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ABSTRACT

Zeolite-based palladium catalysts show high activity in the reduction of NO_x with methane. The addition of cobalt can further improve the SCR activity up to a level required for 'end-of-pipe' applications in gas engines. However, the hydro-thermal stability of the zeolite supported palladium catalysts is poor. CO-chemisorption, H₂-TPR, DRIFT and activity measurements indicate a temperature-induced mechanism of ion migration and sintering to be the ruling mechanism of deactivation. In addition, the process of steam dealumination under reaction conditions likely eases the sintering. Time on stream behaviour of cobalt-palladium-zeolite equals that of palladium-zeolites. Deactivated catalysts are characterised by a palladium peak in the H₂-TPR at lower temperature as compared to the fresh calcined samples. Cerium (and some other additives) stabilises the active Pd species in mordenite to a significant extent. The mechanism of stabilisation is possibly of both steric and electronic nature.

Keywords: NO_x, methane, zeolites, cobalt, palladium, cerium, stability

INTRODUCTION

The emission of NO_x during industrial, domestic and mobile activities still remains a major contributor to the acidification of the atmosphere and soil. NO_x abatement technology based on catalysis is of interest [1,2]. Selective Catalytic Reduction with Hydrocarbons (SCR-HC) is expected to be relatively cost-effective for small-scale DeNO_x applications. For gas engines, especially the use of methane – in the form of readily available natural gas – is very attractive. Moreover, methane is present in the off-gases of gasengines. From a catalytic point of view the challenge is to develop catalysts that operate at the temperature of the off-gases. In practice this means that the catalyst needs to activate the strong C-H bond in methane at temperatures of around 400-450 °C. Cobalt-palladium loaded zeolites were found appreciably active for CH₄-SCR [3,4]. Zeolite stabilised Pd²⁺ cations are believed to activate methane and catalyse the CH₄-SCR of NO_x. The presence of PdO gives rise to complete oxidation of methane and should be limited. On the other hand, cobalt oxide or cobalt-oxo species were reported to being beneficial for SCR activity. These species oxidise NO to NO₂, boosting the SCR reaction [3,4]. Also lanthanides in general and ceria in particular has found widespread attention for applications in oxidation catalysis. The cerium oxide system can exist in a variety of Fluorite crystalline phases of the type CeO_{2-x}, where 0<x<0.5 [5]. The relative rapid change of oxidation state of Ce⁴⁺ ions upon alternating environmental conditions has led to the generally accepted theory of oxygen storage, i.e. redox mechanism. The NO oxidation reaction operates well over ceria and its use in combination with palladium-zeolite is of interest for CH₄-SCR [6].

Nevertheless, the limited hydro-thermal stability of zeolites has been a matter of concern. Leaching of the tetrahedral co-ordinated aluminium out of the framework by creating octahedral aluminium is accelerated by water, usually present in exhaust gases. Therefore, to understand the full potential of the technology, insight in the time on stream behaviour (i.e. the durability) under realistic exhaust conditions is indispensable [3]. The current report describes the overall catalytic performance of zeolite supported palladium catalysts promoted with cobalt and cerium for CH₄-SCR in a feed resembling the off-gases of gas engines.

EXPERIMENTAL

Pd(WIE)-zeolite (0.4 Wt% Pd) was prepared by competitive wet ion exchange in air (16 h at 80 °C) from NH₄-zeolite (ZSM-5 SM27 (Si/Al 11) MOR CBV21a (Si/Al 10), BEA CBV814E from Zeolyst (Si/Al 11) and FER HZ-720a from Tosoh Inc. (Si/Al 9)) and an acidified solution of palladium nitrate. Additional NH₄NO₃ was added and the NH₄⁺/Pd²⁺ ratio initially in the liquid amounted to ca. 20. The pH was 2.2 and was allowed to decrease to 2 during exchange. Following the ion exchange, the catalyst was filtered, washed thoroughly with demineralised water and dried for 16 h at 80 °C. The procedure was preceded by a 3-fold NH₄NO₃ exchange if necessary (MOR CBV10a and CBV90a, FER HZ-720a). Promoted-Pd combination catalysts were prepared by adding cobalt- and lanthanide nitrates (2 to 4 Wt% metal) to Pd(WIE)-zeolite *via* incipient wetness method. The metal loading of the catalyst was examined using ICP elemental analysis. H₂-TPR spectra were recorded with an Altamira AMI-1 apparatus equipped with a TCD detector and a Balzers MS-detector, applying 30 ml/min flow of 10% H₂ in Argon at a heating rate of 20 °C min⁻¹. The same AMI-1 apparatus was also utilised for pulse-chemisorption of CO to determine metal dispersion. The Pd-zeolites were pre-reduced applying 30 ml/min flow of H₂ at 200 °C for 40 minutes. The samples were cooled down to 35 °C under hydrogen and CO was pulsed until saturation was reached.

