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Selective reduction of NO_x by liquid hydrocarbons with supported HPW–metal catalysts

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Abstract

The catalytic multifunctional system based on $H_3PW_{12}O_{40}\cdot 6H_2O$ (HPW), Pt and support (Zr–Ce or Zr–Ti mixed oxides) has been investigated for lean NO_x storage and reduction. It was applied in the NO_x storage and reduction (NSR) concept by including a cyclic operation of short NO_x storage (oxygen rich phase) and reduction (hydrocarbon rich phase: hexane). For NO_x reduction, the assistance of hydrogen is one of the key parameters possibly as a result of the regeneration of metallic sites active for mild oxidation of the hydrocarbon (by forming $C_xH_yO_z$). The difference in oxygen mobility of supports (higher in the case of Zr–Ce than for Zr–Ti) became another strategic parameter for catalyst selection since the possibility of total hydrocarbon oxidation. The influence of temperature was also considered for optimizing NO_x storage and reduction.

Keywords: de-NO_x process; NSR concept; Tungstaphosphoric acid; Platinum; Zr–Ce and Zr–Ti mixed oxides

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1. Introduction

Since the creation of more rigorous nitrogen oxides (NO_x) emissions standards and the economical requirements for gasoline savings (e.g. for vehicles, diesel technology implementation), lean-burning engines and lean NO_x catalytic systems have been a subject of an extensive research. Even though numerous studies have been reported in the literature about the selective catalytic reduction of NO_x by hydrocarbons [1], the de-NO_x mechanism is still a matter of debate among the catalysis community. Recently, a general model was proposed by Djéga-Mariadassou for investigating catalytic sequences from "three-way catalysis" (TWC) to "de-NO_x" reactions [2]. His conclusions are that TWC can occur over both zero-valent (M^0) or cationic (M^{x+}) transitions metals, whereas de-NO_x (lean conditions) mainly occurs over M^{x+} active sites. Nevertheless, M^0 can also be considered [1]. Djéga-Mariadassou insists that in lean conditions, the de-NO_x process, in the presence of cations, needs three kinetically uncoupled functions and, therefore, three catalytic cycles, which have to turn over simultaneously. The first feature allows the oxidation of NO to NO_2; the second one, the partial oxidation of the hydrocarbon via NO_2 and the third corresponds to the decomposition of NO into N_2 and adsorbed oxygen. The partially oxidised hydrocarbons finally achieve their complete oxidation when reacting with the oxygen left over from NO decomposition. This allows the regeneration of the catalytic (cationic) site. In summary, the de-NO_x process proceeds according to an assisted reduction of NO by a hydrocarbon in the presence of an excess of oxygen.

Currently, one of the emergent concepts for gas exhaust treatment is based on the use of a NO_x storage and reduction catalyst (NSR) [3]. In this type of technology, the nitrogen oxides are stored on the catalyst during lean operation and when changing to rich or stoichiometric operation, the stored NO_x are reduced into harmless nitrogen. The first NSR catalyst was developed by Toyota and its composition was based upon that of a three-way catalysts obtained by impregnation of noble metals (essentially Pt) upon alumina with several alkali and alkali earth metals (Na^+, K^+, Ba^{2+}) and rare earth oxides (mainly La_2O_3) [4]. The basicity of the storage component determines the amount of NO_x stored mainly as nitrates. However, the presence of CO_2 and/or SO_2 highly modifies the NO_x storage capacity of barium based catalysts since they can also be stored on the same active sites. In fact, it was established that in a mixture of those three compounds, they are

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preferentially stored according to the sequence: sulphates > carbonates > nitrates [5,6]. To avoid this kind of unequal competition, it could be advantageous to store NO_x in a different way from that of nitrates. Previous works in our laboratory have demonstrated the interest of using a combination of 12-tungstaphosphoric acid hexahydrate (HPW) and metal (e.g. Pt) for de-NO_x processes [7,8]. In fact, HPW presents a high stability to the presence of CO_2 and SO_2 besides its outstanding NO_x storage and desorption properties. This is due to a particular NO_x storage mechanism which consists in the equimolar exchange of structural water molecules of HPW ($(H_2O)H^+(H_2O)$) by NO and NO_2 to form the complex ($(NO_2^-)H^+(NO^+)$) [8]. NO_x storage and desorption efficiency are highly improved by the presence of noble metals [9]. The presence of special interactions between noble metal and the proton of HPW, $(\text{metal–H})^{\delta+}$, seems to be the clue for the important activity of this catalysts [10,11]. However, the presence of ‘‘free’’ metal particles must be also considered. Additionally, the dispersion of HPW on appropriate solid support is crucial for NO_x storage–reduction application but, in order to preserve crystalline structure of HPW, it is necessary to use a support with an isoelectric point near to 6 [12]. We have chosen two types of support with different redox properties and which are able to store NO_x: Zr–Ce and Zr–Ti [9,13].

