From metal-supported oxides to single-metal site zeolites: the next-generation of passive NO_x adsorbers (PNAs) for low temperature diesel engine emission control

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Abstract

Different zeolite-based materials have recently been commercialized as efficient catalysts for the selective catalytic reduction (SCR) of NO_x using ammonia as reducing agents. However, these materials show a limited catalytic activity at low exhaust temperatures, which are particularly achieved during the engine warming up (“cold start conditions”). To overcome this limitation, it has been proposed the inclusion of the passive NO_x adsorber (PNA) as a new component of the emission control system. The PNA is able to adsorb the NO_x species during the cold start at low temperatures and, afterwards, permits their release at higher temperatures where the SCR catalyst can complete the NO_x reduction. In the present revision, the most relevant PNA materials will be discussed, including those based on amorphous oxides and zeolites, together with the fundamental understanding of the NO_x adsorption/desorption mechanisms associated to the PNA materials. The ability to control the dispersion and nature of the metals, the reducibility of the amorphous oxide supports, or the physico-chemical properties of the zeolites, will be key parameters in order to design more active and stable PNA materials.

1.- Introduction

The continuous increase of pollutants in the atmosphere and their irrefutable negative effects on the environment,¹⁻² have made the administrations to increase the emission control legislation.³⁻⁵ Tighter regulations impose short timings to the automotive producers to afford the new more stringent pollutant targets, including carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NOx) and particulate matter (PM).⁶

In general, the automobiles equipped with stoichiometric-burn gasoline engines are able to accomplish with the restrictive emission values for CO-HC-NOx by using the “three-way catalysts”.⁷ In contrast, with those vehicles containing lean-burn diesel engines, such as heavy duty diesel (HDD) vehicles, is more challenging to entirely reduce the NOx pollutants since they work in an oxygen-rich environment.⁶

In the last years, the selective catalytic reduction (SCR) of NOx using ammonia as reducing agent has been introduced in the market to control the NOx emissions in HDD vehicles.^{6,8} The current commercial NH₃-SCR catalysts are vanadium-based or zeolite-based materials, presenting each of them different performance.^{6,9} On the one hand, the vanadium-based catalysts show better resistance against poisoning agents that can be present in the fuels, i.e. sulfur components, but they suffer from irreversible deactivation at operating temperatures above 500°C.^{5,8,10} On the other hand, the zeolite-based catalysts are preferentially based on small pore zeolites doped with copper and/or iron species.¹¹⁻¹³ They perform efficiently under a broader range of operating temperatures (from 200 to 600°C), and show a remarkably higher hydrothermal stability than vanadium-based SCR catalysts. This point is particularly interesting because it allows designing an engine exhaust configuration in where the NH₃-SCR zeolite-based catalyst can be placed downstream of a diesel particulate filter (DPF) (see Figure 1a). Then, the DPF can selectively trap the particulate matter present in the fuel, but the filter regeneration requires high temperatures (above 600°C) and, consequently, the NH₃-SCR catalyst placed downstream must remain stable at elevated temperatures.^{6,8}

Despite the excellent catalytic behavior and hydrothermal stability of the commercial zeolite-based SCR catalysts, they are not active enough at low exhaust temperatures, such as those occurring during the warming up of the catalytic system when the engine has been switched on.¹⁴ This limited cold start NOx control can be explained by the negligible NOx catalytic activity at temperatures below 200°C when using Cu- or Fe-containing SCR zeolite-based catalysts (see

Figure 2), and by the slow rate of urea decomposition into ammonia at low temperatures, limiting the presence of the required reducing agent to undergo the SCR of NO_x.⁶

Recently, it has been proposed the inclusion of a passive NO_x adsorber (PNA) as a new component of the emission control system in HDD vehicles. Its function is to adsorb the NO_x emitted from the diesel engine during the cold start and, afterwards, to release the adsorbed NO_x once the temperature in the SCR catalytic system is high enough to perform adequately the NO_x reduction (see Figure 1b).¹⁵⁻¹⁶ The inclusion of a PNA can adequately complement the NH₃-SCR catalyst, resulting in a very efficient cooperative NO_x emission control technology, even during the cold start period.

