

Lean NO_x reduction with dodecane over cerium and palladium loaded mordenite

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Abstract

The selective catalytic reduction (SCR) of NO_x by dodecane in excess oxygen-containing gas mixtures was studied on Ce and/or Pd-loaded HMOR. Under dry conditions the best fresh bimetallic catalyst, 6.2 wt.% Ce–0.08 wt.% Pd-HMOR, displayed a maximum of about 70% NO_x conversion to N_2 at 350°C and $\text{GHSV} = 30,000 \text{ h}^{-1}$, while either Ce-HMOR or Pd-HMOR exhibited low activity for the SCR reaction. The presence of both Ce and Pd in the zeolite was crucial for high deNO_x activity. The dodecane concentration is very important for the reaction. The catalyst is not active in the absence of the reducing agent and inhibition of NO_x reduction is observed at dodecane concentrations higher than 440–500 ppm. The presence of 40 ppm SO_2 in the gas feed suppresses the reaction. However, the coexistence of 15% H_2O and 40 ppm SO_2 has no appreciable effect on the catalyst activity. Enhanced activity and a broader temperature window was observed in the $\text{NO}_2 + \text{dodecane} + \text{O}_2$ reaction in the presence of 15% H_2O and 100 ppm SO_2 . In this reaction mixture, the catalyst was capable of retaining a stable NO_2 conversion to N_2 for a period of ten days. Characterization by XPS and UV–VIS–diffuse reflectance spectra (UV–VIS–DRS) of selected fresh and aged catalyst samples indicates that Pd exists mainly as Pd^{2+} cations in Ce–Pd-HMOR. Cerium is mostly present as CeO_2 on the surface of the zeolite particles. However, part of the cerium in 6Ce–Pd-HMOR, exists as stable Ce^{3+} species. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cerium; Palladium; Mordenite; Nitrogen oxides; Dodecane; Lean SCR

1. Introduction

Diesel engines have the greatest potential for complying with the stricter emission standards recently adopted by many countries. They have the advantage of lower fuel consumption and lower emission of

greenhouse gases such as CO_2 [1]. However, a larger amount of NO_x is emitted from diesel compared to the gasoline engines equipped with three-way catalysts. Due to the high oxygen content of the exhaust gases the three-way catalyst cannot be applied to diesel engine systems [2]. As a consequence, a catalyst to reduce nitrogen oxides (NO_x) under lean conditions of diesel exhaust is required. A diesel catalyst must operate at lower temperatures than gasoline vehicle catalysts. Besides, a diesel catalyst needs to function over a broad temperature range [1]. Current lean NO_x catalysts require a reductant to achieve NO_x

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conversion but, diesel exhaust contains a relatively low HC/NO_x ratio (≤ 1). Therefore, the addition of HC is necessary to allow adequate NO_x reduction [3].

Over the last several years, many different lean SCR catalysts have been studied including zeolites and metal oxides [4]. Low durability under hydrothermal conditions, low SO_x resistance, or a narrow temperature window are the main drawbacks found for practical application.

Ce-zeolite catalysts have been studied for the lean SCR of NO by propene [5,6]. High selectivity for the NO reduction instead of propene oxidation was found over Ce–Na-ZSM-5. It was postulated [5] that the main role of cerium is to oxidize NO to NO₂. NO₂ reacts with propene to form intermediate organic compounds, containing N and O. The latter compounds are converted to N₂ in the presence of NO_x over Ce sites. The steady-state activity and stability of Ce–Na-ZSM-5 was promoted by alkaline earth metals like strontium. However, Sr-ZSM-5 itself was not active for the reaction. It was concluded that the presence of Sr probably modifies the coordination of Ce ions in the zeolite [6].

During the last few years, catalysts based on Pd–Ce/Al₂O₃ have found wide application in three-way catalysis [7]. Recently, it was reported that Pd promotion by ceria retards the thermal decomposition of PdO [8]. Moreover, Pd–Ce interactions favor N₂ formation over N₂O under stoichiometric conditions [9]. Pd-zeolite catalysts are also active for lean NO_x reduction by methane [10,11]. An important finding for these catalysts is that the presence of acid sites is necessary for achieving high CH₄–SCR activity and selectivity [12,13]. Furthermore, low Si/Al ratios favor NO reduction activity even in the presence of steam [14]. On the other hand, it is recognized that the hydrocarbon type influences lean NO_x reduction [15]. For mobile diesel engines it would be desirable to use a reductant derived from the fuel itself. However, little work has been done using long chain paraffins as reducing agents. In this paper, we examine the lean SCR of NO_x over Pd-HMOR, Ce-HMOR and Pd–Ce-HMOR catalysts, using dodecane as the reducing agent under dry conditions and in synthetic feed gas streams containing water vapor and SO₂. Characterization by XPS and UV–VIS–diffuse reflectance spectra (UV–VIS–DRS) of selected fresh and aged catalyst samples was performed to identify

stable species and potential structural effects of the coexistence of cerium and palladium in HMOR on the activity for the SCR reaction.