In this study, we evaluate the possibility of using *n*-hexane as a representative of a liquid hydrocarbon fraction for reducing NO_x into N_2. We apply the concept NSR by involving a multifunctional catalyst: HPW–metal–support, with the purpose of generating a synergistic effect between all catalytic properties of those three materials for NO_x abatement.

2. Experimental

2.1. Supports

Two types of supports were used: Zr–Ce and Zr–Ti mixed oxides. The molar ratios Zr/Ce and Zr/Ti were optimised and the value 0.5 selected from two previous works [9,12]. These supports present comparable acid–base properties and they are able to preserve the NO_x storage properties of HPW. However, they present marked differences related with oxygen storage and mobility.

Zr–Ce mixed oxides were prepared by sol–gel like method. Zirconium(IV) acetylacetonate (Avocado) and cerium(III) acetate hydrate (Strem) were dissolved into boiling propionic acid. These solutions were mixed in the desired proportions and, after 30 min of stirring, the solvent was evaporated until formation of a resin. Obtained sample was calcined at 680 °C for 4 h. Obtained support has a surface area of ca. 36 $m^2\,g^{-1}$. Details about the characterization were elsewhere published [9].

Zr–Ti mixed oxides were prepared from zirconium(IV) *n*-propoxide (Fluka) and titanium(IV) *i*-propoxide (Strem) by forming an alcoholic solution (1 M) and by mixing with an excess of water. The obtained mixture was filtrated, washed, dried and calcinated at 750 °C for 4 h. Obtained support has a surface area of ca. 36 $m^2\,g^{-1}$. Further details about the characterization of this material can be found elsewhere [13].

2.2. Supported catalysts

Supports were impregnated by an aqueous solution of both 12-tungstaphosphoric acid hexahydrate ($H_3PW_{12}O_{40}\cdot 6H_2O$, HPW) and metal precursor (H_2PtCl_6, Strem) in order to obtain 65 wt.% HPW and 1 wt.% Pt. After adding support with HPW–metal impregnating solution, samples were slowly dried under agitation at 80 °C, followed by drying at 100 °C until wetness [9,13].

2.3. Test procedures

2.3.1. Apparatus and gas composition

A full computer driven reactor system was constructed for including powdered laboratory-scale catalysts. Gas mixtures of NO, NO_2, CO_2, O_2, H_2, air and He are fixed using two independent set of mass flow-meters, each one controlled individually. Tests were made using a lean gas mixture (in volume): $NO = NO_2 = 500$ ppm, $O_2 = 10\%$, $CO_2 = 5\%$, $H_2O = 5\%$ and He as a balance. This modified gas lean mixture is related with an oxidation catalyst previous to the NO_x storage system. In that case, hydrocarbons and CO are oxidised into CO_2 and NO is partially transformed into NO_2. Due to that oxidation catalyst and NO–NO_2 thermodynamic equilibrium, the NO/NO_2 ratio used was fixed to 1.

For reducing conditions, a helium diluted mixture of *n*-hexane (0.4%), 5% water and 1% hydrogen were used (rich gas mixture). Two saturators were used in order to reach the defined water and *n*-hexane content (helium flow was divided and sent throw two saturators).

Former mixtures are introduced into the quartz reactor, of 1 cm diameter, with 300 mg of catalyst (with space time 20,000 h^{-1}). NO and NO_2 concentrations were measured respectively by IR and UV analysers (Binos Rosemont Analytical) over a range of 0–3000 ppm (±10 ppm). Analytical instruments also include a gas phase μ-chromatograph (Agilent 3000, equipped with a molecular sieve column and a thermal conductivity detector) and a quadrupole mass spectrometer (HPR-20, Hiden Analytical).

