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Porous Pt / γ-Al_2O_3 catalytic membrane reactors prepared using mesitylene solvated Pt atoms

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The opportunity of using mesitylene solvated Pt atoms for the deposition of Pt catalyst on inorganic membranes is shown. The catalytic activity of the membrane reactor has been tested using the hydrogenation of benzene as model reaction. The performance of the membrane reactor has been compared with that of a conventional packed bed using γ-Al_2O_3 powder impregnated with Pt. The effect of the feeding configuration has been investigated, and the results show a membrane effect due to the different degrees of accessibility of pores of different size. For alumina powder we have obtained an activation energy of 12.9 kcal/mol, which well agrees with the data reported in literature. The membrane reactor, instead, exhibited an activation energy ca. 60% lower. The preliminary porometry results have shown a slight effect of the platinum deposition process on membrane permeability.

Keywords: Membrane reactors; inorganic membranes; organic precursors; solvated platinum atoms; benzene hydrogenation

1. Introduction

Since the early suggestion of Michaels [1] to use membranes in reaction engineering applications, several investigators have demonstrated the validity of this idea. In particular, the early investigations exploited the separation functionality of membranes by integrating in a single operation the reaction and separation processes. In these applications the main function of the membrane is to provide an effective and selective removal of some of the reacting species (mainly products) during the reaction, so that, for reversible reaction the conversion can be improved above the thermodynamic limit. The pioneering work of Gryaznov on Pd catalytic membranes [2–4] has significantly contributed in proving and divulging the idea of catalytic membrane reactors. In these early works the reactor was a fixed catalytic bed with inert membrane walls.

More recent investigations have dealt with alumina ceramic membranes where the membrane has also the function of catalyst support. Typically, the catalyst is deposited by the conventional wet impregnation process. These inorganic membranes allow relatively high operating temperatures (up to 673–773 K) and are finding a broad spectrum of applications, for instance, in dehydrogenation of hydrocarbons and methanol, and in methane steam reforming [5,6].

A recent study of Sloot et al. [7,8] has successfully proved the opportunity of using catalytic membrane reactors for those applications that require a strict stoichiometric feed ratio of the reactants, such as, the Claus reaction of decomposition of the hydrogen sulphide or the catalytic reduction of NO_x with NH_3. In these applications the main function of the membrane is to provide a way to control the supply of the reactants to the reaction zone.

The work presented here is part of a wide project we undertook to investigate the effect of membrane physicochemical properties and catalyst morphology on the overall performance of catalytic membrane reactors. In this paper we also present a method for the preparation of catalytic membranes based on the use of Pt mesitylene cocondensates, which is alternative to the conventional wet impregnation process.

2. Experimental

2.1. CATALYTIC MEMBRANE PREPARATION

The support for the catalytic phase was a multilayered ceramic membrane (SCT-50) of inner diameter 6.7 mm and outer diameter 10.2 mm. The membrane was 150 mm long but the permeable porous part, located in the central region of the tube, was only 50 mm long since the membrane was sealed by a vitrification process for an extent of 50 mm to both the ends. Scanning electron micrographs of the cross-sections of the multilayered membrane are shown in fig. 1. The three α-Al_2O_3 layers (1–3) are of different thickness and have a decreasing porosity going from layer 1 to layer 3 while the fourth layer of γ-Al_2O_3 has a thickness of about 4 μm and a nominal average pore diameter of 5 nm. Therefore, all the resistance to flow lies in this fourth layer, and the three α-Al_2O_3 layers simply act as a macroporous support for the thin γ-Al_2O_3 layer.