The PNA materials described in the literature are based on noble metal species (i.e. Pt, Pd or Ag) on amorphous oxide supports (i.e. Al₂O₃, TiO₂ or CeO₂, among others)^{15, 17-18} or crystalline zeolites with different pore topologies (i.e. BEA, MFI or CHA).¹⁹⁻²¹ However, the design of a very efficient and stable low-temperature PNA requires a rapid adsorption of NO_x at temperatures below ~100°C, and desorption of the NO_x components at intermediate temperatures (i.e. 200-350°C). Moreover, they should be stable at high temperatures in presence of steam and active in presence of potential poisons (i.e. sulfur components, CO, or water, among others). Thus, according to all these premises, the adsorption/desorption mechanisms of NO_x on those materials has to be understood to fine-tune the physico-chemical properties of the PNA materials.

Within the present revision, the most relevant PNA materials based on amorphous oxides and zeolites will be described together with the fundamental understanding of the adsorption/desorption mechanisms associated to the different components of the PNA materials. The last includes the nature or oxidation state of the metal, reducibility nature of the support, and pore topology or chemical composition of the zeolite. This understanding can help to design more efficient and stable PNA materials.

2.- Supported noble metal oxides as former PNA materials: towards a comprehensive mechanistic assessment

One of the first descriptions in the literature describing the combination of two catalyst components to treat exhaust gases generated by a diesel engine was reported by researchers at Ford.²² These authors proposed the use of an oxide support carrying a precious metal, Pt/Al₂O₃, as a NO_x adsorbent, followed by an SCR catalyst able of converting the exhaust gases, including the NO_x desorbed from the previous adsorbent, when hydrocarbons or ammonia are employed

as reducing agents (see Figure 1b). In particular, the authors demonstrate that Pt/Al₂O₃ shows a storage efficiency of ~80% at 160°C when measuring the cold start NO_x emission from 50°C with a temperature increase of 15°C/min. A complete release of the NO_x adsorbed occurs at 230-430°C (see Figure 3).

These preliminary results combined with the new environmental scenario created by the more constrained regulations, have induced in the last years to several research groups to rationalize the preparation of improved PNA materials to overcome deficiencies in the diesel exhaust purification methods, particularly during the cold start period.

2.1.- Nature of the noble metal species: the chemistry involved in the NO_x adsorption/desorption

The adsorption/desorption abilities of the PNAs will directly depend on the NO_x species present in the exhaust gases together with the stability of the adsorbed NO_x species as nitrites (-NO₂) or nitrates (-NO₃).²³ In this sense, Theis et al. studied the NO_x storage and release performance of Pt/Al₂O₃ and Pd-rich/Al₂O₃ materials by transient tests that simulate the real cold-start period. For doing that, the feed was treated from 70 to 300°C with a temperature ramp of 10°C/min (feed composition: 110 ppm NO, 5% CO₂, 5% H₂O, 10% O₂).²⁴ These authors observed that the Pt-containing alumina materials exhibited limited NO_x storage during the initial 200 s compared to the Pd-rich/Al₂O₃ materials, and, in addition, Pt/Al₂O₃ materials required higher temperatures to desorb the NO_x species (see Figure 4).²⁴ The analysis of the released NO_x products revealed that the Pd-rich/Al₂O₃ material mostly desorbs NO (see Figure 4b), whereas the Pt/Al₂O₃ materials released preferentially NO₂ at higher temperatures (see Figure 4a), suggesting the preferential formation of nitrite and nitrate species in the Pd-rich/Al₂O₃ and Pt/Al₂O₃ materials, respectively. The authors speculated that the limited NO_x storage capacity of the Pt/Al₂O₃ materials at low temperatures could be attributed to the low efficiency of Pt to store NO combined with the weak NO oxidation ability at temperatures between 70 and 150°C. Indeed, the storing capacity of the Pt/Al₂O₃ materials increased at longer times (above 500 s, with a temperature of ~200°C, see Figure 4a), fact that can be explained by the higher NO oxidation capacity of Pt to form NO₂ at temperatures above 200°C material.²³