2. Experimental

2.1. Catalyst preparation

The parent sodium mordenite zeolite (Si/Al \cong 6) was synthesized by a known procedure [16]. Catalyst samples were prepared by first exchanging Na-MOR with 100 ml of aqueous 1 M ammonium chloride solution per gram of zeolite during 8 h at 80°C. The samples were then filtered, rinsed with de-ionized water, and dried at 50°C overnight. Ce/NH₄-MOR and Pd/NH₄-MOR were prepared by incipient wetness impregnation at room temperature. The precursor salts were Ce(NO₃)₃·6H₂O and Pd(NH₃)₄Cl₂·H₂O, respectively, with the content of cerium and palladium equaling the desired amount. The solids were then dried in an oven at 60°C and pretreated at 500°C in flowing He for 3 h to obtain Pd-HMOR and Ce-HMOR catalyst samples. Bimetallic Ce–Pd-HMOR catalysts were obtained by impregnating the required amount of Pd(NH₃)₄Cl₂·H₂O over Ce-HMOR, drying at 60°C as above and pretreating at 450°C in flowing He for three additional hours. For comparison, a Ce–Pd catalyst supported on γ -alumina was prepared in the same way using a γ -alumina sample from Alfa Aesar, 120 m²/g. Selected samples were analyzed by inductively coupled plasma emission spectrometry (ICP, Perkin-Elmer Plasma 40) and their BET surface areas determined in a Micromeritics ASAP 2000. Table 1 lists the bulk elemental composition and the corresponding surface areas of several zeolite supported catalysts prepared in this work.

2.2. Catalytic activity tests

Steady-state SCR conversion measurements were carried out in a fixed-bed microreactor operating isothermally. The reactor was a Pyrex tube 3/8 in o.d. containing a quartz frit to hold the catalyst. Typically, 150 mg catalyst (40–60 mesh) was used. Reactant gases were fed from separate mass flow controllers (Brooks 5850E). The gaseous reaction mixture consisted of 900 ppm NO, 100 ppm NO₂, 30 ppm N₂O,

Table 1
Bulk chemical composition and surface area of catalysts

Code	Catalyst	Si/Al	Na/Al	Ce/Al	Pd/Al	Surface area (m ² /g)
Na-MOR	Na-MOR	5.1	0.98	–	–	–
NH ₄ -MOR	NH ₄ -MOR	6.3	0.02	–	–	–
Pd-HMOR	0.07 wt.% Pd-HMOR	5.7	0.02	–	0.0025	–
1Ce-Pd-HMOR	0.6 wt.% Ce–0.06 wt.% Pd-HMOR	6.5	–	0.02	0.0025	–
5Ce-HMOR	5.1 wt.% Ce-HMOR	5.4	–	0.14	–	315
5Ce-Pd-HMOR	5.4 wt.% Ce–0.053 wt.% Pd-HMOR	6.6	–	0.18	0.0022	300
6Ce-HMOR	6.1 wt.% Ce-HMOR	6.3	0.02	0.20	–	276
6Ce-Pd-HMOR	6.2 wt.% Ce–0.08 wt.% Pd-HMOR	6.9	0.01	0.25	0.0042	262
6Ce-Pd-HMOR (aged, H ₂ O)	–	–	–	–	–	73

6% O₂, 400–500 ppm C₁₂H₂₆, and balance helium. Dodecane was added by saturating half of the helium feed with dodecane through a sealed glass bubbler with a medium pore frit. The bubbler was wrapped with a heating tape and insulated. By adjusting the temperature of dodecane, the desired dodecane level could be obtained. The effect of water was determined by adding about 15% water vapor to the feed using a heated H₂O saturator. The tolerance to SO₂ was tested by adding about 40 ppm SO₂ to the reactant mixture. However, 100 ppm SO₂ was used in some experiments. The total flow rate was maintained at 150 ml/min. The gas hourly space velocity (GHSV) was 30,000 h⁻¹ (STP) based on the bulk density of the zeolite, 0.5 g/cm³. The feed and effluent gases were condensed before being analyzed by an on-line gas chromatograph (Varian Star 3400) equipped with a TCD detector. A molecular sieve 5A column was used to separate O₂, N₂ and CO and a Poparapak Q to separate CO₂. In some runs, a FTIR multicomponent gas analyzer (Temet, model Gaset DX 4000, cell length 2.4 m, cell volume 1.01, cell temperature 120°C) was used to follow NO, NO₂, N₂O, NH₃, CO, CO₂, SO₂, H₂O and dodecane concentrations. To avoid condensation of water vapor, the line between reactor and the gas analyzer was heated and the temperature was controlled at 120°C. Spectra from each run were processed at the end of each experiment using a software program known as Calcmet (Temet). The NO_x conversion was calculated from the disappearance of NO_x and the N₂ yield as the ratio of twice the number of moles of N₂ produced at each temperature (from GC measurements) to the initial moles of NO_x. Good correspondence between these

