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Catalysis Today 113 (2006) 87–93

CATALYSIS TODAY

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FT-IR operando study on selective catalytic reduction of NO_x species by ammonia: A comparison between zeolitic and GAPON compounds

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Abstract

Zeolitic materials are currently studied as potential catalysts for NO_x SCR using ammonia as reducing agent. It was recently evidenced that a higher activity can be reached when an appropriate ratio between NO and NO_2 is reached in the flow. To obtain this composition, oxidation catalysts are used in addition to the zeolitic compound. Nevertheless, the oxidation catalyst is easily poisoned by the SO_2 normally present in a real flow. The use of an acidic material to prevent the SO_2 effect and containing an oxidising function seems to be a very good alternative to improve the efficiency of the SCR process. Therefore, we have tested the possibility to perform such kind of reaction in two ammonium galloposphates (representing nanoporous compounds alternative to zeolites), containing transition elements in the crystal structure. The study has been carried out in real temperature and VHSV conditions using an IR transmission reactor cell coupled with a gas analysis system constituted by a IR gas cell and a mass spectrometer. The different analyses are performed on line, under flow, at the time resolution of 1 s.

Keywords: Zeolitic materials; SCR process; Transition elements

1. Introduction

The global equation representing the NO_x SCR with ammonia is as follows:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad \text{or}$$

$$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O$$

Therefore this process, because of its stoechiometry, appears to be particularly advantageous for practical applications. Among catalysts, the most used for this reduction process are Ti supporting vanadium with tungsten or molybdenum as promoters, the reaction temperature being between 573 and 673 K [1]. Nevertheless, in cement or glass industry where exhaust gas treatment is required, the chimney temperature can be as low as 393 K [2]. To avoid an additional cost due to the heating of the gas until the operative reduction temperature, it was necessary to look for low temperature effective SCR catalysts. A good understanding of the different steps of this process will permit us to optimise the operating conditions: temperature, catalytic material composition and decrease of the ammonia gas leaking. With this aim, a careful study of both gas phase and surface was carried out using infrared operando spectroscopy.

Starting from literature data [3], we decided first to reinvestigate the selective catalytic reduction of NO_x by preadsorbed NH_3 over zeolites (as NH_4^+ on Brønsted sites or as ammonia coordinated on Lewis acidic sites), which could be suitable materials for this particular application, taking into account the relatively low temperature of the process. It seemed that such catalysts could be very efficient and easily regenerated by an ammonia flow. In particular we have chosen to study the Y type zeolite because of its well known acid behaviour: the NH_3 storage capacity is in fact rather high and it is possible to modify both the number and the strength of acid sites on such material.

It has been shown as well that the presence of NO_2 in the flow is needed to increase the activity and selectivity in nitrogen [4–6]. So, to improve NO → NO_2 conversion, at a first step we have mixed an oxidation catalyst to our zeolites. Successively, we have considered the possibility to synthesise new materials directly containing an oxidising function and the appropriate NH_3 storage properties, submitting them to reaction tests in real

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0920-5861/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.cattod.2005.11.012

conditions, followed by our IR operando system, which permits the analysis of both gas phase and surface during the reaction.

2. Experimental

2.1. The choice of the samples

A HY_{SA} zeolite was tested, having a structural Si/Al_{IV} ratio of 11.2. This sample was obtained from the mother zeolite ($Si/Al_{IV} = 2.72$) vapour-treated at 823 K. It contains Lewis acidity induced by extraframework aluminium species.

Pt/SiO_2, CeO_2 and two modified ceria samples were used as oxidation catalysts to convert NO to NO_2 at low temperatures.

Three other samples, containing ammonium inside the structure, were prepared in hydrothermal conditions. Their formula are $(NH_4)_3Ga_2(PO_4)_3$, $(NH_4)[Mn(H_2O)_2]Ga(PO_4)_3$, $(NH_4)[Co(H_2O)_2]Ga(PO_4)_3$ [7–10]. Their framework is constituted by corner-sharing GaO_5 trigonal bipyramids and PO_4 tetrahedra. The resulting $[Ga_2(PO_4)_3]_\infty$ three-dimensional framework presents intersecting tunnels running along the [0 0 1], [1 0 1] and [1 0 $\bar{1}$] directions. In the structure of $(NH_4)_3Ga_2(PO_4)_3$, the ammonium cations sit at the intersections of these tunnels, on two independent crystallographic sites. The largest channel, parallel to the $\vec{c}$ axis, has the approximate dimensions of 6 Å × 4 Å. In the Mn and Co containing compounds, only one of the two NH_4^+ cations is still present, the second site being occupied by a water molecule. The divalent transition element (Mn or Co) takes place also in these tunnels, in a distorted octahedral coordination constituted by four oxygen atoms of the $[Ga_2(PO_4)_3]_\infty$ framework and two of the water molecules inserted in the tunnels (Fig. 1).

