APPLICATION OF ION BEAM PROCESSING TECHNOLOGY IN PRODUCTION OF CATALYSTS

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Abstract: In this paper, the applicability of Ion Beam Processing Technology for making catalysts has been investigated. Ceramic substrates of different shapes and metal fibre tablets were implanted by platinum ions and tested in nitrogen oxides (NO_x) and carbon monoxide (CO) conversion reactions. Effectiveness of the implanted catalysts was compared to that of the commercially produced platinum catalysts made by impregnation. Platinum-implanted catalyst having fifteen times less platinum content showed the same CO conversion efficiency as the commercially produced catalyst. It was revealed that the effectiveness of the platinum-implanted catalyst has complex dependence on the process parameters and the optimum can be achieved by varying the ions energy and the duration of implantation. Investigation of the pore structure showed that ion implantation did not decrease the specific surface area of the catalyst.

Key words: Catalyst, Ion Implantation, Noble metals.

1. INTRODUCTION

Growing concern of the world society over clean environment impels manufacturers to look for new, environmentally-friendly technologies. Catalysts are widely used to clean industrial and automobile exhausts from oxides of nitrogen (NO_x), carbon monoxide (CO) and unburned hydrocarbons (HC).

Catalysts are produced by the well-established impregnation technology[1]. With this technology a ceramic substrate is impregnated by a solution of nitrates of catalytic metals. This step is followed by drying and calcination. The whole cycle is carried out in several steps and takes around 50 hours. High water consumption and emission of NO_x to the atmosphere accompany this process. Other drawbacks of this method have to be accounted for. The properties of the carrier are said to be changed, and in some cases the specific area of a catalyst is reduced[2]. Unequal distribution of catalytic materials on the carrier surface and their agglomeration has been also observed. The growing of the catalytic material crystals with time leads to the blockage of pores during catalyst exploitation[3]. High expense of catalytic materials is inherent to impregnation technology and this is of very importance when noble metals are used as catalysts.

In this connection new technologies of catalyst coating have to be sought and investigated. Ion Beam Processing Technology (IBPT) has been already recognised as a competitive method of surface modification. Ion implantation has been used to enhance materials engineering performance in areas such as hardness, friction and wear, and corrosion[4-6]. Direct metal ion implantation as a part of IBPT has some features that make it applicable for making catalysts. The ion implantation allows virtually any chemical element to be implanted into the surface of any solid. Apart from ceramic pellets other carriers such as metallic type or metallic wire may be used as a substrate of a catalyst[7]. It was also found that when a catalyst on a substrate is in the form of atoms its catalytic activity increases[8]. This is additional evidence in favour of an ion implantation.

2. ION IMPLANTATION INSTALLATION

The ion implanter used for catalyst fabrication includes a vacuum chamber, source of metal ions, a vacuum pumping-out system and power supplies. The 1 m^3 vacuum chamber has a hatch for loading the substrate to be coated, a branch pipe for connection with a vacuum pump, an observation port, an air inlet valve for gas and a flange on which a metal ion source is located. The ion source on the basis of a discharge in crossed ExH fields with the cathode sputtering of metals has allowed an ion beam to be obtained along with diameter 200 mm, current density 130 $\mu A/cm^2$ and non-uniformity of 5% along the cross section. The vacuum chamber can accommodate several ion sources. The ease of changing the target in the ion source enables different materials to be implanted. The energy of ions can be controlled from 0 to 40 keV.

With an ion implantation technique, catalysts are fabricated in a single cycle. The vacuum chamber is loaded with the substrates and a vacuum of up to 0.013 Pa is created. Coating then starts. This process, in turn, comprises two steps: surface degassing and coating. The first step is fulfilled at the voltage of 10 kV for about 10 minutes. The voltage of the second step determines the depth of ion penetration into the carrier and de-

pends on materials processed. In our case it was around 20 kV. The duration of the second step depends on the catalytic material loading required.

