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Experimental study of catalytic CO oxidation over CuO/Al_2O_3 deposited on metal sheets

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ABSTRACT

Novel catalytic coatings excluding noble metals were deposited employing plasma spray technology in order to avoid uneven distribution of the catalyst in the washcoat and instability of substrate. The copper oxide (5–15 wt.%) supported on alumina were coated on metal substrate and multitubular catalytic monolithic reactors (CMR) were manufactured. The morphology and surface performances of washcoat were studied by scanning electron microscopy (SEM), BET surface area and X-ray diffraction (XRD). Results indicated that coatings containing CuO remain stable and keep an excellent adhesion up to 1000 °C, and show a high activity in CO oxidation. The CuO/Al_2O_3 catalyst according to the catalytic properties showed the similar behaviour as coatings containing noble and expensive metals, but the surface area of presented catalytic coatings is noticeably lower.

1. Introduction

Modern catalytic monolithic reactors prepared by chemical impregnation of platinum group metals are expensive and often fail because of the fusion of honeycombs caused by ceramic substrate overheat. A new generation of catalytic converters based on metallic substrate contains much cheaper metal oxides, zeolites and other materials that serve as effective catalysts and slowly replace noble metals [1,2].

Applying plasma spray technology and modifying parameters of plasma process, formation of high-quality coatings with high specific surface area and required porosity as well as desirable elemental surface structure becomes possible. Besides, plasma spray method may suit for the formation of desirably thickness coatings, the washcoat of which well adheres to the substrate.

There is a large amount of data in the worldwide scientific literature describing the results of experimental works on CMR made of noble metals, but there is a lack of date regarding the mass and heat transfer processes that occur during investigation of CMR made of non-noble metal catalysts and the factors that influence the reaction. In particular the results on examination of CMR made employing plasma spray technology are very limited and catalytic properties of such reactors are unstudied in practice. Therefore, the correlation of CO conversion in the gas downstream from CMR, exhaust gas flow rate and temperature, initial pollutant concentration and conversion process duration are described in this study. Coatings were deposited using specific plasma spray installation in order to escape uneven distribution [3] of the catalyst. Disadvantages of the traditional ceramic coatings: instability of substrate and usage of expensive materials, were also similarly avoided.

2. Experimental

2.1. Preparation of catalytic coatings and CMR

We have already reported [4] that the significant increase in CO oxidation observed in the case of the simple, when catalytic coating was prepared from a mixture containing the pure copper. So, this base metal oxide was chosen in order to reach the aim of the further work. Three simples of catalytic coatings 90 μm of total thickness using starting mixture of 5 wt.%, 10 wt.% and 15 wt.% Cu with the rest amount of aluminium hydroxide were formed on both sides of stainless steel foil applying plasma spray technology [5]. Multitubular CMR 30×10^{-3} m of diameter and 90×10^{-3} m of length were manufactured from those coatings (plain and corrugated). Such $0.26\,m^2$ surface CMR consist of 410 small triangle channels (thread is 3×10^{-3} m and height is 0.7×10^{-3} m).

2.2. Measurements of catalytic characters

The prepared CMR samples were characterized before and after the catalytic test by several techniques, such as XRD, SEM and BET. The crystal structure of CuO/Al_2O_3 was investigated by XRD. Diffraction intensities were measured by scanning from 10° to

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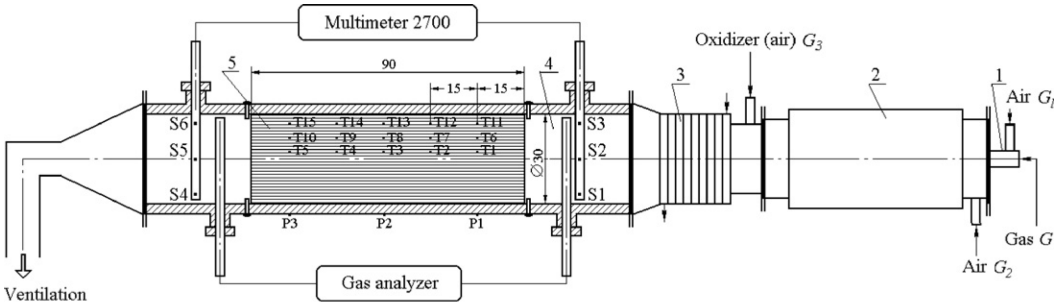

Fig. 1. Scheme of the experimental set-up for the investigation of catalytic coatings' properties: S1–S6, T1–T15, P1–P3 – thermocouples; 1 – burner; 2 – gas combustion chamber; 3 – stabilization section; 4 – catalytic combustion chamber; 5 – CMR.

