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Porous Pt/SiO_2 catalytic membranes prepared using mesitylene solvated Pt atoms as a source of Pt particles

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Abstract

The preparation of silica catalytic membrane reactors as well as their characterization are discussed. The deposition of platinum by the Pt mesitylene co-condensate method has proved to provide high Pt loading with good catalyst dispersion, also on SiO_2 support. The catalytic activity of the silica membrane has been assessed using the hydrogenation of toluene as model reaction.

1. Introduction

In the recent years much interest has been paid to catalytic membrane reactors (CMR) because they show great promise for a wide range of reaction applications, such as hydrocarbon and methanol dehydrogenation, methane steam reforming, Claus reaction, reduction of NO_x with NH_3, and hydrocarbon partial oxidations, etc. [1–3].

Among the techniques employed to prepare catalytic membranes, the one based on the use of solvated metal atoms allows to deposit catalyst particles in an active form at room temperature or lower, thus avoiding the calcination and activation steps of the conventional wet deposition and impregnation processes [4]. This paper deals with preparation and porosimetric as well as catalytic characterization of porous Pt/SiO_2 membranes using mesitylene solvated Pt atoms as source of Pt particles.

The silica thin layer has been deposited via the sol–gel method described elsewhere [5].

A preliminary comparison with the properties of similarly prepared Pt/γ-Al_2O_3 [6] is also reported.

2. Experimental

2.1. Catalytic membrane preparation

The SiO_2 surface layer has been prepared by the sol–gel process, starting from a commercial colloidal sol (LUDOX^R ASGI-Dupont) containing 40% wt. SiO_2 in water (ammonium stabilized sol). After water dilution, polyvinyl alcohol (PVA —Polyvinylalcohol Rhodoviol^R 25/140-Rhône Poulenc) has been added to the sol. A thin sol layer is deposited by slip-casting on an asym-

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metric α-alumina tubular support (150 mm long) supplied by SCT-US Filter. The layer drying is performed at 10°C and the firing treatment at 600°C under air flow. The membrane is sealed by a vitrification process for an extent of 25 mm to both ends.

The platinum is deposited on the permeable part of the SiO_2 thin surface layer, by using mesitylene solvated Pt atoms, using the technique described elsewhere [7]. The membrane tube (fitted with teflon stoppers at both ends) was filled with the mesitylene solution stored at -20°C and warmed up to room temperature. The mesitylene solution rapidly turns from red–brown to clear and is siphoned out after ca. 2 h. The residual solvent is removed under vacuum.

2.2. Catalyst characterization

The platinum distribution on a SiO_2 layer has been evaluated using a scanning electron microscope (SEM, Leika Cambridge Stereoscan 440) fitted with a EDS capability analysis (Oxford, Isis). This EDS capability has also allowed us to evaluate the silica interdispersion within the α-Al_2O_3 support. The Pt loading has been determined by atomic absorption after reduction of the membrane to powder and a subsequent chemical attack by a mixture of hydrofluoric acid and aqua regia.

The size distribution of the Pt has been evaluated by transmission electron microscope (TEM, Joel DIEM 2000 EX/T). We do not report data obtained via chemisorption, because in the case of catalytic membrane reactors this technique cannot be proved statistically due to the small amount of catalyst deposited on the membrane.

2.3. Membrane characterisation

The membrane pore size distribution has been evaluated by liquid–liquid displacement porosimetry (LLDP) [8] and, N_2 adsorption/desorption measurements (Micromerities ASAP 2000). The membrane morphology has been observed by scanning electron microscopy (SEM).

2.4. Reaction runs

The catalytic characterization of the membranes has been carried out by using the hydrogenation of toluene to methylcyclohexane as model reaction. The runs have been performed in the 343–373 K temperature range using a hydrogen to toluene molar ratio of 27. A helium stream has been used as a carrier for toluene; the toluene partial pressure was controlled via a thermoregulated saturator located before the CMR. The transmembrane pressure, measured as the ΔP between the shell side and the internal pressure, was in the 100 mbar range.

3. Results and discussion

Both SiO_2 and Pt distributions, as obtained from SEM X-ray microanalyses, are shown in Fig. 1 in an arbitrary scale. The results indicate the occurrence of a spread interface between the silica thin layer and the α-Al_2O_3 support. As a consequence, a small amount of Pt is also found in the α-Al_2O_3 layer. This finding differs from that observed for γ-Al_2O_3 membranes [6] which exhibit a sharp interface between the deposited thin layer and the support. The difference may be due to the different morphological properties of SiO_2 and γ-Al_2O_3 layers. Indeed, while the former is constituted by small grains ca. 20–30 nm in diameter (cf.

