysts under He flow at 250°C. After saturation with ammonia at room temperature, the sample (200mg) was heated at 10°C/min up to 700°C under He flow. A KOH-based trap selectively removed water possibly desorbed which can mask the TCD signal of ammonia. NH_3-TPD tests were also repeated using a P_2O_5-based trap (which removed both H_2O and ammonia simultaneously) in order to distinguish the possible contribution to the TPD curve due to the products of reaction between adsorbed ammonia and lattice oxygen (i.e. N_2, NO, N_2O and O_2). O_2-TPD runs were carried out following the same procedure (but without adsorbing ammonia) in order to evaluate the possible release of oxygen from supported MnO_x.

2.3 NH_3-SCR tests

Catalytic activity tests were carried out in a lab-scale experimental rig (Figure 1) consisting of down-flow quartz reactor with annular section (inner d =6mm, outer D=10mm) placed in a tubular furnace and operated at nearly atmospheric pressure in the temperature range 50–250°C. Powder catalysts (300 mg, particle size: 200–300 μm) were sustained by a quartz foam disk. The temperature of the catalytic bed was measured by a K-type thermocouple located inside the inner quartz tube. The feed, containing 500 ppmv NO, 500 ppmv NH_3 and 8% vol. O_2 (balance He) was obtained by mixing high purity gas streams (He (99.999%), O_2(99.95%), NO/He (1 vol. %; NO_2 impurity <100ppmv) and NH_3/He (900 ppmv)) regulated by independent MFCs. The total inlet flow rate was set at 30 Sl/h. The concentrations of NO and NO_2 were measured with a Emerson X-Stream XEGP continuous analyzer after removing water and unconverted NH_3 in the product gas using a Sycapent (P_2O_5) trap.

3. Results and discussion

3.1 Basic characterization of catalysts

In Table 1 a list of the catalysts is reported with their nominal manganese loading and the corresponding BET surface area after calcination at 250°C in air. The original surface area of the two supports was 125 m^2/g and 400 m^2/g for TiO_2 and ZSM5 respectively: thus a Mn loading of 6 and 20 wt % roughly corresponded to the theoretical mono-layer coverage for TiO_2 and ZSM5 respectively [13]. The deposition of MnO_x caused a limited loss of the original surface area of TiO_2 even for loadings exceeding the theoretical mono-layer, suggesting a quite effective dispersion of the active phase. On the contrary, the BET surface area significantly decreased for ZSM5-supported catalysts already at low loadings, indicating some blocking of the zeolite pores had occurred. Finally, in agreement with Peng et al. [12], a negligible effect of potassium addition on the surface area was observed. As a consequence, in the following discussion about the loss of activity caused by KCl poisoning this parameter has been not taken into account.

Preliminary TPR experiments were carried out in order to evaluate the type of manganese oxides dispersed on the supports: the typical reduction profiles are presented in Figure 2 (a,b) and compared with those obtained with some pure reference manganese oxides (c). With both supports the reduction process started at ca. 150°C and showed a characteristic two step feature, well evident for relatively high Mn loadings (above 10%), whilst the second peak appears as a shoulder for lower Mn contents. The characteristic temperatures for the main reduction events and the overall H_2/Mn ratios, in the range 0.8 to 0.95 (Table 1), indicate the predominance of Mn^{4+} species (as in MnO_2) with a smaller fraction (ca 15-40%) of Mn^{3+}

species (as in Mn_2O_3), which are all finally reduced to Mn^{2+}[30, 31]. These results are in agreement with Fang et al. [28] who found that TiO_2 supported manganese oxide prepared from nitrate precursor mainly consisted of MnO_2. Peng et al. [12] also reported a double peaked TPR curve for MnO_x/TiO_2 catalyst corresponding to the H_2 uptake necessary to the reduction of a mixture of MnO_2 and Mn_2O_3. Moreover, TPR analysis of the reference unsupported MnO_x sample indicated a lower average oxidation state of Mn with respect to supported catalysts, with roughly 30% of the metal present as Mn^{4+}. That suggests the initial oxidation state of manganese is mainly determined by the calcination temperature and increases following dispersion on a support.

3.2 NH_3-SCR tests

In Figure 3 the catalytic performances of 10Mn/T and 10Mn/Z catalysts are compared with that of a commercial V_2O_5-WO_3/TiO_2 sample tested under identical conditions in the temperature range 80-250°C. In agreement with several previous reports [12-19] Mn-based catalysts displayed significant SCR activity already at low temperatures where the commercial V-based catalyst gave poor performance: at 150°C the NO conversion over V_2O_5-WO_3/TiO_2 catalyst was ca. 15%, whilst it was 30% over 10Mn/Z catalyst, and slightly above 80% for 10Mn/T catalyst. Those results confirm an important promotional effect of using TiO_2 as a support [12, 13,15-18] at fixed Mn content. NO_2 formation was never detected during catalytic tests. In fact the production of N_2O in addition to N_2 in the upper part of the temperature range explored is expected (but could not be measured in the experimental rig): indeed, N_2O was detected at T>175°C by Ettireddy et al. [13, 16] and in general a N_2 selectivity far below 100% was observed at 200°C for Mn/TiO_2 catalysts [21, 22].

Regarding the effect of Mn loading in the TiO_2 supported catalysts, Figure 4a shows that the SCR activity (on a mass basis) reached a clear maximum for the monolayer coverage (6Mn/T catalyst), and further Mn addition was not effective, probably due to the formation of larger and poorly dispersed MnO_x aggregates. On the other hand NO conversion plots obtained over ZSM5- supported catalysts at various Mn loadings (Figure 4b) appear almost overlapped in spite of the large differences in their active phase content. For ZSM5-supported samples the best performance was associated to a nominal sub-monolayer coverage (14%Mn). It can be argued that manganese oxides were poorly dispersed already at rather low loadings and preferentially formed bulk-like structures on the outer shell of the zeolite grains that block inner pores (as confirmed by the significant drop of surface area, Table 1).