80° (2θ) with a step size of 0.02° on a DRON-UM1 diffractometer using Cu Kα radiation and a graphite single-crystal monochromator. Crystalline structures were identified using PDF-2 database [6]. The BET surface area of the CMR samples was performed by means of nitrogen sorption isotherms at 77 K using Micromeritics M2100D instrument. The SEM (JEOL JSM 5600) was used to observe the morphology of the washcoat.

2.3. Catalytic activity testing

The activity of catalytic coating as well as mass transfer and thermal processes in CMR was analyzed using constructed specific experimental setup (Fig. 1). All tests were carried out using real combustion products. The temperature was monitored by thermocouples and registered by a data gathering system (Keithley's Multimeter 2700). The flow rate of the feed gas was controlled by mass flow controllers. The concentrations of gases (CO, CO_2, O_2, HC) were continuously measured by a stack gas analyzer (Tecnotest, Multigas 488).

An exhaust gas mixture containing 2%, 3% or 4% CO was passed through the CMR at three different total flow rates – 1 g s^{-1}, 1.5 g s^{-1} and 2 g s^{-1} at standard conditions, and the corresponding space velocity was 50,000 h^{-1}, 75,000 h^{-1} and 100,000 h^{-1}. Experiments were performed at atmospheric pressure and at the exhaust gas inlet temperatures between 70 °C and 450 °C.

3. Results and discussion

3.1. Characterization of catalysts

The SEM views of fresh catalytic coatings confirm that the washcoat is evenly distributed, homogeneous, dense and porous (Fig. 2a). The extreme mechanical treatment showed the excellent CuO/Al_2O_3 adhesion with the substrate; after corrugation of coatings no mechanical violations were noticed. The morphological research of thermal treatment show no substantial changes till 850 °C (Fig. 2b), while at 1000 °C the washcoat became thinner in some places (Fig. 2c), but mass losses does not exceed 10%. After affect in higher temperatures the washcoat agglomerates, anneals and crumbles away (Fig. 2d).

It was determined that the specific surface area of fresh catalytic coating equals about 3 m^2/g and after heat treatment at 560 °C for 1.5 h increased for 8 times. But after the exposition of catalytic coating in the reacting medium at 1000 °C, in the case of