The platinum phase was deposited on the permeable part of the γ-Al_2O_3 layer by using mesitylene Pt atoms as source of active particles [9]. Platinum vapor and mesitylene were cocondensed at 77 K in a typical glass reactor [10] yielding a red brown solid matrix. The flask was heated up to 233 K and the resulting yellow brown solution of mesitylene solvated atoms was isolated under argon and handled at low temperature. Platinum particles were rapidly deposited by filling the mem-

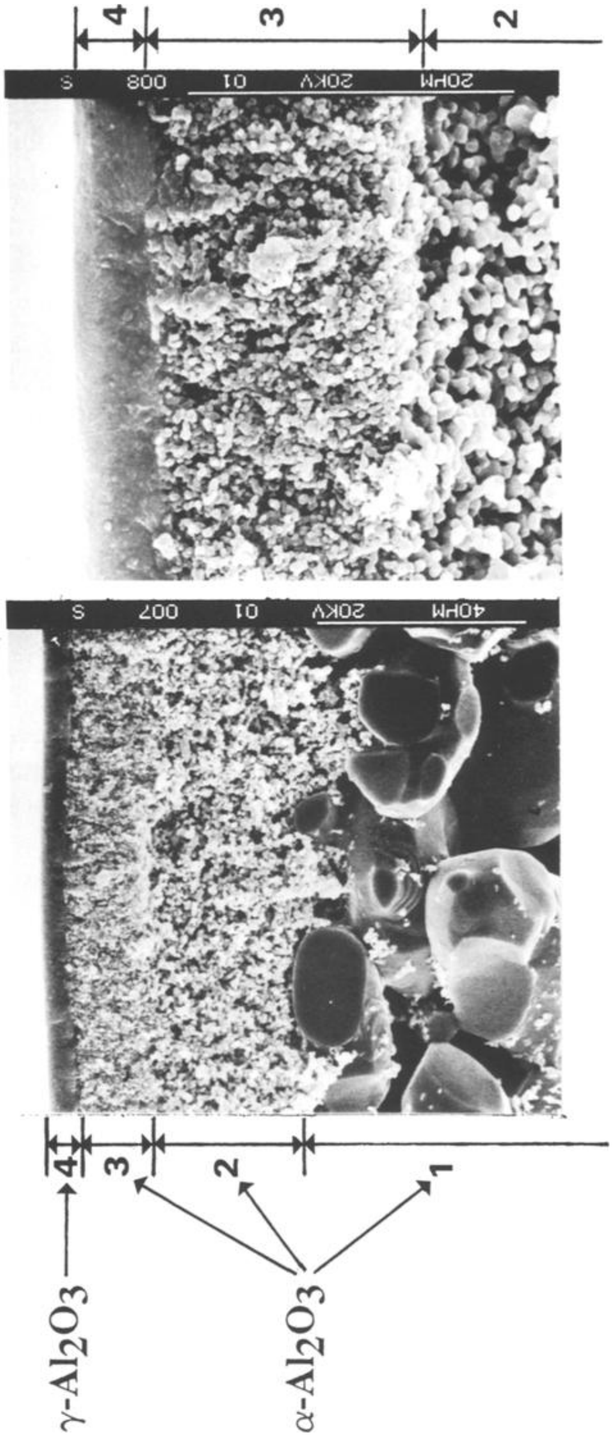

Fig. 1. Scanning electron micrographs of the cross section of the multilayered ceramic membranes at different magnification.

brane tube (fitted with teflon stoppers at both ends) with the above solution and heating up to room temperature. The deposition method can be schematized as follows:

$$\mathrm{Pt} + \text{mesitylene} \xrightarrow{77\,\mathrm{K}} [\mathrm{Pt/mesitylene}]_{\text{solid matrix}} \xrightarrow{233\,\mathrm{K}} \begin{bmatrix} \text{yellow brown} \\ \text{solution stable at} \\ \text{low temperature} \end{bmatrix}$$

$$\xrightarrow[\gamma\text{-}\mathrm{Al_2O_3}]{298\,\mathrm{K}} \mathrm{Pt}/\gamma\text{-}\mathrm{Al_2O_3}\,.$$

The main advantage of this deposition process is that the Pt is deposited directly in an active form, so that, the calcination and activation processes of the conventional wet deposition method are not required. This reduces the probability to introduce defects on the thin layer of γ-Al_2O_3. Furthermore, previous measurements [11] show that this technique may increase the activity of the deposited catalyst.