In Figure 5(a,b) the effect of KCl-poisoning on the SCR activity is shown for the two best performing catalysts (6Mn/T and 14Mn/Z).A significant loss of NO conversion upon 1% wt. KCl addition was observed for the TiO2 supported MnOx catalyst, in good agreement with the results by Peng et al. [12], who however added KNO3 to poison their MnO_x/TiO_2 catalysts. On the other hand, the 14Mn/Z catalyst showed a much higher tolerance for the same KCl level (1% wt), so that its NO conversion at T>150°C resulted higher than on 6Mn/T_1K counterpart. For 14Mn/Z catalyst the effect of increasing KCl content was also investigated: Figure 5b shows a general progressive loss of activity along with the amount of KCl added, although the NO conversion plots for 14Mn/Z_2K and 14Mn/Z_3K were substantially superimposed in the low temperature range up to 180°C.

3.3 Temperature programmed desorption of NH_3

Ammonia was used as probe molecule in the TPD experiments because it is both a basic molecule to test surface acidity and is one of the reactant for SCR. Before discussing TPD results it must be reminded that the TC detector employed for those experiments is not selective and cannot distinguish a priori a gaseous species from another. As a consequence some tricks were taken in order to identify peaks.

Typical TPD profiles, saturating (NH_3-TPD) or not (O_2-TPD) the sample with ammonia before heating under flowing helium, are reported in Figure 6 for 6Mn/T and 14Mn/Z catalysts chosen as representative. Moreover it should be noticed that NH_3-TPD profiles are reported using either a KOH based trap to remove water or a P_2O_5 trap to remove water and ammonia simultaneously. NH_3-TPD profiles (KOH trap) show two main signals peaked at 160 °C and 360 °C and a shoulder at about 485 - 500°C which prolonges up to ca. 700 °C. The ratio between the first and the second signal is higher for $6Mn/TiO_2$. O_2-TPD showed a broad desorption peak in the range 250-400°C and a stronger peak at about 550°C for both catalysts.

In order to determine the contribution of supports and manganese oxide NH_3 TPD (KOH) and O_2-TPD experiments were also carried out over both bare TiO_2 and ZSM5 supports and unsupported MnO_x. The corresponding profiles are reported in Figure 7. The O_2-TPD experiments showed that both TiO_2 and ZSM5 supports give a negligible signal according to the good thermal stability of those phases up to 700°C. On the contrary, unsupported MnO_x thermally decomposed releasing oxygen from roughly 400 °C with a peak centered at 580°C, i.e. in the same temperature range where the additional high temperature peak was detected for the O_2-TPD of supported manganese oxide catalysts (Fig. 6), thus suggesting that those

signals can be reasonably associated to the decomposition of larger aggregates of MnO_x on the support. Unsupported MnO_x sample did not significantly adsorb ammonia, as suggested by the overlapping of NH_3-TPD and O_2-TPD profiles (Fig. 7c). Therefore the signal detected in the NH_3-TPD of bulk MnO_x was actually oxygen and not ammonia.

On the contrary, both the supports adsorbed large amounts of NH_3 on acid sites of different strengths. Two main acid sites with a further contribution at high temperature were reported for TiO_2 and zeolites [33, 34]. Lewis acid sites were attributed to anatase TiO_2 peaked at about 400°C [32]. On the other hand Watanabe et al. [33] detected an additional contribution at low temperature (around 200°C) and reported a NH_3-TPD profile more similar to that observed by us. The relatively strong contribution of the low temperature signal for the TiO_2 investigated in this work is likely related to the rather low pre-treatment temperature (250°C) which is not sufficient to remove surface hydroxyls, thus leaving a significant residual Brønsted acidity. H-ZSM5 shows two main resolved signals respectively at 200-300°C (consisting of two partially overlapped peaks) and around 500°C, as also reported in [35]. Comparing the NH_3-TPD profile of supported Mn catalysts (Fig. 6) with those of their corresponding bare supports (Fig. 7), a new and stronger signal appears at ca. 360°C. In order to understand if manganese oxide provided some extra acidity or if a species different from ammonia was formed in that temperature range, an unusual "negative" NH_3-TPD experiment was carried out by trapping also ammonia (red trace in Figure 6). The appearance of a similar peak in both repeated NH_3-TPD profiles demonstrates that it corresponds to the emission of products of ammonia oxidation. In other words, adsorbed ammonia reacted with oxygen from the lattice of the supported manganese oxide to give nitrogen or nitrogen oxides starting roughly from 150°C. In fact, repeating those measurements with the continuous analyzer for NO/NO_2 it was possible to exclude any significant formation of those nitrogen oxides at temperatures up to 450°C, thus suggesting that the products of ammonia oxidation with lattice oxygen should be N_2 and N_2O. Finally, the (anticipated) consumption of easy labile oxygen from MnO_x via the reaction with ammonia explains the absence of the typical O_2 emission at 500-600°C in the NH_3-TPD of the 6Mn/T and 14Mn/Z catalysts.

The effect of MnO_x loadings on NH_3-TPD profiles was investigated for ZSM5- supported catalysts and results are presented in Figure 8. Both signals typical of the zeolite support decrease with increasing the MnO_x loading as a consequence of ZSM5 acid sites blocking. Nevertheless a new peak at 300-400°C, related to the product of ammonia oxidation, progressively increases along with Mn content before reaching a maximum for 14% Mn. Noticeably the catalyst displaying the best SCR activity in the series (Fig. 4) was also the one

which provided the highest ammonia oxidation peak during NH_3-TPD. A similar feature was observed for TiO_2 supported catalysts, suggesting that a correlation between the TPD peak related to the oxidation of adsorbed ammonia and the SCR activity should exist, at least in the contest of TiO_2 or ZSM5 supported catalysts.