Possible deposits on the catalyst surface were traced for by simultaneous analysis of C, H, N, and S using a LECO CHNS-932 analyser. Infrared spectroscopic (IR) measurements were performed with diffuse reflectance spectroscopy (DRIFT) on a BIORAD FTS-175 spectrometer equipped with a Harrick HV-DR2 flow cell. Spectra were recorded in the Kubelka-Munk mode at 350 °C. The spectra were recorded with a spectral resolution of 4 cm⁻¹. Catalytic tests were carried out in a feed consisting of 500 ppm NO, 2500 ppm CH₄, 5 % O₂ and 5 % H₂O in nitrogen. This composition is denoted standard: other concentrations were also tested and explained in the text. Conversion of NO_x is defined $(1 - (\text{NO}_2 + \text{NO})_t) / (\text{NO}_2 + \text{NO})_o * 100 \%$, conversion methane is defined $(1 - (\text{CH}_4)_t) / (\text{CH}_4)_o * 100 \%$, based on dry flow.

RESULTS

The NO_x removal efficiency at T ≥ 350 °C over Pd-zeolites decreases in the order Pd-HZSM-5 > Pd-HMOR > Pd-HBEA > Pd-FER. The addition of cobalt to the Pd-zeolites results in a significant increase of the activity of all catalysts without changing the order of highest activity (see Figures 1a and 1b). The function of cobalt in the combination catalyst is mainly to oxidise NO toward the (more) reactive NO₂ [3]. Time-on-stream trends for Co-Pd-zeolites are depicted in Figure 2a (NO_x conversion) and Figure 2b (methane conversion). None of the catalysts show stable behaviour. The cobalt-palladium-zeolites deactivate similarly as the palladium only Pd-zeolites (not shown). ZSM-5, FER and BEA deactivate most significantly. H₂-TPR, CO-chemisorption and IR were used to identify the process that is responsible for the deactivation. TPR shows a peak around 380-420 °C in

fresh Pd-zeolite that is shifted in part toward lower temperature (50 to 100 °C) in used Pd-zeolite. Obviously, the deactivation of promoted-palladium-mordenite is characterised by this shift. CO uptake is somewhat lower on used samples. On line MS analysis of released species during the H₂-TPR indicate significant amounts of carbon deposits in the case of BEA. The absence of (a-) symmetric CH, CH₂ and CH₃ intensity in IR spectra indicates that the carbon is of graphitic nature. IR analysis indicates extra-framework aluminum on all zeolites after reaction. Generally, the deactivation becomes less significant at lower reaction temperature [4].

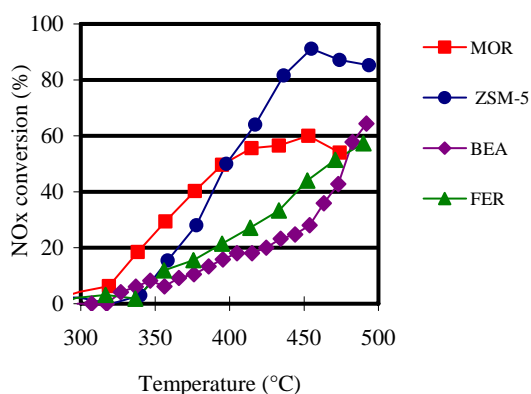


Figure 1a. NO_x conversion of Co(IMP)-Pd(WIE)-zeolites, 500 ppm NO, 2500 ppm CH₄, 5% O₂ and 5% H₂O GHSV = 20,000 h⁻¹ (FER at 10,000 h⁻¹).