Ag-based catalysts have been deeply studied along the years in the literature for the SCR of NO_x reaction using hydrocarbons²⁵⁻²⁶ or ammonia²⁷⁻²⁸ as reducing agents. In general, it has been described the promoting effect of hydrogen in the reaction feed to favor the low temperature SCR reduction efficiency when using Ag/Al₂O₃ as catalysts.²⁵ Recently, the potential ability of Ag-

containing Al_2O_3 as effective low-temperature PNA materials has also been explored.²⁹⁻³⁰ As it can be seen in Figure 5a, the presence of hydrogen clearly influences the NO_x adsorption capacity of the $\text{Ag}/\text{Al}_2\text{O}_3$ material, increasing the total NO_x storage below 180°C from 0.07 g/L to 0.19 g/L, when the H_2 concentration in the exhaust feed is increased from 0 to 500 ppm, respectively.²⁹ In-situ Fourier-transform infrared (FTIR) characterization revealed the preferential presence of monodentate nitrate species when H_2 is present, and the authors suggest that H_2 could favor the reduction of Ag_2O clusters to Ag metal, which would catalyze the low-temperature NO oxidation.²⁹ As it could be expected by the preferential formation of stored nitrate species, the $\text{Ag}/\text{Al}_2\text{O}_3$ material shows a considerably higher NO_x release temperature compared to a benchmark Pt/Pd based catalyst ($\sim 430^\circ\text{C}$ versus 280°C , respectively, see Figure 5b). Therefore, considering that effective PNA materials should mostly desorb NO_x below 350°C for consecutive cold-start cycles, the current NO_x desorption step achieved using $\text{Ag}/\text{Al}_2\text{O}_3$ may preclude its potential use as PNA for low-temperature diesel engine emission control.

In general, it has been observed that NO and NO_2 species are preferentially stored as nitrites and nitrates, respectively, being the stored nitrates more stable than nitrites and, therefore, nitrates should require higher temperatures to be released.²⁴ Thus, the design of optimal PNA materials for low temperature diesel engine emission control would require to preferentially store NO_x as NO species, which would be more easily released when increasing the temperature of the start, favoring efficient cold start adsorption-desorption consecutive cycles. From the different metals that have been described in the literature, Pd seems to possess the most effective dual performance, both during the low-temperature NO adsorption and during the intermediate NO release temperatures.

2.2.- Influence of metal PNA promoters and oxide supports

The former 3-way catalyst described for automotive lean-burn engines combined the presence of a precious metal (Pt), aluminum oxide as support, and a second metal compound as NO_x storage component (i.e. Barium).²³ In this early work, the authors proposed the NO_x storage and reduction mechanisms based on fundamental kinetics and spectroscopic studies. On the one hand, the NO is oxidized on the precious metal and, subsequently, the NO_x storage compound is able to trap NO_x species as nitrate ions (see Figure 6a). This fact can be explained by the high basicity of the NO_x storage compound, which can react with two NO_2 species, forming the highly stable $\text{Ba}(\text{NO}_3)_2$ (see Figure 6a). On the other hand, the formed nitrates can be decomposed into NO_x at high temperatures in the presence of reducing agents (i.e. hydrocarbons) on the precious metal (see Figure 6b) and, under stoichiometric ratios of reducing agents, the resultant NO_x

species are adequately reduced to N_2 on precious metals (see Figure 6b). Nevertheless, the high stability of the $Ba(NO_3)_2$ species requires temperatures above $350^\circ C$ to mostly desorb the stored nitrates, limiting the optimal efficient cold start adsorption-desorption consecutive cycles.

Besides barium, lanthanum has also been proposed as a NO_x storage compound in the $Pt/La/Al_2O_3$ system.¹⁷ In this case, the higher basicity of La_2O_3 compared to Al_2O_3 , increases the NO_x adsorption capacity at low temperatures. However, despite the NO_x adsorption efficiency is remarkably increased for the La-promoted Pt/Al_2O_3 system, this material cannot be completely regenerated at intermediate temperatures, i.e. $250-300^\circ C$, and most of the NO_x stored species are released at temperatures above $400^\circ C$ (see Figure 7). The high desorption temperature can be explained, by the preferential storage of nitrate species, as occurred above for the $Pt/Ba/Al_2O_3$ system. Moreover, the Pt dispersion along the $Pt/La/Al_2O_3$ catalyst is substantially reduced after different cyclic operations, which can be explained by the competitive role between platinum and lanthanum to occupy the defect sites in the Al_2O_3 structure, leading towards significant metal sintering.