In Figure 9 a,b the oxygen release by thermal decomposition of supported manganese oxide, is compared among all TiO_2 and ZSM5 supported catalysts and with bulk MnO_x, after normalization of the signal for Mn weight content. In agreement with the previous hypothesis, it was found that 14Mn/Z catalyst provided the largest amount of oxygen from MnO_x decomposition, mostly at low temperature (250-400°C). This type of oxygen is lower for the other catalysts and totally absent for bulk MnO_x sample which thus shows a reduced oxygen mobility. The signal at higher temperature, present for all catalysts, is similar to the single peak of unsupported MnO_x suggesting that it is generated by bulk-like structures.

A similar trend was observed for TiO_2 supported catalysts. At low coverage (2%) the very high dispersion of supported manganese oxide gave rise mainly to an oxide with a very labile oxygen with a poor contribution of larger aggregates. The latter prevails by increasing the Mn content in the catalyst whilst the fraction of highly dispersed MnO_x decreases. Of course, the total amount of oxygen released at low temperature from this type of extremely active manganese oxide was maximum for 6Mn/T sample, which in turn showed the best SCR activity. Nevertheless, if the NO conversion rate at each temperature is referred to the weight of manganese in the catalyst, the 2Mn/T sample results unquestionably the most active. That emphasizes the role of dispersion of manganese oxide: when approaching the monolayer coverage less dispersed manganese oxide was formed with a lower specific activity at low temperature. The generally higher SCR activity of TiO_2 supported catalysts compared to ZSM5 supported counterparts can be explained by similar considerations.

3.4 Effect of KCl poisoning on acid and redox properties

The effect of KCl-poisoning on the acid properties was investigated for 14Mn/Z catalyst in view of its better tolerance to poisoning. In Figure 10a NH_3-TPD profiles obtained with the standard procedure (KOH trap) are compared for the fresh sample and after poisoning at two different KCl levels. The addition of 1.0%KCl induced a general decrease of both main peaks of the fresh catalyst, as expected due to the alkaline nature of potassium. Nevertheless, the poisoning of the sample with a higher KCl level (3.0%) provided a marked increase of the first signal and the appearance of a peak at high temperature (500-600°C). That latter peak can be reasonably assigned to oxygen resulting from the decomposition of manganese oxide,

thus implying that the reaction between adsorbed ammonia and oxygen from MnO_x is somewhat inhibited. Furthermore, the increase of the first NH_3 signal suggests that ammonia originally involved in this oxidation reaction was more easily desorbed between 100 °C and 200°C due to KCl poisoning effect.

Poisoning by KCl induced a significant effect on the oxygen release as well: O_2-TPD traces in Figure 10b indicate that the release of oxygen at low temperature (below 480°C) was strongly limited or did not occur at all if KCl was added to the catalyst. On the other hand, the release of oxygen at high temperature was almost unaffected by the presence of KCl. The loss of lattice oxygen availability at low temperature is proportional to the amount of KCl added to the catalyst (Figure 11). This result agrees with that reported by Peng et al. [12] who found that K restrains the oxidation ability of MnO_x/TiO_2 catalyst also reducing the formation of NO_2 from the reaction between adsorbed NO and lattice oxygen. Moreover, the rough linear correlation between the temperature of 50% NO conversion and the oxygen released at low temperature reported in Figure 11 seems to confirm the direct relation between SCR activity and oxygen availability.

It must be pointed out that modification of oxygen availability cannot be unambiguously attributed to potassium because chlorine has not been certainly removed at 250°C. The high electronegativity of this element could be responsible for the redox changes observed. On the other hand, chlorine can also affect the acidity, as reported for V_2O_5/TiO_2 catalysts [24]. For those reasons further studies are in progress with different counteranions.

4. Conclusions

MnO_x-based catalysts, mainly containing MnO_2 supported on TiO_2 or ZSM5 displayed a remarkable activity towards NH_3-SCR of NO at low temperature (100-180°C), providing definitely better performance than traditional V_2O_5-WO_3/TiO_2 catalysts and confirming their possible application in diesel engine emission control.

NH_3- and O_2-TPD studies evidenced that the SCR catalytic activity was directly related to oxygen mobility/availability in MnO_x at low temperature which was able to react with adsorbed ammonia. Highly dispersed manganese oxides guaranteed a superior oxygen mobility and availability. TiO_2 promotes a significantly higher MnO_x dispersion compared to ZSM5 support providing a higher NO conversion and a better utilization of active phase.

KCl was selected as representative of most concerning poisons for marine diesel application of SCR after a Sea Water Scrubber unit. It was found that KCl inhibits the low temperature SCR reaction mainly affecting the oxygen mobility/availability of MnO_x species. However,

ZSM5 supported catalysts, although less active as unpoisoned, seems to tolerate higher KCl levels probably due to the more acid character and sorbent capacity of the zeolite. In turn a zeolite layer may serve as a trap for the poisoning agent and could be placed in front of the most active catalyst (MnO_x/TiO_2) in order to preserve its functionalities.

5. References

[1] Janssen, F., Van den Kerkhof, F., Bosch, H., Ross, J.R.H., "Mechanism of the Reaction of Nitric Oxide, Ammonia, and Oxygen over Vanadia Catalysts. 1. The Role of Oxygen Studied by Way of Isotopic Transients under Dilute Conditions", *J. Phys. Chem.* 91: 5921-5927 (1987)

[2] Wood S.C., "Select the Right NO_x Control Technology", Chem. Eng. Progr. 90: 32-38 (1994)

[3] Dumesic, J.A., Topsoe, N.-Y., Topsoe, H., Slabiak, T., "Kinetics of Selective Catalytic Reduction of Nitric Oxide by Ammonia over Vanadia/Titania" *J.Catal.* 163: 409-417 (1996)

[4] Twigg, M.V., "Catalytic control of emissions from cars", Catalysis Today 163: 33-41 (2011)

[5] Wang, T.J., Baek, S.W., Kwon, H.J., Kim, Y.J., Nam, I.-S., Cha, M.-S., Yeo, G.K., "Kinetic Parameter Estimation of a Commercial Fe-Zeolite SCR", *Industrial and Engineering Chemistry Research* 50: 2850-2864 (2011)