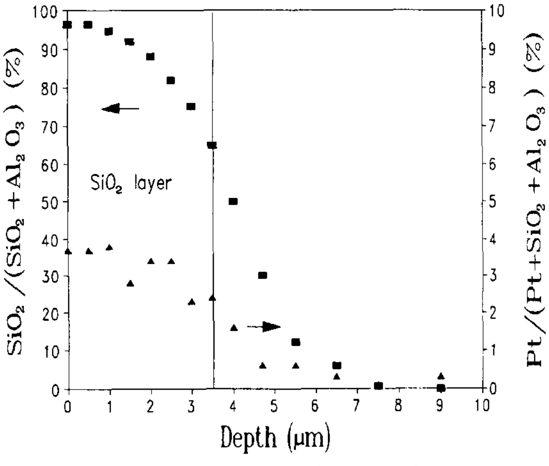

Fig. 1. Silica and platinum distribution within the membrane.

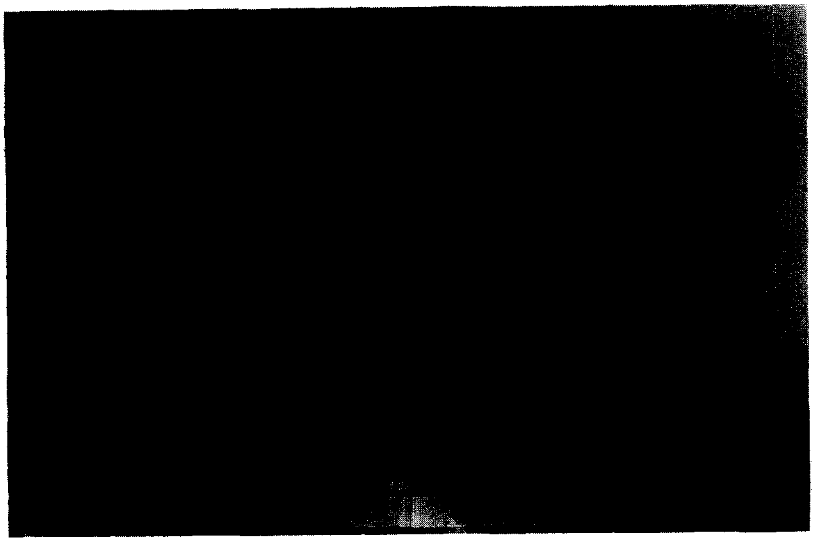

Fig. 2. SiO_2 and Pt particles TEM micrograph.

Fig. 2), also confirmed by SEM measurements, the latter exists of thin plates [9] ca. 240×320 nm. This may explain the presence of the silica grains within the pores of α-Al_2O_3 layer which have a nominal size of 0.2 μm.

Fig. 2 represents a typical TEM micrograph showing the catalyst dispersion onto the silica support, while the histogram of Fig. 3 illustrates the Pt particle size distribution. Fig. 2 clearly shows that the SiO_2 thin layer is constituted of grains ca. 20 nm in diameter. This has been also confirmed by independent FESEM measurements [10]. The average volume/area particle size (dva), as obtained from Fig. 3, is 2.4 nm and the percentage dispersion (DM) is 47.35%. These values are comparable to the ones obtained by the same deposition method on γ-Al_2O_3 membranes [6]. Furthermore, independently from the nature of the support, the cocondensate deposition route allows one to attain high Pt loadings without affecting the catalyst dispersion.

For the membrane of Fig. 2, obtained by Pt deposition from a mesitylene solution, the platinum loading, referred only to the SiO_2 skin layer, is 1.4% which corresponds to 0.36 mg of catalyst. The loading can be increased by selecting a proper solvent. For instance, the deposition from 1-hexene solution has led to loadings in the range of 4 to 5%, most probably, this has to do with the higher diffusion rate, within the porous matrix, exhibited by the Pt complexes of linear molecules.

The results of porosimetric and gas permeability measurements, before metallic deposition, are shown in Fig. 4 and Fig. 5, respectively. Fig. 4 shows that the overall permeability is a result of the contribution of a spread family of pores.

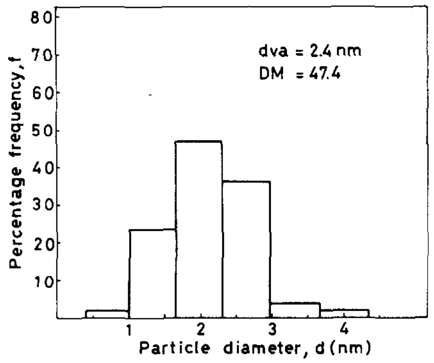

Fig. 3. Pt particles distribution.