These results suggest that the use of barium or other alkaline-earth metals may not be adequate for PNA formulations, because the high temperature required to decompose the nitrate species. As alternative, it has been recently proposed the use of Pd-containing on ceria/zirconia (CZO) as low-temperature PNA materials.^{18, 31} The oxidized form of the Pd/CZO material is able to store significantly more NO_x species at bed temperatures below $200^\circ C$ than the Pd/Al_2O_3 material (see Figures 8a and 8b, respectively). The authors suggest that the improved NO_x adsorption capacity observed using the Pd/CZO sample could be explained by a preferential NO adsorption at the interface of a Pd oxide site and nearby ceria site, possibly through a spill-over process.¹⁷⁻¹⁸ Interestingly, most of the NO_x desorption occurs at intermediate temperatures, i.e. $220-270^\circ C$, being almost exclusively released as NO. This fact clearly indicates that the NO was initially stored as nitrites, which can decompose at lower temperatures. Thus, the ceria-based Pt-zirconia PNA could be entirely purged for cold start adsorption-desorption consecutive cycles.

2.3.- Hydrothermal stability and poisoning of the PNA catalysts

For the long-term active in a diesel-engine performing under lean conditions, the PNA material must show high (hydro)thermal stability and tolerance against sulfur compounds, which are present in the fuel. It is particularly important to design PNA catalysts able to efficiently perform in presence of sulfur contaminants, because these S-based molecules can be easily oxidized to SO_2 in presence of noble metals under lean conditions, and stored as sulfates in the PNAs.²³ The

adsorbed sulfates are more stable than nitrates, diminishing the NO_x adsorption capacity of the PNA material and, in addition, they require higher temperatures to be released (i.e. above 700°C).

The PNA performance of the Pd/Al₂O₃ catalyst has been studied in presence of SO₂ to evaluate how the sulfur poisoning and its posterior desulfation would influence the NO_x adsorption-desorption processes.²⁴ After 7 or 14 hours of exposing the Pd/Al₂O₃ catalyst to a 5 ppm SO₂-containing feed, the NO_x adsorption efficiency is severely reduced (see for instance after 14 h SO₂ in Figure 9). However, if the poisoned Pd/Al₂O₃ catalyst is exposed to lean conditions at high temperatures (~750°C), most of the NO_x adsorption capacity can be recovered (see “after DSO_x at 750C” in Figure 9).

Different authors have described that the base strength of the doped-PNA supports defines the decomposition temperatures of the adsorbed sulfur components in the PNA catalysts.³²⁻³³ Thus, Tsukamoto et al. have proposed the addition of an acidic material to the support to weaken the base strength, then including titania in the formulation of the Ag/Al₂O₃ catalyst.³⁰ The resulting Ag/TiO₂/Al₂O₃ system not only requires a remarkably lower temperature to decompose the adsorbed sulfates (below 600°C), but also presents an enhanced NO_x trapping capacity compared to the analogous TiO₂-free Ag/Al₂O₃ catalyst.³⁰ A plausible explanation for the better NO_x trap capacity is that the TiO₂ inclusion favors the Ag dispersion, resulting in smaller Ag particles with more NO_x adsorption sites in the Ag/TiO₂/Al₂O₃ catalyst.

Besides sulfur poisoning, it has been described that the presence of water also provokes an inhibiting effect on the NO_x storage at temperatures below 100°C, being suggested that water was physically blocking the NO_x storage sites.^{18, 34} In this sense, the increase of the starting bed temperature of the catalyst results in an enhancement of the NO_x adsorption capacity by mitigating the inhibiting effects of water (see Figure 10). Nevertheless, the increase of the starting bed temperature would also favor the NO_x release at low temperatures and, under these conditions, the SCR catalyst could not be operative. Thus, the search for new low-temperature water-resistant PNA materials able to retain the NO_x species until achieving temperatures where the SCR catalyst become active, is still an active field of research.

