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Efficiency of Pd impregnated sol-gel derived γ-alumina porous spheres as catalyst

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Abstract. Porous γ-alumina spheres having surface area as large as 300 m^2/gm are obtained by using sol-gel process. γ-alumina supported Pd catalyst is synthesized by soaking it in $PdCl_2$ solution followed by drying and heating at 300 °C/1 hr in hydrogen atmosphere. Specific Surface Area of Pd coated alumina remained unaltered. The scanning electron microscopy revealed uniform coating of Pd metal on the surface. The equivalent spherical diameter (ESD) of the coated Pd metal particles is estimated to be 50. The catalytic efficiency is evaluated by H_2-O_2 combination reaction. The performance of this supported catalyst is found to be much superior in comparison with Pd catalyst realized on commercially available alumina having surface area of 80 m^2/gm. The improved efficiency of the catalyst could be co-related to enhanced surface of nano-structured Pd available for catalytic action. The added advantage of spherical shape of the support material appeared in uniform and homogeneous loading of the catalyst bed. The results highlight the important role played by support material in these type of catalysts.

PACS. 61.82.-d Radiation effects on specific materials – 68.47.-b Solid-gas/vacuum interfaces: types of surfaces

1 Introduction

The study of catalysts is essentially a study of the surface chemistry. The efficiency of the catalyst is its interaction with an environment. In surface assembled metal catalyst, metal is distributed in the form of fine particles on support material. The classification of support material is done in terms of porosity and surface area. An enormous increase in activity could be obtained if an appropriate support material could be synthesized. Generally, the metals like ruthenium, rhodium, palladium, silver, platinum and gold are used as catalyst while alumina, silica, magnetia etc. are used as supports. The supported catalyst have several advantages over simple catalyst like, large area of metal is exposed, sintering of metal is reduced and accessibility of the catalyst surface to reactant is improved. There is also possibility to modify activity and selectivity of catalyst. The heat produced in an exothermic reaction is dissipated. The supported catalyst are generally prepared by either impregnation, co-precipitation or decomposition. The approach allows the controlled use of expensive materials, since they are more or less confined to the surface of the support. The activity of a supported catalyst for a given reaction should be referred to unit area of metal surface exposed to reactants. The activity per unit area of accessible surface is called the surface activity. The rapid ability of the catalyst to interact with a reacting system to give a certain chemical composition and structure is desirable. Synthesis of variety of supported metal catalyst including bimetallics are reported and their functioning has been extensively studied by various groups [1–7]. It is very apparent from the literature that the efficiency of the catalysts are highly influenced by the quality of the support material. The large surface area and porosity of γ- alumina synthesized through novel sol-gel process developed in our laboratory, motivated us to test it as catalyst support.

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2 Experimental

Porous γ-alumina spheres having high specific surface area are obtained by using newly developed sol-gel process [8]. In which the sol consisting of suspended aluminium hydroxide particles is geleted by means of chemical dehydrating agent. To obtain geleted material in spherical shape, column technology is adopted (Fig. 1). The drying and calcination at 400° converts geleted spheres into γ-Al_2O_3 phase. The details of the procedure are reported earlier [8]. These sol-gel derived γ-Al_2O_3 spheres of the size 0.4-0.5 mm are composed of particles which are 4-5 nm in size. The other characteristics of the γ-Al_2O_3 spheres are as follows: Specific Surface Area (SSA): 300 m^2, Pore volume: 1.28 cc/gm, Adsorption activity: 2.9 mole/gm. The known quantity of γ-alumina spheres is then soaked in $PdCl_2$ solution of known concentration. After soaking for few hours, $PdCl_2$ solution is decanted out and the change in concentration is determined

Table 1. Catalytic efficiency of Pd impregnated alumina.

