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Pt and Nb species on various supports: An alternative to current materials for NO_x removal

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Abstract

Meso- or micro/mesoporous supports (NbMCM-41 and NaY + NbMCM-41, respectively) were tested for Pt loading. The effects of the support structure and composition on the metal oxidation and on nitrate storage properties were pointed out in the SCR for NO_x removal. Nitrate species were found directly related to the catalytic performance of Pt. Niobium from NbMCM-41 matrix in Pt/NbMCM-41 play the role of NO_x storage species, whereas in the presence of NaY in the support, sodium cations act as storage for NO_x.

Keywords: Pt/NbMCM-41; Pt/Y + NbMCM-41; NO_x storage

1. Introduction

Diesel, *lean-burn* direct-injection gasoline (GDI) and port-fuel injected (PFI) engines have the potential to offer reduced fuel consumption relative to the stoichiometric engines, which is beneficial to spare energy and to lower CO_2 emissions. Nevertheless, the EURO V planned regulations will force car manufactures to introduce particulate matter (PM) and nitrogen oxides (NO_x) control devices for light-duty vehicles. In particular, NO_x reduction in oxidizing atmosphere and in the presence of sulphur compounds is still one of the hottest and unresolved problems. Many solutions have been attempted, among them HC-SCR and NO_x-trap processes, both using in the majority of cases Pt as the active phase. Actually, the most promising NO_x catalytic converter is a NO_x storage and reduction catalyst (NO_x-trap), which has been developed in the mid 1990s by Toyota [1–3]. It mainly consists of a storage component based on an alkali or alkaline-earth metal oxide, precious metals (generally Pt and Rh) and a high surface area supporting material (essentially based on γ-Al_2O_3). The use of a NO_x-trap catalyst infers that the engine operates periodically under lean and rich atmospheres: during the lean period, NO_x present in the exhaust gas are oxidized to NO_2 by Pt [3,4] and stored onto the catalyst, whereas during rich spikes the atmosphere is driven fuel rich for a brief time to reduce NO_x into N_2. Mechanisms involved in this process are complex and a large number of studies has thus been carried out, both by industrial and scientific community in order to precise mechanistic details of NO_x storage and reduction reactions. But all the authors seem to agree on the central role of Pt sites for NO_x-trap process.

MCM-41 mesoporous molecular sieves, due to their uniform molecular structure and high surface area, are attractive new supports for Pt. On the other hand, the presence of Nb in NbMCM-41 matrix enhances the oxidative properties of the catalyst [5]. For these reasons, we have investigated Pt/NbMCM-41 and Pt/NaY + NbMCM-41 samples for NO_x reduction by propene as well as for NO_x storage and reduction.

2. Experimental

Purely siliceous mesoporous molecular sieves of MCM-41 type were synthesised according to the procedure described in Ref. [6] and modified in the preparation of NbMCM-41 according to Ref. [7]. Si/Nb atom ratio was 128 as assumed.

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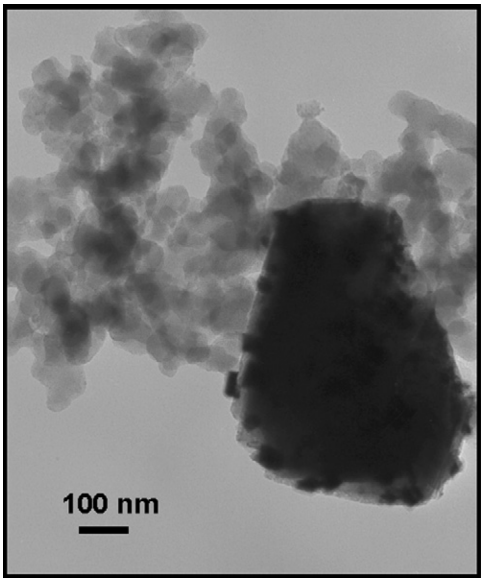

Fig. 1. TEM micrograph of Pt/NaY + NbMCM-41 catalyst.

