Development of monolithic catalysts with low noble metal content for diesel vehicle emission control

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Monolith washcoated catalysts with potential for diesel emission control have been developed. Two types of catalysts have been prepared for further study: (1) MnO\textsubscript{2} supported on granulated γ-Al\textsubscript{2}O\textsubscript{3}, (2) MnO\textsubscript{2} supported on cordierite monolith washcoated with γ-Al\textsubscript{2}O\textsubscript{3}. Both catalysts have been calcined at 500 and 900 °C and subsequently modified by doping with 0.1–1.0 wt% of Pt or Pd. The influence of the concentration of both manganese oxide (0–10 wt%) and noble metals Pt and Pd in the range 0–1.0 wt% on the catalytic activity in methane oxidation has been studied. Comparison of the catalytic activity of MnO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} and MnO\textsubscript{2} + Pt(Pd)/Al\textsubscript{2}O\textsubscript{3} with that of a standard 1 wt%Pt/Al\textsubscript{2}O\textsubscript{3} catalyst shows the existence of a synergetic effect. This effect is more pronounced for the samples calcined at 900 °C. The developed monolithic catalyst MnO\textsubscript{2} + Pt(Pd)/Al\textsubscript{2}O\textsubscript{3} demonstrate higher activity and thermal stability (up to 900 °C) compared to the commercial monolithic catalyst (TWC's).

KEY WORDS: manganese-alumina catalyst; multicomponent catalyst; washcoated catalyst; automotive exhaust purification; diesel emission control; catalytic combustion.

I. Introduction

Over the last several years the environmental legislation has imposed increasingly stringent limits for automotive exhaust gas emissions. There is a strong motivation for the development of new improved automotive catalysts. It is known that for practical applications the catalyst must be active at relatively low temperatures and show high selectivity to carbon dioxide. The catalyst must also be able to destroy effectively low concentrations of incomplete fuel combustion products (CO, hydrocarbons and VOCs) at very high flow rates with little or no deactivation, i.e. by keeping its thermal stability and resistance to poisons.

Supported Pt, Pd and Rh are most commonly used catalysts, TWC’s, for the automotive exhaust gas purification [1,2]. Each of these noble metals has its own application area conditioned by its advantages and limitations. Palladium is more active for oxidation of carbon monoxide, and, possibly, unsaturated hydrocarbons [2,3], and methane [1,2]. Platinum is more suitable for oxidizing alkanes such as butane [3,4]. However, these noble metals are relatively expensive, and can be rapidly deactivated in the presence of sulfur compounds or other metals in the exhaust stream. Pd was said to be more resistant to thermal sintering in an oxidizing environment than Pt [4], whereas Pt was found to have higher sulfur resistance [5].

The second class of deep oxidation catalysts is based on metal oxides. Some of the most active ones are based on Mn, Cu, Co, which are a cheaper alternative to noble metals. Copper and manganese oxides have sufficient catalytic activity in the reactions of CO and hydrocarbon oxidation [6,7], although they are less active than noble metals at low temperatures. They are sensitive to sintering at higher temperatures and less stable against sulfur poisoning than noble metals. In comparison with copper oxide, manganese oxides have a lower volatility at high temperatures in the presence of water vapor, and slightly interact with alumina forming MnAl\textsubscript{2}O\textsubscript{4} spinel [8]. On the other hand, formation of high temperature compounds between Mn and Al, e.g. hexaaluminates of different composition, provides high stability of Mn containing catalysts in the case of supports made of alumina modified with La\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2} and MgO [7,9]. In addition, for some applications the higher overall loading of metal oxides in the catalysts makes them more tolerant to poisons than noble metals.

The deposition of a La\textsubscript{2}O\textsubscript{3} modified Mn–Al–O catalyst on the surface of reticulated foam materials allows to obtain new and thermally more stable and efficient catalysts [9–11]. These catalysts outperform the known Pt/Al\textsubscript{2}O\textsubscript{3} and La–Co–Al–O-containing catalysts [10] deposited in the same way on reticulated foam materials and exhibit higher thermal stability. The modified Mn–Al–O catalyst supported on the surface of highly porous reticulated foam materials may be used for automotive exhaust gas purification [10] and for high temperature oxidation of hydrocarbon fuel [9,11].

Multicomponent catalysts containing noble metals and copper or manganese oxides are known to exhibit a large synergetic effect and thermal stability in the oxidation of hydrocarbons [1,4,12,14–17], CO [13,16,17], and N-containing hydrocarbons [4]. So, partial or complete substitution of noble metals Pt, Pd

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and Rh for transition metal oxides is one of the promising ways for the development of less expensive catalysts for diesel emission control.

The present work is directed to the development of a monolithic catalyst with low content of noble metals for neutralization of diesel engine exhaust gases, with high activity in low temperature oxidation of light and heavy hydrocarbons, and high thermal stability. The influence of the concentrations of both manganese oxide (0–10 wt%) and noble metals Pt and Pd (0–1.0 wt%), and calcination temperature on the catalytic activity in a model reaction of methane oxidation have been studied. BET, X-ray diffraction (XRD), X-ray microanalysis, and small angle X-ray scattering (SAXS) have also been used for catalysts characterization and understanding of the beneficial effect of the addition of manganese oxide.