2.3.2. Standard test procedure

NO_x storage and reduction was made isothermally at 170 and 250 °C. These temperatures where chosen from a previous work where the properties of NO_x storage for HPW were optimised [8,9]. It was shown that a procedure with short storage and reduction cycles leads to an increase of the reduction percentage of NO_x into N_2 [7] compared to the one where catalyst is saturated by NO_x (long cycles). For this reason we have used short cycles in this work. The furnace was heated from room temperature to selected temperature, with a ramp of 4 °C min^{-1}. At the same time, the complete mixtures of gases were stabilized by the by-pass. Afterwards, fuel lean mixture was changed from by-pass to reactor. NO_x storage is manifested itself by the drop of NO and NO_2 concentrations signals. After 2 min, gas mixture flowing throw the reactor was changed to rich mixture during 1 min completing the first cycle. Cycles were repeated successively. After 12 cycles, a final procedure of cooling to room temperature under wet air (5% H_2O) allows us to verify if there is some NO_x remaining in HPW structure. The amount of NO_x stored and released upon desorption–reduction was estimated by integration of the curve below or above the base line for storage or desorption, respectively, and expressed in mol NO_x g^{-1} HPW. The efficiency of storage process was defined as the ratio between the amounts of NO_x stored during the lean period (2 min) to the total of NO_x fed during this period of time.

3. Results

3.1. Cycles of NO_x storage and reduction with HPW–Pt

3.1.1. Reduction with n-hexane

The reductive properties of *n*-hexane were first evaluated with HPW–Pt as catalyst. The results are presented in Fig. 1. The first cycle of NO_x storage and reduction is typical of HPW based catalysts. In fact, after a sequence of gas stabilization, the NO_x storage (St. in Fig. 1) is evidenced from the simultaneous drop in NO and NO_2 concentrations (first 2 min). The change to rich mixture of gases (0.4% *n*-hexane) generates a concomitant desorption of NO and NO_2 (less important for this last one). Conversely, for the succeeding cycles, a large NO desorption peak was observed during lean excursions. Such NO evolution can be attributed to the reduction of NO_2 into NO by remaining *n*-hexane (or derivate compounds) after changing gas mixtures from rich to lean. A marked deactivation can be observed by the diminution of NO desorption and the increase of NO_2 desorption with the increase in cycles number. Those results are summarised in Fig. 2.

After 12 cycles, NO_x reduction percentage decreases continually from 30% to 5%. This deactivation is permanent. However, storage efficiency presents a more stable behaviour (or a less marked deactivation rate) of around 40%. In fact, the storage function of this catalyst (HPW) is not affected while the reduction function, which involves the noble metal, is markedly decreased. It is possible to propose that the expected mild hydrocarbon oxidation (to generate active $C_xH_yO_z$ oxygenated compounds), possible at this temperature range [14], continues up to CO_2 formation or that hydrocarbon is not oxidised at all and poisons the active sites by covering them. The first hypothesis is more probable since CO_2 is detected by mass spectrometry. The decrease of reduction function could be observed from the increase in NO_2 desorption instead of NO reduction (Fig. 1). Process is more like if the quantity of active reductive agent were not enough.

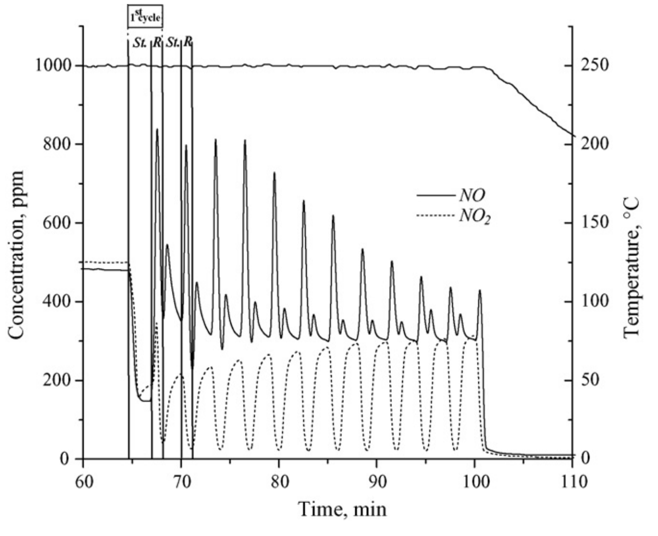

Fig. 1. NO_x storage–reduction cycles with HPW–Pt at 250 °C and using 0.4% C_6H_{14} as reductive agent. The two first cycles of NO_x storage (St.) and reduction (R) are revealed indeed.