2.2. CATALYST CHARACTERIZATION

The distribution of the platinum deposited on the γ-Al_2O_3 layer was evaluated by a scanning electron microscope (SEM, Cambridge 250 Stereoscan MK2) equipped with a microprobe for X-ray analysis (Link System 860 Analyzer LTD). The Pt loading was measured via a colorimetric technique after reduction of the membrane to powder followed by chemical attack with a mixture of hydrofluoric acid and aqua regia. The size distribution of the Pt particles was evaluated by transmission electron microscope (TEM, Jeol JEM 2000 EX/T).

We have also characterized the platinum on the powder of γ-Al_2O_3 in terms of Pt distribution, Pt loading, and particle size distribution.

2.3.MEMBRANE CHARACTERIZATION

The pore size distribution of membranes was evaluated before and after the Pt deposition by liquid–liquid displacement porometry (LLDP) [12,13]. LLDP is a non-destructive method which is based on the use of a proper "displacement" liquid which is forced through the membrane filled with a "wetting" liquid chosen to be immiscible with the displacing one. From the measurement of the pressure drop through the membrane for a given flux of the displacing liquid and from the knowledge of the interfacial tension between the two liquids, a pore permeability versus pore radius curve is obtained through Cantor's equation [12]. The membrane permeability is defined as the ratio of the flux to the pressure drop.

As displacing liquid we used the light phase obtained from the phase demixing at 293 K of a mixture of methanol, isobutanol, and water in volumetric ratio 70 : 150 : 250; the heavy phase was used as wetting liquid. The interfacial tension between the two immiscible phases was 0.35 mN/m [12,13]. The flux and pressure measurements were performed with the automatic instrument described in ref. [13].

It is noteworthy to emphasize that LLDP allows to evaluate only the open pores of the surface layer of γ-Al_2O_3, which, as previously mentioned, govern the transport properties of the membrane.

2.4. REACTION RUNS

The reaction runs were designed to test the catalytic activity of the membrane reactor, as well as the effect of membrane porometry characteristics on reactor performance. The hydrogenation of benzene to cyclohexane was selected as model reaction because it is well accepted that such reaction is structure insensitive [14–16] over Pt/γ-Al_2O_3 catalyst, even though a recent study [17] has shown that it becomes structure sensitive for high catalyst dispersion. The runs were performed in the 333–523 K range and with several hydrogen to benzene ratios. A helium stream was used as a carrier for benzene; the benzene partial pressure was controlled via a saturator thermoregulated at 283 K. We have also investigated the effect of the feeding mode on the membrane reactor performance; the flow configurations used in this study are shown in fig. 2. The lower pressure differences (measured as the Δp between the shell side and the internal pressure) were attained with flow configurations M_1 and M_2 (ca. 10–30 mbar), while with the feeding mode M_3 the pressure differences were typically in the 200–700 mbar range.

During the experiments carried out at high temperature, we have observed a slow deactivation of the catalytic membrane. However, a mild regeneration was sufficient to reestablish the initial catalyst activity. The regeneration was carried out by passing through the membrane reactor a hydrogen flow (ca. 1.38 ml/s) at 523 K for 2 h.

The performance of the catalytic membrane reactor was also compared with that of a conventional packed bed reactor where the catalyst was γ-Al_2O_3 powder

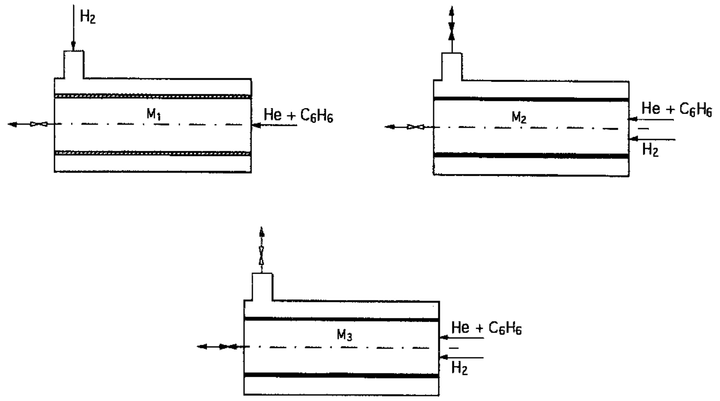

Fig. 2. Schematic of the investigated flow configurations.