values was found in all experiments. Dodecane conversion was calculated from the percent ratio of 1/12 outlet (CO + CO₂) to the initial moles of dodecane.

2.3. Catalyst characterization

Selected fresh and aged catalyst samples were characterized by XPS and UV–VIS–DRS. The fresh samples were used as prepared without further treatment. Aged samples were obtained by exposing the fresh catalyst samples to a gas stream containing 900 ppm NO, 100 ppm NO₂, 30 ppm N₂O, 6% O₂, 400–500 ppm C₁₂H₂₆, 15% H₂O, 40 ppm SO₂ and balance helium at 500°C for 72 h.

A Perkin-Elmer Model 5100 X-ray photoelectron spectroscope (XPS) with 2 mm spatial resolution was used to determine surface composition of catalyst samples. The Al K α anode X-ray source was operated at 300 W. A layer of catalyst sample in powder form was pressed on a copper adhesive tape mounted on the sample holder. The sample was then introduced into the XPS vacuum chamber. The base pressure of the vacuum chamber was below 5×10^{-8} Torr. Each sample was exposed to the X-ray beam for about 40 min for data acquisition. Atomic ratios of cerium to silicon on the surface region (3–4 nm) of the zeolite particles were determined based in the core level spectra of Ce and Si.

UV–VIS–DRS of Ce-HMOR, Pd-HMOR and Ce–Pd-HMOR were collected in a HP 8452A diode array spectrometer coupled with a Harrick diffuse reflectance attachment and a reaction chamber which could be heated up to 600°C. The spectra were recorded in the range of 180–820 nm with a resolution

of 2 nm. High purity MgO (99.998%, Johnson Matthey) was used as reference material. In situ reduction and oxidation experiments were performed with 10% H₂-He and 10% O₂-He gas mixtures, respectively, at a flow rate of 20 ml/min (STP).

3. Results and discussion

3.1. Catalytic activity tests

3.1.1. Effect of cerium loading

Fig. 1 shows the total NO_x conversion to N₂ versus temperature over Ce-Pd-HMOR catalysts under dry conditions and in the absence of SO₂. The conversion of NO_x increases with cerium loading up to about 6 wt.%. A maximum NO_x conversion to N₂ around 70% at 350°C is observed for 6Ce-Pd-HMOR in Fig. 1. Further increase of the amount of loaded cerium nitrate by 5 wt.% (Ce-Pd-HMOR*) lead to a decrease of NO_x conversion. Higher cerium loading might result in larger cerium oxide particles which were not active for the SCR of NO_x. The Pd loading in these samples was maintained approximately constant between 0.05 and 0.08 wt.%. The choice of such a low loading of Pd is based on our previous findings [17] that a very small amount of Pd added to a Pt-HMOR has a promoting effect on NO_x reduction by methane.

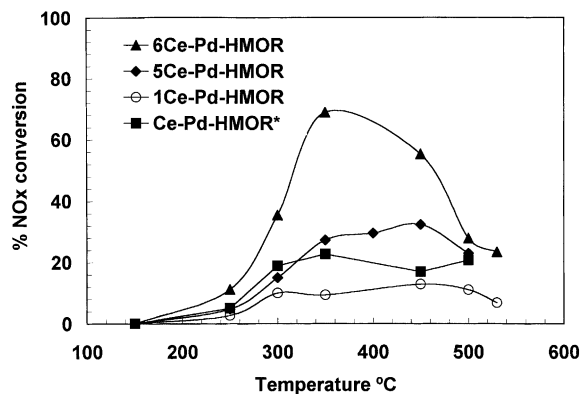


Fig. 1. Effect of Ce content on the lean SCR of NO_x by dodecane over Ce-Pd-HMOR catalysts maintaining Pd at about 0.07%. Dry feed: 900 ppm NO, 100 ppm NO₂, 30 ppm N₂O, 6% O₂, 400–500 ppm C₁₂H₂₆, and balance helium, GHSV = 30,000. In Ce-Pd-HMOR* Ce loading is about 5% higher than 6Ce-Pd-HMOR.