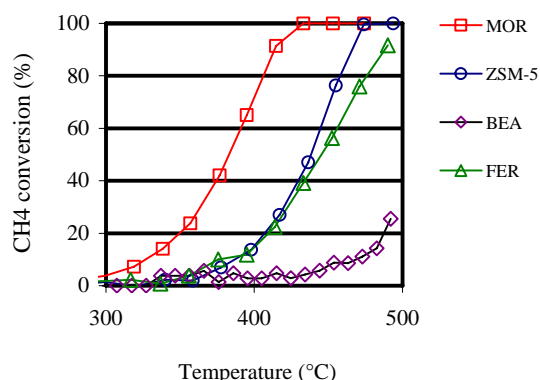


Figure 1b. Methane conversion of Co(IMP)-Pd(WIE)-zeolites, 500 ppm NO, 2500 ppm CH₄, 5% O₂ and 5% H₂O GHSV = 20,000 h⁻¹ (FER at 10,000 h⁻¹).

Remarkably, SCR-activity of MOR increases in the first hours on stream. However, deactivation was observed in a later stage. Total methane conversion decreases instantaneously (see figure 2b, i.e. the SCR-selectivity increases) and is by far incomplete.

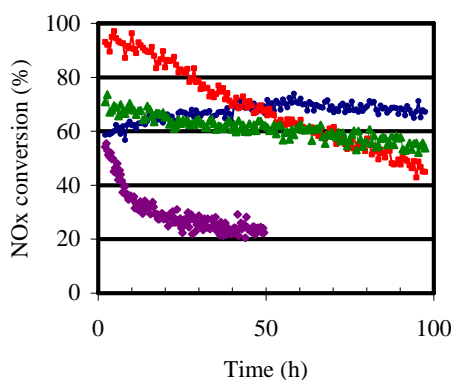


Figure 2a. Stability of Co(IMP)-Pd(WIE)-zeolites, 500 ppm NO, 2500 ppm CH₄, 5% O₂ and 5% H₂O GHSV = 20,000 h⁻¹ (FER at 10,000 h⁻¹). T = 450 °C. NO_x conversion.

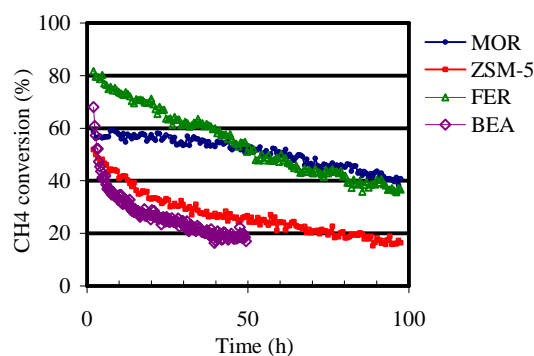


Figure 2b. Stability of Co(IMP)-Pd(WIE)-zeolites, 500 ppm NO, 2500 ppm CH₄, 5% O₂ and 5% H₂O GHSV = 20,000 h⁻¹ (FER at 10,000 h⁻¹). T = 450 °C. CH₄ conversion

Cerium promoted palladium-mordenite

Palladium-mordenite was promoted with cerium by (dry) impregnation of ceriumnitrate. Compared to palladium-MOR cerium led to increased SCR activity up to the activity level

of cobalt-palladium-MOR. Methane combustion activity of cerium-palladium-MOR is, however, somewhat lower compared to cobalt-palladium-MOR. Within the 100 hours test periods no activation followed by deactivation behaviour as opposed to (cobalt-) Pd-MOR was found at standard conditions (see also Figure 4). Test conditions were also changed according to gas compositions of off-gases of gas engines currently in use in the Netherlands, denoted A1, A27 and M1. Especially the water content is much higher (see Table 1). The activity at the various conditions is compiled in Figure 3.