2. Experimental

Two types of catalysts have been prepared for further study: (1) MnO$_x$ supported on cordierite monolith washcoated with γ-Al$_2$O$_3$. Both catalysts were treated at 500 or 900 °C and then modified with Pt or Pd.

Granulated alumina was prepared by hydrocarbon-ammonia moulding from pseudoboehmite aluminum hydroxide resulting from the thermal decomposition of gibbsite in a catalytic heat generator [18]. After calcination at 550 °C the granulated alumina contained 85–90% of γ-Al$_2$O$_3$ and 10–15% of χ-Al$_2$O$_3$. The specific surface area of alumina was 170 m$^2$/g and the total pore volume was 0.5 cm$^3$/g.

The washcoated monolithic supports were synthesized via immersion of cordierite monoliths (Corning, cell density of 400 cpsl) in a slurry, containing 80% of γ-Al$_2$O$_3$ powder and 20% of a binding agent (calculated for Al$_2$O$_3$) made from aluminum hydroxide with pseudoboehmite structure. The excess slurry was removed by blowing air through the channels. Several dips followed by drying at 110 °C were needed to obtain a washcoat loading of approximately 15 wt% of the total support weight. Finally, the cordierite monolith washcoated with γ-Al$_2$O$_3$ was calcined at 500 °C.

The manganese oxides were introduced by wet impregnation of the granulated γ-Al$_2$O$_3$ or the γ-Al$_2$O$_3$ washcoated cordierite monolith with a manganese nitrate solution followed by drying at 110 °C. Both catalysts were calcined at 500 and 900 °C for 4 h. The manganese loading was 5 or 10 wt% as MnO$_2$ of alumina weight.

The Pt or Pd was introduced by wet impregnation of both catalyst types, preliminary calcined at 500 and 900 °C, with a chloroplatinic acid or chloropalladic acid solution, drying at 110 °C and calcining at 500 °C. The noble metal loading was ranged from 0.1 to 0.5 wt% for granulated catalysts and from 0.25 to 1.0 wt% for the washcoat, counted as Al$_2$O$_3$.

To investigate the thermal stability of the catalysts, all unmodified and modified catalysts were calcined at 900 °C for 14 h and at 1200 °C for 4 h.

The catalytic activity of fresh and thermally treated catalysts was studied in the reaction of methane oxidation using a flow reactor in the temperature range 200–700 °C at a space velocity 1000 h$^{-1}$. The methane concentration in the initial gas mixture was 1 vol% in air. For testing 0.5 g of the granulated catalyst or 1 cm$^3$ of the monolith catalyst was used. The catalytic activity was characterized by the temperature of 50% methane conversion ($T_{50\%}$).

The monolithic catalysts were subjected to DIESEL tests at the Electrochemical Plant (Novouralsk, Russia). The space velocity was 50 000 h$^{-1}$, the temperature was 400 °C, and the gas mixture contained: 14.5 vol% O$_2$, 300 ppm NO, 1900 ppm CO, 200 ppm C$_2$H$_6$, 300 ppm C$_3$H$_6$, 2500 ppm CO$_2$, 2.5 vol% H$_2$O, nitrogen being the balance. Tests were performed on three replicate samples of the monolithic catalyst 25 mm in diameter and 75 mm in length. The alumina washcoat contained 5 wt% MnO$_2$ doped with 0.5 wt% Pd. The catalytic activity was characterized by an average value (for three replicate samples) of the temperature at which 50% conversion of hydrocarbons (HC) and carbon monoxide CO was obtained and by an average value (for three replicate samples) of HC, CO, and NO conversion at 400°C. Three samples were aged at 800 °C for 7 h in dry air and examined in DIESEL tests at similar conditions.

XRD was performed using a HZG-4 diffractometer supplied with Cu K$_\alpha$ radiation. The observed diffraction patterns were identified using the JCPDS-data base [19]. The distribution of the main active components (Mn, Pt) on the catalyst surface was studied using a MAP-3 microanalyzer. K$_x$Al, K$_x$Mn, K$_x$Pt lines were analyzed.

3. Results and discussion

The effect of the alumina modification (γ- γ + χ-Al$_2$O$_3$) on the catalytic performance of pure MnO$_x$/Al$_2$O$_3$ catalysts has been discussed previously [9,11]. The phase composition of the used alumina support has practically no effect on the catalytic activity of manganese catalysts calcined at 900 °C. The phase composition of the support has significantly affected the catalytic activity of the above catalysts when the calcination temperature was sufficiently high (1100 and 1300 °C) [9]. The local catalyst overheating can only reach 800–900 °C at diesel engine operation. So, all studied alumina modifications are usable for the preparation of a multicomponent catalyst.

Table I presents data on the activity of granulated MnO$_x$/Al$_2$O$_3$ catalysts, unmodified and modified by...