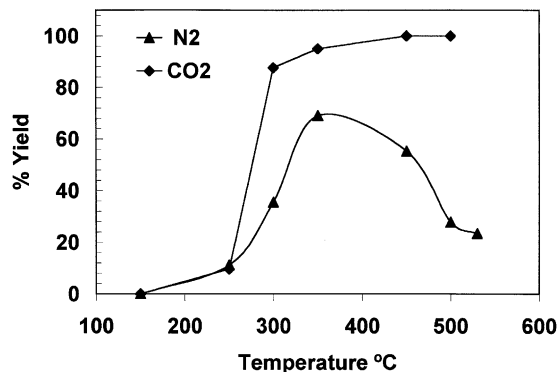


Fig. 2. N₂ and CO₂ yield over 6Ce-Pd-HMOR for the lean SCR. Dry feed: 900 ppm NO, 100 ppm NO₂, 30 ppm N₂O, 6% O₂, 400–500 ppm C₁₂H₂₆, and balance helium, GHSV = 30,000.

A promoting effect was also observed in NO_x reduction with propene by the addition of small amounts of palladium to In/TiO₂-ZrO₂ [18]. Similarly, a small amount of Pd added to Ag-MOR promotes the SCR of NO_x when oxygenates are used as reductants [4]. Fig. 2 compares N₂ and CO₂ yields versus temperature on the most active catalyst, 6Ce-Pd-HMOR, under dry conditions. According to stoichiometry, about three molecules of NO are reduced for every C₁ consumed but, dodecane is partitioned between NO and O₂ combustion. Therefore, it is clear that dodecane combustion occurs in the whole temperature range, starting at temperatures above 250°C. The high O₂ concentration typical of diesel exhaust contributes to low catalyst selectivity.

3.1.2. Composition effects

As shown in Fig. 3, to evaluate the role of cerium, palladium and proton species, separate activity tests were carried out with 6Ce-HMOR, Pd-HMOR (0.07% Pd on an average) and HMOR. Under dry conditions, the monometallic Pd-HMOR catalyst exhibits low NO_x conversion (12%) over a broad temperature range. The activity of HMOR (17% NO_x conversion) is similar within experimental error to Pd-HMOR. These results are expected, given the low Pd loading of Pd-HMOR. The monometallic Ce-HMOR exhibits a volcano-type curve with a maximum of about 40% NO_x conversion at 500°C. Thus, the bimetallic catalyst, 6Ce-Pd-HMOR, is much more active than the corresponding monometallic Ce-HMOR and

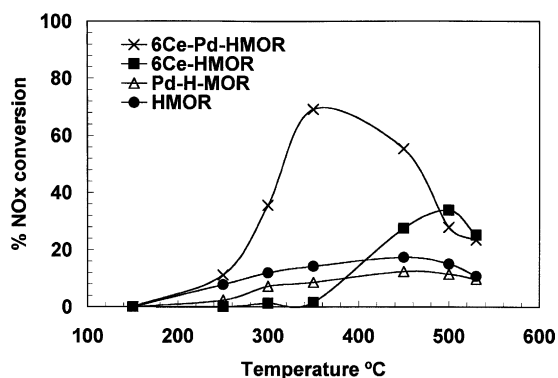


Fig. 3. Effect of the individual species Ce, Pd and, proton on HMOR for the lean SCR of NO_x by dodecane. Dry feed: 900 ppm NO, 100 ppm NO_2 , 30 ppm N_2O , 6% O_2 , 400–500 ppm $\text{C}_{12}\text{H}_{26}$, and balance helium, GHSV = 30,000.

Pd-HMOR. A similar promoting effect by the addition of cerium was observed on Pd-ZSM-5 [19] and Ag-ZSM-5 used as catalysts for the SCR of NO with CH_4 [20,21].

3.1.3. Effect of the support

The effect of the support was briefly studied by comparing the activity of 6Ce–Pd–HMOR with 6Ce–Pd/ Al_2O_3 . As can be seen in Fig. 4, Al_2O_3 is an inferior support for Ce and Pd for the lean SCR of NO_x by dodecane, at least under the present preparation conditions.