Catalist support	Surface area of support material	Pd/100 gm of support material	Catalytic efficiency
Sol-gel alumina	300 $m^2\,gm^{-1}$	0.698 gm	100%
Commercial alumina	80 $m^2\,gm^{-1}$	0.50 gm	93%

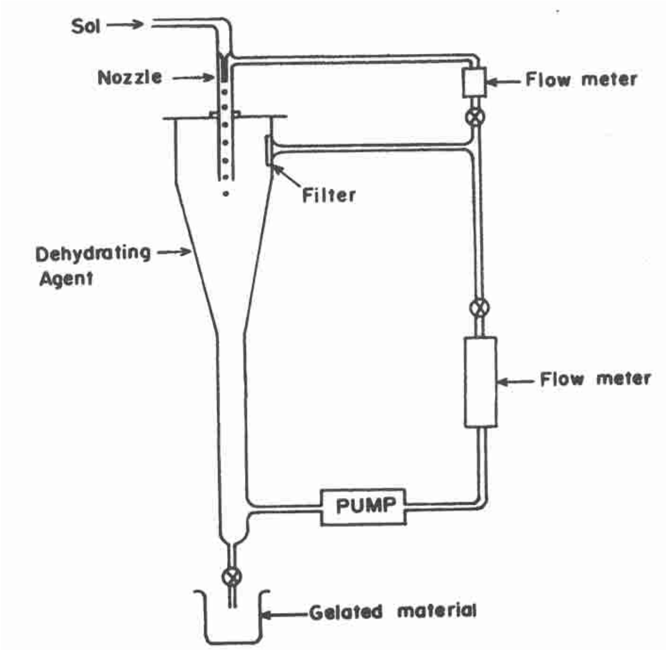

Fig. 1. Glass column used for geletion process.

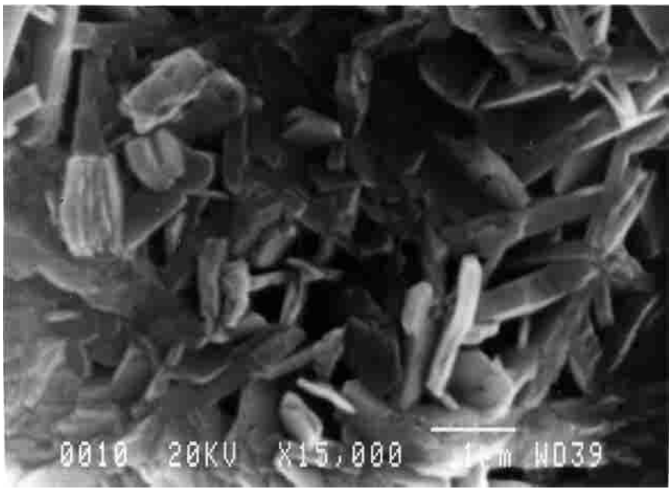

Fig. 2. SEM picture of alumina sphere.

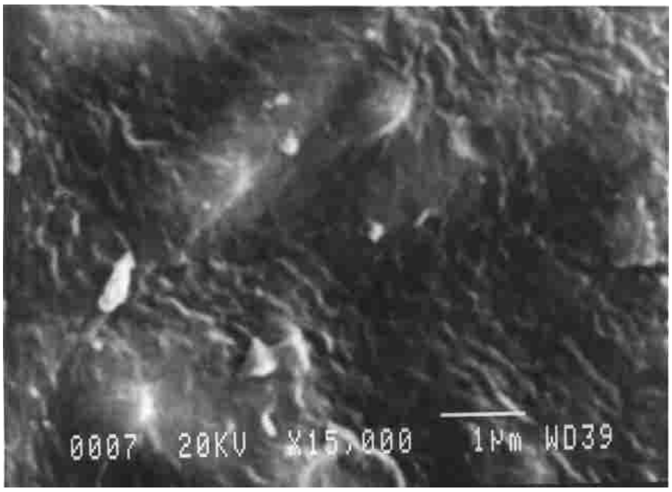

Fig. 3. SEM picture of Pd impregnated alumina sphere.

by spectrophotometric method. From the decrease in concentration, the exact quantity of Pd impregnated/gm of γ-alumina could be calculated. To convert $PdCl_2$ to Pd metal, the material is dried and heated in hydrogen atmosphere at 300°/1 hr. For comparative study, commercially available γ-alumina support material is also impregnated with Pd under identical conditions.