Samples main properties are reported in Table 1.

2.2. Sample operando characterisation

2.2.1. The reaction system

Our operando system is constituted by a classical gas lines device connected to an IR reactor cell. Gases are introduced into the lines (heated at 333 K) by mass flow controllers, while vapour phases can be sent via a saturator purged by 10 cm^3/min carrier gas (argon) flow. Two independent gas mixtures can be realized at the same time in our system (activation and reaction flow or oxidising and reducing flow, for example), then sent to the reactor cell described below. The system allows the analysis of the reactants and/or of the reaction products by quadrupole mass spectrometry (Balzers TCP 121), FTIR spectroscopy (via a gas microcell of 0.088 cm^3 volume) and gas chromatography (Varian micro GC CP-4900). IR spectra are collected with a Nicolet Magna 750 FT-IR spectrometer, equipped with MCT detectors, at the maximum speed of a spectrum every 50 ms. Normally, to ameliorate the signal/noise ratio, we accumulate 64 scans at a resolution of 4 cm^{-1}, to have a spectrum per second. The same time resolution is obtained in the case of the QMS analysis.

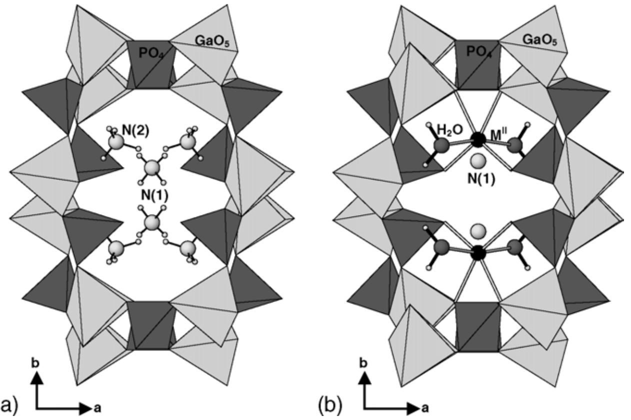

Fig. 1. View of the tunnel parallel to the [0 0 1] direction in the $[Ga_2(PO_4)_3]_\infty$ framework, showing the location of cations and water molecules in the different studied gallophosphates: (A) in $(NH_4)_3Ga_2(PO_4)_3$, the tunnel host ammonium cations distributed over two independent crystallographic sites (labelled N(1) and N(2)); (B) in $(NH_4)[M(H_2O)_2]Ga_2(PO_4)_3$ compounds (with M = Mn, Co), there is still an ammonium cation on the N(1) site, but a water molecule replaces N(2) and the divalent M^{II} transition metal is inserted in the tunnels in a distorted octahedral coordination made of four oxygen atoms belonging to the $[Ga_2(PO_4)_3]_\infty$ host lattice and two water molecules.

2.2.2. The reactor cell

Our IR reactor cell consists of a cylinder of stainless steel carrying a toroidal sample holder in its centre, where the catalyst is placed in the form of a self-supported wafer of 10 mg cm^{-2}. The rest of the space is filled by KBr windows, which limit the dead volume to 0.12 cm^3. The external windows can be also in CaF_2 or BaF_2 to widen the transparency range. The heating system guarantees a maximum temperature of 773 K on the sample; the experiments are carried out at atmospheric pressure. Additional details are given in reference [11].

Table 1
Structural and morphologic properties of the investigated compounds

Zeolite	Cell parameters (Å)	V_{N_2} (cm^3/g)	Si/Al[a]$_{total}$	Si/Al[b]$_{IV}$
HY_{SA} (vapour-treatment)	24.38	0.350	6.41	11.20

GAPON compounds	Cell parameters			
	a (Å)	*b* (Å)	*c* (Å)	*β* (°)
$(NH_4)_3Ga_2(PO_4)_3$	13.3948 (16)	10.3138 (9)	9.0361 (9)	111.323 (7)
$(NH_4)[Co(H_2O)_2]Ga(PO_4)_3$	13.323 (3)	10.245 (1)	8.886 (2)	108.43 (2)
$(NH_4)[Mn(H_2O)_2]Ga(PO_4)_3$	13.543 (4)	10.2302 (15)	8.894 (3)	108.54 (3)

[a] Elemental analysis.
[b] From NMR.