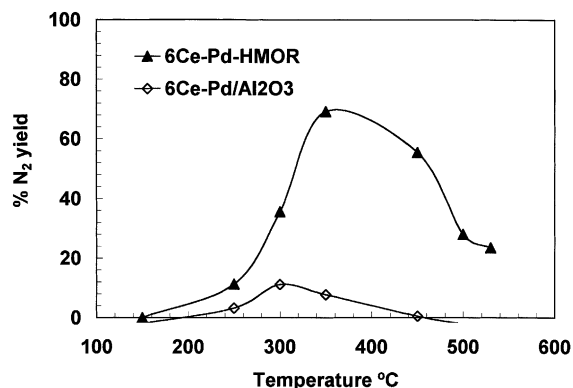


Fig. 4. Effect of the support on the lean SCR of NO_x by dodecane. Dry feed: 900 ppm NO, 100 ppm NO_2 , 30 ppm N_2O , 6% O_2 , 400–500 ppm $\text{C}_{12}\text{H}_{26}$, and balance helium, GHSV = 30,000.

3.1.4. Effect of H_2O , SO_2 and combined effect of H_2O and SO_2

Fig. 5 shows that the addition of 40 ppm SO_2 to the dry reaction mixture drastically decreases the N_2 yield over the 6Ce–Pd–HMOR catalyst. However, the loss of N_2 formation is much smaller when 15% water vapor is added to the feed gas. In the presence of both SO_2 and water vapor, little difference from the wet-gas data is observed. Thus, the maximum N_2 yield is about 60% at 350°C. This indicates that SO_2 cannot inhibit the reaction in the presence of water. The NO_x activity window of 6Ce–Pd–HMOR in the wet reaction mixtures is narrower than that exhibited under dry conditions. Table 2 lists the product yields in the dry feed and in the presence of water and both water and SO_2 for 6Ce–Pd–HMOR. Low N_2O , NH_3 and CO yields are observed. The yield of CO_2 increases with temperature, while the N_2 yield passes through a maximum followed by a decrease when most dodecane is consumed. Selectivity always decreases with temperature, as dodecane combustion becomes predominant at high temperatures. As shown in Fig. 6, when H_2O or both water and SO_2 are present in the feed gas stream, the conversion of dodecane to CO_2 is decreased, i.e. selectivity increases.

Fig. 7 shows the conversions of NO_2 to N_2 for NO_2 + dodecane + O_2 reaction in the presence of H_2O and SO_2 over 6Ce–Pd–HMOR. Enhanced activity and a broader operating temperature window is observed. Based on the results from Figs. 5 and 7

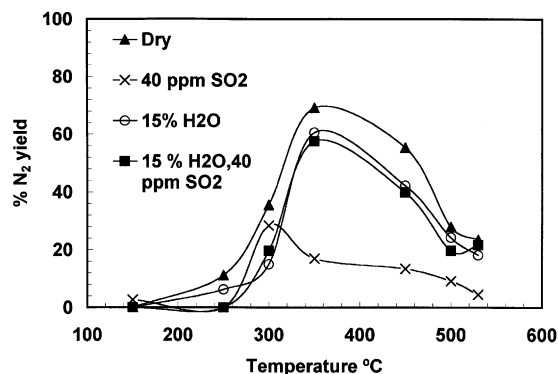


Fig. 5. Effect of the addition of 15% water vapor, 40 ppm SO_2 or both 15% water vapor and 40 ppm SO_2 over 6Ce–Pd–HMOR. Dry feed: 900 ppm NO, 100 ppm NO_2 , 30 ppm N_2O , 6% O_2 , 400–500 ppm $\text{C}_{12}\text{H}_{26}$, and balance helium, GHSV = 30,000.

Table 2
Lean NO_x reduction with Dodecane over 6Ce–Pd–HMOR — product distribution

Feed	Yield (%)	Temperature (°C)						
		150	250	300	350	450	500	530
Dry	N ₂	0	11.2	35.5	69.1	55.4	27.9	23.4
	N ₂ O	0.3	5.9	2.8	1.6	0	0	0
	NH ₃	0.1	0.4	0	0	0	0	0
	CO ₂	0	10	88	95	100	100	–
	CO	0	0	0	0	0	0	–
15% H ₂ O	N ₂	0	6.2	15.0	60.6	42.2	24.2	18.2
	N ₂ O	0.5	0.5	0	3.1	0	0	0
	NH ₃	0	0	0.8	0.4	0	0	0
	CO ₂	0	4	19	61	98	100	–
	CO	0	0	0	1	5	0	–
15% H ₂ O, 40 ppm SO ₂	N ₂	0	0	19.6	57.5	39.8	19.6	21.6
	N ₂ O	0.6	1.0	1.4	3.2	0	0	0
	NH ₃	0	1.4	0.5	0	0.2	0	0
	CO ₂	0	1	1	5	63	72	–
	CO	0	0	0	0	0	2	–

it appears that H₂O inhibits NO oxidation to NO₂ on 6Ce–Pd–HMOR. Kikuchi et al. have previously reported that NO oxidation is hindered by water adsorption on the Lewis acid sites of zeolites [22]. The long-term catalyst stability evaluated at 350°C in the gas reaction mixture containing 1000 ppm NO₂, 400–500 ppm dodecane, 6% O₂, 15% H₂O and 100 ppm SO₂ is shown in Fig. 8. The N₂ yield was maintained around 60% for a period of 10 days.