3.- Zeolite-based PNA materials: the next-generation of low temperature NO_x adsorbers

Alternative to the metal-supported oxides as PNA materials, the use of metal zeolite catalysts for the low temperature NO_x trapping during the cold-start period in diesel engines has been recently proposed.^{19, 35} In fact, researchers at Johnson Matthey have developed the Diesel Cold

Start Concept (dCSC™) based on this technology.^{15, 36-37} Preliminary results with the zeolite-based PNA materials have shown an improved NO adsorption capacity together with a better (hydro)thermal stability and poisoning resistance compared to the metal-supported PNA oxides.¹⁹ The acquired knowledge during the design of metal-supported PNA oxides, combining the catalyst syntheses and mechanistic assessments on NO_x adsorption/desorption, together with the experience obtained during years of research in the design of Pd-containing zeolites as potential hydrocarbon SCR catalysts,³⁸⁻⁴⁰ have allowed the proposal of different metal-containing zeolites as efficient passive NO_x adsorbers.

3.1.- Influence of the zeolite structure

The influence of the zeolite structure on the low-temperature NO_x adsorption has been evaluated by two different research groups for different Pd-containing zeolites with small-, medium- and large-pores (Pd/CHA, Pd/MFI and Pd/BEA, respectively, see pore dimensions and chemical compositions in Table 1).^{19, 41} The NO storage has been studied using a gas mixture containing 200 ppm NO, 200 ppm CO, 50 ppm *n*-C₁₀H₂₂, 12% O₂, 5% CO₂, and 5% H₂O at 100°C. As seen in Figure 11a, the three Pd-zeolites showed an excellent NO trapping efficiency with values above 90%, being this outstanding efficiency higher maintained when Pd/BEA was used as PNA.¹⁹ The overall NO storage capacity of the Pd-zeolites were 48, 58, and 64 μmol of NO per gram of zeolite for the Pd/CHA, Pd/MFI and Pd/BEA materials, respectively. Interestingly, the characterization of the Pd-zeolites by in-situ FTIR spectroscopy using NO as probe molecule, suggested a preferential stabilization of the adsorbed NO when decreasing the size of the zeolite pores. The authors propose that the different NO bond strength within the zeolite structures could influence the NO desorption profiles depending on the pore topology. To demonstrate this point, the NO desorption profile was studied after adsorbing NO at 100°C followed by a rapid temperature increase up to 500°C (ramping rate of 100°C/min). As expected, the observed temperature for the maximum NO_x desorption peak increases with decreasing the pore size, being 260, 275 and 360°C for the Pd/BEA, Pd/MFI and Pd/CHA, respectively (see Figure 11b).¹⁹ However, besides the different NO bonding strength proposed by the authors, the presence of chromatographic effects influencing the molecule diffusion out from zeolite crystallites with different pore sizes cannot be ruled out.⁴²⁻⁴³

These results show that the NO_x adsorption/desorption properties could be fine-tuned by properly selecting the zeolite support structure, opening new possibilities for designing specific PNA materials for each particular model of vehicle with possible different exhaust temperature profiles.

As stated above, an important issue for the PNA materials is their ability to maintain the adsorption capacity at low temperatures in the presence of some poisoning components in the feed, such as water and SO₂. In fact, the Pd-containing zeolite-based PNA materials mostly retain their NO adsorption efficiency almost intact in presence of water, and after being exposed to 100 ppm SO₂ gas mixture (see Figure 11c).¹⁹ In contrast, the metal-supported oxides, i.e. Pd/CeO₂, lose almost completely their ability to adsorb NO_x at low temperatures when sulfated compounds are present in the exhaust mixture (see Figure 11c). The authors suggest that the SO₂ adsorption may preferentially occur on the residual PdO aggregates formed on the external surface of the zeolite crystals, clearly indicating that the highly dispersed Pd cationic species at the exchangeable sites would be able to selectively store NO at low temperatures without being influenced by the SO₂ species in the gas mixture.