[6] Xie, J., Fang, D., He, F., Chen, J., Fu, Z., Chen, X., "Performance and mechanism about MnO_x species included in MnO_x/TiO_2 catalysts for SCR at low temperature", Catalysis Communications 28: 77–81 (2012)

[7] Kim, D.S., Lee, C.S., Improved emission characteristics of HCCI engine by various premixed fuels and cooled EGR, *Fuel* 85: 695-704 (2006)

[8] International Maritime Organization, Revised MARPOL Annex VI, Regulations for the Prevention of Air Pollution from Ships and NO_x Technical Code 2008 (2009 edition ISBN 978-92-801-42-43-3) www.imo.org

[9] Gregory D., A practical guide to exhaust gas cleaning systems for the maritime industry, EGCSA Handbook 2013, London, UK

[10] Magnusson, M., Fridell, E., Ingelsten, H.," The influence of sulfur dioxide and water on the performance of a marine SCR catalyst", *Appl. Catal. B: Envir.* 111–112: 20-26 (2012)

[11] Armor, J.N., *Proc. Environmental Catalysis 205th National ACS Meeting* (1994) p. 206

[12] Peng, Y., Li, J., Si, W., Li, X., Shi, W., Luo, J., Fu, J., Crittenden, J., Hao, J., "Ceria promotion on the potassium resistance of MnO_x/TiO_2 SCR catalysts: An experimental and DFT study", *Chem. Eng. J.*, 269: 44-50 (2015)

[13] Ettireddy, P. R., Ettireddy, N., Mamedov, S., Boolchand, P., Smirniotis P. G., Surface characterization studies of TiO_2 supported manganese oxide catalysts for low temperature SCR of NO with NH_3, *App. Catal. B: Environmental* 76:123–134 (2007)

[14] Kim, Y. J., Kwon, H. J., Heo, I., Nam, I-S., Cho, B. K., Choung, J. W., Cha, M-S., Yeo, G. K., "Mn–Fe/ZSM5 as a low-temperature SCR catalyst to remove NO_x from diesel engine exhaust", *Appl. Catal. B: Environ*. 126: 9–21 (2012)

[15] Peña, D. A., Uphade, B. S., Smirniotis, P. G., "TiO_2-supported metal oxide catalysts for low-temperature selective catalytic reduction of NO with NH_3: I. Evaluation and characterization of first row transition metals", *J. Catal.* 221: 421-431 (2004)

[16] Ettireddy, P. R., Ettireddy, N., Boningari, T., Pardemann, R., Smirniotis, P. G., "Investigation of the selective catalytic reduction of nitric oxide with ammonia over Mn/TiO_2 catalysts through transient isotopic labeling and in situ FT-IR studies", *J. Catal.* 292: 53–63 (2012)

[17] Thirupathi, B., Smirniotis, P. G., "Nickel-doped Mn/TiO_2 as an efficient catalyst for the low-temperature SCR of NO with NH_3: Catalytic evaluation and characterizations", *J. Catal.* 288: 74–83 (2012)

[18] Thirupathi, B., Smirniotis, P. G., "Co-doping a metal (Cr, Fe, Co, Ni, Cu, Zn, Ce, and Zr) on Mn/TiO_2 catalyst and its effect on the selective reduction of NO with NH_3 at low-temperatures", *Appl. Catal. B: Environmental* 110: 195– 206 (2011)

[19] Park, T.S., Jeong, S.K., Hong, S.H., Hong, S.C., "Selective Catalytic Reduction of Nitrogen Oxides with NH_3 over Natural Manganese Ore at Low Temperature", *Ind. Eng. Chem. Res.* 40: 4491–4495 (2001)

[20] Pourkhalil, M., Moghaddam, A.Z., Rashidi, A., Towfighi, J., Mortazavi, Y., "Preparation of highly active manganese oxides supported on functionalized MWNTs for low temperature NO_x reduction with NH_3", *Appl. Surf. Science* 279: 250-259 (2013)

[21] Qi, G., Yang, R.T., "Low-temperature selective catalytic reduction of NO with NH_3 over iron and manganese oxides supported on titania", *Appl. Catal. B: Environmental* 44: 217–225 (2003)

[22] Wu, Z. B., Jin, R.B., Liu, Y., Wang, H.Q., "Ceria modified MnO_x/TiO_2 as a superior catalyst for NO reduction with NH_3 at low-temperature", *Catal. Commun.* 9: 2217–2220 (2008)

[23] Kristensen, S.B., Due-Hansen, J., Putluru, S.S.R., Kunov-Kruse, A.J., Fehrmann, R., Jensen, A. D., "Alternative alkali resistant deNOx technologies: PSO Project 7318" DTU Chemistry (2011) 95 p.

[24] Lisi, L., Lasorella, G., Malloggi, S., Russo, G., "Single and combined deactivating effect of alkali metals and HCl on commercial SCR catalysts", *Appl. Catal. B: Environmental* 50: 251-258 (2004)

[25] Tang, F., Xu, B., Shi, H., Qiu, J., Fan, Y., "The poisoning effect of Na^+ and Ca^{2+} ions doped on the V_2O_5/TiO_2 catalysts for selective catalytic reduction of NO by NH_3", *Appl. Catal. B: Environmental* 94: 71–76 (2010)

[26] Larsson, A-C., Einvall, J., Andersson, A., Sanati, M., "Targeting by Comparison with Laboratory Experiments the SCR Catalyst Deactivation Process by Potassium and Zinc Salts in a Large-Scale Biomass Combustion Boiler", *Energy & Fuels* 20: 1398-1405 (2006)

[27] Kling, Å., Andersson, C., Myringer, Å., Eskilsson, D., Järås, S. G., "Alkali deactivation of high-dust SCR catalysts used for NO_x reduction exposed to flue gas from 100 MW-scale biofuel and peat fired boilers: Influence of flue gas composition", *Appl. Catal. B: Environmental* 69: 240–251 (2007)

[28] Kröcher, O., Elsener, M., "Chemical deactivation of $V_2O_5/WO_3–TiO_2$ SCR catalysts by additives and impurities from fuels, lubrication oils, and urea solution: I. Catalytic studies", *Appl. Catal. B: Environmental* 75: 215- (2008)