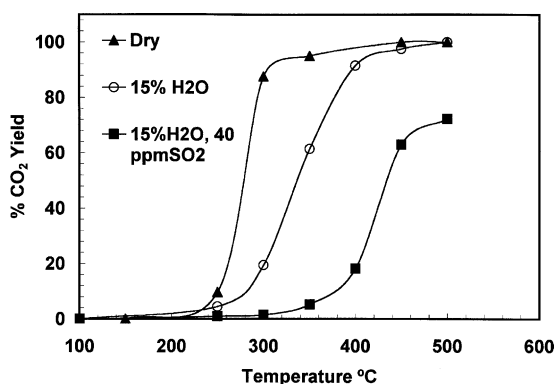


Fig. 6. CO₂ yield vs. temperature over 6Ce–Pd–HMOR under dry conditions and in the presence of 15% H₂O and both 15% H₂O and 40 ppm SO₂. Dry feed: 900 ppm NO, 100 ppm NO₂, 30 ppm N₂O, 6% O₂, 400–500 ppm C₁₂H₂₆, and balance helium, GHSV = 30,000.

3.1.5. Effect of dodecane concentration

Fig. 9 illustrates the N₂ yield versus dodecane concentration profile over 6Ce–Pd–HMOR with no addition of water and SO₂ to the feed. All runs were performed with the same catalyst sample. After each run the catalyst was treated for 1 h at 500°C in the gas reaction mixture containing the lowest possible dodecane level to remove carbonaceous deposits. The isotherms show a maximum NO_x reduction peak around 440–500 ppm dodecane. Higher dodecane concentrations appear to decrease the NO_x

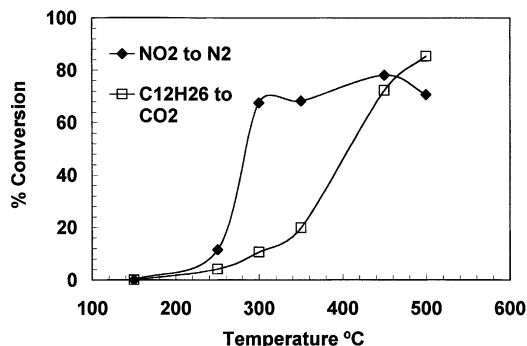


Fig. 7. Yield of N₂ and CO₂ vs. temperature over 6Ce–Pd–HMOR. Feed: 1000 ppm NO₂, 30 ppm N₂O, 400–500 ppm C₁₂H₂₆, 6% O₂, 15% H₂O, 100 ppm SO₂ and helium balance, GHSV = 30,000.

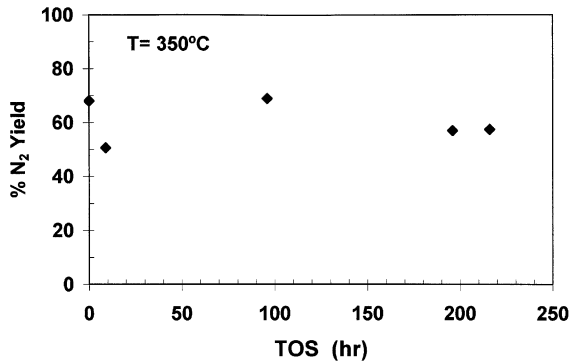


Fig. 8. Yield of N₂ vs. time-on-stream (TOS) on 6Ce-Pd-HMOR. Feed: 1000 ppm NO₂, 30 ppm N₂O, 400–500 ppm C₁₂H₂₆, 6% O₂, 15% H₂O, 100 ppm SO₂ and helium balance, GHSV = 30,000, T = 350°C.

reduction activity, mainly at temperatures below 350°C. Furthermore, in the absence of dodecane no NO_x decomposition activity is observed. Therefore, it is very important to control the level of dodecane in the gas reaction mixture.

