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Low-temperature SCR of NO_x with NH_3 over carbon–ceramic cellular monolith-supported manganese oxides

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Abstract

This work describes the development and use of carbon–ceramic cellular monoliths as catalyst supports for the low-temperature selective catalytic reduction (SCR) of NO_x with ammonia. Manganese oxide was selected as catalyst and deposited over the support, which was obtained by coating the cellular ceramics with a polymeric film. The coated material was cured, carbonised and activated prior to impregnation of the active phase. The produced catalysts showed a good NO_x reduction (in the range 34–73%) at 150°C for a space velocity of $\sim 4000\,h^{-1}$. Gasification of the support was negligible at the mentioned conditions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: NO_x reduction; SCR catalyst; Manganese oxide; Carbon–ceramic; Monolith

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1. Introduction

Carbon–ceramic cellular materials consist of a monolithic structure with a carbon layer coating the ceramic support. These materials combine the properties of ceramics, such as high mechanical strength and low pressure drop, with those of carbonaceous materials (i.e. adjustable surface properties). These materials are also more abrasion resistant than the non-coated material, with a high axial crushing strength, a lower pressure drop in the system and a high textural development. Consequently, carbon–ceramic monoliths are materials with wide possibilities of application.

The carbon–ceramic monoliths have been studied for their application in adsorption [1] and catalysis [2]. They have also been investigated for methane storage [3], VOCs' adsorption [4], as catalyst supports [5] and as electrocatalysts [6]. In our lab, a procedure to prepare microporous carbon–ceramic cellular monoliths has recently been developed [7].

The selective catalytic reduction (SCR) of NO_x with NH_3 is a well-proven technique for the removal of NO_x from stationary sources [8]. A number of catalysts have been developed in which the active phases are different metallic oxides. Manganese oxides have been employed by several authors [9–12] for the low-temperature (100–300°C) SCR of NO_x with good results. The objective of this work is to prepare catalysts consisting of manganese oxides deposited on carbon–ceramic monolithic supports and to analyse the effect of the support surface properties on the catalytic performance of the resulting materials for the low temperature reduction of NO_x.

2. Experimental

Support. Cordierite monolithic supports by Corning (Celcor®), with 31 channels cm^{-2}, were dip-coated in a phenolic novolac resin supplied by Fers Resins

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S.A. After the contact, the excess of solution was drained by rotating the coated support at high speed. Dip-coated monoliths were cured at 150°C in air at atmospheric pressure and subsequently carbonised (N_2, 700°C). In order to increase the carbon content of the monoliths, successive coating, curing and carbonising cycles were performed. The material obtained has a 14 wt.% carbon, a micropore volume of $0.32\,\mathrm{cm^3\,g^{-1}}$ C and a S_{BET} of $427\,\mathrm{m^2\,g^{-1}}$ C. Carbonised monoliths were activated by gasification with a steam/nitrogen gas mixture (25%, w/w) at 700°C. Activated monoliths were oxidised with nitric acid (40 wt.%) at 90°C for times between 1 and 4 h.

Catalyst. The oxidised coated supports were generally Na-exchanged with a 0.05 M NaOH solution for 20 h prior to equilibrium adsorption impregnation. For this, an aqueous solution of manganese(II) acetate tetrahydrate supplied by Prolabo was used. The carbon–ceramic monoliths were maintained in a 0.068 M solution during 24 h, then thoroughly washed with deionised water and finally dried at 120°C for 1 h. In order to produce the manganese oxides on the catalyst surface, the catalyst was heated (400°C) under inert atmosphere for 1 h.

Characterisation. A scanning electron microscope (SEM, Zeiss, DSM 942) was used to obtain qualitative information on manganese distribution on the monolith. CO_2 adsorption experiments at 20°C were performed in a thermogravimetric analyser (C.I. Electronics). Analysis of CO_2 adsorption data was carried out by means of the Dubinin–Raduskevich equation. N_2 adsorption was performed at −196°C to obtain the BET surface area. Axial crushing strength tests were conducted over both ceramic substrates and carbon–ceramic monoliths using an electromechanical Instrom analyser by applying a constant load rate of $299\,\mathrm{N\,min^{-1}}$ (ASTM C-133-97 for insulating materials). An atomic absorption spectrometer (AAS, IL Video 12) was used to obtain the manganese content in the catalyst. The surface acidity of the oxidised support was measured by titration. An Orion pH electrode was used for determining the equivalence point.