3.2.- Enhancing NO_x adsorption by maximizing the metal dispersion in zeolites

The studies on different Pd-zeolites proposed by Chen et al.¹⁹ have been extended by Zheng et al.⁴¹ to provide a more atomic understanding on Pd dispersion and site requirements for NO adsorption. In this sense, the Pd dispersion along the Pd-exchanged zeolites, including BEA, MFI and CHA, has been studied by FTIR spectroscopy using CO as probe molecule, XPS and scanning TEM microscopy.⁴¹ These authors describe the presence of several Pd species under different oxidation states along the three Pd-zeolites, resulting in diverse local metallic structures that can influence the NO_x adsorption/desorption mechanisms by inducing complex chemical reactions. For instance, XPS analyses of the different Pd-zeolites clearly reveal the formation of diverse Pd species depending on the zeolite structure, being particularly surprising the higher proportion of Pd(IV) within the Pd/CHA zeolite compared to Pd/BEA and Pd/MFI zeolites (see Figure 12). This characterization indicates the higher fraction of PdO₂ clusters on the external surface of the preoxidized Pd/CHA crystals, whereas the Pd/BEA and Pd/MFI initially presents a higher portion of Pd(II) in cationic positions.⁴¹ The authors propose that the small pores of the CHA structure can limit the cationic Pd diffusion into the CHA crystals as a plausible reason for its inadequate Pd dispersion compared to Pd/MFI and Pd/BEA.

According to the characterization and the NO_x adsorption/desorption profiles, Zheng et al. have proposed different NO_x trapping mechanisms for the Pd(II) and Pd(IV) species depending if the feed also contains water and/or CO.⁴¹ In absence of water and CO, the exposed Pd(IV) species, which are mainly present at the surface of PdO₂ clusters, would be able to adsorb two NO molecules, one of those being transformed to NO₂ and the other remaining molecularly adsorbed (see Figure 13-right). In presence of water, the authors suggest that only the well-

dispersed monomeric Pd sites are not inhibited for NO_x adsorption, being the PdO₂ clusters located on the external surface inactive for the NO_x adsorption.

Interestingly, in presence of H₂O and CO, the authors noticed a clear increase of the NO_x trapping efficiency compared to the studies performed in absence of CO.⁴¹ This improved NO_x adsorption behavior when CO is present in the feed also results in an increase of the NO_x temperature desorption (see Figure 14).⁴⁴ Different groups have recently studied the possible role of CO in the NO_x adsorption enhancement.⁴⁴⁻⁴⁵ On the one hand, Vu et al. have studied the influence of CO in the Pd-containing BEA zeolite using FTIR, concluding that CO would act as a reductant agent, being able to lower the Pd oxidation state.⁴⁴ This partially reduced Pd can strongly bond the NO_x species via the strengthening of the covalent bond by π -backdonation.⁴⁴ On the other hand, Khivantsev et al. studied the NO_x storage capacity promotion by CO on Pd-containing CHA using TPD and FTIR spectroscopy.⁴⁵ These authors have proposed the selective formation of a carbonyl-nitrosyl Pd complex [Pd(II)(NO)(CO)], which would explain the high resistance to water poisoning when CO is present in the feed and the shift towards higher temperatures for the NO_x release (above 320°C).⁴⁵

According to these previous studies, one can conclude that maximizing the metal distribution along the zeolite crystals, if possible as single cationic species, will be beneficial to increase the NO_x adsorption/desorption performance, both in terms of adsorption capacity and (hydro)thermal and poisoning stability. Having that in mind, recent studies have focused on the evaluation of the metal loading, the Si/Al molar ratio and the metal dispersion treatments in different zeolites, particularly MFI and CHA, and their influence in the low-temperature NO_x adsorption/desorption processes.²⁰⁻²¹ In a very complete experimental design, Lee et al. have first evaluated the influence of the activation treatment on the metal dispersion, detecting that an oxidative treatment at 750°C allows the atomically dispersion of the Pd species within the MFI crystals (see EXAFS spectra in Figure 15), which maximizes the total amount of adsorbed NO species ($\sim 24.6 \mu\text{mol/g}_{\text{catal}}$).²⁰ Afterwards, a large number of Pd-containing MFI zeolites, with different Si/Al molar ratios (from 11 to 150, see Table 2) and Pd contents (from 0.5 to 5.5%wt Pd, see Table 2) have been evaluated by the same authors.²⁰ The achieved results are summarized in Table 2, where it can be concluded that the Pd/MFI zeolite prepared with a Si/Al molar ratio of 15 and a $\sim 2\%$ wt Pd content shows the highest amount of adsorbed NO (see Pd(2)/MFI(Si/Al=15)). The combination of a relatively Al-rich MFI zeolite with an intermediate Pd content mostly suppresses the undesired PdO sintering, while favoring the metal dispersion by better coulombic interactions between the cationic Pd species and the Al-rich MFI support.