NbMCM-41 and NaY (Si/Al = 2.6) were impregnated in an aqueous solution of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, Aldrich) with a platinum loading of 1 and 2 wt.%, respectively. The produced Pt/NaY sample was further mechanically mixed with NbMCM-41 (1:1) in order to provide a catalyst with the same global Pt loading (1 wt.%) as the Pt/NbMCM-41 sample. Catalysts were successively dried at 363 K for 11 h and calcined at 773 K for 3 h in air, then reduced in H_2 (5 vol.% H_2/N_2) at 773 K for 3 h.

The surface area and pore volume of the MCM-41 materials were measured by nitrogen adsorption at 77 K using the BET conventional technique on a Micromeritics 2010 apparatus.

Catalytic properties of materials were characterised using an infrared *operando* device, equipped with gas flow line controllers and two different analysis systems [8]. The catalysts in the form of a self-supported wafer of ~5 mg cm^{-2} was placed inside the IR reactor-cell with KBr windows. IR spectra were recorded with a Nicolet Magna 750 FTIR spectrometer. Gas products were analysed by Quadrupole Mass Spectrometer (Varian Star 3400) and by FTIR in a gas microcell with a

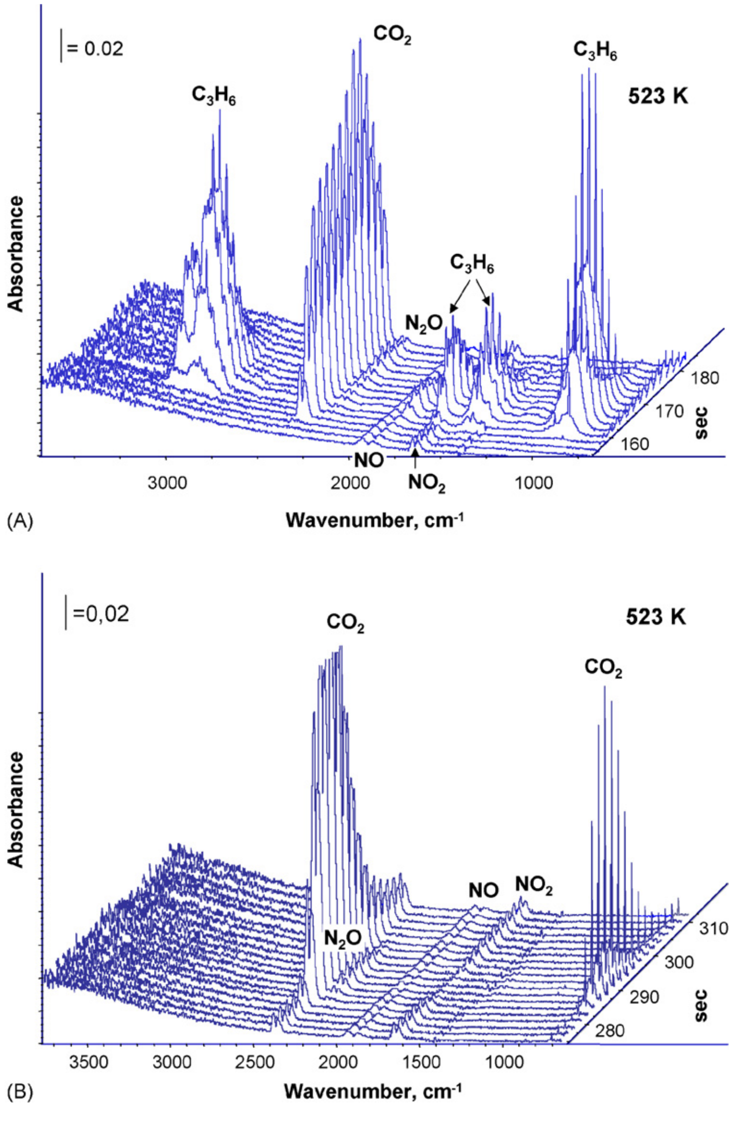

Fig. 2. FTIR spectra of gas phase after sending a flow of NO + O_2 followed by C_3H_6 pulses at 523 K on a Pt/SiMCM-41 (A) and on a Pt/NbMCM-41 (B) samples.

volume of 0.088 cm^3. Prior to each experiment the catalyst was activated in situ by heating in a flow of Ar (12.5 $cm^3\ min^{-1}$) at 573 K for 5 h, followed by cooling to the reaction temperature 523 K. Spectra were corrected by subtracting the spectrum of the activated surface which was used as a background. The concentrations of NO, C_3H_6 and O_2 in the gas mixture were 500, 500 ppm, and 10% with Ar balance, respectively. A pulse reaction was also performed to examine in detail the reactivity of NO_x species. The catalyst was exposed to NO/O_2/Ar, and then three consecutive pulses of C_3H_6 (20 μl) were injected into a flow of NO/O_2/Ar at 523 and 573 K.

