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Wire-mesh honeycomb catalyst for selective catalytic reduction of NO_x under lean-burn conditions

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ABSTRACT

The selective catalytic reduction of NO_x by propene under lean-burn conditions was investigated over Pd/$Ce_{0.66}Zr_{0.34}O_2/TiO_2/Al_2O_3$ catalysts supported on wire-mesh honeycomb and was compared with pellet catalysts and ceramic monolithic catalysts. The wire-mesh honeycomb possessed high geometric surface area (GSA) of 43.0 in.^{2} in.$^{-3}$ and large open frontal area (OFA) of 86.6%. The wire-mesh honeycomb catalyst exhibited high NO_x conversion at lower temperatures and could be stabilized in shorter time after temperature elevation than that of ceramic monolithic catalyst in the unsteady-state experiment. The wire-mesh honeycomb catalyst also exhibited characteristics of fast light-off.

1. Introduction

Selective catalytic reduction of NO_x by hydrocarbon (HC-SCR) is a promising method to control emission from lean-burn engines. This technology uses unburned hydrocarbons present in the engine exhaust as reductants, which does not need to supply the storage or transportation devices. So, extensive investigations performed on this issue and a large number of catalysts had been evaluated in HC-SCR [1–5]. However, most of researches were made by testing the catalysts deposited over powders or pellets, which could not meet the demand of the practical application. The popular design for the automotive exhaust catalysts is the monolith catalysts now. A monolith has a honeycomb structure with parallel and usually straight channels or cells, and the catalysts are dispersed on the channel's wall. Compared with packed-bed reactors loaded with pellet catalysts, the monolith has the low pressure-drop (up to two orders of magnitude) [6]. Ceramic monoliths are the common monolith substrate which had been one of the most significant and promising developments in the fields of heterogeneous catalysis and chemical engineering, especially in environmental protection. However, there are some disadvantages in honeycomb reactors, such as the absence of radial mixing [7], the low interphase mass- and heat-transfer rate [8,9].

In recent years, metal wire had received much interest as catalytic carriers [10]. Wire-mesh catalysts combined the excellent mass- and heat-transfer characteristics of pellets catalysts with a relatively low pressure-drop of monolith, which was mainly attributed to the high porosity of the wire-mesh structure [8,11]. Ahlström-Silversand and Odenbrand compared the performances of wire-mesh, monolith and pellet catalysts and found that wire-mesh catalysts showed high mass- and heat-transfer numbers, moderate pressure-drop, insignificant effects of pore diffusion and axial dispersion [8,12]. Nevertheless, little attention has been paid to the configuration of wire-mesh catalysts.

Wire-mesh honeycomb was manufactured by stacking alternatively corrugated and plain wire-mesh sheets, which combined the characteristics of wire-mesh catalyst and the monolith. This structure not only enhanced the external mass-transfer rate and gave a more uniform distribution of fluids across the entire bed diameter, which offered better efficiencies of gas–solid containing, but also was easily installed. Furthermore, wire-mesh honeycomb, like other metallic monoliths, had high thermal conductivity and mechanical strength, which had been applied in catalytic oxidation of 1,2-dichlorobenzene [13], ethyl acetate [14,15] and volatile organic compounds in air [11]. However, there were few literatures on using wire-mesh honeycomb as catalytic substrate for selective catalytic reduction of NO_x under lean-burn conditions.

Supported precious metal catalysts had received much interest in the SCR of NO_x due to the high catalytic activity at low temperature and excellent stability [16,17]. In this paper, the Pd/

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$Ce_{0.66}Zr_{0.34}O_2/TiO_2/Al_2O_3$ wire-mesh honeycomb catalyst was prepared using sol–gel and impregnation method, and the selective catalytic reduction of NO_x by propene under lean-burn conditions was evaluated. The catalytic activities of different catalysts, ceramic monolith catalysts and pellets catalysts, were also investigated and compared experimentally.

2. Experimental

2.1. Preparation of alumina washcoat over wire-meshes and ceramic monolith

Because the surface areas of metal wire were very low and the catalysts could not be dispersed directly, it was necessary to deposit the ceramic oxide washcoat with a high surface area over the wire-mesh substrate. Electrophoretic deposition (EPD) method had been employed to deposit alumina washcoat on the wire-mesh substrates. The alumina suspension was prepared with γ-alumina (γ-Al_2O_3) powders gritted from γ-alumina pellets (Shanghai Chemical Laboratory). Polyscylic acid and aluminum isopropoxide were used as additives.