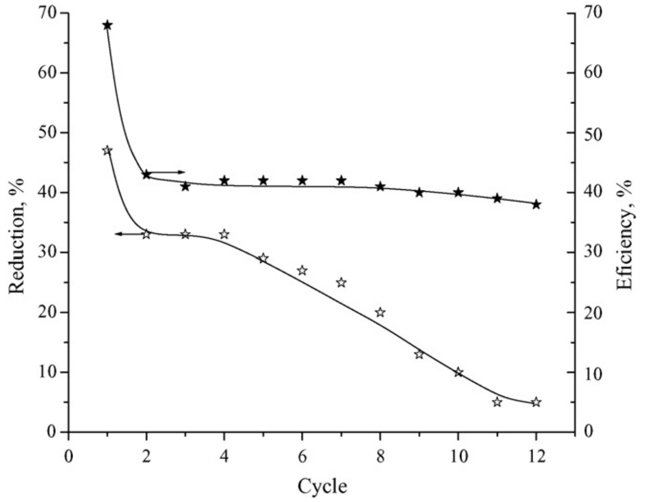

Fig. 2. NO_x reduction percentage and storage efficiency with HPW–Pt after 12 storage–reduction (0.4% C_6H_{14}) cycles at 250 °C.

3.1.2. Reduction with n-hexane and hydrogen

Reductive mixture of gases was modified by addition of 1% hydrogen. In fact, we had demonstrated in a previous work the possibility of using a mixture of H_2 and CO for reducing NO_x with supported HPW–Pt [9,10]. Several conclusions were obtained:

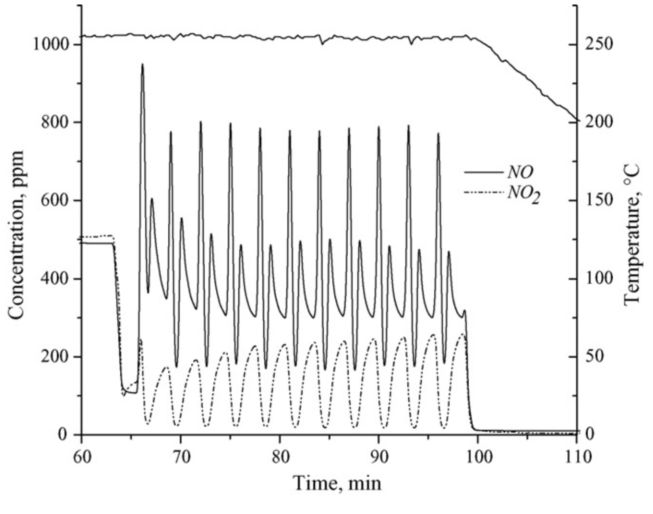

Fig. 3. NO_x storage–reduction cycles with HPW–Pt at 250 °C and using 0.4% C_6H_{14} + 1% H_2 as reductive agent.

- With H_2, NO_2 is reduced only into NO.
- With CO, the mechanism of NO_2 reduction concerns the production of CO_2 and NO. A low N_2 formation was also detected.
- Addition of H_2 to CO accelerates the reduction process. This could be attributed to two independent possible phenomena: one related to the formation of metallic particles by hydrogen (where NO_2 is reduced into NO with H_2O formation); and a second one related to the formation of formyl species ($C_xH_yO_z$) [15], which are actives for de-NO_x process [2].

It seems that hydrogen, as a promoter of NO_x reduction, serves to ‘‘clean the catalytic sites for the suitable activation of HC (partial oxidation)’’. The influence of hydrogen presence in the reductive mixture is revealed by comparing Figs. 1 and 3 for NO_x reduction. Even if the NO desorption peak remains during NO_x storage phase, the catalyst performance is more stable. NO_x reduction and storage efficiency percentages are summarised in Fig. 4. The reduction percentage reaches rapidly a stable value of 48%. This fact confirms the role of assistance played by hydrogen for NO_x reduction. As expected, a NO_x storage efficiency of 45% is obtained with or without hydrogen (Fig. 2 compared with Fig. 4) after 12 cycles.