Table 1. Gas composition in various types of gas engines currently in use in the Netherlands

Gas engines	standard	A1	A27	M1
NO (ppm)	500	240	117	245
CH ₄ (ppm)	2500	1750	2260	881
H ₂ O (vol.%)	5	10.9	10.6	11.3
O ₂ (vol.%)	5	8.5	8.8	6.4

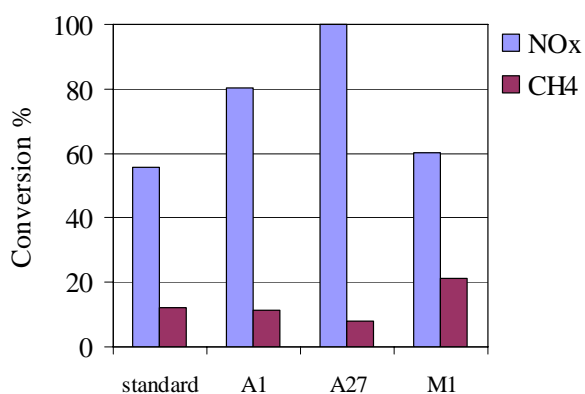


Figure 3. Influence of exhaust gas composition on the conversion, Ce(IMP)-Pd(WIE)-MOR, 385 °C, $\pm 17,000 \text{ h}^{-1}$.

The activity of the catalysts is higher for A1 and A27 gas compositions and quite similar for M1 as compared to the standard test conditions. From the results it follows that the methane to NO ratio affects the activity most. Figure 4 shows the time on stream behaviour of cerium-palladium-mordenite with 11 % water in the feed. Some deactivation is noticed within 100 hours on stream.

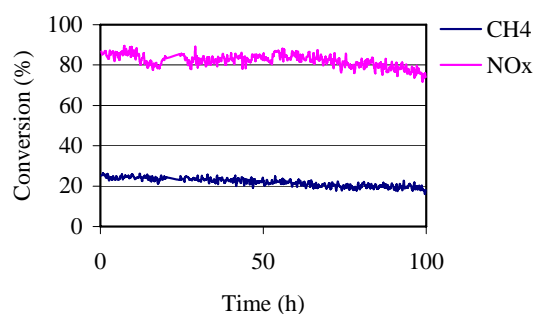
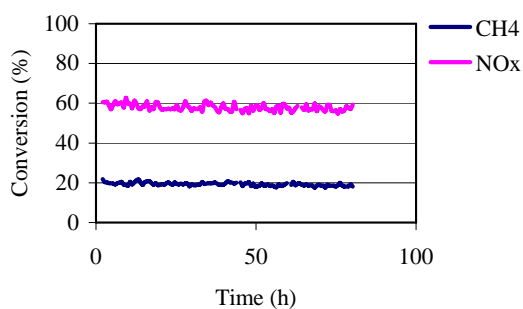


Figure 4. Stability of Ce(IMP)-Pd(WIE)-MOR, 375 °C, $\pm 17,000 \text{ h}^{-1}$, 5 % water (standard). Figure 5. Stability of Ce(IMP)-Pd(WIE)-MOR, 400 °C, $\pm 15,000 \text{ h}^{-1}$, 11 % water.

DISCUSSION

Metal-cation-containing zeolites are widely studied as catalysts for SCR-HC [2,3,4]. Palladium loaded zeolites were found appreciably active for SCR with methane [2,3]. Gaz de France [7] and Ogura et al. [8] quoted the enhanced catalytic performance of zeolite supported Pd combination catalysts by addition of cobalt. Synergistic effects between cobalt and palladium were proposed to explain the enhanced performance compared to the single metal systems. The catalysts based on MOR and ZSM-5 zeolites were found to be most active. MOR has also high methane combustion activity tackling both emissions adequately.

Despite high activity usually achieved, the limited hydro-thermal stability of zeolites has been a matter of concern. High reaction temperature in combination with the wet conditions usually encountered in practical situations gives rise to the process of steam dealumination. Tetrahedral co-ordinated aluminium is leached out of the framework by creating octahedral co-ordinated aluminium (EFAL). Crystallinity loss and a decreased number of exchange sites to disperse metal are the consequence. Due to these problems, studies on metal loaded oxide catalysts have found renewed interest. Unfortunately the oxidic materials are also less active when compared to zeolites [9]. Presumably the unique ability of the zeolite to generate highly dispersed metal ions at charge compensating sites (stabilised by the electrostatic field around the oxygen atoms in the pores) in the interior of the zeolite micropore system is of crucial importance in establishing high SCR activity. As catalysts based on oxides support materials show yet too little conversion at practical off-gas temperatures, research that focuses on stability improvements of zeolites is important. Automotive catalysts are exposed to a wide range of temperatures and an excellent heat-tolerance is required for SCR catalysts [10]. Application of zeolites in the field of the stationary pollution control, i.e., without large temperature excursions, seems less challenging. A few examples of potential markets for zeolite based HC-SCR are treatment of flue gases stemming from nitric acid factories, small sized boiler installations, combined-cycle devices, and (lean-burn) gas engines and transformers. In some cases, the high activity that can be accomplished with zeolites lowers the (required) minimum temperature of operation and therefore poses fewer demands with regards to (hydro-) thermal stability of the material. In the case of end-of-pipe applications in gas engines the zeolite should withstand temperatures between 400 and 500 °C, i.e. the temperature of the exhaust gas.