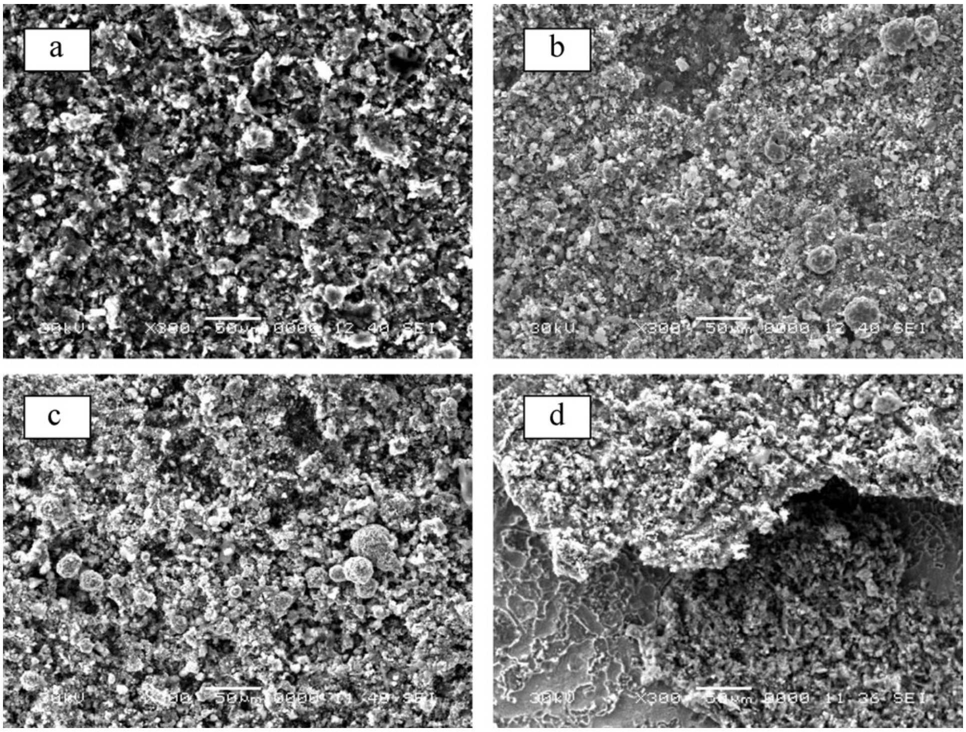

Fig. 2. SEM images of the fresh coated CuO/Al_2O_3 (a) and thermally treated at 850 °C (b), 1000 °C (c) and 1100 °C (d).

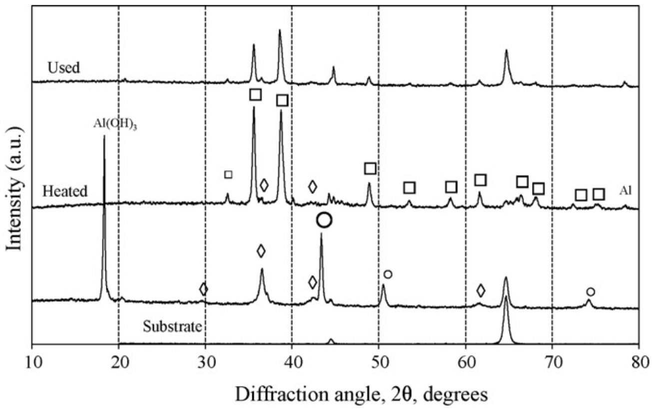

Fig. 3. XRD patterns of the fresh, thermal processed and used coating containing CuO(5 wt.% Cu)/Al_2O_3. ◊ – Cu_2O, ○ – Cu, □ – CuO.

reduction of porosity, mechanical force and thermal hardness the specific surface area reduces for 3 times.

Results on XRD analysis of fresh catalytic coating show the domination of pure copper and Cu_2O (Fig. 3), however, a significant amount of the desired active component CuO appeared after heat treatment. XRD analysis of coatings after CO catalytic combustion about 1000 °C shows that the phase composition did not change, however it is observed simultaneous decrease in the intensity of CuO peaks and increase in the intensity of the peaks of metallic substrate (Fig. 3) because of possible overheating of the CMR during its exploitation under extreme conditions. These changes in the XRD patterns agree well with a clearly seen washcoat crumbling away observed in the SEM views (Fig. 2c and d).

3.2. Activity testing

The highest degree of CO conversion was obtained using catalytic coatings formed of starting mixture containing 5 wt.% Cu without Cr_2O_3 additives. It is known that mechanically more resistant, though 10% less active catalytic coatings are formed using mixtures with chromium oxide. Using presented CMR's CO oxidation starts at 260–280 °C and further intensifies gradually. As compared the CMR containing CuO/Al_2O_3 with the commercial one supported by noble metals, the latter showed the highest CO conversion degree progressing more intensively, however, the light-off temperature differs only slightly.

3.3. Factors impact on CO conversion

It was observed that the light-off temperature of CuO/Al_2O_3 catalyst increases up to 23–16% with increasing the space velocity from 50,000 h^{-1} to 100,000 h^{-1} at the constant amount of CO while the pollutant conversion degree reduces up to 40% (Fig. 4). When CO concentration reduces from 4% to 2% in the feed gas, the light-off point of the catalyst respectively 15–10% moves to the lower temperature region.

While delivering the exhaust gas of 300–400 °C temperature at $G = 1$, 1.5, 2 g s^{-1} the highest CO conversion obtained is 40–70%. According to the research results of gas temperature (t) influence the calculating method is created for determining the conversion degree:

$$\nu_{CO} = 0.0008t - 0.1874, \quad R^2 = 0.7334,$$
$$X = \frac{100F\nu_{CO}}{GC_0},$$

where ν_{CO} is the reaction rate $(g\,(s\,m^2)^{-1})$, X the CO conversion degree (%), F the catalytic surface area (m^2), G the gas flow rate $(g\,s^{-1})$, C_0 is the initial pollutant concentration (%).