Ion implantation dose (D) is proportional to the current density (I), surface area processed (S) and duration of implantation (t):

$$D = \frac{I \cdot t}{S \cdot 1.6 \times 10^{-19}}. \quad (1)$$

The mass of the substance implanted (m):

$$m = D \cdot m_a \cdot 1.66 \times 10^{-27} \quad (2)$$

where m_a is the average atomic mass of the chemical element implanted. Catalyst loading in wt% is determined as a ratio of mass of catalytic material to mass of substrate.

3. EXPERIMENTAL PROCEDURE

Carbon monoxide conversion efficiency of catalyst was measured in the test bed, which comprised the twin cylinder naturally aspirated diesel engine with a bore of 85 mm and a stroke of 110 mm, laboratory catalytic reactor, and gas analysers. Design of the laboratory catalytic reactor is described by Zlobin et al.[9]. Exhaust temperature at the reactor inlet could be changed from 100ºC to 500ºC by an electric heater. GIAM-14 gas analyser was used for measuring CO concentration in the exhaust at the reactor's inlet and outlet. All engine performance parameters, except exhaust temperature, were maintained as follows: engine speed 1000 rpm, engine brake power 1 kW, air mass flow rate around 37 kg/hr, relative ratio of $\lambda = 4.2$. Exhaust flow could bypassed the reactor to maintain constant volume flow rate through the reactor. The space velocity was 38,000 hr^{-1}.

Some industrial processes are accompanied by emission of harmful NO_x. Reduction of NO_x can be achieved using a suitable catalyst in presence of ammonia (NH_3) as shown in the following equation:

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \quad (3)$$

In this investigation, NO_x conversion efficiency of catalysts was measured by model gas activity tester. Model gas was composed of oxygen (O_2), nitrogen (N_2) and nitric oxide (NO). Mass flow rate of NH_3 was 0.2% that of the model gas, and volume of the catalytic reactor was 40 cm^3, space velocity was 15,000 hr^{-1}. Nitric oxide content in the outlet gas was measured by chemiluminescent gas analyser (344-CL-01).

The conversion efficiency of a catalyst was calculated as a ratio of mass of contaminant in gas outflow to that in gas inflow. The pore structure of catalysts was investigated by mercury porosimetry and nitrogen physisorption (BET) methods.

4. RESULTS AND DISCUSSION

Several samples of catalyst on various substrates with different platinum loading were prepared. The first set of experiments was a preliminary investigation on the applicability of an ion implantation technique as a means of manufacturing catalysts. Alumina (γ-Al_2O_3) extrudate (ø4-6 mm, L5-7 mm), alumina rounded granules (ø3-7 mm) and tablets (ø70 mm, L5 mm) made from metal fibre (ø0.1 mm) were implanted with platinum. This resulted in catalysts C1 (Pt = 0.110%), C2 (Pt = 0.110%), and C3 (Pt = 0.114%) respectively. The implantation dose was chosen in a such way as to obtain a platinum loading of catalysts two times less than that of commercially produced platinum catalyst, C5 (Pt = 0.2%). The commercial catalyst C5 was manufactured by impregnation method.

Catalysts obtained were tested in reaction of NO_x with NH_3 at temperature of 280ºC, and results are shown in Fig. 1. All catalysts showed satisfactory conversion efficiency but platinum content was still too high to make an ion implantation technique the competitive one.

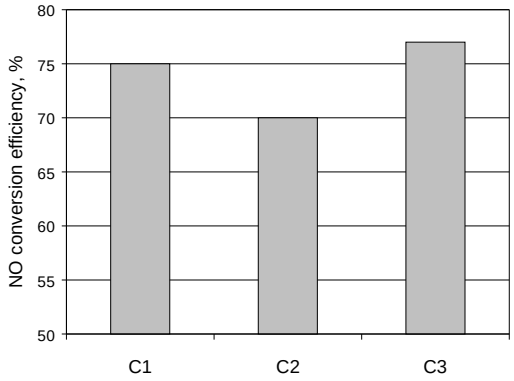

Fig. 1: NO_x conversion efficiency of catalysts.

The natural question arises: what regime parameters of an implantation process are to be chosen to obtain maximum efficiency of the catalyst at the minimum expense of a catalytic material?