3.2. Cycles of NO_x storage and reduction with supported (HPW–Pt)

Fig. 5 presents the results obtained with HPW–Pt when using Zr/Ce (molar ratio equals to 0.5) as support and the mixture hexane and hydrogen for reducing. With (HPW–Pt)/(Zr/Ce = 0.5), the NO desorption peak observed after changing from rich to lean mixtures is very similar to that observed during rich phase. However, the former becomes smaller with the number of cycles. The important concentration of NO during lean phase decreases drastically the performance of this catalyst. No improvement in the performance of HPW–Pt was observed after supporting on Zr–Ce mixed oxides as evidenced in Fig. 5. A different scenario was observed for (HPW–Pt)/(Zr/Ti = 0.5) catalyst as presented in Fig. 6. Several interesting characteristics could be noticed for Zr–Ti support based catalyst. First, the NO desorption peak is no longer detected when changing from rich to lean. Second, a small desorption peak of NO_2 is now present in concomitance with the NO peak when changing to rich mixture. The performances at 250 °C of supported catalysts are compared in Fig. 7. From these results it is possible to propose that:

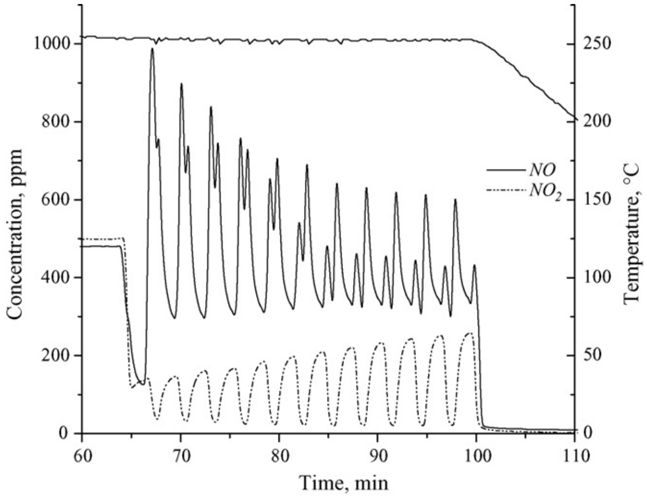

Fig. 5. NO_x storage–reduction cycles with (HPW–Pt)/(Zr/Ce = 0.5) at 250 °C and using 0.4% C_6H_{14} + 1% H_2 as reductive agent.

(a) The difference in oxygen storage capacity and mobility between Zr–Ce and Zr–Ti materials is one of the key parameter for using (or selecting) a specific reductive agent and support for NO_x reduction.
(b) Zr–Ce support is too oxidant and promotes the oxidation of *n*-hexane into CO_2 [16]. It was also reflected from the low NO_x reduction activity: 35%. The absence of $C_xH_yO_z$ diminishes the possibility of N_2 formation. The reduction of NO_2 into NO during lean (storage) phase has for

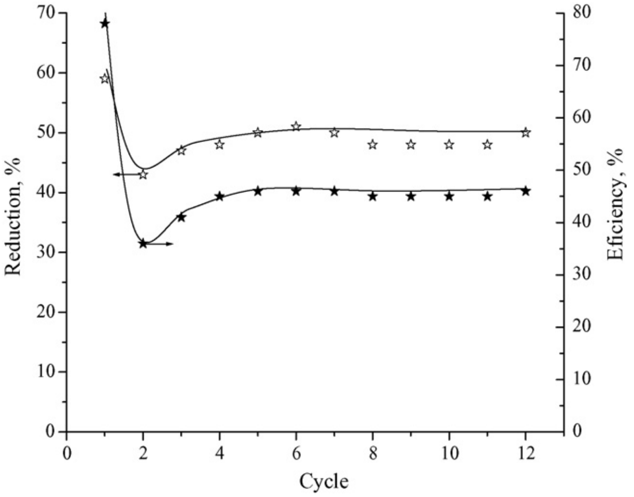

Fig. 4. NO_x reduction percentage and storage efficiency with HPW–Pt after 12 storage–reduction (0.4% C_6H_{14} + 1% H_2) cycles at 250 °C.