[29] Putluru, S. S. R., Riisager, A., Fehrmann, R., "Alkali resistant Cu/zeolite deNO_x catalysts for flue gas cleaning in biomass fired applications", *Appl. Catal. B: Environmental* 101: 183-188 (2011)

[30] Cimino, S., Colonna, S., De Rossi, S., Faticanti, M., Lisi, L., Pettiti, I., Porta, P., "Methane Combustion and CO Oxidation on Zirconia-Supported La, Mn Oxides and $LaMnO_3$ Perovskite", *J. Catal.* 205: 309-317 (2002)

[31] Fang, D., Xie, J., Hu, H., Yang, H., He, F., Fu, Z., "Identification of MnO_x species and Mn valence states in MnO_x/TiO_2 catalysts for low temperature SCR", Chem. Eng. J. 271: 23-30 (2015)

[32] Gandhe, A. R. , Fernandes, J. B. , Varma, S., Gupta, N.M., "TiO_2: As a versatile catalyst for the ortho-selective methylation of phenol", *Journal of Molecular Catalysis A: Chemical* 238: 63–71(2005)

[33] Watanabe, M., Aizawa, Y., Iida, T., Nishimura, R., Inomata, H., "Catalytic glucose and fructose conversions with TiO_2 and ZrO_2 in water at 473 K: Relationship between reactivity and acid–base property determined by TPD measurement", *Appl. Catalysis A: General* 295: 150–156 (2005)

[34] Katada, N., Igi, H., Kim, J., and Niwa, M., "Determination of the Acidic Properties of Zeolite by Theoretical Analysis of Temperature-Programmed Desorption of Ammonia Based on Adsorption Equilibrium", *J. Phys. Chem. B* 101: 5969–5977 (1997)

[35] Al-Bogami, S.A., de Lasa, H.I., "Catalytic conversion of benzothiophene over a H-ZSM5 based catalyst", *Fuel* 108: 490–501 (2013)

Table 1. List of MnO_x based catalysts supported on either TiO_2 (T) or ZSM5 (Z) with their corresponding nominal content of Mn and eventually KCl, BET surface area after calcinations at 250°C, and specific H_2 consumption during TPR experiments.

Catalyst ID	Mn wt%	KCl wt%	BET area m^2/g	H_2/Mn mol/mol
2Mn/T	2.15	-	107	-
6Mn/T	6.00	-	104	0.79
10Mn/T	9.40	-	100	0.85
2Mn/Z	2.27	-	370	-
6Mn/Z	5.60	-	270	-
8Mn/Z	7.78	-	303	-
10Mn/Z	10.0	-	305	0.91
14Mn/Z	14.2	-	288	0.94
20Mn/Z	20.0	-	264	-
6Mn/T_1K	6.00	1	112	-
14Mn/Z_1K	14.2	1	292	-
14Mn/Z_2K	14.2	2	291	-
14Mn/Z_2K	14.2	3	287	-

Figure Captions

Figure 1. Scheme of the experimental rig for NH_3-SCR tests.

Figure 2. H_2-TPR profiles for MnOx supported catalysts: 6Mn/T and 10Mn/T (a); 10Mn/Z and 14Mn/Z (b). Panel (c) presents reference TPR profiles for pure bulk MnO_2, Mn_2O_3 and Mn_3O_4 [30].

Figure 3. NO conversion by NH_3-SCR as a function of reaction temperature for 10Mn/T, 10Mn/Z and a commercial V_2O_5- WO_3/TiO_2 reference catalyst.

Figure 4. Effect of Mn loading on NO conversion by NH_3-SCR as a function of the reaction temperature for TiO_2 supported (a) and ZSM5 supported catalysts (b).

Figure 5. Effect of ex-situ poisoning with increasing amounts of KCl over 6Mn/T (a) and 14Mn/Z (b) catalysts: NO conversion by NH_3-SCR as a function of the reaction temperature.

Figure 6. NH_3-TPD profiles obtained with KOH trap (line 1), P_2O_5 trap (line 2) and corresponding O_2-TPD profile (dashed line 3) for 6Mn/T (a) and 14 Mn/Z (b) catalysts. TCD signal was normalized by the weight of the sample.

Figure 7. (a) NH_3-TPD for TiO_2 and H-ZSM5 supports. (b) O_2-TPD for TiO_2 and bulk MnO_x, as well as NH_3-TPD for the same MnO_x sample. TCD signal was normalized by the weight of the sample.

Figure 8. NH_3-TPD profiles obtained with KOH trap for Mn/Z catalysts at various loadings and for the bare H-ZSM5 support.

Figure 9. O_2-TPD profiles for bulk MnO_x and catalysts with MnO_x on TiO2 (a) or ZSM5 (b) at different loadings. TCD signal was normalized by the Mn weight content in each sample.

Figure 10. Comparison between NH_3-TPD with KOH trap (a) and O_2-TPD profiles (b) of fresh 14Mn/Z catalyst and after poisoning with 2 different KCl levels. TCD signal in (b) was normalized by the Mn weight content, as in Figure 9.

Figure 11. Effect of KCl poisoning level on the temperature for 50% NO conversion (T_{50}) and on the amount of oxygen released at low temperature (<480°C) during O_2-TPD for 14Mn/Z catalyst.

Figure 1

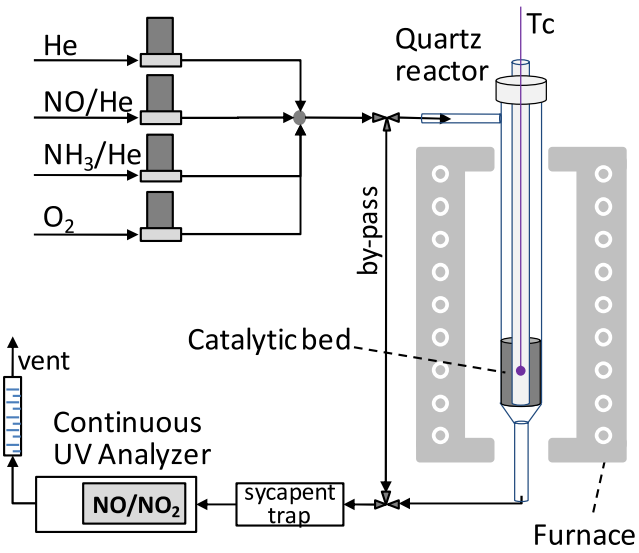

Figure 1.