Recently, Ryou et al. have performed a similar systematic study on the Pd/CHA zeolite.²¹ As it has been exposed above, the introduction of metal species with large ionic radii within small pore zeolites can suffer severe diffusion limitations, frequently precluding an optimized metal dispersion along the small pore zeolite crystals.⁴⁶⁻⁴⁸ Ryou et al. have evaluated different metal incorporation procedures (incipient wetness impregnation, wet impregnation, ion exchange or solid-state ion exchange) and metal loadings (from 0.2 to 4.7%wt Pd), with the aim of maximizing the metal dispersion along the CHA crystals.²¹ The authors found that regardless the metal incorporation treatment employed, the NO adsorption ability of the Pd/CHA materials can considerably be increased if the Pd-containing samples are previously treated at 750°C with an oxidative atmosphere (15%O₂, 10%H₂O in N₂). This hydrothermal treatment induces the transformation of bulk PdO into Pd²⁺ cations along the zeolite, thus favoring the low-temperature NO_x adsorption process. From these results, the authors have found that the optimum Pd loading in the Pd-CHA based PNA material is ~ 2%wt, leading to an overall NO_x adsorption value of ~30 μmol/g_{catal}.²¹

4.- Conclusions and perspectives

Along the present review, it has been shown how the fundamental understanding of the chemical processes involved in the complex NO_x adsorption/desorption steps has allowed to advance in the design of low-temperature PNA materials with not only higher NO_x adsorption capacities but also higher resistances against the presence of poisoning agents, such as water, sulfated components or CO. The early studies on metal-supported oxides have paved the way to well-defined single metal sites stabilized in zeolitic matrixes, as a next generation of novel and efficient PNA materials. The recent descriptions on Pd-containing CHA or MFI materials, among other zeolites, allows envisioning that these metal-zeolites will play a crucial role in the control of the automotive exhaust emissions, where the new upcoming scenario, with more restrictive legislation, will force to the manufacturers to include efficient PNA materials to prevent the cold-start NO_x emissions.

Undoubtedly, the design of new zeolite-based PNA materials with improved low-temperature NO_x performance will be an important challenge in the following years. In this sense, the use of advanced characterization techniques will help in the determination of the structure-storage property relationships for different and/or new metal-containing zeolites, where the presence of particular secondary building units or chemical compositions within the zeolite frameworks could remarkably increase the NO_x adsorption/desorption capacities and/or the PNA stability under realistic conditions.

In addition, the preparation of the zeolite-based PNA materials for their industrial implementation may require the rationalization of their synthesis recipes in order to decrease the costs associated to their manufacture. Therefore, the preparation of efficient one-pot methods or the synthesis of particular zeolite frameworks using less-expensive OSDAs or under OSDA-free conditions, will be of interest.

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Figure 1. Simplified scheme configurations for SCR-based NO_x abatement technologies: (a) DOC/DPF before SCR and (b) PNA added before SCR. (DOC: Diesel Oxidation Catalyst; DPF: Diesel Particulate Filter; SCR: Selective Catalytic Reduction; PNA: Passive NO_x adsorber)

Figure 2. Standard NO conversion profiles observed for the selective catalytic reduction (SCR) of NO_x with ammonia using Cu-containing and Fe-containing zeolites as catalysts.

Figure 3. NO_x storage efficiency using Pt/Al₂O₃ when measuring the NO_x release from 50°C with a temperature ramp of 15°C/min (Feed: 85 ppm NO, 720 ppm CO, 245 ppm H₂, 5% CO₂, 4.6% H₂O). Reproduced from reference ²².

Figure 4. NO_x slip on low temperature transient tests for Pt/Al₂O₃ (a) and Pd/Al₂O₃ (b) materials. Reproduced from reference ²⁴ with permission from Elsevier.

Figure 5. (a) Steady-state NO_x storage using 1.3%wt Ag/Al₂O₃ at 180°C with different H₂ concentrations and, (b) NO_x release temperatures when using 1.3%wt Ag/Al₂O₃ compared to a commercial PNA (Pt:Pd=1:1). Reproduced from reference ²⁹ with permission from Elsevier.