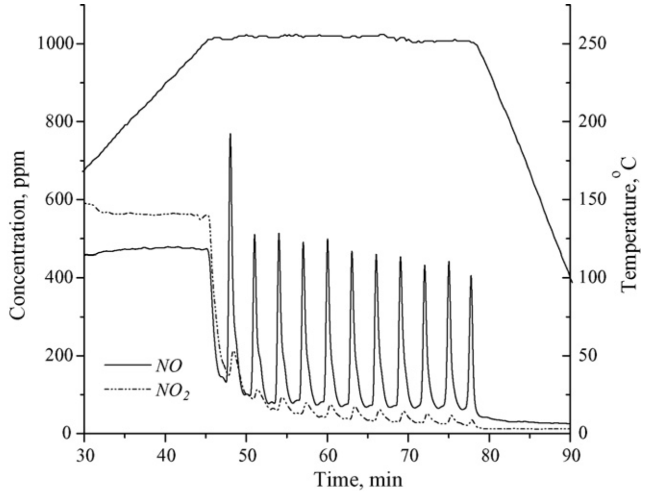

Fig. 6. NO_x storage–reduction cycles with (HPW–Pt)/(Zr/Ti = 0.5) at 250 °C and using 0.4% C_6H_{14} + 1% H_2 as reductive agent.

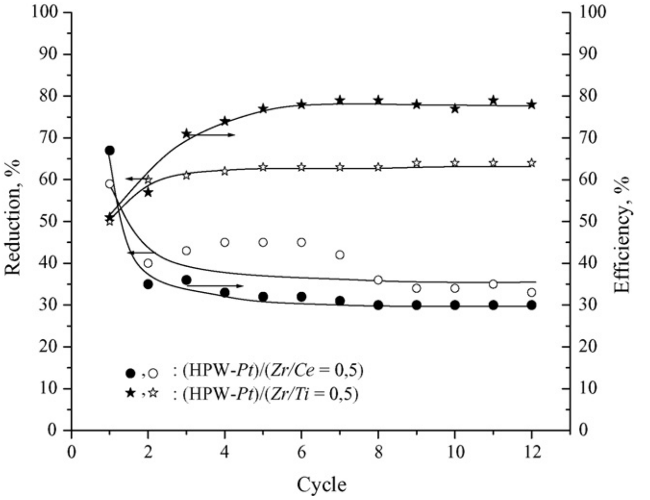

Fig. 7. Comparison of NO_x reduction percentage and storage efficiency between (HPW–Pt)/(Zr/Ce = 0.5) and (HPW–Pt)/(Zr/Ti = 0.5) after 12 storage–reduction (0.4% C_6H_{14} + 1% H_2) cycles at 250 °C.

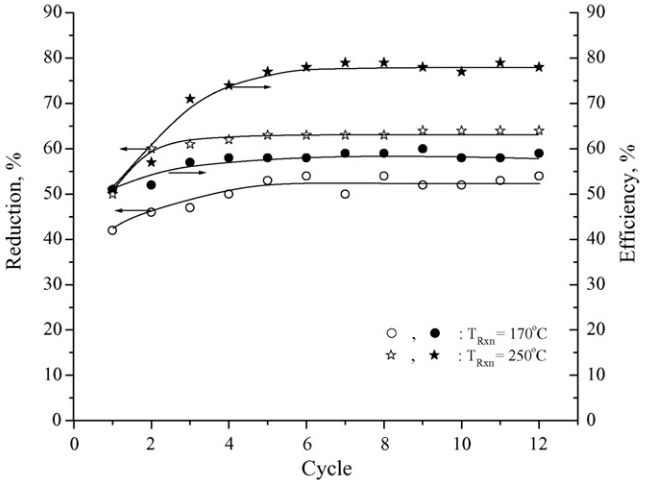

Fig. 9. Comparison of NO_x reduction percentage and storage efficiency with (HPW–Pt)/(Zr/Ti = 0.5) after 12 cycles of storage–reduction (0.4% C_6H_{14} + 1% H_2) at 250 °C and 170 °C.

consequence the modification of NO/NO_2 ratio and so the decrease in the storage performance with Zr–Ce based catalyst.