Catalytic activity tests. The catalytic activity tests were conducted under isothermal conditions at temperatures between 100 and 300°C. In each test, a cellular catalyst containing ∼300 mg of carbon was placed in a quartz reactor heated by a vertical Carbolite furnace. Before each experiment, the sample was dried in He at 200°C for around 10 min. During the experiments, the gas flow rate was fixed at $300\,\mathrm{cm^3\,min^{-1}}$, which corresponds to space velocities (GHSV) in the range $3500–4500\,\mathrm{h^{-1}}$. The inlet gas was a mixture which was set by mass flow controllers to be 700 ppm NO, 800 ppm NH_3, 3 vol.% O_2 and He to balance, although due to dilution effects, the inlet NO concentration varied between 610 and 650 ppm. The NO/NO_2 concentration of the inlet and outlet gases was analysed by means of a chemiluminiscence analyser (Rosemount Analytical, Model 951A), whereas the CO_2 and N_2O concentration in the outlet gases was measured with a gas chromatographer (HP 6890 Series).

The directly measured NO_x reduction degree (conversion) was evaluated as $X = 1-C^{\mathrm{r}}_{\mathrm{NO}_x}/C^{0}_{\mathrm{NO}_x}$, where $C^{\mathrm{r}}_{\mathrm{NO}_x}$ is the outlet NO_x concentration during reaction at the steady state and $C^{0}_{\mathrm{NO}_x}$ the NO_x concentration in the inlet gas mixture. A normalised volume conversion (X_{v}), referred to a fixed space velocity of $3750\,\mathrm{h^{-1}}$, which averages those used in all the experiments, and to a fixed inlet NO_x concentration of 700 ppm, was determined as: $\ln(1-X_{\mathrm{v}}) = [700\times 4.8/(C^{0}_{\mathrm{NO}_x}V)]\ln(1-X)$, where V is the true volume of the monolith. Parameter X_{v} permits a better comparison of catalytic performance among the prepared materials.

A kinetic rate constant for the reaction rate related to the monolith volume, k_{v} [$\mathrm{mol(cm^3\,s\,Pa)^{-1}}$], was calculated assuming integral type reactor and first order dependence in NO partial pressure, by using the following equation: $k_{\mathrm{v}} = -F_{\mathrm{NO}}/(Vp^{0}_{\mathrm{NO}})\ln(1-X)$. Selectivity of the desired reaction was calculated as the ratio of N_2O production to NO_x removal, $S = 1 - C_{\mathrm{N_2O}}/(XC^{0}_{\mathrm{NO}_x})$, where $C_{\mathrm{N_2O}}$ is the outlet N_2O concentration. Gasification of the catalyst was expressed in terms of a gasification rate k_{g} estimated by the CO_2 concentration in the outlet gas ($C_{\mathrm{CO_2}}$, ppm) during the SCR of NO_x. This constant was calculated as $k_{\mathrm{g}}\,(\mathrm{mg\,mg^{-1}\,s^{-1}}) = (\mathrm{d}w/\mathrm{d}t)/w_0 = 8.185\times 10^{-12}(C_{\mathrm{CO_2}}F/w_0)$, where F is the total gas flow rate ($\mathrm{cm^3\,min^{-1}}$) and w_0 the carbon mass of the catalyst.

3. Results and discussion

The method developed for the preparation of manganese oxide–carbon–ceramic monoliths provides a uniform carbon distribution over the monoliths [7].