Figure 6. NO_x storage and reduction mechanisms using Pt/Ba/Al₂O₃ catalysts (b).
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Figure 7. NO_x desorption temperatures for Pt/Al₂O₃ and Pt/La/Al₂O₃ catalysts. Reproduced from reference ¹⁷ with permission from Elsevier.

Figure 8. NO_x slip and bed temperature for transition tests using Pd/CZO (a) and Pd/Al₂O₃ (b) with 110 ppm NO, 5%CO₂, and 10% O₂ after 700°C. Reproduced from reference ¹⁸ with permission from Elsevier.

Figure 9. NO_x adsorption on the Pd/Al₂O₃ catalyst before and after different poisoning treatments with SO₂. Reproduced from reference ²⁴ with permission from Elsevier.

Figure 10. NO_x adsorption using the Pd/CZO catalyst and different starting bed temperatures in presence of a water-containing feed (5%H₂O). Reproduced from reference ¹⁸ with permission from Elsevier.

Figure 11. (a, b) NO_x adsorption at 100°C (a), and the NO_x release at increasing temperatures (b) using different Pd-containing zeolites. (c) NO_x adsorption capacity of different Pd-containing zeolites after being exposed to a gas mixture with 100 ppm SO₂. Reproduced from reference ¹⁹ with permission from SpringerNature.

Figure 12. Pd 3d XPS spectra of (a) fully oxidized Pd/BEA (top) and Pd/CHA (bottom) and (b) after reaction with 2000 ppm NO at 150°C. Reproduced from reference ⁴¹ with permission from the American Chemical Society.

Figure 13. Different proposed active sites for the NO_x adsorption/desorption processes in Pd-containing zeolites. Reproduced from reference ⁴¹ with permission from the American Chemical Society.

Figure 14. Effect of the presence of CO in the exhausts on the NO_x desorption temperatures.
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Figure 15. Pd K-edge EXAFS Fourier transformations for different Pd/MFI zeolites after being treated with air at 500 or 750°C. Reproduced from reference ²⁰ with permission from Elsevier.

Table 1. Framework topology and chemical compositions of the different Pd-containing zeolites prepared in reference ¹⁹.

Sample	Framework type	Dimensionality	Pore sizes	Si/Al ratio	%wtPd
Pd/CHA	CHA	3D	3.8x3.8	11	~1.0
Pd/MFI	MFI	3D	5.1x5.6	12	~1.0
Pd/BEA	BEA	3D	6.6x6.7	14	~1.0

Table 2. Chemical analyses and total amount of NO_x species desorbed for the different Pd-containing MFI zeolites (note: the different Pd/MFI zeolites have been first activated at 750°C in air). Reproduced from reference ²⁰.

Sample	Pd content (%wt)	NO _x desorbed (μmol/g _{catal})		
		Below 300°C	Above 300°C	Total amount
Pd(1)/MFI(Si/Al=11)	1.10	2.9	2.3	5.2
Pd(2)/MFI(Si/Al=11)	2.02	9.4	6.3	15.7
Pd(3)/MFI(Si/Al=11)	2.71	9.1	8.0	17.1
Pd(4)/MFI(Si/Al=11)	3.73	7.1	4.9	12.0
Pd(0.5)/MFI(Si/Al=15)	0.51	0.3	4.9	5.2
Pd(1)/MFI(Si/Al=15)	0.91	3.7	11.7	15.4
Pd(2)/MFI(Si/Al=15)	1.90	8.9	15.7	24.6
Pd(3)/MFI(Si/Al=15)	2.97	6.6	6.3	12.9
Pd(6)/MFI(Si/Al=15)	5.46	0.6	5.4	6.0
Pd(0.5)/MFI(Si/Al=25)	0.54	0.0	4.9	4.9
Pd(1)/MFI(Si/Al=25)	1.02	0.0	8.3	8.3
Pd(2)/MFI(Si/Al=25)	1.88	0.0	4.6	4.6
Pd(2)/MFI(Si/Al=50)	1.98	0.0	2.3	2.3
Pd(2)/MFI(Si/Al=150)	1.02	0.0	2.9	2.9

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