3.2. Catalyst characterization

The superficial Ce/Si atomic ratios of the tested catalysts are compared with the bulk Ce/Si ratios in Table 3. The superficial Ce/Si atomic ratios of the

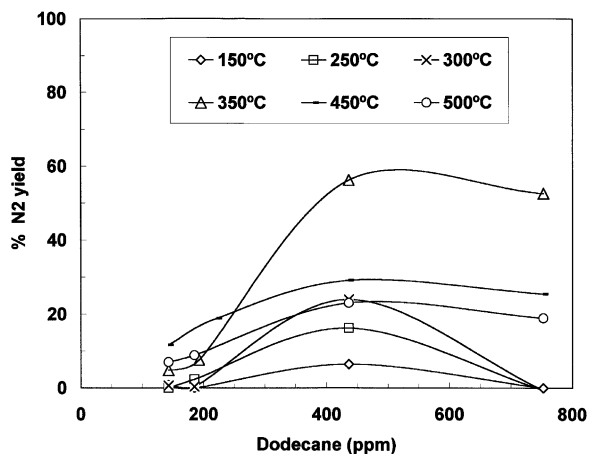


Fig. 9. N₂ yield vs. dodecane concentration profile for the lean SCR of NO_x over 6Ce-Pd-HMOR. Feed: 900 ppm NO, 100 ppm NO₂, 30 ppm N₂O, 6% O₂, dodecane varied between 0 and 750 ppm and helium balance, GHSV = 30,000.

Table 3

Comparison of bulk versus surface Ce/Si atomic ratios

Catalyst sample ^a	Surface Ce/Si ^b	Bulk Ce/Si ^c
6Ce-HMOR	0.652	0.032
5Ce-Pd-HMOR	0.216	0.028
6Ce-Pd-HMOR	0.303	0.031
6Ce-Pd-HMOR (aged)	0.341	0.031

^a Fresh samples.

^b By XPS analysis.

^c By ICP analysis.

used and fresh mono- and bimetallic catalyst samples are significantly higher than the corresponding bulk ratios. Thus, the surface of the mordenite particles is enriched with cerium oxide. This is similar to what has been reported by Li and Flytzani-Stephanopoulos [20,21] for Ce-loaded ZSM-5 samples. In that work, the cerium oxide was present in nanoparticles of less than 3 nm size.

The oxidation states and electronic transitions of Ce and Pd during reduction and oxidation of mono- and bimetallic catalysts were obtained by UV-VIS-DRS. Fig. 10 shows the diffuse reflectance UV-VIS spectra of Pd-HMOR during successive reduction and oxidation treatments at temperatures in the range 25–600°C. During reduction, a band at about 240 nm that grows with temperature is observed. This band has been assigned [23] to the formation of palladium clusters of different sizes at high temperature. No significant

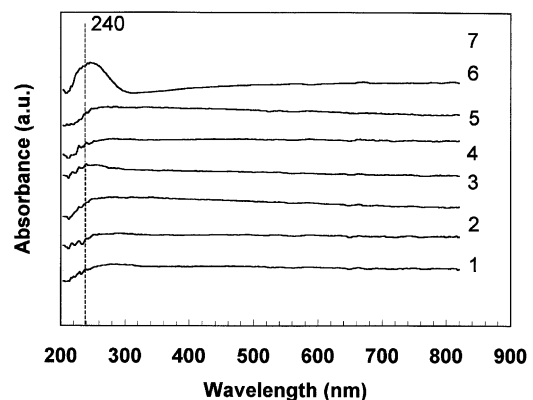


Fig. 10. In situ UV-VIS-DRS for the reduction and oxidation behavior of Pd-HMOR. (1) 25°C in He; (2) 25°C in O₂; (3) 300°C in O₂; (4) 600°C in O₂; (5) 25°C in H₂; (6) 300°C in H₂; (7) 600°C in H₂. Reduction gas, 20 ml/min 10% H₂ in He. Oxidation gas, 20 ml/min 10% O₂ in He.

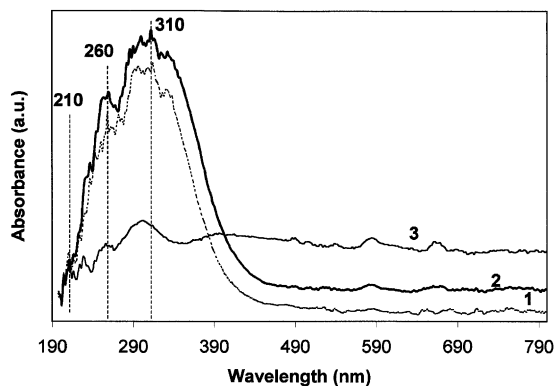


Fig. 11. UV-VIS-DRS of (1) 6Ce-Pd-HMOR; (2) 6Ce-HMOR; (3) 1Ce-Pd-HMOR in 20 ml/min He flow at 25°C.

changes are observed during the oxidation treatment at different temperatures when compared to the fresh sample at 25°C. Therefore, it appears that in the fresh catalyst palladium exists in an oxidized state.