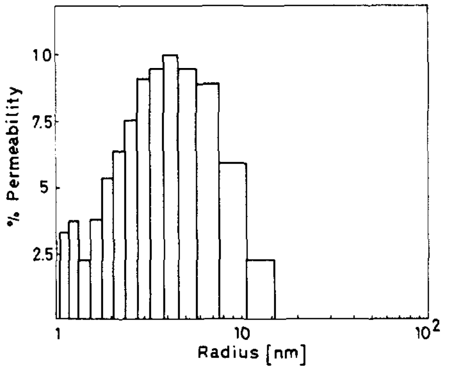

Fig. 4. Percentage permeability vs. pore radius.

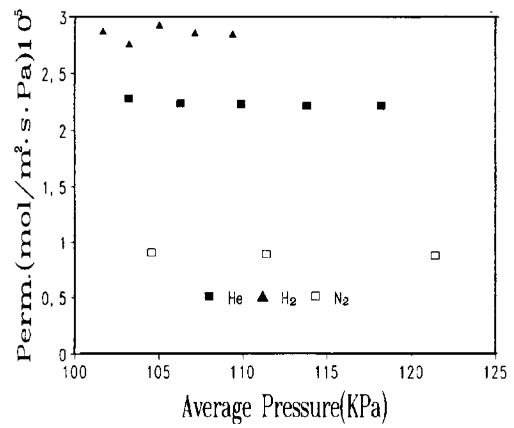

Fig. 5. Gas permeability at 383 K, as a function of average pressure.

The permeability ratios K_{H_2/N_2} and $K_{H_2/He}$ obtained from Fig. 5 are 3.19 and 1.24 and compare well to the square root of reciprocal molecular weight ratios, $\sqrt{M_{N_2}/M_{H_2}}=3.47$ and $\sqrt{M_{He}/M_{H_2}}=1.41$. This indicates that the gas mass transport across the membrane prevalently occurs in the Knudsen regime.

The catalytic activity of the membrane reactor has been assessed, in the temperature range 343–373 K, using the hydrogenation of toluene as model reaction. Here, we present only the results for the all-through configuration where all the reactants are forced through the membrane layer [6]. The toluene consumption as a function of the reciprocal temperature is shown in Fig. 6. In the insert the apparent activation energy, E_a, is also reported. The E_a value is slightly smaller than the values which are usually found for such a reaction (11–12 kcal/mol). The lower E_a value we found is mainly due to the wide pore size distribution, more than to mass transport resistances (cf. the comparison paper [11])

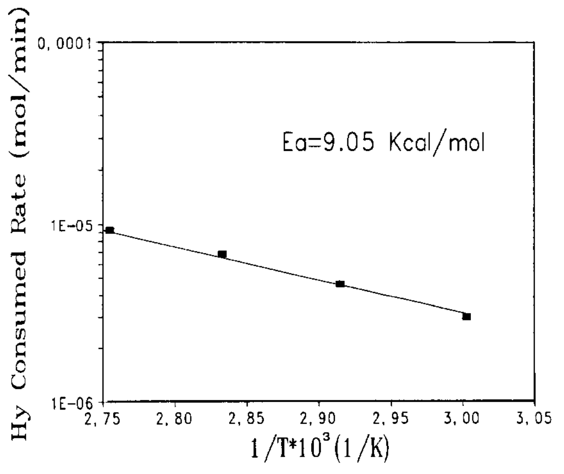

Fig. 6. Toluene consumption rate vs. reciprocal temperature (Q = 195 ml/min; $H_2/H_y=27$).

The silica-based CMR exhibits a much higher specific activity (expressed as molecule of consumed toluene per atom of Pt per h) than the similarly prepared Pt/γ-Al_2O_3 membranes. Indeed, for the membrane of Fig. 6 we have evaluated a specific activity of 947 which has to be compared with the value of 87.6. At present time, we do not have an explanation for this finding yet, considering that the Pt dispersion is rather similar for the two membranes and a so large support effect is rather unlikely. Different catalyst accessibility within the porous matrix could explain the experimental finding. The silica membranes have pores with nominal pore diameter of 10 nm while the γ-Al_2O_3 membranes have pores with nominal diameter of 5 nm.

Further investigations are underway to fully clarify the reason for such a high reactivity of the SiO_2 CMR.

4. Conclusion

It clearly appears from the reported data the usefulness of solvated Pt atoms is depositing active Pt particles under very mild conditions. The method can be used for γ-Al_2O_3 or SiO_2 membranes. The membrane porosity and the nature of organic solvating compounds allow good control of the Pt loadings, presumably via the solvent diffusion in the membranes. Even at high Pt contents, substantially good metal dispersion can be obtained.

Preliminary experiments show that the SiO_2 based membranes exhibit higher catalytic activity than the corresponding γ-Al_2O_3 ones. Further studies, however, are necessary, in order to better understand the reasons for this behaviour. At present, considering that there is no appreciable difference in the metal dispersion, the observed differences can be due to a support effect and/or to a different Pt accessibility within the membrane.

The latter justification is supported by the fact that the two membranes exhibit different porosimetric characteristics.

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