2.1 Characterization

The specific surface area of the samples is determined using BET technique (Table 1). Scanning electron microscopy is used to check surface morphology of γ-alumina spheres before and after Pd impregnation (Figs. 2 & 3). Hydrogen-oxygen combination reaction was used to determine the catalytic efficiency of Pd impregnated γ-alumina spheres. The schematic diagram of the system used for testing is shown in the Fig. 4. The catalyst bed is prepared using known quantity of the impregnated samples. The mixture of hydrogen and air is passed over the catalyst through inlet tube. The out coming stream of gas is checked for hydrogen using gas chromatography. The experiment is repeated under identical conditions for commercially available γ-alumina impregnated with Pd metal. Results of this study are shown in Table 1.

3 Results and discussion

Table 1 clearly indicates that though both alumina samples are soaked under identical conditions, the amount of Pd impregnated on sol-gel alumina is more. This could be attributed to higher adsorption activity of the material. Since the specific surface area of the sol-gel derived sample is almost 4 times higher than the commercially available material, Pd on sol-gel alumina is distributed over larger surface. With the result larger surface is available for the catalytic reaction. γ-alumina is a well known for its adsorption capacity. Hence, adsorption of Pd on the surface of alumina is more likely than absorption. SEM pictures also indicate uniform coating of Pd on the surface (Figs. 2 & 3). Equivalent

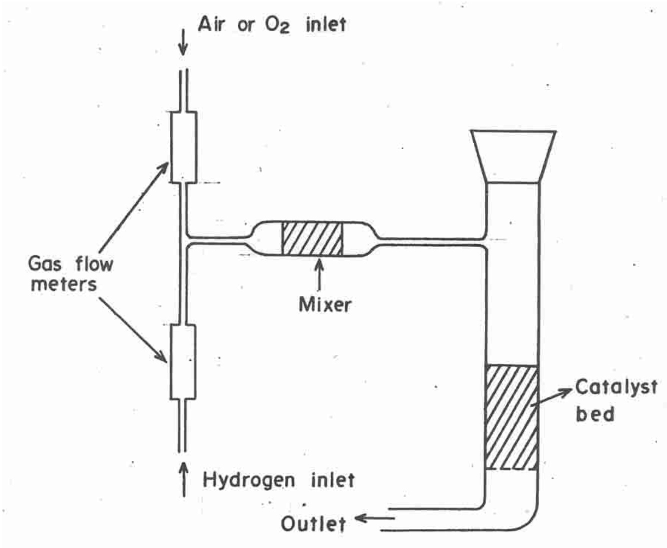

Fig. 4. System used for H_2-O_2 combination reaction.

spherical diameter as calculated from specific surface area indicates that the Pd particle size could be of the order of 5 nm. Enhanced surface of nanostructured Pd available for catalytic action has helped to improve the catalytic behavior. Spherical shape of alumina is advantageous in forming uniform packing of the catalyst bed. In summary it is possible to conclude that the availability of enhanced surface of nanostructured Pd for catalytic reaction leads to superior behavior. The results obtained in the test study once again prove the important role played by the quality of the base material in supported catalyst.

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References

1. A. Hoek, M.F.M. Post, J.K. Minderhoud, P.W. Ldnor, US Patent **4**, 499 (1985); *ibid.* 209 (1985).
2. M.P. Rosynek, C.A. Polansky, Appl. Catal. **73**, 97 (1991).
3. E. Iglesia, S.L. Soled, R.A. Fiato, J. Catal. **137**, 212 (1992).
4. P. Arnoldy, J.A. Moulijin, J. Catal. **93**, 38 (1985).
5. A.C. Krauth, E. Wolf, MRS Symp. Proc. **368**, 157 (1995).
6. M. Haruta, T. Kobayashi, N. Yamada, Chem. Lett. **405** (1987).
7. M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. **115**, 301 (1989).
8. V.R. Palkar, Nanostruct. Mat. **11**, 369 (1999).