Preliminary work carried out to change the process parameters and the catalyst with low platinum content has been obtained. Figure 2 shows that the new catalyst C4 (Pt = 0.0135%) has the same CO conversion efficiency at 340ºC as that of catalyst C5 (Pt = 0.2%), even though it contained fifteen times less platinum. Also shown in Fig. 2 is the conversion efficiency of the commercially produced cuprum-chromium catalyst C6 ($CuO : Cr_2O_3$ = 5% : 5%). It is only half as effective as platinum catalysts.

Effectiveness of any catalyst, other things being equal, depends on the catalytic material loading, specific surface area and temperature of reaction. First two properties, in turn, depend on the method of coating. Coating obtained by impregnation has a finite thickness and only catalyst on the exterior surface is exposed to reagents whereas the rest does not contribute to reaction. Obviously with this technology the maximum catalytic loading must exist over which catalyst effectiveness does not increase. While selecting ion implantation process parameters the following factors are to be taken into account. Energy of ions determines the depth of their penetration into the surface of a substrate. If ions are implanted at depth more than 1 μm, they probably will not be accessible to reagents. Loading of catalytic

material is directly proportional to the duration of implantation and current density. In turn both duration of ion bombardment and current density can affect the specific area significantly. For instance nickel ion bombardment with the dose of $5x10^{16}$ ions/cm^2 increased the specific area by factor of four compared to that of an unprocessed sample[4]. Thus, duration of implantation affects both platinum loading and surface properties of the carrier.

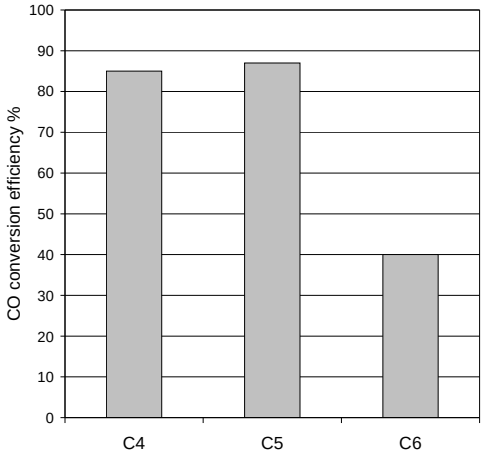

Fig. 2: CO conversion efficiency of catalysts.

To estimate the influence of duration of implantation on efficiency of the platinum catalyst the following experiment was carried out. Several catalysts were implanted with platinum at different duration of implantation and the same current density. Catalysts were tested in CO conversion reaction at different temperatures. Figure 3 shows that the relative conversion efficiency of catalysts is a non-linear function of the implantation dose. Temperature of reaction at which maximum efficiency of each catalyst was observed is a function of duration of implantation as well. Moreover, the maximum conversion efficiency in this experiment was obtained at lower temperatures.

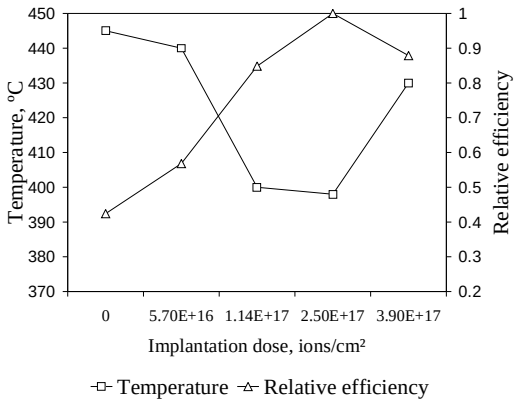

Fig. 3: Effect of implantation dose on the relative efficiency.

This experiment could not be used to predict the optimum parameters of an ion implantation process but showed that properties of catalysts produced by an ion implantation could not be explained just by catalytic material loading. Possible surface modification caused by an ion bombardment must be taken into account and investigated. As a first step in this direction, the pore structure of carrier and catalysts was investigated by the mercury porosimetry technique.

Figure 4 shows that curves of pore volume distribution versus pore radius have nearly the same shape for all samples tested. Pore structure of samples is characterised by two kinds of pores: macropores with radius from 200 to 1000 nm, and mesopores with radius from 3.7 to 8 nm.