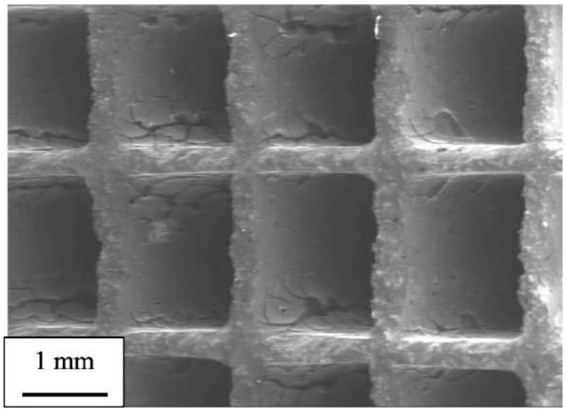

Fig. 1. SEM image of a carbon–ceramic cellular monolith (14 wt.% of carbon).

The procedure considers the removal of impregnating solution excess by fast spinning (5000 rpm), and the adjustment of the concentration and viscosity of the polymeric solution and impregnation temperature to values that ensure a high infiltration of the solution into the ceramic substrate. A SEM microphotograph of the monolith obtained by this method is shown in Fig. 1. In this figure, no carbon accumulation on the corners of the cells is observed. The impregnated monoliths have enhanced mechanical strength (16 MPa) as compared to that of the original substrate (10 MPa).

The qualitative manganese distribution of a catalyst was examined by SEM–EDX inspection. In Fig. 2, a SEM microphotograph of a manganese impregnated carbon–ceramic monolith and a Mn mapping view obtained by EDX are displayed. Mn (white points in Fig. 2b) was found to be associated only to the carbon substrate (dark grey areas in Fig. 2a).

The effect of textural development on the catalytic performance was studied from carbon–ceramic monoliths with different activation degrees (*burnoff*). Catalytic activity tests were conducted over impregnated monoliths with burnoff degrees between 0 and 40 wt.%. The conversion degrees achieved with these materials are shown in Table 1 together with the values of micropore volume and manganese loading.

As a consequence of activation, a porosity enlargement of the carbonaceous support (W, refer to footnote ‘a’ of Table 1) takes place. A comparison of micropore volumes for the non-oxidised, oxidised and impregnated materials shows that this parameter is not affected by impregnation until a burnoff degree of 40 wt.%. Nevertheless, the increase in manganese content with activation degree between 0 and 20 wt.% could be due to an increase in pore volume associated to larger pores (>2 nm). The catalytic activity (X_v, k_v) of monoliths increases with the activation degree from $X_\mathrm{v} = 0.34$ (0 wt.% burnoff) up to $X_\mathrm{v} = 0.73$ (40 wt.% burnoff). Moreover, the selectivity hardly changes with burnoff. The increment of the catalytic activity with burnoff is a direct consequence of the increase in Mn loading.

The non-activated support has a weak acidic character (0.36 meq g^{-1} C). The acidity is improved by oxidation with concentrated HNO_3 at 90°C for times between 1 and 4 h. The values of acidity of the oxidised materials are shown in Table 2. The

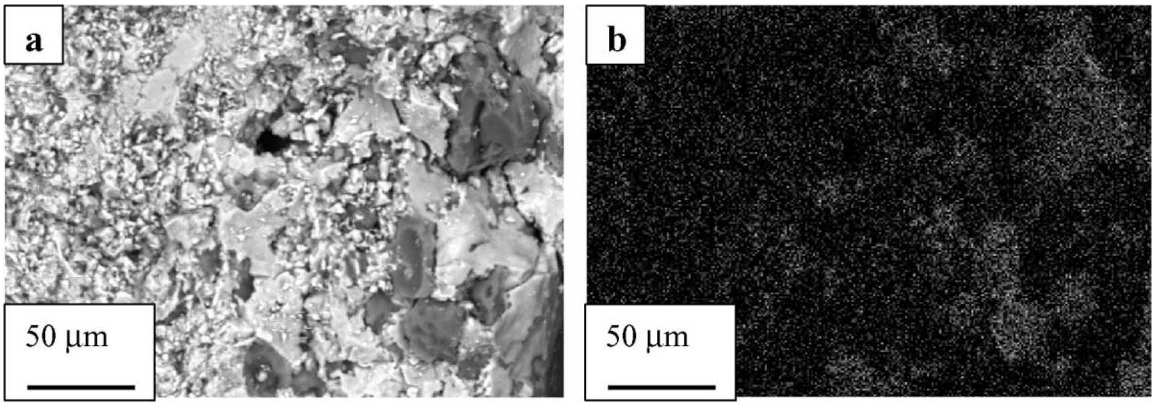

Fig. 2. SEM image of a manganese impregnated carbon–ceramic monolith: (a) SEM image; (b) Mn mapping of the same view.