(ca. 1 μm in diameter) with platinum deposited by the organic precursor route. In order to reduce the pressure drop along the reactor the catalyst powder was diluted in a ratio of 1 : 28 with glass pellets, ca. 500 μm in diameter.

3. Results and discussion

The membrane permeability represents the most important feature which, for some applications, makes membrane reactors more advantageous over conventional reactors. Thus, as a first step we have evaluated the effect of the catalyst deposition on the membrane pore permeability. Preliminary results on pore distribution are shown in fig. 3a as histograms and in fig. 3b as cumulative curves. The figures indicate that the deposition of the active phase has only a slight effect on the permeability and that the partial occlusion of some of the pores leads to the formation of smallest pores. The values of the average pore radius calculated from these permeability distributions are 3.8 and 4 nm for membranes with and without catalyst, respectively. These findings agree with the results of a recent study by Champagnie et al. [18].

The results of the SEM/X-ray microanalysis are illustrated in fig. 4 where the distribution of Pt, in an arbitrary scale, is given as a function of the penetration depth. The figure shows that most of the metal is deposited on the γ-Al_2O_3 surface layer and no deposition occurs on the support layers of α-Al_2O_3. The total Pt loading was 1.65% of the surface layer of γ-Al_2O_3. The typical distribution of platinum particle size, as obtained from TEM micrographs, is shown in fig. 5 which indicates that most of the particles have size in the 1.5–3.0 nm range. The average volume-area particle size (DVA), as obtained from fig. 5, is 2.4 nm which is comparable with the average size of Pt particles obtained via the wet deposition route (ca. 2.5 nm [19]).

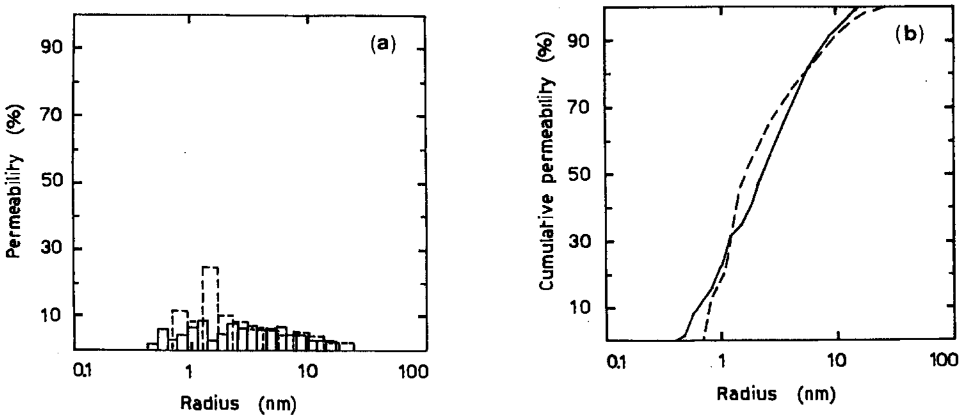

Fig. 3. Permeability of ceramic membranes as a function of pore radius; (a) pore permeability distribution functions, (b) cumulative pore permeability; (- - -) before catalyst deposition; (——) after catalyst deposition.

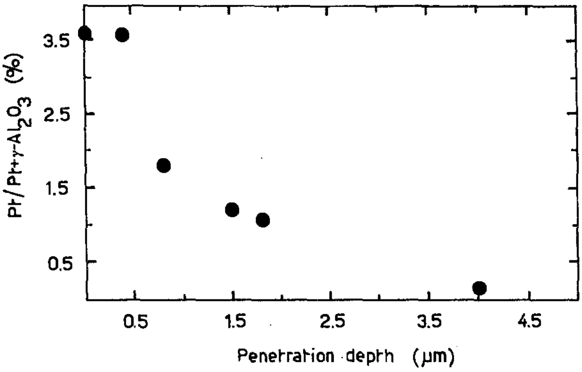

Fig. 4. Platinum distribution in the surface layer of γ-Al_2O_3 evaluated from the SEM/X-ray microanalysis.