Alumina-coated plain sheets and corrugated sheets (3.5 cm × 2.0 cm in size) were adopted for the formation of the wire-mesh honeycomb. The two types of sheets were shacked alternately to prepare the wire-mesh honeycomb having a cuboid shape with a size of 3.5 cm × 3.5 cm × 2.0 cm.

For the comparison of catalytic activity, the two ceramic monolith catalysts were prepared. The two ceramic monoliths made of cordierite had different channels structure and cell density: one with 50 cpsi had channels of square crosssection and another with 400 cpsi had triangle channels. The cordierite monoliths with the size of 3.5 cm × 3.5 cm and length of 2.0 cm were cleaned with 1.6 mol L^{-1} oxalic acid. The slurry of alumina washcoat consisted of 20.0 g alumina in 100 mL of water and pH of slurry was adjusted to 3–4. The washcoating was carried out by immersing the cordierite monoliths in this slurry for 5 min, and then the samples were dried at 110 °C for 5 h. This procedure was repeated in order to increase the amount of washcoat. Finally, the ceramic monoliths were calcined at 500 °C for 3 h.

2.2. Preparation of different catalysts

The $Pd/Ce_{0.66}Zr_{0.34}O_2/TiO_2/Al_2O_3$ catalysts over different catalytic substrates were prepared. Firstly, the TiO_2 coat was prepared by sol–gel method. The Al_2O_3-coated wire-mesh honeycomb, ceramic monoliths and alumina pellets were impregnated in titania sol which was prepared by hydrolysis of tetra-*n*-butyl titanate [$Ti(OC_4H_9)_4$] (Shanghai Reagent Company), and then the impregnated samples were dried at 110 °C for 3 h and calcined at 500 °C for 2 h in air. Subsequently, the $Ce_{0.66}Zr_{0.34}O_2$ washcoat was introduced by sol–gel method. Polyethylene glycol and citric acid (Guangzhou Reagent Company) were added into the mixture of $Ce(NO_3)_3{\bullet}6H_2O$ and $Zr(NO_3)_4{\bullet}5H_2O$ (Shanghai Reagent Company) at 80 °C under vigorous stirring to prepare the CeZr sol with a mole Ce/Zr ratio of 2/1. The samples were dried at 110 °C for 3 h and calcined at 500 °C for 2 h in air. $Pd/Ce_{0.66}Zr_{0.34}O_2/TiO_2/Al_2O_3$ catalysts were obtained by impregnation with an aqueous solution of $PdCl_2$ (99%, Shenyang Reagent Company), and the Pd loading was determined by atomic absorption spectrometer (AAS) with graphite furnace (AAnalyst 700, PerkinElmer). The catalysts were then dried at 110 °C for 12 h and calcined at 500 °C for 2 h in air. These catalysts were not reduced before the catalytic activity test.

In the case of pellet catalysts, the catalysts were loaded into a reactor made of stainless steel mesh with the size of 3.5 cm × 3.5 cm × 2.0 cm also.

2.3. Catalytic activity

Catalyst performance was evaluated under steady-state conditions using a square-shape reactor (4.0 cm × 4.0 cm in width) made of stainless steel with a total bead length of 100 cm. The catalysts were placed inside the reactor at a distance of 10 cm from the top. The temperature was controlled with a temperature controller. The reactant gases flowed into the reactor and the activity measurements were performed in the temperature range from room temperature to 260 °C. Typically, the composition of the reactant gas was 2000 ppm NO, 2000 ppm C_3H_6 and 6% O_2 in N_2. The total flow rate was 100 L h^{-1} which corresponded an hour space velocity (GHSV) of 4325 h^{-1}. NO and propylene (purity 99%) used for the experiments were provided by Guangming Research and Design Institute of Chemical Industry, Dalian. Before the selective catalytic reduction of NO_x, the catalysts had been exposed to the reactant gas for 2 h in order to eliminate the influence of the adsorption on the catalysts and in the pipe-lines.