3. Results and discussion

The samples, after synthesis, were analysed from the point of view of structural, textural and morphological properties (Table 1; Fig. 1). It was observed that the presence of Pt on mesoporous matrix only slightly reduces the surface area and the mesopore volume of the catalysts, whereas Pt/NaY admission significantly changes these parameters. Interestingly, TEM image (Fig. 1) of Pt/NaY + NbMCM-41 shows the localization of Pt particles on the edges of the zeolite crystal, far from the mesoporous phase. It is the contrary in Pt/NbMCM-41 in which Pt crystals were located close to the Nb species in the mesoporous matrix [9].

Table 1
Textural data of the catalysts used

Catalyst	Surface area BET ($m^2\ g^{-1}$)	Mesopore volume BJH-KJS ($cm^3\ g^{-1}$)	Pore diameter BJH-KJS (nm)
SiMCM-41	1073	0.99	3.9
Pt/SiMCM-41	980	0.88	3.6
NbMCM-41	961	0.83	3.6
Pt/NbMCM-41	910	0.74	3.3
Pt/NaY + NbMCM-41	819	0.41	3.4

The here used model catalysts have been tested for NO_x reduction by propene in the range of temperature 423–673 K but we will only report results obtained at 523 K. Studies under transient conditions are often sources of precious information. As it is shown in Fig. 2, sending a pulse of propene in a NO + O_2 stream results in C_3H_6 oxidation to CO_2 and H_2O, partial for the Pt/SiMCM-41 compound, while complete for Pt/Nb containing support. Concomitantly, NO

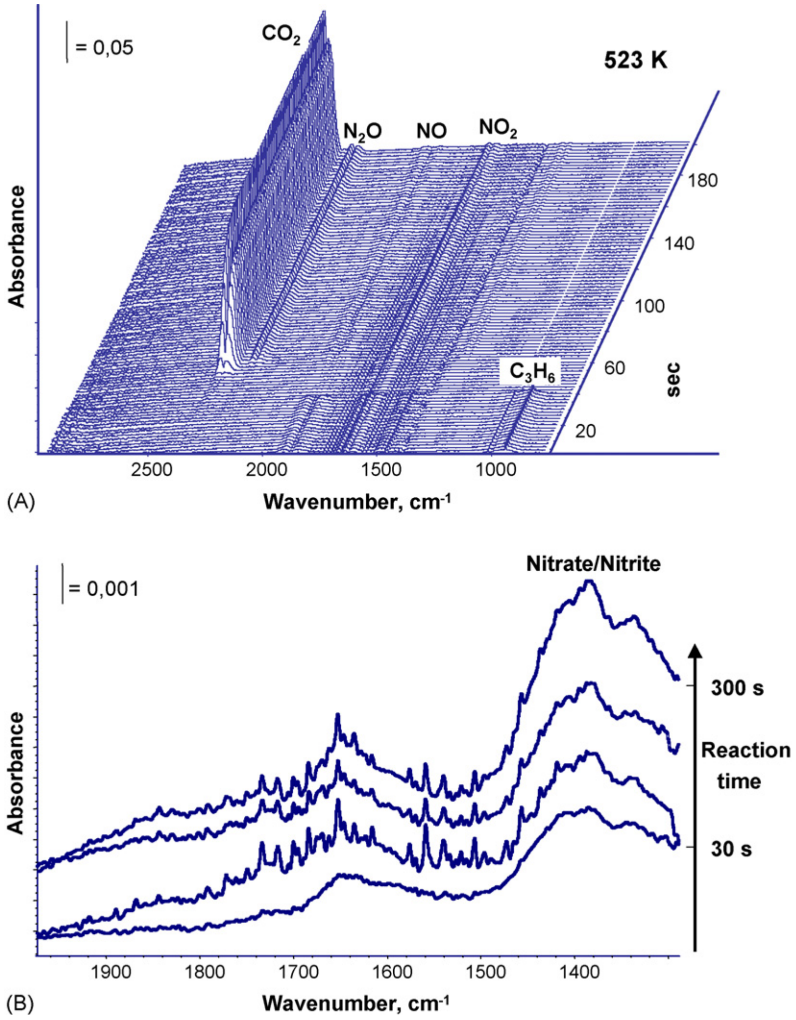

Fig. 3. FTIR spectra of Pt/NbMCM-41 sample after sending a flow of NO + O_2 + C_3H_6 at 523 K; gas phase (A) and catalyst surface (B).