Figure 2

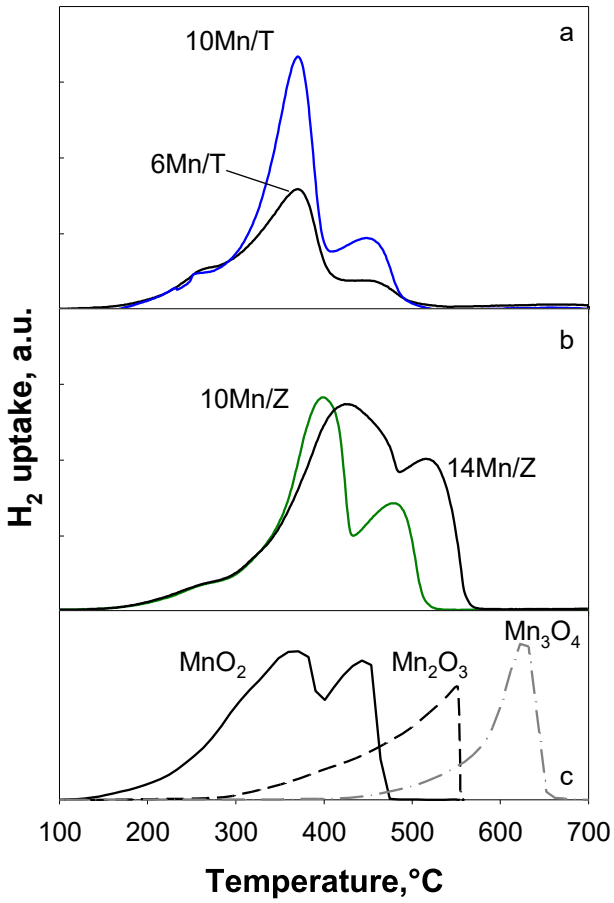

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Figure 3

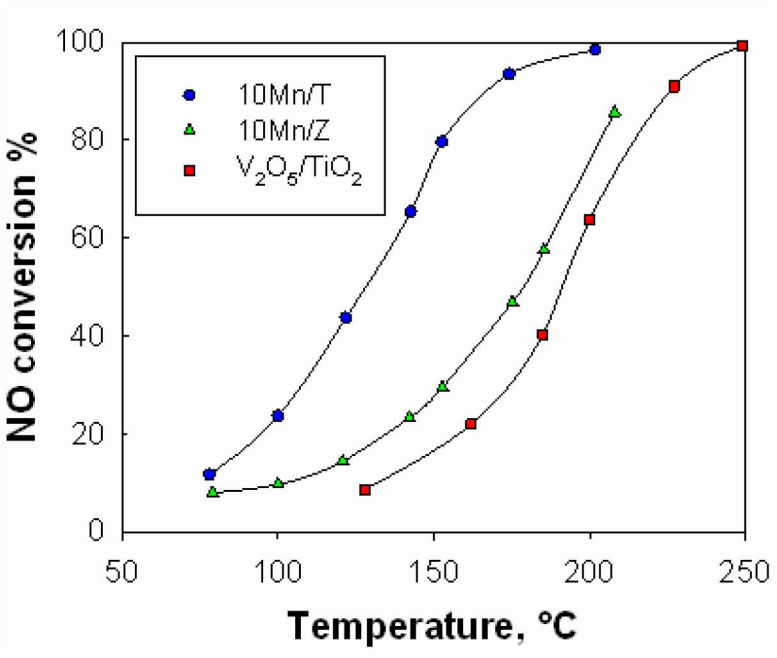

Figure 3.

Figure 4

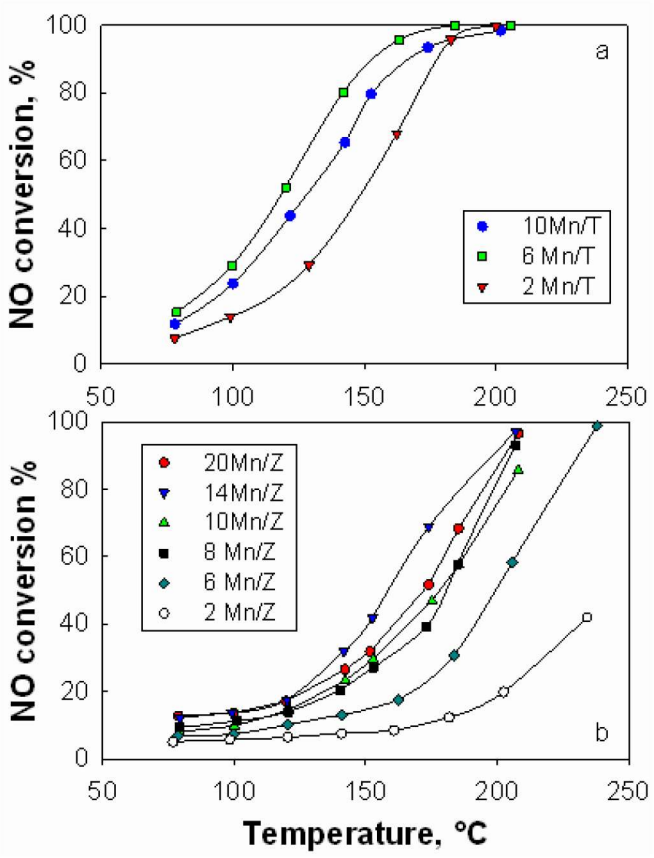

Figure 4.