The inlet and outlet gases were analyzed with a gas chromatograph (Shimadzu GC-14C) equipped with a switched dual columns system and with two columns (Porapak Q, for the separation of CO_2, N_2O, H_2O and C_3H_6, and Molecular Sieve 5A for O_2, N_2, and CO). The activities were evaluated in terms of NO_x conversion determined according to the following equation:

$$NO_x\ \text{conversion}\ (\%) = \frac{[NO_x]_{\text{inlet}} - [NO_x]_{\text{outlet}}}{[NO_x]_{\text{inlet}}}$$

where $[NO_x]_{\text{inlet}}$ and $[NO_x]_{\text{outlet}}$ were the concentrations of NO_x at the inlet and outlet of the reactor, respectively.

3. Results and discussion

3.1. Characteristics of catalysts

The substrate was an integral part of the catalysts. Its primary function was to bring the active catalyst into maximal effective exposure with the exhaust gases. However, it was interestingly noted that many parameters affecting the performance of a catalytic converter were influenced by the substrate [17]. Cell density, geometric surface area (GSA), open frontal area (OFA), hydraulic diameter (D_h), mechanical integrity factor and bulk heat transfer of the substrate affected both the performance and durability of the catalytic converter.

Wire-mesh honeycomb, cordierite monoliths and pellets catalysts were prepared (Fig. 1), and their characteristics were shown in Table 1. The palladium loadings were kept at the similar value. To facilitate the comparison of wire-mesh honeycomb substrate and cordierite honeycomb substrate, their geometric properties should be first addressed. From Table 1, wire-mesh honeycomb substrate offered 88% higher GSA and 33% greater OFA than ceramic substrate of 50 cell density. Furthermore, GSA of wire-mesh honeycomb was only 25% lower than that of ceramic honeycomb with 400 cpsi. The high GSA of the ideal substrate was necessary in order to obtain the high conversion efficiency under steady-state [18].

The pressure-drop characteristic of monolith was one of the most important factors to take into consideration in most applications. The high OFA and large D_h could help to minimize the backpressure. The wire-mesh honeycomb had a larger D_h of 0.0201 in and a greater OFA of 86.6% than ceramic honeycomb. It was evident that wire-mesh honeycomb had a good pressure-drop