2.2.3. The reaction stream

The two reacting gas compositions for the tests on zeolitic compounds are the following:

- reaction flow: 500 ppm NO, 10% O_2;
- ammonium regeneration flow: 600 ppm NH_3.

Total flow = 12.5 ml min^{-1}; gas vector: Ar.

On GAPON samples the reaction stream has the following composition:

- 500 ppm NO, 10% O_2, 500 ppm NH_3.

Total flow = 12.5 ml min^{-1}; gas vector: Ar.

These reaction streams lead to space velocities (VHSV $\approx$ 30,000 h^{-1} calculated from the total flow) very close to the industrial ones.

3. Results and discussion

3.1. NH_4-zeolites

We have replaced the protons in a HY_{SA} zeolite by ammonium ions. The step of ammonia saturation was carried out using a flow of 600 ppm of NH_3 in argon. Due to the high number of acidic sites (and acidic strength) of this compound, the totality of ammonia is adsorbed in the zeolite until the saturation limit is reached (Fig. 2). The total quantity of adsorbed ammonia (obtained by the integration of the dashed surface: 2.06 mmol/g) is in good agreement with the theoretical number of acidic sites calculated from the Si/Al_{IV} ratio (2.24 mmol/g).

3.1.1. NO reduction at 473 K

Using the previously described operando system, which allow us to correlate adsorbed species and gas flow composition, we managed to show that NH_3 coordinated on Lewis acidic sites are the most active species for the reduction of a flow containing 500 ppm of NO and 10% of O_2 diluted in argon at 473 K (Fig. 3). Considering the gas phase, we observed by both infrared and mass spectroscopy the disappearance of 12% of the NO contained in the inlet flow, reacting with the ammoniacal species adsorbed on the surface, until we reach their overall consumption. In these conditions, the remaining NO (88%) was always detected in the outlet gas and moreover a small quantity of NH_3 (around 6% of the total amount of adsorbed species) was noticed in the exhaust as well, probably due to a local increase of temperature (exothermal SCR reaction). So, we can affirm that the reactivity showed by NO in these conditions is not enough to apply the present catalyst (HY_{SA}) and process to industrial plant, at least at low temperature.

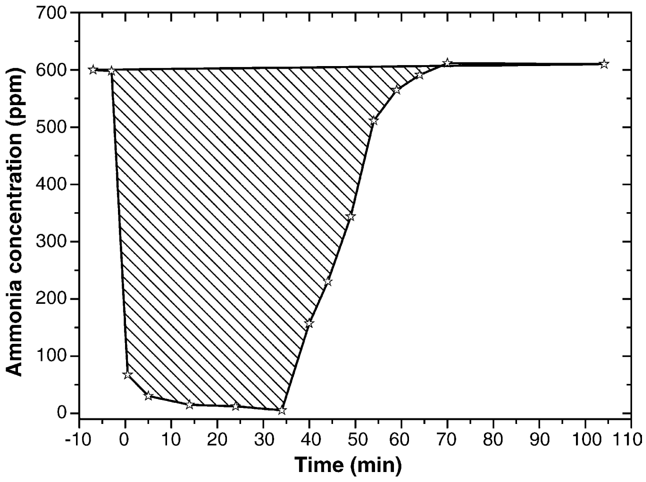

Fig. 2. Evolution of the ammonia flow (IR-gas) during the adsorption step (473 K) on a HY zeolite.

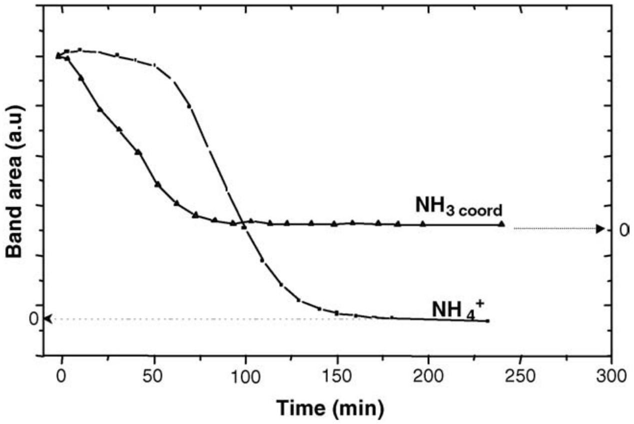

Fig. 3. Evolution of surface species during NO reaction on a NH_4Y zeolite at 473 K.