Table 1
Effect of burnoff degree over textural development, Mn loading and catalytic activity at 150°C (14 wt.% C, HNO_3 90°C, 1 h)

Burnoff (wt.%)	Micropore volume ($cm^3\,g^{-1}$ C)			Mn (wt.%) (g Mn/100 g C)	X_v	S	k_v ($\times 10^{-11}$)
	W^a	W^b	W^c				
0	0.32	–	0.31	2.2	0.34	–	17
10	0.41	–	0.34	2.1	0.55	0.96	33
20	0.44	0.37	0.40	4.0	0.63	0.97	40
40	0.47	0.45	0.27	5.3	0.73	0.92	42

[a] Micropore volume of non-oxidised materials.
[b] Micropore volume of oxidised materials.
[c] Micropore volume of manganese impregnated materials.

Table 2
Effect of oxidation over Mn loading and catalytic activity at 150°C

Burnoff (wt.%)	Oxidation time (h)	Acidity (meq/g C)	Mn (wt.%)	X_v	S	k_v ($\times 10^{-11}$)
20	0	0.36	1.0	0.05	0.85	2.2
	1	2.33	4.0	0.63	0.97	40
	4	4.14	8.2	0.63	0.93	42
40	1	1.75	4.7	0.63	0.92	42
	4	3.99	7.5	0.73	0.88	59

non-oxidised sample hardly shows catalytic activity ($X_V = 0.05$). Moreover, there is a clear correlation between acidity and Mn loading. For oxidation times longer than 1 h, the conversion hardly changes. Oxidation creates new functional groups for anchoring and dispersing manganese cations from solution. The increase in oxidation time produces a small decrease in selectivity. The selectivity is also lower for monoliths activated at 40 wt.% than for those activated at 20 wt.%. Nevertheless, the values of selectivity are always high, over 0.85.

The effect of reaction temperature on catalytic activity was evaluated for a non-impregnated carbon–ceramic monolith (14 wt.% C, burnoff: 20 wt.%) and for a carbon–ceramic monolith (14 wt.% C, burnoff: 20 wt.%) oxidised for 1 h, treated with NaOH for 20 h and impregnated with manganese acetate for 24 h. The results of these experiments are shown in Table 3. As observed, both materials show different trends. For the non-impregnated material, conversion drops as temperature increases whereas for the impregnated material, conversion increases with temperature.

The NO_x conversion mechanism for non-impregnated materials at low temperatures involves physical adsorption of NO on the carbon surface [13]. Increasing temperature provokes a decrease in physical adsorption and consequently a decrease in NO_x removal. At temperatures over 200°C, NO chemisorption on

Table 3
Effect of temperature on catalytic activity of non-impregnated and impregnated monoliths (burnoff: 20%)

Temperature (°C)	Without Mn				With Mn (4 wt.%)			
	X_v	S	k_g ($\times 10^{-8}$)	k_v ($\times 10^{-11}$)	X_v	S	k_g ($\times 10^{-7}$)	k_v ($\times 10^{-11}$)
100	0.162	1.00	<1	7.4	0.53	0.99	2	32
150	0.071	0.98	4	3.1	0.76	0.79	7	61
200	0.035	0.90	8	1.5	0.85	0.48	80	81
300	0.044	0.64	60	1.9	0.88	0.48	5000	87

the surface provokes a small increase in NO_x removal. Addition of the metal oxide causes an important increase in catalytic activity, which is enhanced by temperature, which corresponds to an activated process. From these results, the apparent activation energies for both carbon-catalysed and metal-catalysed processes were obtained. For the non-impregnated monolith the activation energy is $-23\,kJ\,mol^{-1}$, whereas for the impregnated monolith, it is $14\,kJ\,mol^{-1}$. Its value is similar to that obtained by Kapteijn et al. [14]. Selectivity decreases with temperature in both cases from 1 at 100°C to 0.64 at 300°C for the non-impregnated monolith and from 0.99 at 100°C to 0.48 at 300°C for the impregnated monolith. For the impregnated monolith, there is a clear change in the slope of $\ln(k_v)$ vs. $1/T$ at $T > 200°C$, which is probably related to the existence of diffusion restrictions.