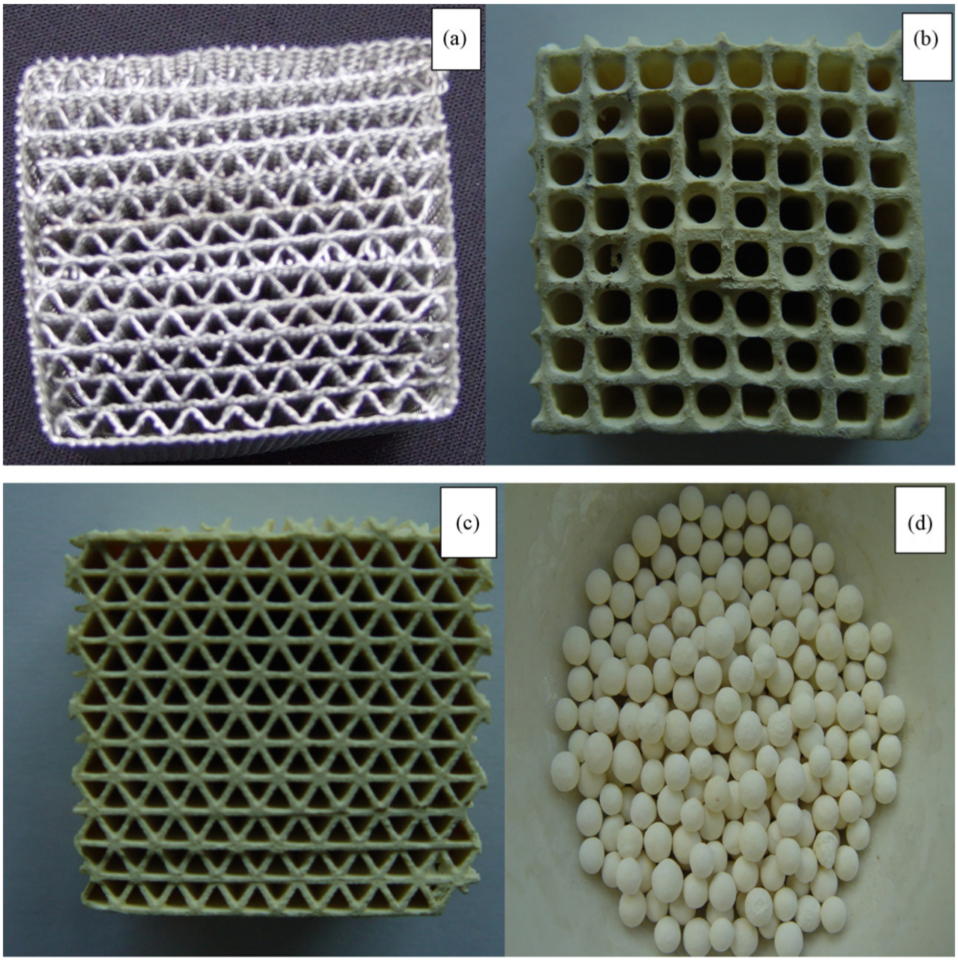

Fig. 1. The photographs of different catalysts: (a) wire-mesh honeycomb catalyst; (b) cordierite monolithic catalyst with square channels (50 cpsi); (c) cordierite monolithic catalyst with triangle channels (400 cpsi); (d) pellet catalysts.

performance. Additionally, the accumulation of alumina washcoat in the corners of the channels could be avoided with the wire-mesh honeycomb substrate, as shown in Fig. 1.

3.2. Selective catalytic reduction of NO_x over different catalysts

In order to test the effect of the wire-mesh honeycomb as the catalytic support, the catalytic activity of selective catalytic reduction of NO_x by propene was compared with those of the other conventional catalysts (ceramic catalysts and pellets catalysts). The Pd loading and the experimental conditions were the same and the results were shown in Fig. 2. From Fig. 2(a), it could be found that wire-mesh honeycomb catalyst exhibited better performance than the other catalysts, giving the maximum of NO_x conversion (74.0%) at 140 °C. The ceramic monolithic catalysts displayed a similar behaviour as the wire-mesh honeycomb catalyst. It was interesting that the high NO_x removal could be observed in the range from room temperature to 80 °C, which could attribute to NO_x adsorption or organo-nitrogen-containing species formation due to the interaction of NO_x with propylene. It needed to be explored in further work. On the other hand, the typical volcano-shape of the NO_x conversion was obtained at higher temperatures (>80 °C) [19]. The pellets catalysts showed the lowest catalytic activity of NO_x in all catalysts. The NO_x conversion increased tardily with increasing temperature and reached the maximum of 46.1% at 200 °C. It was

Table 1
Characterization of different catalysts

	Wire-mesh honeycomb catalyst	Ceramic honeycomb catalysts		Pellets catalysts
Materials	Stainless steel	Cordierite	Cordierite	γ-Al_2O_3
Cell density (cpsi)	60	50	400	–
Cell shape	Sine wave	Square	Triangle	–
GSA ($in.^2\ in.^{-3}$)	43.0	22.8	57.67	–
OFA (%)	86.6	64.9	37.2	–
D_h (in.)	0.0201	0.0285	0.0064	–
Al_2O_3 washcoat (g)	0.3934	0.4820	0.3162	–
TiO_2 washcoat (g)	0.1890	0.2780	0.1839	0.2813
CeZr washcoat (g)	0.0225	0.0329	0.0289	0.0357
Pd (wt.%)	0.23	0.23	0.25	0.26