We carried out a first series of kinetics runs on the impregnated γ-Al_2O_3 powder to evaluate the intrinsic apparent activation energy. The absence of external mass transfer resistance was confirmed by the observed linear dependence of benzene conversion on the reciprocal total flowrate. In fig. 6 the benzene consumption rate is shown in an Arrhenius like plot in the temperature range 333–473 K. From the slope we have evaluated an apparent activation energy of 12.9 kcal/mol which well agrees with the values reported in the literature [17,20–22]. In these experiments, as well as in those carried out with the membrane reactor, the effect of the reverse reaction (dehydrogenation of cyclohexane to benzene) was negligible because the conversion per-pass was maintained below the 15% limit.

The catalytic membrane reactor was studied in the temperature range 373–573 K and in operating conditions which made the external mass transfer resistance negligible. For illustrative purposes, the dependence of benzene conversion on the total flowrate ($Q_{He} + Q_{H_2}$) is shown in fig. 7 for the flow configuration M_1.

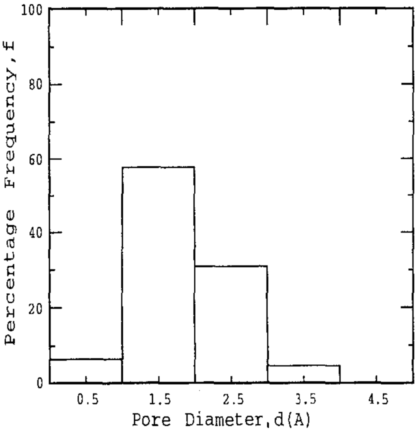

Fig. 5. Platinum particle size distribution as obtained from TEM micrographs.

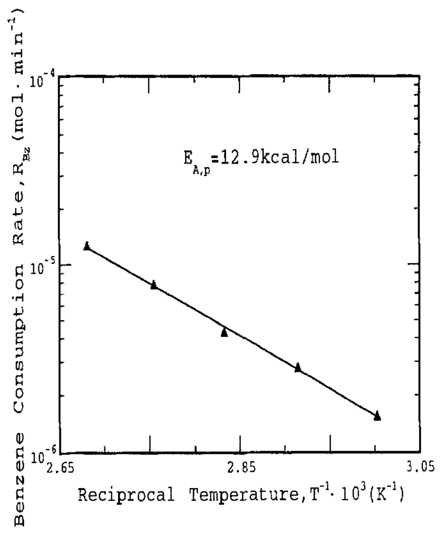

Fig. 6 Benzene consumption rate, R_{Bz}, as a function of the reciprocal temperature for the packed bed reactor. Hydrogen/benzene ratio: 28.1.

The effect of the feeding mode is illustrated in fig. 8 where the benzene conversion, χ, is shown as a function of the reciprocal temperature. The results show that the flow configuration slightly affects the activation energy, on the contrary, the conversion depends on the feeding mode, and in particular higher conversions are attained with the flow configuration M_3. The higher internal pressure realized with this configuration cannot account for the observed increase in the conversion.

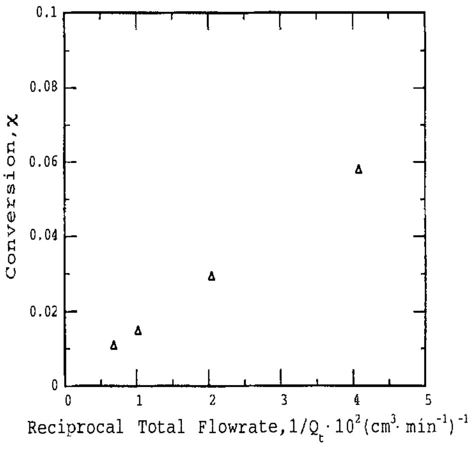

Fig. 7. Benzene conversion as a function of the reciprocal total volumetric flowrate, Q_t, for the flow configuration M_1. $T = 383$ K, hydrogen/benzene ratio: 29.2.