(c) When using Zr–Ti as support, catalyst performance is improved for NO_x reduction (60%) and more clearly for NO_x storage efficiency (74%). It could be proposed that active $C_xH_yO_z$ oxygenated compounds are formed and present in sufficient amount for increasing reduction of NO_x into N_2. The increase of this reduction rate has for consequence that more absorption sites are regenerated during the period in rich conditions. It is also possible to understand why the storage efficiency is improved with Zr–Ti.

3.3. Influence of temperature

In order to reduce the oxidation ability of the support and so increase the concentration of $C_xH_yO_z$ oxygenated compounds, a solution can be to decrease the temperature. In addition, in the previous publication [8], it was evidenced that NO_x storage on HPW depends on temperature (with a maximum at 170 °C). We tested first the performance of (HPW–Pt)/(Zr/Ti = 0.5) at this temperature to see if it is possible to improve the performance of this catalyst. Results are presented in Fig. 8. The performance at 170 °C is characterised by the presence of a small NO desorption peak during lean phase but also the concomitant desorption of NO_2 with NO during rich phase. This NO_2 desorption is more important at 170 than at 250 °C (compare Figs. 6 and 8). This behaviour could be related to the NO_x reduction dependency on temperature. Results are compared in Fig. 9.

As explained before, a slower regeneration of the absorption sites at 170 °C may explain the fact that storage efficiency decreases with the temperature whereas values at 170 °C compared to 250 °C are equivalent for the first cycle. Additional tests where made with Zr–Ce based catalysts at 170 °C. The results are presented in Fig. 10.

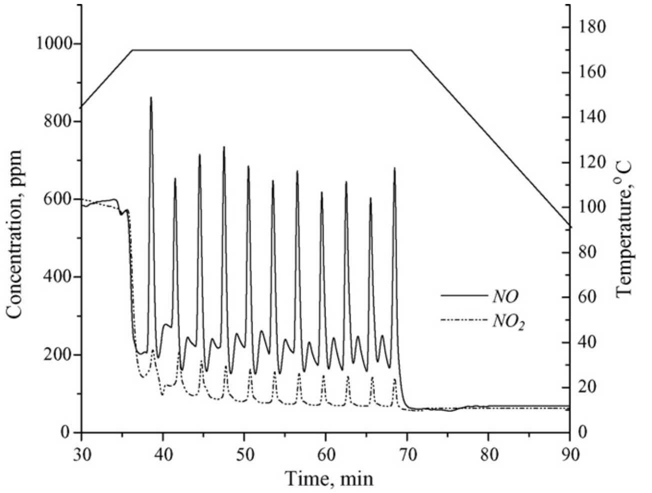

Fig. 8. NO_x storage–reduction cycles with (HPW–Pt)/(Zr/Ti = 0.5) at 170 °C and using 0.4% C_6H_{14} + 1% H_2 as reductive agent.

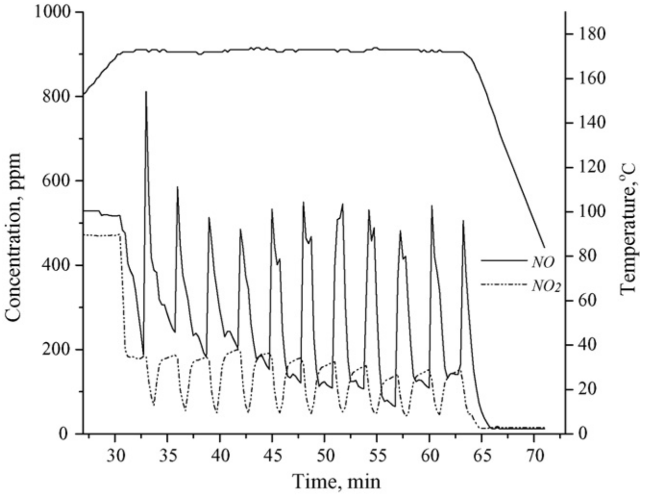

Fig. 10. NO_x storage–reduction cycles with (HPW–Pt)/(Zr/Ce = 0.5) at 170 °C and using 0.4% C_6H_{14} + 1% H_2 as reductive agent.