Figure 5

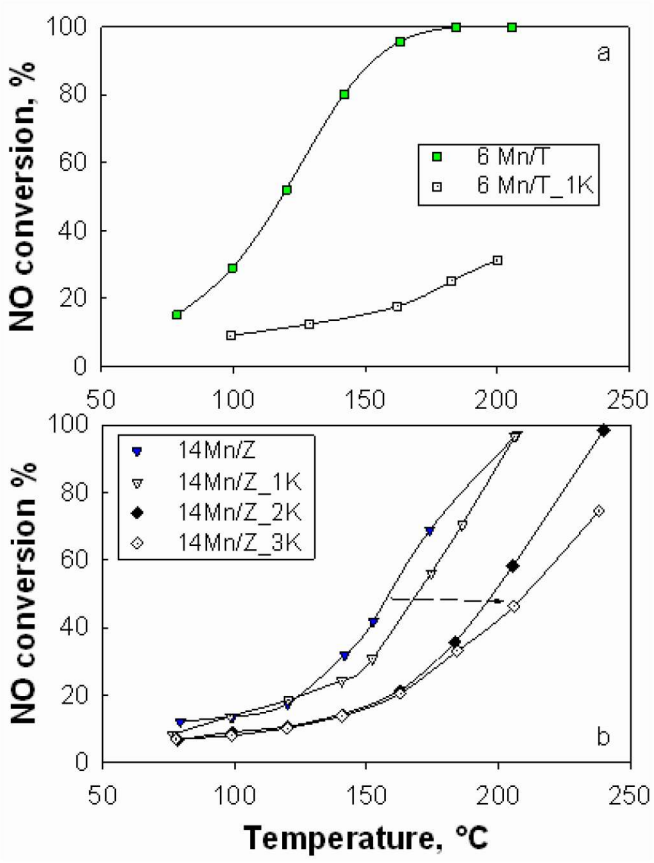

Figure 5.

Figure 6

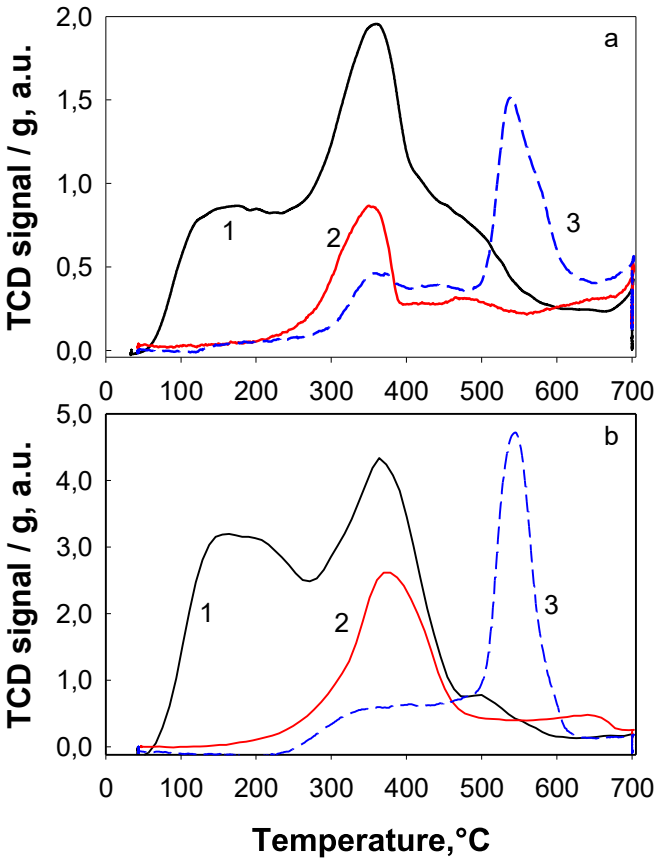

Figure 6.

Figure 7

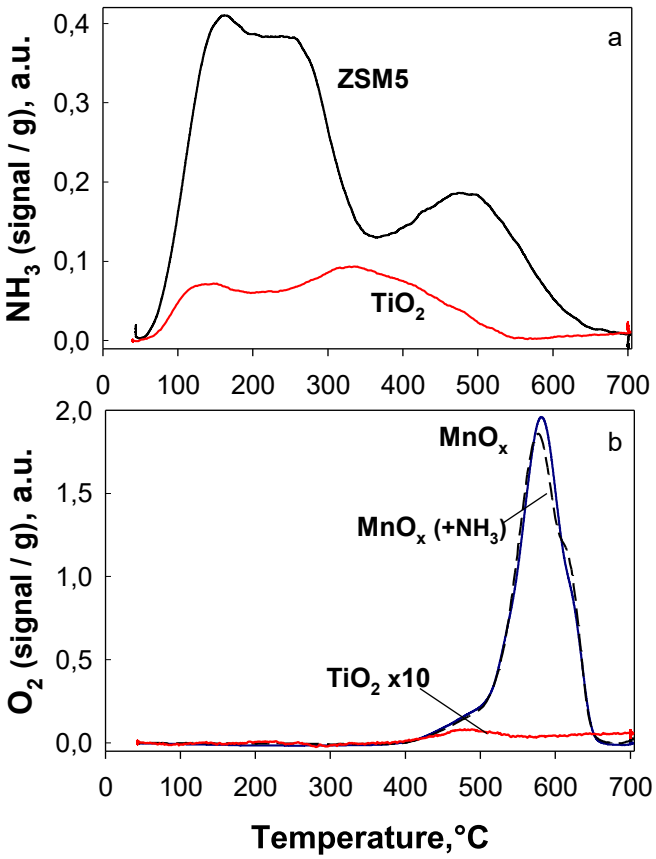

Figure 7.