Nevertheless, the zeolite supported palladium catalyst deactivates at the conditions applied in this study. Palladium cations in zeolites seem to migrate during the reaction. From TPR work we infer that Pd either migrated toward locations that are more easily reduced or has changed nature, e.g. increased oxidic character. The formation of larger amounts of PdO is, however, unlikely. PdO is a very good methane oxidation catalyst. However, during the course of the reaction the lower SCR activity is never paralleled by increased methane combustion activity. A more plausible theory to explain the changes is to consider different locations in the zeolite micropore system following the classification of Kauckcy et al. [11,12]. Three typical cationic sites for divalent transition metal ions referred to as α , β and γ sites were defined. Studies on cobalt (Co^{2+}) siting showed that the location, the accessibility and activity of various locations might differ among the zeolites. The size of the Pd^{2+} ion exceeds the size of Co^{2+} and this is likely to result in different spatial limitations and interaction with the walls of the pores. As a consequence, the siting, i.e. the occupation of α , β and γ sites may be different. The migration of cations during reaction is a reasonable explanation for the activity changes. IR analysis indicated the presence of some EFAL in deactivated samples that may have

eased migration. Descorme et al. [13] attributed the activity increase observed with Pd-MOR to the migration of Pd ions to the more accessible positions.

It appears that cerium stabilise active palladium sites to some extent. Other additives can give similar stabilisation phenomena [6,14]. The addition of cobalt to palladium-zeolite does not result in increased durability. The mechanism of stabilisation by promotor additives is not yet clear. According to the theory of migration, a plausible explanation seems that the promotor metal occupies some locations that would otherwise be occupied by palladium cations after migration. The success of stabilisation may than be governed by the size of the voids in relation to the ion radii of the promotor cations or their nanoclusters formed during preparation and post-modification treatments. To form nanoclusters of critical size, the method of deposition of the promotor is expected to be important too. On the other hand, some synergy between cerium and palladium is indicated by the suppression of the methane combustion reaction. In this respect, it is interesting to note that Mitome et al. [14] report that the influence of cerium in cerium-palladium-TiO₂ catalyst for CH₄-SCR is to prevent Pd from being oxidised.

Future research includes the challenging tasks to further increase the durability of the zeolite catalysts while combining high SCR activity with sufficient methane combustion activity. Also the presence of additional catalysts poisons in the off-gases of gas engines, e.g. phosphate, caesium, calcium and sulfate [15], stemming from natural gas or from lubricating oils, will effect catalysts and are subject of study.

CONCLUSION

Zeolite-based palladium catalysts show high activity in the reduction of NO_x with methane. The addition of additive promotors can further improve the SCR activity up to a level required for 'end-of-pipe' applications in various types of gas engines. The addition of additives is also necessary to improve the stability of the catalysts. The use of cobalt for this purpose is inadequate. CO-chemisorption, H₂-TPR, DRIFT and activity measurements indicate a temperature-induced mechanism of ion migration and sintering to be the ruling mechanism of deactivation of Pd-zeolite catalysts. In addition, the process of steam dealumination under reaction conditions likely eases the sintering. Deactivated catalysts are characterised by a palladium peak in the H₂-TPR at lower temperature as compared to the fresh calcined samples. Cerium (and some other additives) stabilises the active Pd species in mordenite to some extent. The mechanism of stabilisation is possibly of both steric and electronic nature. Future research will face the challenging tasks to further increase the durability of the zeolite catalysts while combining high SCR activity with sufficient methane combustion activity. Apart from the water and oxygen resistance of the catalysts, deactivation by trace elements as usually present in the off-gases need to be considered too.

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