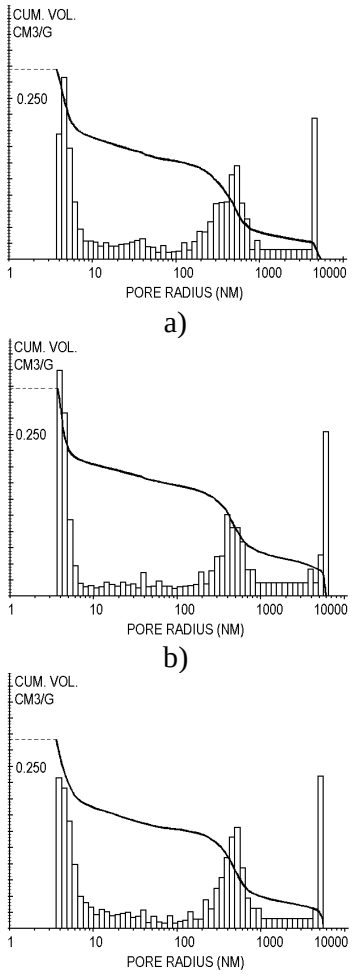

Fig. 4: Pore volume distribution: (a) carrier (γ-Al_2O_3 pellets), (b) catalyst C4, (c) catalyst C6.

With mercury porosimetry method only pores with radius of more than 3.7 nm are accessible. Thus if sample contains pores with radius less than 3.7 nm its surface area can be underestimated. Therefore surface area of samples was also measured by the BET method with which pores with radius up to 0.32 nm are accessible.

As shown in Fig. 5, specific surface areas of catalysts measured by mercury porosimetry and BET methods differ significantly. This difference indicates the presence of tiny pores with radius from 0.32 to 3.7 nm in the catalyst samples. This is also confirmed by the in-

complete shape of the integral curves in Fig. 4. Figure 5 shows that specific surface areas of carrier and catlysts C4 and C6 are not much different from each other. When assessing these data the accuracy of measurement must be taken into account. P. Fauchais and J. C. Labbe suggest that measurement error of methods used can reach 20%[10]. Thus, the surface area difference observed is comparable with measurement error. To investigate the effect of an ion bombardment on the surface area additional tests will have to be carried out. Nevertheless, the firm conclusion can be made that ion implantation does not decrease the surface area of catalyst.

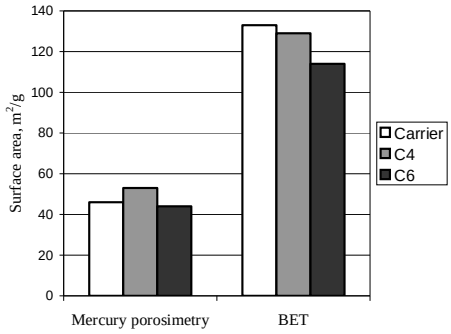

Fig. 5: Surface area of catalysts.

5. CONCLUSION

Based on the results of the work reported in this paper the following conclusions are drawn:

1. The ion implanter for coating of catalysts has been developed. The installation allows implanting any catalytic materials on various substrates.
2. Several samples of catalysts on various substrates have been prepared and tested. Platinum-implanted catalyst having fifteen times less platinum content showed the same CO conversion efficiency as the commercially produced catalyst.
3. Effectiveness of implanted catalysts and temperature at which maximum efficiencies have been achieved had non-linear dependence on the implantation dose.
4. Investigation of the pore structure showed that ion implantation did not decrease the specific surface area of the catalyst. Modification of surfaces treated with an ion beam demands further investigation.
5. Ion beam processing technology may be considered as the potential method of production of noble-metal-based catalysts and research in this direction shall be continued.

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LIST OF SYMBOLS AND ABBREVIATIONS

1.6×10^{-19}, C: elementary charge

1.66×10^{-27}, kg: atomic mass unit

D , ion/cm^2: ion implantation dose

I , A/cm^2: ion beam current density

(IBPT): Ion Beam Processing Technology

m , kg: mass of the substance implanted

m_a: atomic mass

S , cm^2: surface area processed

t , s: duration of implantation

λ: relative ratio

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