The UV-VIS spectra, in flowing He at 25°C, of 6Ce-HMOR is compared with those of Ce-Pd-HMOR catalysts containing different Ce loadings in Fig. 11. Three bands are observed at 210, 260 and 310 nm. The peak at 210 nm corresponds to dispersed Ce^{3+} species [2] and the one at 260 nm is due to the 4f–5d interconfiguration transitions of Ce^{3+} species [24]. The band at 310 nm has been assigned to CeO_2 [23–25] and increases with cerium loading. Therefore, a mixture of cerium species in 3+ and 4+ states coexists in Ce-HMOR and in Ce-Pd-HMOR catalysts. This is similar to what has been reported for Ce-loaded ZSM-5 [19–21]. However, these analyses alone cannot identify which of the two states of cerium is responsible for the SCR activity.

The UV-VIS spectra for the reduction oxidation behavior of 6Ce-Pd-HMOR are shown in Fig. 12. The reduction and oxidation treatments, even at high temperatures, do not significantly affect these bands, suggesting that the cerium species in HMOR are stable. The UV-VIS spectra of 6Ce-Pd-HMOR, after exposure to H_2O and SO_2 is compared with the spectrum of the fresh sample in Fig. 13. The aged sample does not exhibit significant changes in the absorption bands suggesting redox stability of the active cerium species. Notwithstanding, it is not clear which sulfated species are formed upon exposure to SO_2 and water. Presumably the active sites are not affected

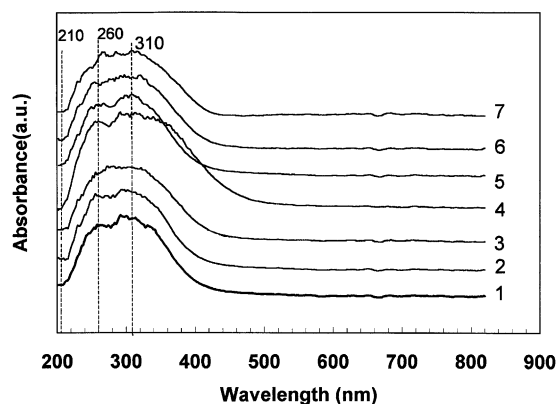


Fig. 12. In situ UV-VIS DR spectra for the reduction and oxidation behavior of 6Ce-Pd-HMOR. (1) 25°C in He; (2) 25°C in O_2 ; (3) 300°C in O_2 ; (4) 600°C in O_2 ; (5) 25°C in H_2 ; (6) 300°C in H_2 ; (7) 600°C in H_2 . Reduction gas, 20 ml/min 10% H_2 in He. Oxidation gas, 20 ml/min 10% O_2 in He.

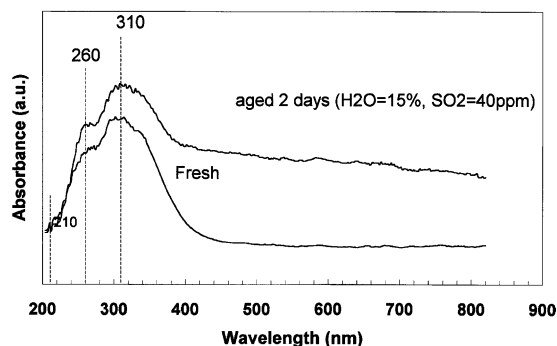


Fig. 13. UV-VIS-DRS of fresh and aged 10Ce-Pd-HMOR in 20 ml/min He flow at 25°C.

much, based on the little deactivation observed on 6Ce-Pd-HMOR in the presence of H_2O and SO_2 .

4. Conclusions

The bimetallic 6Ce-Pd-HMOR catalyst was found to display high activity for the lean SCR of NO_x with dodecane even in the presence of water and SO_2 . Also, N_2O , NH_3 and CO yields are very low. The presence of water inhibits deactivation by SO_2 ; while SO_2 alone is detrimental for the catalyst, the two together ($\text{H}_2\text{O} + \text{SO}_2$) have a negligible effect. A N_2 yield around 60% was obtained over a period of 10 days

when NO₂ instead of NO was used in the wet gas reaction feed containing SO₂. Exactly how Pd promotes the activity is still unclear and more work to clarify this is recommended.

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