The gasification rate of both non-impregnated and impregnated monoliths increases with temperature. Impregnated and non-impregnated monoliths show low gasification rates at temperatures below 150°C. In this temperature range, the support gasification is negligible. The presence of manganese considerably enhances the gasification rate of the carbonaceous support at temperatures above 200°C. This evidences the limitations of these materials as catalyst supports for their use in oxidising environments at temperatures over 200°C.

In principle, the adsorption equilibrium impregnation is going to be affected by the ionic exchange properties of the support surface. In order to assess the performance towards impregnation of other ionic exchange centres, the protonated acid groups of the oxidised support were previously exchanged with Na^+ by impregnation with a NaOH solution (0.05 M). This permits to compare the ionic exchange power of the Na-surface with that of the H-surface for the subsequent impregnation with Mn^{2+}. The results obtained are included in Table 4.

Table 4
Effect of NaOH exchange on catalytic activity ($T = 150°C$) and Mn loading

Burnoff (oxidation time)	No NaOH exchange		NaOH exchange	
	X_v	Mn (wt.%)	X_v	Mn (wt.%)
20 wt.% (2 h)	0.51	2.2	0.59	3.1
40 wt.% (4 h)	0.49	6.4	0.73	7.5

As observed, the previous Na-exchange of the acidic surface provokes an increase in catalytic activity due to the increase in the manganese content of the monolith. The conversion achieved by the catalyst with a burnoff degree of 40 wt.% increases from 0.49 to 0.73 due to the increase from 6.4 to 7.5 wt.% in manganese loading.

A comparison between the catalysts prepared in this work and other Mn SCR catalysts supported on carbon materials can be given in terms of the apparent rate constant on carbon mass basis, k_m. Thus, the rate constant measured at 150°C for the most active catalyst prepared in this work (Table 4, *burnoff* = 40 wt.%) was $k_m = 10.5 \times 10^{-9}\,mol\,NO\,g^{-1}\,C\,s^{-1}\,Pa^{-1}$. These results are comparable to those for other Mn–carbon catalysts reported in literature: (a) $k_m = 16.7 \times 10^{-9}\,mol\,NO\,g^{-1}\,C\,s^{-1}\,Pa^{-1}$ for a carbon supported catalyst with 15.5% Mn [13] and (b) $k_m = 3.0 \times 10^{-9}\,mol\,NO\,g^{-1}\,C\,s^{-1}\,Pa^{-1}$ for Mn-supported activated carbon fibres with 10.0 wt.% Mn [12].

4. Conclusions

A new type of low-temperature SCR catalyst in monolithic shape is presented. It consists of manganese oxides supported over a carbon–ceramic cellular monolith. The catalyst developed shows a good catalytic activity for the reduction of NO_x with NH_3 at low temperatures (NO_x reduction of around 60–70% at 150°C and space velocities of $\sim 4000\,h^{-1}$). Increasing temperatures provoke an increase in catalytic conversion but a loss in selectivity takes place. The existence of diffusion restrictions was confirmed for $T > 200°C$.

Support activation produces an increase in the micropore volume and in the manganese loading that enhances NO_x reduction. Oxidation of the support permits to obtain an acidic carbon surface that enhances Mn loading during impregnation and, therefore, improves the catalytic activity of the impregnated material. Previous Na^+-exchange of the oxidised support produces a further increment in catalytic activity.

The best catalytic results are obtained by using carbon–ceramic monolith as a catalyst support with a burnoff degree of 40 wt.%, oxidised with nitric acid (90°C) for 4 h and Na-exchanged prior to impregnation (NO_x reduction: 73% at 150°C and $4000\,h^{-1}$).

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