3.1.2. NO–NO_2 reduction at 473 K

The reaction was then undertaken introducing a 500 ppm NO_x mixture corresponding to a 55% NO_2 and 45% NO molar composition at the entrance of the reactor cell. As observed in Fig. 4, in this case we noticed the total disappearance of NO_2 as long as some adsorbed NH_3 species remained on the zeolitic surface, inferring a nitrogen dioxide conversion of 100%. Moreover, N_2O was never detected in the outlet gas phase, illustrating the high selectivity of the reaction in these conditions. N_2 yield was confirmed by mass 28 in MS spectra, a reliable signal in these particular conditions due to the absence of carbonaceous species in the flow. Other tests were undertaken at lower temperature (433 and 373 K), as well as at

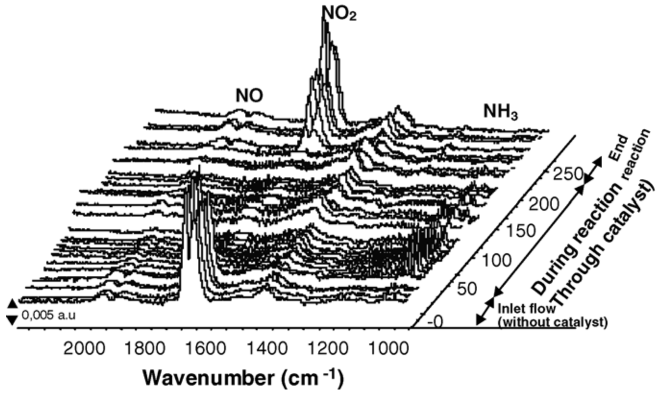

Fig. 4. Gas phase evolution during NO_2 reaction at 433 K on NH_4Y zeolite at 473 K.

different NO_2 concentrations and the results were the same: NO_2 was completely reduced to dinitrogen during the reaction. On the contrary, NO was only partially converted, the unreacted quantity being rejected in the exhaust gases.

The obtained information from these preliminary experiments allow us to confirm that the presence of NO_2 in the reaction flow is needed to obtain a total elimination of 500 ppm NO_x at temperatures lower than 473 K. Therefore, an oxidation step is required in the process.

3.1.3. NO → NO_2 oxidation using an oxidation catalyst

From the last results, we decided to look for a catalyst able to oxidise a fraction of NO into NO_2 during the first step of the SCR reaction. For this purpose we studied the oxidation activity of four different catalysts (Pt/SiO_2, CeO_2 and two modified ceria samples) and isolated the most adapted to our case: CeO_2 modified with transition elements. Pt/SiO_2 was not suitable for our alternative process because the platinum reduction during the NH_3 regeneration step leads to N_2O production during the NO_x reduction step. SCR experiments performed at 433 K with a mechanical mixture of the chosen oxidising compound (modified CeO_2) and HY_{SA} led to the complete (within the experimental error range) NO_x consumption at rather low temperature (Fig. 5). These results are in a good agreement with those reported by Koebel et al. [5], nevertheless we believe that the mechanism in our case is different. In continuous NO_x–NH_3 mixture over V, W, Ti based materials, it was reported that at temperature below 473 K the main deNO_x activity goes through ammonium nitrates formation and further decomposition. In the case of a mechanical mixture of oxidation catalyst and ammonium zeolites, we never observed in the outlet gas any N_2O which would be expected from ammonium nitrates decomposition nor on the surface the rising of nitrates typical IR bands around 1380 cm^{-1}. It seems improbable to displace the ammonium countercations in strong interaction with the zeolitic framework oxygen atoms (ZO^-) to form [ZNO_3^- NH_4^+] species without SCR reaction. Concerning the selectivity, solely N_2 and H_2O were detected as reaction products showing that the modified CeO_2 has not effect on the high selectivity (Fig. 6).