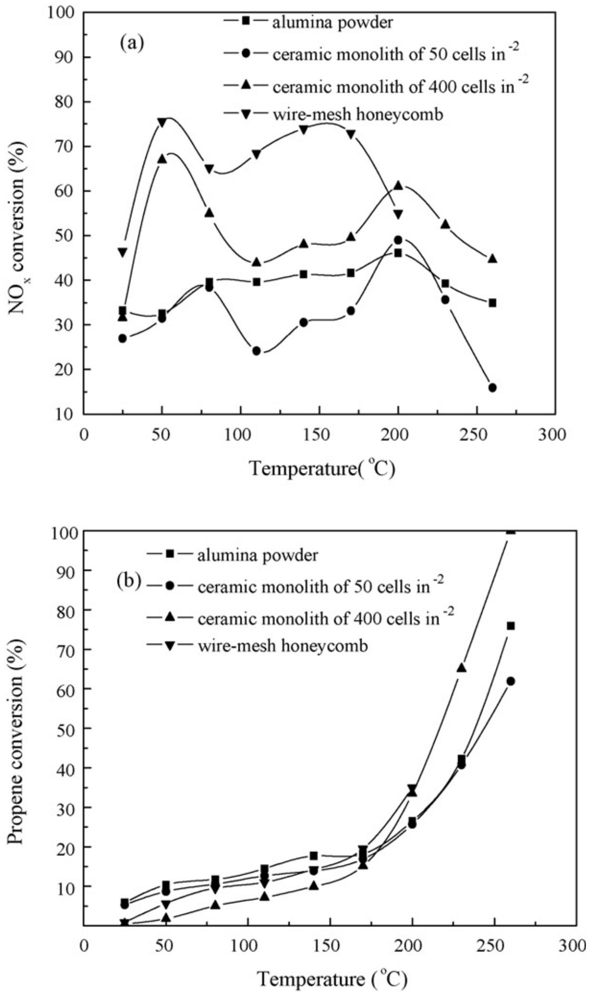

Fig. 2. NO_x conversion as a function of temperature over different catalysts. Reaction gas: 2000 ppm NO_x, 2000 ppm C_3H_6, 6% O_2 and N_2 as balance.

interesting that the temperature corresponding to the maximum of NO_x conversion on wire-mesh honeycomb catalyst was much lower than that on ceramic monolithic catalysts and pellet catalysts. Fig. 2(b) showed that the C_3H_6 conversions over different catalysts were also consistent with the fact that the wire-mesh honeycomb catalyst exhibited the best catalytic activity.

Heck et al. reported that the substrate should have large GSA for high conversion [18]. The wire-mesh honeycomb possessed larger GSA than cordierite monolith with similar cell density, and it exhibited higher NO_x conversion. The cordierite monolith with 400 cpsi had larger GSA of 57.67 $\text{in.}^2\,\text{in.}^{-3}$ than the wire-mesh honeycomb, but it showed the lower NO_x conversion. This could be ascribed to the support material since the metallic substrate could have promotional effect on NO_x conversion at low temperatures. It was also found that N_2O was detected in the outlet flow only when the catalysts were supported on the pellets. The result indicated that the structure of substrate could have some effects on the selectivity of NO_x to N_2 and the selectivity of NO_x was higher with the monolith catalysts. Therefore, the potential advantages of wire-mesh honeycomb substrate were the higher conversion efficiency and selectivity of NO_x to N_2.

3.3. Unsteady-state tests

In order to investigate the characteristics of thermal response of wire-mesh honeycomb catalyst and ceramic monolithic catalyst, the unsteady-stated tests were continuously performed. For each experimental step, temperature was rapidly increased within 5 min and kept this temperature for 60 min. The NO_x concentration at outlet was measured every 10 min and the results were shown in Fig. 3. Clearly, the NO_x conversion over the wire-mesh honeycomb catalyst could be quickly reached the steady-state after 10 min. However, the NO_x conversion over the ceramic monolithic catalyst was slowly changed after temperature elevation and could be stabilized after 30 min.

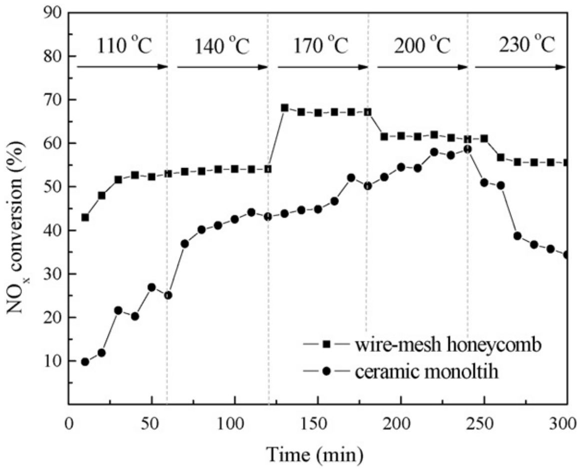

Fig. 3. Thermal response in selective catalytic reduction of NO_x by propene over different catalysts. Reaction gas: 2000 ppm NO_x, 2000 ppm C_3H_6, 6% O_2 and N_2 as balance.

Obviously, the substrate material of honeycomb affected the activity of supported catalysts. It was well-known that high thermal conductivity of the metal substrate provided a radial heat-transfer coefficient in the catalytic bed compared to cordierite at the same condition. The wire-mesh honeycomb was made of stainless steel. So, the catalysts supported on wire-mesh honeycomb could be warmed quickly to reach the same temperature as ambience. On the other hand, the higher thermal response of wire-mesh honeycomb catalyst could be attributed to its especial structure. The wire-mesh honeycomb catalyst had channels whose walls were interconnected with each other through the openings in the wire-mesh sheet. The gases entering the wire-mesh honeycomb catalyst could flow in three-dimensional direction, promoting the axial mixing within channels. Ahlström-Silversand and Odenbrand had reported that the wire-mesh catalyst had a better thermal response than the monolith catalyst due to the combination with the negligible radial temperature gradients [8].