and NO_2 intensities decrease, whereas N_2O appears in the gas phase, indicating that nitrogen oxides have been reduced. Therefore, we can infer that Pt is an active element for the NO_x reduction, even when the support is based on silica [10]. However, the presence of Nb in the support enhances the activity (propene is totally converted, not only at 523 K; Fig. 2B, but also at lower temperatures). The consumption of NO_2 after C_3H_6 admission is clearly visible and indicates the role of NO_2 as oxidation agent in the HC-SCR process. On the other hand the higher conversion of C_3H_6 on Pt/NbMCM-41 than on Pt/SiMCM-41 is supposed to favour hydrocarbon activation, enhancing its reduction properties.

Looking carefully at spectra in Fig. 2A, we observe that N_2O species are preceded by propene excess peak and by hydrocarbon oxidation. This infers that the reaction pathway is based on a mechanism proposed by Burch et al. (e.g. [11]), in which Pt reduced particles are able to dissociate NO. The high selectivity towards N_2O more than N_2 is due to the high oxygen concentration on the catalytic surface, leading to a partial recombination of nitrogen atoms with oxygen or NO species adsorbed on the metallic sites [10]. After sending a steady flow of NO + O_2 + C_3H_6 at 523 K on the Pt/NbMCM-41 sample, we still observe the total conversion of propene. Moreover, this oxidation is again associated to NO and NO_2 decreasing and to N_2O production (Fig. 3A). By mass spectrometry (not reported here), nitrogen output is detected as well. Therefore, we can affirm that the tested catalyst is effective also under continuous flow. The selected IR spectra of the surface (Fig. 3B) indicate the formation of nitrate/nitrite characterized by bands at 1390 and 1370 cm^{-1}. The rather weak intensity of these bands increases with the reaction time. Previously [12], it has been indicated on the basis of in situ IR experiments (under controlled atmosphere) that such kind of nitrate/nitrite species interacts with C_3H_6. It was also shown that nitrates can be considered intermediate species in the SCR of NO_x by propene via the formation of ciano-compounds [13], not observed here. We can propose that on the present catalytic surface CN and NCO species are involved in fast reaction steps, so that their