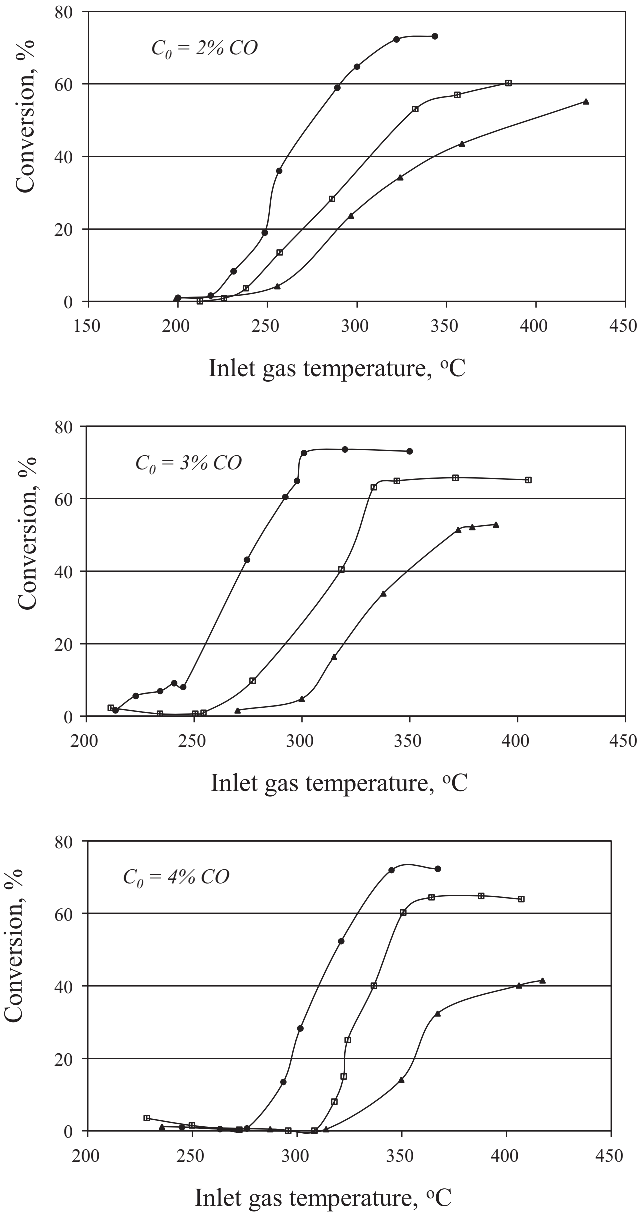

Fig. 4. Catalytic activity of CuO(15 wt.% Cu)/Al_2O_3 at the different space velocity: ● – 50,000 h^{-1}, ■ – 75,000 h^{-1}, ▲ – 100,000 h^{-1}.

It has been found that CO conversion under constant temperature and flow rate of feed gas does not change in the course of time. When the temperature of catalytic system is rising and pollutant concentration in the exhaust gas, independently of flow rate, is increasing from 2% to 4%, the conversion process time reduces by 2.5 times.

While comparing the obtained results with results reported by other authors [2,7–9], very similar peculiarities of pollutant conversion variation were observed. While initial studies were carried out with positive results, the experimental equipment for the CO + NO_x redaction is under construction.

4. Conclusions

CMR manufactured from the catalytic coatings, deposited by plasma spray technology with active component CuO, reduce effectively the amount of CO in the exhaust gas and according to the activity are comparable to the CMR containing noble metals. The washcoat of formed catalytic coatings is homogeneous, dense, porous, and has excellent adhesion with the substrate; the microstructure, mechanical and thermal strength of deposited coatings remain constant at the temperature up to 1000 °C. It was determined that CO conversion, depending on the change of the mentioned factors, varied in agreement with mass transfer and catalytic reactions' kinetics theories.

The investigated 0.26 m^2 surface area CMR operates optimally when the temperature of the feed gas is 320 °C, CO concentration is 3% and space velocity is 75,000 h^{-1}. Unfortunately, CO conversion degree did not exceed 80% in any of the experiments described, but it is possible that the degree of pollutant conversion would increase on increasing the catalytic surface area. Nevertheless, information accumulated on the basis of the obtained research results could be used in creating, designing and calculating CO oxidizing CMR, they can also enlarge database of modelling programs since there is a lack of experimental data on the processes occurring in such sort of CMR.

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