In spite of the promising results obtained for the mechanical mixture with a flow containing NO and oxygen, when 50 ppm of SO_2 was added to the inlet flow, a strong decrease of the activity was observed. A careful study of both zeolite and oxidation catalyst showed that the SO_2 is a poison for the oxidation catalyst itself, and an important decrease of its oxidation capacity is produced during the reaction in these conditions. Taking into account that SO_2 is always present in the industrial exhausts gases, an improvement of the catalytic system is required for real applications.

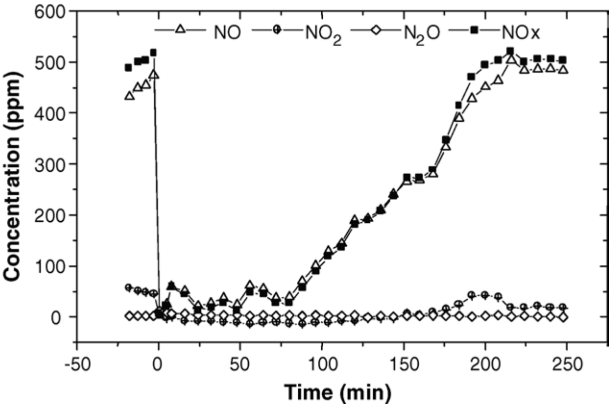

Fig. 5. IR gas phase species analysis during NO_x reaction at 433 K with NH_4Y zeolite mechanically mixed with the oxidation catalyst.

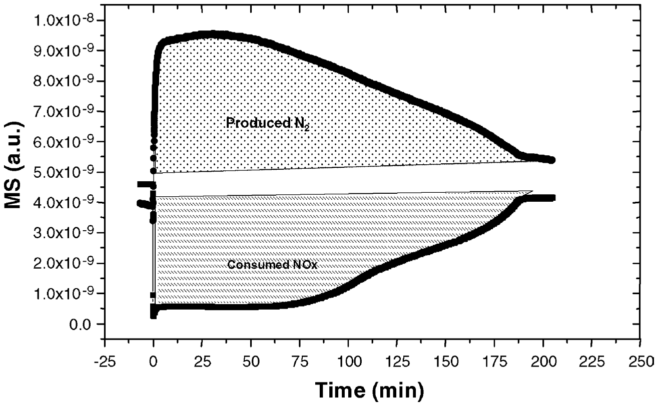

Fig. 6. NO_x conversion and N_2 production detected by MS during reaction at 433 K with NH_4Y zeolite mechanically mixed with the oxidation catalyst.

Theoretically, a catalytic system showing acidic properties should be a good solution to improve the thioresistance of the material because SO_2 is an acid gas, which would not interact with an acidic support. It is already known that phosphate compounds present a high acidic strength [12,13], and therefore, the use of this type of compounds may lead to a better thioresistance. So, three ammonium gallophosphates were synthesised: $(NH_4)_3Ga_2(PO_4)_3$, $(NH_4)[Mn(H_2O)_2]Ga(PO_4)_3$ and $(NH_4)[Co(H_2O)_2]Ga(PO_4)_3$. The first (only containing ammonium) permit us to test the structural ammonium reactivity, while the other two compounds (including a transition metal in their structure) are useful to check the role of a potential oxidising function in the SCR process.

Initially, it was necessary to verify that these compounds already show an adequate activity when SO_2 is not present in the inlet flow.

3.2. Compounds containing NH_4^+ as a template in their structure

At a first time, a GAPON compound previously described [14] $(NH_4)_3Ga_2(PO_4)_3$ was tested at 433 K in a flow of 500 ppm NO, 500 ppm NH_3 and 10% O_2 in Ar, as performed in the case of zeolitic compounds, to compare the respective activities. The presence of ammonia in the stream (additional component respect to the experiment with zeolites) is justified by the fact that ammonium ions are here constitutive elements of the material structure: their ablation will lead to a structural crash, as verified during the TPD experiment. We recall that the process implies in fact a reaction between NO_x molecules from the gas phase and structural NH_4^+ ions, the latter being supposed to be continuously regenerated by the ammonia flow.