3.4. Light-off tests

It should be noted that roughly 50–80% of total HC emissions are emitted within the first 200 s of the cold start phase due to the long time for the catalyst to reach light-off temperature [20]. While more and more demanding regulations were introduced, minimization of warm-up HC emissions had become a major problem in automotive pollution abatement [21].

An alternative approach for the catalysts applied in cold start was to develop new catalysts presenting the characteristic of fast light-off, such as high activity at low temperature. The experiment of C_3H_6 oxidation was performed over wire-mesh honeycomb, ceramic and pellets catalysts. The composition of the reactant gas was 2000 ppm C_3H_6 and 6% O_2 in N_2 (GHSV of 4325 h^{-1}) and the result was shown in Fig. 4. It was found that C_3H_6 conversion increased with increasing the temperature. At low temperatures (<140 °C), there existed a relatively small difference in the curve

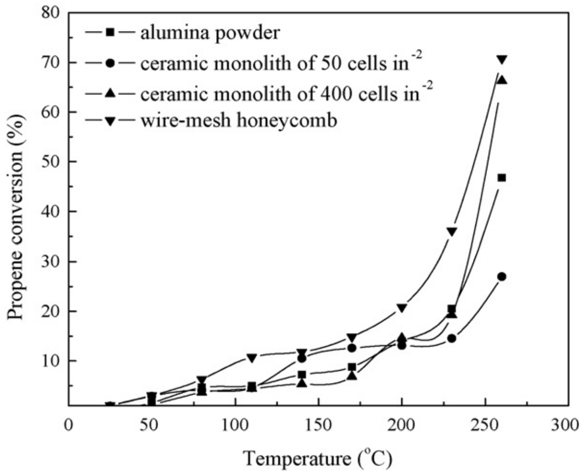

Fig. 4. Propene conversion as a function of temperature over different catalysts. Reaction gas: 2000 ppm C_3H_6, 6% O_2 and N_2 as balance.

pattern among these catalysts and C_3H_6 conversions were below 20.0%. However, these catalysts showed different catalytic activities at higher temperature. The wire-mesh honeycomb catalyst exhibited the highest C_3H_6 conversion, and the ceramic catalyst with 400 cpsi, the pellet catalysts and the ceramic catalyst with 50 cpsi followed orderly, as reported by Ahlström-Silversand and Odenbrand [12]. In order to evaluate catalyst light-off, the light-off temperature was defined as the temperature required for 50% C_3H_6 conversion. It was noted that the light-off temperature over the wire-mesh honeycomb catalyst was around 240 °C and was the lowest among these catalysts.

The location of the light-off point depended on the thermal conductivity of the support [22]. For the high thermal conductivity, the warm-up of metallic support from the cold state was faster than that of ceramic support under the same process conditions. Therefore, the temperature of wire-mesh honeycomb catalyst igniting the homogeneous gas-phase combustion of propene could be lower. Kołodziej and Łojewska proved that the wire gauze structures had higher mass-transfer coefficients than monolith with same cell density [23]. Therefore, the high C_3H_6 conversion of the wire-mesh honeycomb catalyst in the mass-transfer dominated region (high temperature) could be attributed to good mass-transfer characteristics [12].

4. Conclusions

The wire-mesh honeycomb, compared to ceramic monolith with similar cell density, had higher GSA, larger OFA and lower pressure-drop. Its structure could enhance internal mass transfer due to channels interconnected with each other through the openings in the wire-mesh sheet.

This study had been devoted to the evaluation of various catalysts supported different substrates for the selective catalytic reduction of NO_x by propene under lean-burn conditions. Compared with pellet catalysts and ceramic monolithic catalysts, the wire-mesh honeycomb catalyst exhibited higher activity for selective catalytic reduction of NO_x by propene at low temperatures, and NO_x conversion over wire-mesh honeycomb catalyst was quickly stabilized in a short time after temperature elevation in unsteady-state experiment. Therefore, the best utilization of the wire-mesh honeycomb catalyst could be as a start-up catalyst due to the low light-off temperature and the high thermal conductivity.

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