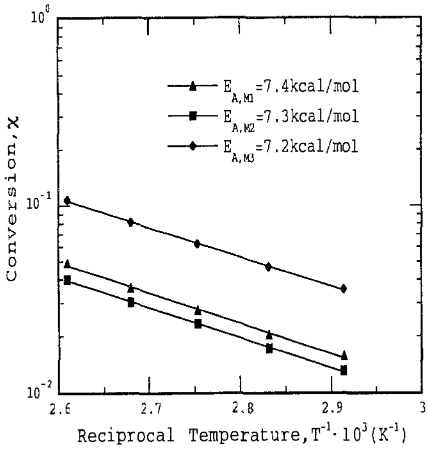

Fig. 8. Benzene conversion, χ, as a function of the reciprocal temperature for the three flow configurations of fig. 2. Hydrogen/benzene ratio: 29.2.

This finding may be better explained in terms of pore accessibility. With low ΔP, as realized with feeding modes M_1 and M_2, the permeation through the membrane mainly occurs by molecular diffusion and Knudsen flow and only a small region of the surface layer is penetrated by benzene, thus, only a fraction of the total deposited platinum is reached by both the reactants. In the flow configuration M_3, the reactants are forced through the surface layer, and in this case the reactants have the chance to reach all the active sites. This results in an increase of the observed conversion. This picture may also account for the slight decrease of the conversion when passing from the flow configuration M_1 to M_2. While in the first configuration, hydrogen is forced through the membrane, in the latter one hydrogen has to diffuse across the surface layer along with benzene, and thus, one expects a decrease in conversion. The slight decrease is justified by the high permeability of hydrogen. The mass transport across pores of various sizes also results in an apparent activation energy which is an average between the values corresponding to purely kinetic and diffusional regimes. This accounts for the observed constancy of E_A.

The effect of the hydrogen to benzene ratio on conversion is shown in fig. 9, where the benzene conversion is shown as a function of temperature for three values of the ratio H_2/C_6H_6. The conversion curves in fig. 9 show the typical behavior observed for a reversible reaction. At temperatures higher than 403–423 K the reverse reaction (dehydrogenation of cyclohexane to benzene) becomes important and this leads to a significant decrease of conversion at temperatures above 473 K. these findings are in agreement with previous observation reported in the literature [23].

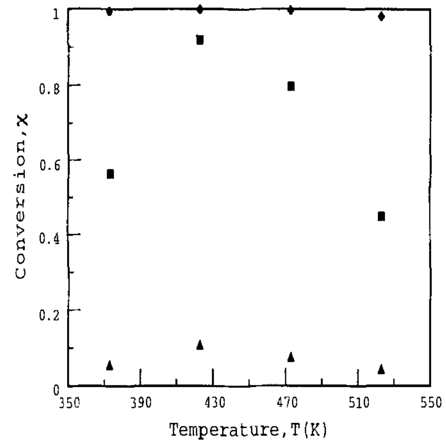

Fig. 9. Benzene conversion, χ, as a function of the temperature for various hydrogen/benzene ratios: (▲) 6.8; (■) 17.1; (◆) 28.3; Q_t: 0.16 ml/s.

4. Conclusions

We have shown that the deposition of the active phase via Pt mesitylene cocondensates may be successfully used in preparing catalytic membranes. The technique is a valid alternative to the conventional wet deposition process because it does not require the high temperature calcination step which may introduce defects in the surface active layer of γ-Al_2O_3. Work is in progress to address this issue in a more systematic way.

The preliminary experimental results on the benzene hydrogenation have shown the importance of the role of the mass transport accross the membrane on the overall reactor performance. The nonuniform pore size distribution results in a decrease of the apparent activation energy, compare $E_{A,p}$ (12.9 kcal/mol) with $E_{A,M1-3}$ (7.2–7.4 kcal/mol). Work is in progress to address this issue in a more systematic way by also developing a detailed membrane reactor model.

The potentiality of membrane catalytic reactors has not yet been fully investigated, except perhaps for the dehydrogenation reactions and there are new opportunities for developing new interesting applications.

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