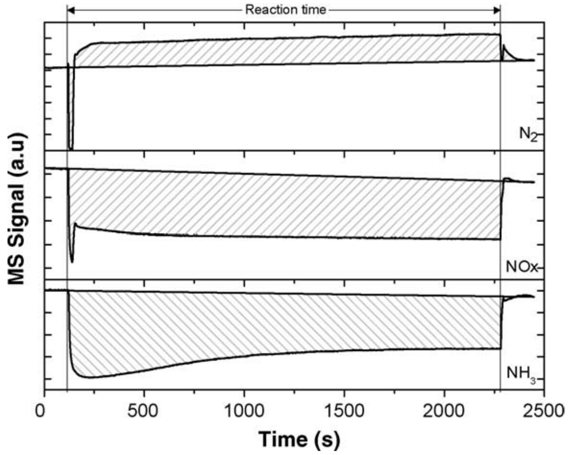

Fig. 7. Evolution of reactants and product during reaction of a NO–NO_2 mixture on a $(NH_4)_3Ga_2(PO_4)_3$ sample at 433 K.

Studying the gas phase by IR spectroscopy and MS, no consumption of NO or NH_3 was observed at this temperature. However, the test with NO_2 replacing the NO gives very different results: consumption of NO_2 and ammonia as well as N_2 production were observed when the gas flow passed through the catalyst. The obtained results from IR-MS analysis are shown in Fig. 7.

Quantitative analysis calculations of the NO_x conversion and N_2 yield have given very similar results for both analytical techniques, IR and MS, such as 64%. The fact that the produced nitrogen amount well matches with N-compounds consumption is also confirmed by the absence of N_2O and/or nitrogen-containing species adsorbed on the surface, as verified by IR spectral analysis. We therefore conclude that a selectivity value around 100% is reached in these conditions (Table 2). Thus, it is obvious that the presence of NO_2 in the reaction stream promotes the activity on these materials as well as on zeolites. Therefore, we can say that NO oxidation to NO_2 is again the primary step in the reaction pathway. According to that, the insertion of a potential oxidising function in the structure compounds, favouring NO oxidation, should improve the activity when a flow containing NO and O_2 is used. With this aim, the synthesis of two new compounds containing, respectively, Mn and Co in the structure was carried out.

3.3. Compounds containing an oxidising function in their structure

Two formulations were prepared and tested, containing Mn and Co, typical transition elements showing oxidative properties [15–17].

Table 2
Reactants and product quantities from SCR reaction on $(NH_4)_3Ga_2(PO_4)_3$ (433 K)

	IR	MS
Consumed NH_3 (mmol/g)	0.25	0.26
Consumed NO_x (mmol/g)	0.29	0.22
Produced N_2 (mmol/g)	–	0.23

But the oxidation capacity is very influenced by the temperature of operation: normally an increase in the reaction temperature will lead to an enhancement of the conversion. So, to establish the temperature working range, it is necessary to have some information about the thermal stability of these compounds. Since both compounds (containing a transition metal) have the same structure, the thermal stability should be very similar (this point was verified by DTG-DTA). With the aim to verify it in conditions similar to those of the reaction, we have submitted the $(NH_4)[Mn(H_2O)_2]Ga(PO_4)_3$ compound to a TPD experiment (2 K/min in an Ar flow). Our system is adequate to obtain the quantity of desorbed ammonia during the TPD experiment; simultaneously possible changes in the compound structure may be detected. Thus, some interesting results were obtained: the TPD study clearly shows the presence of only one type of ammonium in the structure (only one peak in TPD analysis, see Fig. 8), contrarily to what was measured in the parent $(NH_4)_3Ga_2(PO_4)_3$ compound [14]. This is coherent with the fact that in the present case ammonium species have been partially replaced by water molecules. The ammonia uptake has been quantified from Fig. 8 (6.16 mmol/g), showing that it agrees with the chemical formula established by structural analysis (6.29 mmol/g).

From surface characterisation (Fig. 9), the possible changes in the structure may be determined and for the tested catalyst the structural stability limit was measured at around 673 K. Therefore, the use of both Mn and Co modified GAPON for deNO_x applications should be limited to temperature lower than 673 K in order to avoid structural ‘‘crash’’ leading to severe activity lost.

With the aim to test the efficiency of the different transition elements in the deNO_x reaction, being basically related to their oxidation capacity, the sample containing Co was first tested in flow of NO, ammonia and oxygen in a temperature range of 433–623 K (according to the previously established stability limit). In these experiments, no activity in deNO_x reaction was found, nor activity in oxidation.