Figure 8

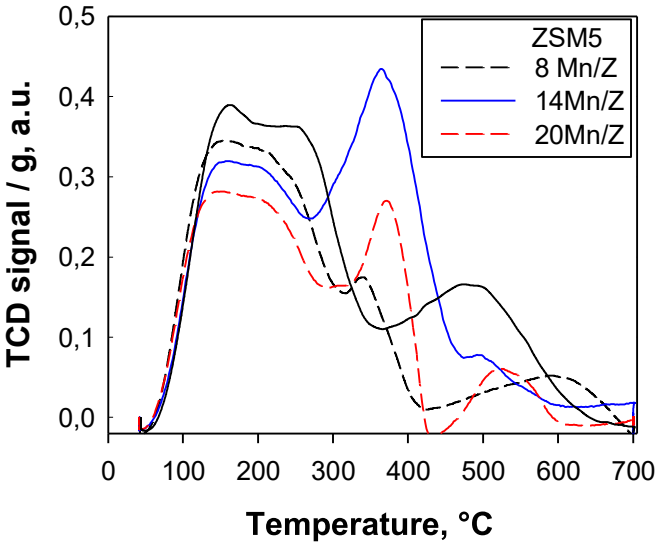

Figure 8.

Figure 9

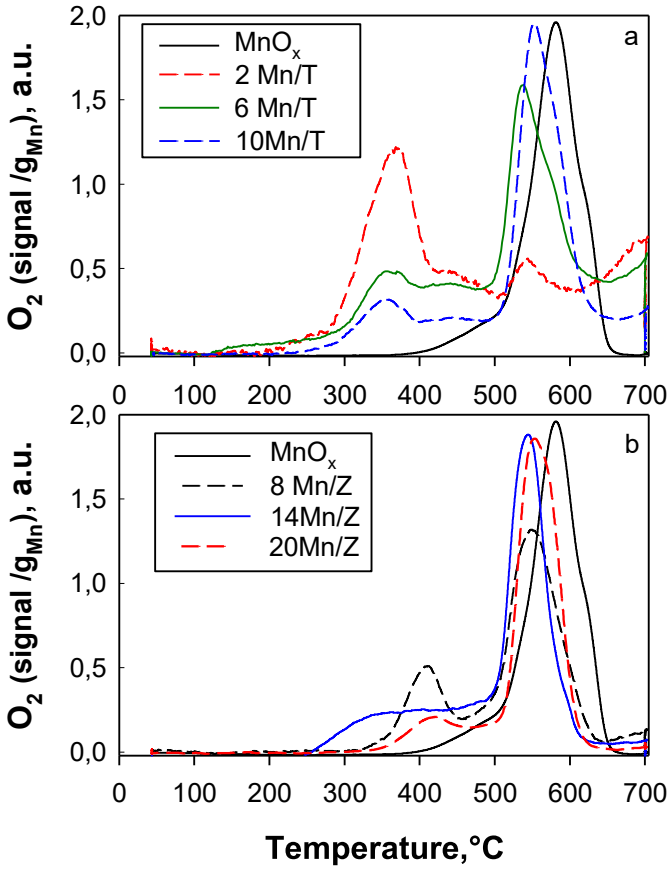

Figure 9.

Figure 10

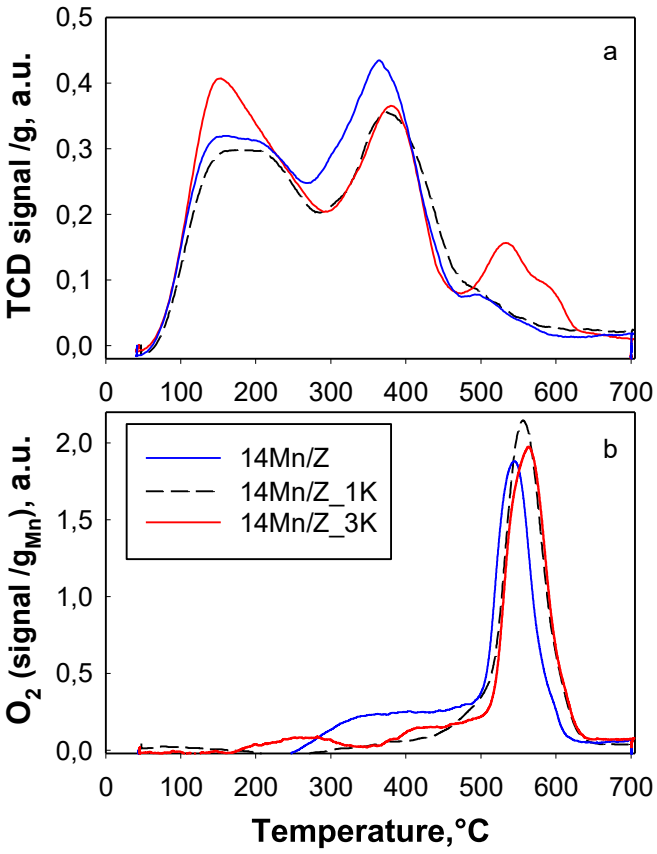

Figure 10.

Figure 11

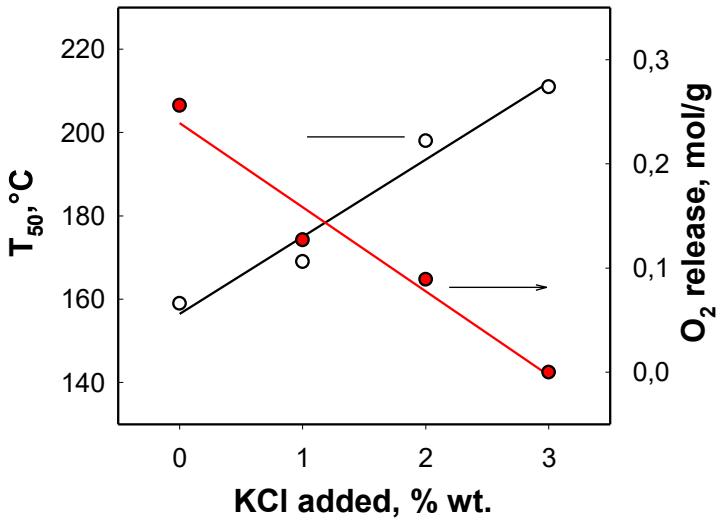

Figure 11.