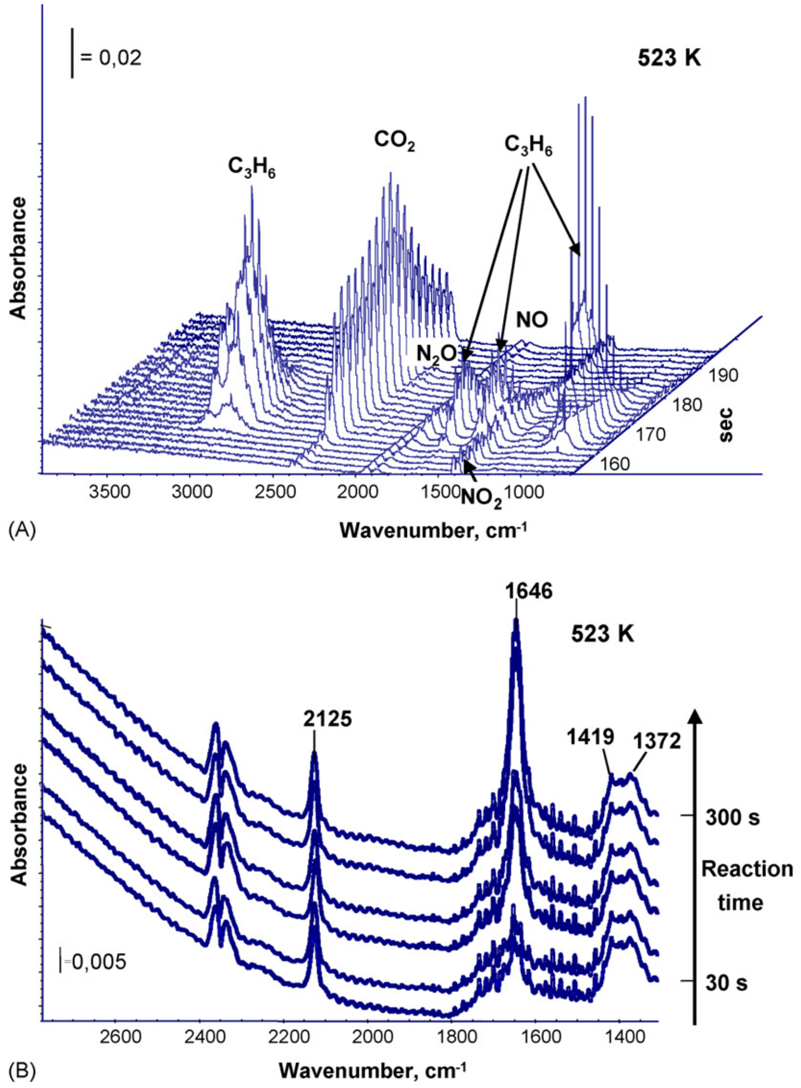

Fig. 4. FTIR spectra of gas phase after sending a flow of NO + O_2 followed by C_3H_6 pulses (A) and of the catalyst surface after sending a flow of NO + O_2 + C_3H_6 (B) at 523 K on a Pt/NaY + NbMCM-41 sample.

average life-time is too slow to allow IR detection. It could also be suggested that under dynamic conditions the rate of nitrate/nitrite formation is higher than that of their decomposition via an interaction with propene. Therefore, one can conclude that NbMCM-41 matrix (i.e. Nb species in this material) holds nitrogen oxides (in the form of nitrate/nitrite species) too strongly for their effective interaction with propene. It appears therefore that Pt/NbMCM-41 sample can also act as nitrate storage compound.

An alternative behavior for platinum activity was obtained depositing the metal on a zeolitic compound such as NaY. The application of a microporous matrix (for NO oxidation) and mixing with NbMCM-41 (for NO_x storage) led to a different reaction pathway. The gas spectra after sending $NO + O_2$ followed by C_3H_6 pulse (Fig. 4A) on Pt/NaY + NbMCM-41 differ from those reported in Fig. 2B—the consumption of NO_2 after C_3H_6 pulse is not visible due to the low propene conversion. As for the results presented in Figs. 2 and 3, it is clear that NO_2 is an intermediate product, in the case of Pt/NaY + NbMCM-41 the presence of nitrogen dioxide is further increased on the surface, as shown by the intense band at 1646 cm^{-1} (Fig. 4B). As a consequence, the nitrate intensity has at least doubled and a new band appeared at 2125 cm^{-1}, assigned to NO^+ species [14,15]. The high nitrosonium concentration is related to the NO_2 disproportionation, which occurs in basic zeolites: NO^+ become the zeolitic compensation cation whereas nitrates of the initial alkaline cations are formed which explains the different wavenumbers (1419–1372 instead of 1390–1370 cm^{-1} on Pt/NbMCM-41). The most important result is that the analysis of mass spectra (not reported here) showed an increase in the nitrogen oxides elimination and dinitrogen production by a factor five related to that found on Pt/NbMCM-41.

The above observation indicate that in Pt/NaY + NbMCM-41 catalyst, the niobium containing part of the support does not play the role of NO_x storage due to the long distance between Pt and Nb species (see TEM image—Fig. 1).

4. Conclusions

This work has evidenced the effect of the support structure and composition (meso- or micro/mesoporous) on the metal activity in HC-SCR of NO_x. Platinum acts as an oxidation site for hydrocarbons and a reduction centre for NO molecules. Furthermore, NO_x removal activity appeared to be correlated with nitrogen storage on the support. However, the storage species differs depending on the support nature. In the case of Pt/NbMCM-41 catalyst, it is Nb species responsible for the NO_x storage, whereas in Pt/NaY + NbMCM-41 system sodium cations from NaY zeolite hold NO_x in the form of sodium nitrates.

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