Even if this sample was not able to produce the necessary quantity of NO_2 to obtain SCR activity, the role of the structural ammonium was tested, using a flow of NO_2 in the presence of

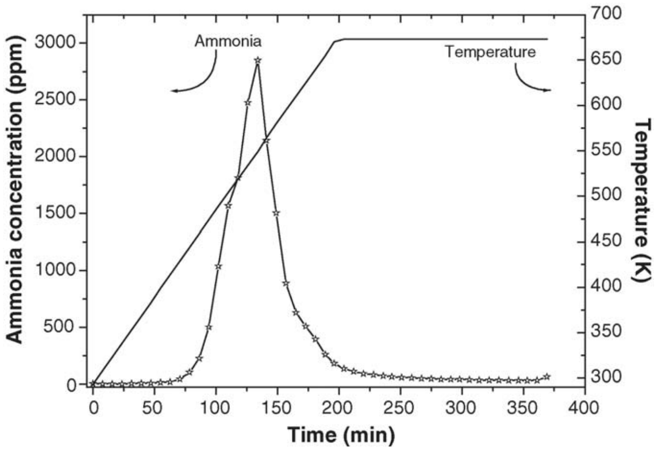

Fig. 8. Ammonia desorption from $(NH_4)[Mn(H_2O)_2]Ga(PO_4)_3$ sample during the TPD experiment.

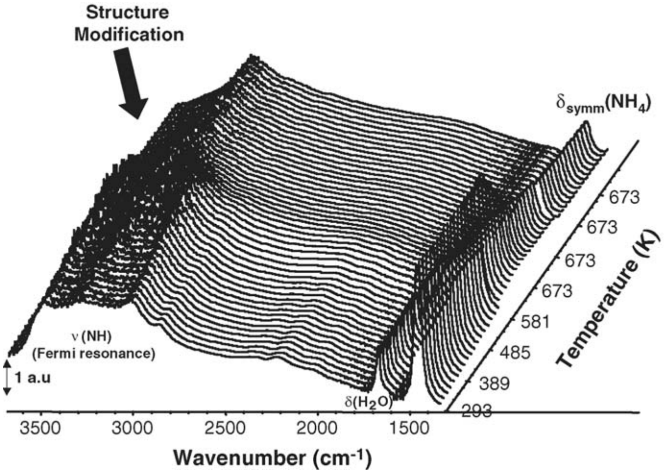

Fig. 9. Surface evolution of $(NH_4)[Mn(H_2O)_2]Ga(PO_4)_3$ sample during the TPD (determination of the stability temperature range).

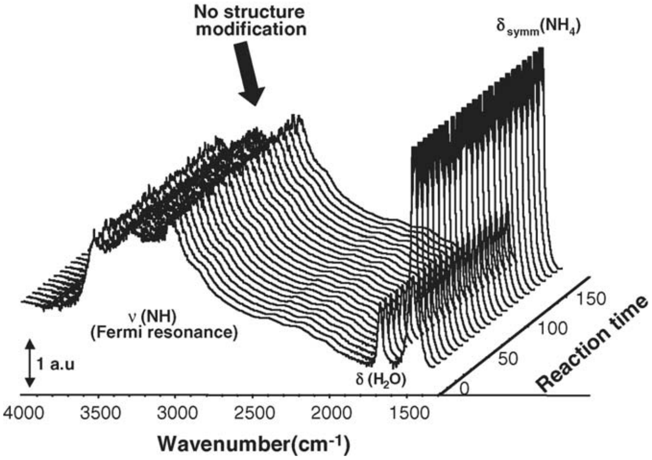

Fig. 11. Surface behaviour during reaction on $(NH_4)[Co(H_2O)_2]Ga(PO_4)_3$ sample with NO_2 and NH_3 at 623 K.

ammonia and Ar as a carrier gas. The aim was to test if the ammonium present in the structure was able to react with an adequate gas phase.

The reaction in the presence of NO_2 gives, as expected, better results. From Fig. 10, we can observe a decrease in both NH_3 and NO_2 concentrations. Also, the formation of N_2 can be observed (MS spectra, not shown here). This fact confirms that the ammonium ions of the structure are able to react (although at rather high temperature: 623 K) with the NO_2 present in the flow, being replaced by the ammonia present in the gas phase (no changes are detected in surface spectra). The study of IR spectra of the surface shows that the structure is not altered during the reaction (Fig. 11).