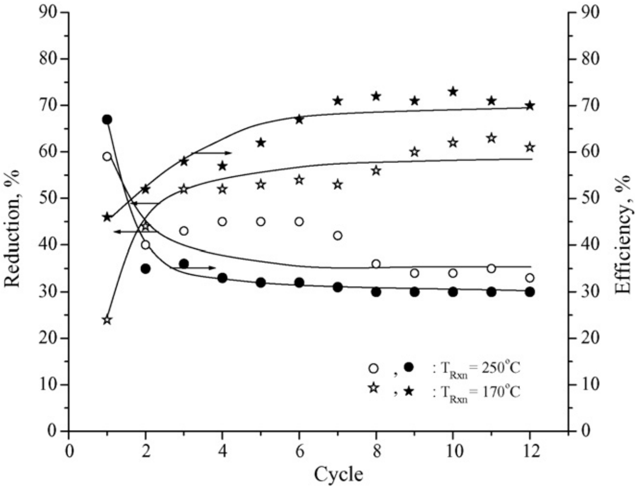

Fig. 11. Comparison of NO_x reduction percentage and storage efficiency with (HPW–Pt)/(Zr/Ce = 0.5) after 12 cycles of storage–reduction (0.4% C_6H_{14} + 1% H_2) at 250 °C and 170 °C.

The influence of temperature decrease is evident when comparing Figs. 5 and 10. In fact, the important NO desorption peak observed during lean phase is not longer detected. NO peak obtained during reduction excursions is wider at 170 °C. These characteristics are also reflected in an evident improvement of NO_x reduction and storage capacity at 170 °C as presented in Fig. 11. The increase of reduction at 170 °C could be explained by the increase of $C_xH_yO_z$ species concentration due to a milder oxidating power of the support. As the reduction percentage is improved, the faster regeneration of absorption sites explains the increase of the storage efficiency. Two other factors could also explain the improvement of the efficiency. First, the presence of $C_xH_yO_z$ compounds stored inside HPW by exchange with water molecules enlarges HPW void space [17]. Secondly, during lean excursion, the NO/NO_2 ratio is preserved since no NO desorption peak is observed during this phase.

4. Discussion

The use of a cyclic operation for NO_x lean reduction by including a short periodic switching of storage (lean phase) and reduction (rich phase) – NSR concept – shows a high application potential. For that, the use of a multifunctional catalyst like HPW–metal–support seems to be very appropriate. The presence of hydrogen is one of the key parameters since it assists the reduction process by generating active sites for mild oxidation of hydrocarbons (in this case, *n*-hexane). However, a high oxygen mobility of support (like in the case of Zr–Ce) can result unfavourable when using *n*-hexane as reductive agent since the possibility of its complete oxidation depending upon temperature. Finally, in the case of *n*-hexane, Zr–Ti is a potential candidate for supporting HPW–Pt. Accordingly to the experimental results, it can be proposed that NO_x storage and reduction process with supported HPW–Pt can concern the following steps.

i. NO_x storage

In HPW, NO and NO_2 are simultaneously and equimolecularly stored by exchange of water structural molecules.

ii. NO_x reduction

The presence of two types of active sites can be suggested: (a) metallic sites (M^0) generated from platinum reduction by hydrogen and (b) cationic site (M^+) from both: (i) the reduced surface of support and/or (ii) the interaction of noble metal with HPW proton (metal–$H^{\delta+}$) [10]. After NO_x adsorption, the mild oxidation of *n*-hexane by NO_2 on metallic sites could generate $C_xH_yO_z$ active compounds to assist the reduction of NO into N_2. In fact, NO can be adsorbed on cationic sites generating N_2 and adsorbed oxygen. These last oxygens will complete the oxidation of $C_xH_yO_z$ compounds generating CO_2 and H_2O and regenerating the cationic sites for a new cycle.

An excessive hydrocarbon oxidation by the oxygen provided by the support leads to CO_2 formation instead of $C_xH_yO_z$ compounds and decreases the NO_x reduction into N_2. A decrease of temperature will diminish the oxidation power of the support (Zr–Ce) and favour NO reduction.

5. Conclusions

It has been proved the possibility of reducing a representative lean NO_x emission by using the multifunctional catalyst HPW–Pt/support and hexane (with and without H_2) as reductant. Several key parameters were identified from the experimental results: the assistance effect of hydrogen in the de-NO_x process, the redox and oxygen mobility properties of supports (and their functionality with temperature). From these facts, it was possible to propose the presence of mild oxidation hydrocarbons as necessary intermediate compounds for this catalytic de-NO_x process.

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