The $(NH_4)[Mn(H_2O)_2]Ga(PO_4)_3$ sample was tested as well in reaction conditions (500 ppm NO, 500 ppm NH_3, 10% O_2 and Ar) very similar to the real ones. The continuous screening (by MS and IR gas analyses) of the gas phase when the flow pass through the catalyst in steady state indicates that no variations in the gas composition and concentration take place during the reaction. Also, no changes in the catalyst surface were detected by IR spectroscopy. This means that no catalytic activity is detected on this sample in these conditions. The IR gas analysis, permitting to distinguish between NO and NO_2, allows us to verify the absence of NO oxidation to NO_2 in these operating conditions. We can therefore conclude that the absence of an efficient oxidation function on this compound (in our operating conditions) implies the absence of catalytic properties of the solid.

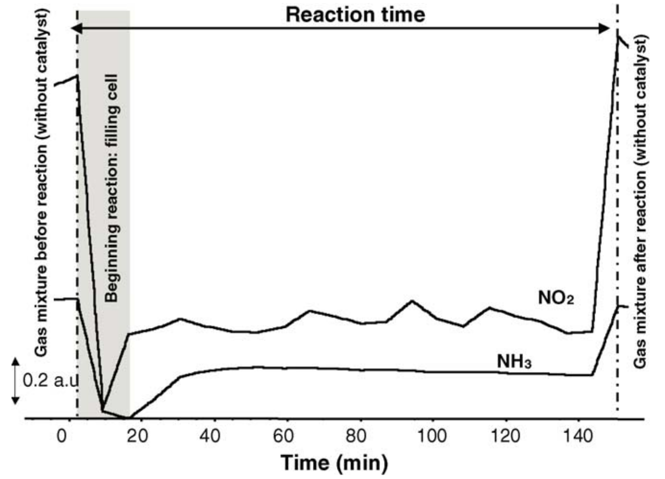

Fig. 10. Ammonia and NO_2 evolution during reaction at 623 K (IR) on $(NH_4)[Co(H_2O)_2]Ga(PO_4)_3$ sample.

Comparing the obtained results for the two last samples (ammonium gallophosphates containing a potential oxidising function), we deduce that the cationic position in such structures should not permit the change in the metal oxidation state, that is the necessary prerogative to observe redox phenomena. So, some changes in the oxidation element coordination will be necessary to obtain a catalyst with a higher activity.

4. Conclusions

In the present work we have demonstrated the feasibility of an efficient and very selective SCR of NO_x on zeolitic compounds pre-saturated with ammonium and/or ammonia. The NH_3 storage capacity must be considered carefully when choosing the type of zeolite, because the SCR reaction goes on until the overall consumption of the adsorbed species.

The presence of NO_2 in the reaction stream seems to be necessary to oxidise the adsorbed NH_3 species. To obtain an optimal NO/NO_2 ratio, the presence of modified CeO_2 together with a Y zeolite containing NH_3 adsorbed species allows to obtain a satisfactory SCR efficiency at low temperatures.

Concerning the GAPON samples, from the obtained results in this study we can conclude that these catalysts could be used only in processes at low temperatures, because their structure is strongly modified at temperatures higher than 673 K (and the compounds are not active after the structure modification). The ammonium ions present in the structure are able to react in the presence of an adequate quantity of NO_2 and ammonia giving significant conversion and selectivity. Unfortunately, the introduction in their structure of transition elements to generate oxidising functions (as performed) is not able to produce the required quantity of NO_2. Probably, due to the position of the transition element inside the structure, the cation is in a fixed oxidation state, without having the possibility to manifest redox properties. An improvement of the catalysts for deNO$_x$ applications (at low temperatures) could be possible if the position of the oxidising element in the structure may be changed to allow different redox states. Conversely, we have verified that ammonium active species inside the structure can be easily regenerated by ammonia from the gas phase, giving rise to a good activity.

In fine we can stress that a complete analysis using an operando system gives rise to important conclusions about catalyst behaviours. The parallel following of both the gas phase and the surface during the reaction in real conditions allows establishing all the parameters influencing the catalyst functionalities. Therefore, it is possible to conceive the necessary modifications in the formulation of the catalyst to improve its performances.

Acknowledgements

The authors would like to thank the Conseil Regional de la Region Basse-Normandie and ADEME for the support given to the present study.

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