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Carbon membrane-based catalysts for hydrogenation of CO

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Hollow-fibre carbon membranes with different pore sizes were tested as catalyst supports in the hydrogenation of CO. The factors which contributed to the uniformity of the porous structure and to an increase in the specific surface area of the membranes also resulted in enhanced performances of the catalysts.

Keywords: carbon membrane; hydrogenation; pore-size distribution

The use of carbon fibres as supports for catalysts is an area of intensive investigation. Among the advantages of this type of catalytic system are those inherent to the commonly used mineral compounds, such as: developed specific surface area, homogeneous surface properties, stability in harsh environments and resistance towards the active metal phase, in addition to the unique features which are characteristic only of carbon. The latter include: high heat and electrical conductance, shorter diffusion paths due to the small diameter of the fibrils and lower hydraulic resistance [1]. Catalytic processes require high porosity and an optimal micropore/macropore ratio of the carbon fibre supports [2,3]. Certain methods of impregnation of metals and the subsequent treatments of fibres are also required [4,5].

During the last decade attention was paid to stereoselective catalytic systems [6], some of them were based on zeolites and carbon molecular sieving adsorbents. In a recently published survey it was emphasized that stable inorganic membranes, especially hollow fibre membranes, were one of the most promising types of catalyst support [7]. Hollow-fibre carbon membranes originated from the work of Koresh et al., who produced them by gradual pyrolysis of cellulose and other commercial membranes manufactured from carbonizable materials [8]. Later, polyacrylonitrile (PAN)-based hollow fibers, some of which had been subjected to

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different treatments, were employed in the production of carbon membranes, mainly because of the remarkable mechanical properties and stability of PAN-derived carbonized materials [9–11].

The production of highly asymmetric carbon membranes by the authors has been discussed in a previous paper [12]. These membranes were produced by thermo-oxidative stabilization and carbonization of specially prepared hollow-fibre asymmetrical precursors which were cast from solutions of PAN-based copolymers using the phase-inversion technique. The membranes possessed remarkable flexibility and stability in harsh environments. The diameters and shapes of pores could be easily varied by changing the precursor precipitation technique, stabilization atmosphere and carbonization temperature [13].

It has been reported that carbon-supported iron catalysts [14,15] and nickel and cobalt catalysts on various supports, including activated carbon fibres [16–18], can be successfully used in the Fischer–Tropsch process for the synthesis of methane from a carbon monoxide and hydrogen mixture. In the present study the Fischer–Tropsch synthesis was chosen as the model reaction for the investigation into the feasibility of hollow-fibre carbon membranes as catalyst supports.

Asymmetric hollow-fibre carbon membranes, with increased porosity, were obtained by carbonization of hollow-fibre precursors produced from polyacrylonitrile-based polymers of two intrinsic viscosities: 2.35 and 3.21 [12]. The precursors also contained large quantities of polymers which give low-carbon residuals upon pyrolysis, such as polyethylene glycols (PEG) of molecular mass 20 000 and polyvinylpyrrolidone (PVP) of molecular mass 40 000, as has been described previously [19]. Two different carbonization methods were used: carbonization in an inert atmosphere or carbonization with activation; their details are given in table 1. The activation was carried out in a CO_2 atmosphere; an activation time, during which the mechanical properties of the membranes did not deteriorate seriously, was chosen. Examination of hollow-fibre carbon membranes produced, by means of mercury-intrusion porosimetry, showed that the pore-size distributions were markedly narrower than were those of the carbon membranes reported earlier [13], although the compatibility of low carbon-residual additives with the PAN-based precursor material seriously affected the mesopore dimensions. Fig. 1 shows the results of

Table 1
Conditions of carbon membrane preparation

Membrane No.	[*n*] of PAN	Additive to PAN precursor solution	Activation conditions (temp.+time)	Carbonization temperature (°C)
1	3.21	PEG	–	800
2	3.21	PVP	–	800
3	2.35	PVP	250°C, 4 h 800°C, 0.5 h	800
4	3.21	PVP	250°C, 4 h 800°C, 0.5 h	800

mercury-intrusion analysis of hollow-fibre carbon membranes produced from precursors containing low-carbon residual polymers. It is clear from this figure that the carbonization of precursors containing the more compatible PVP material resulted in the formation of membranes having pores with sharper radii cut-offs than in the cases of the PEG-containing precursors.

At first an attempt was made to prepare the catalysts by soaking the membrane precursors in solutions of cobalt salts prior to the carbonization operation. When carbonized, both in the inert or in the activating atmosphere, the resulted membranes did not exhibit substantial activity in the synthesis of methane. Although CO conversion reached 70%, by membrane 4, the main product was CO_2 which formed according to Bell–Buduar reaction. In this case, carbon depositions on the membrane surfaces were seen with the naked eye.

Carbonized membranes were then impregnated with cobalt nitrate according to the method described by Lapidus et al. [17] to give carbon-based hollow-fibre catalysts. All the catalysts were specially prepared to contain 2% cobalt, the optimum for the carbon fibre-based catalysts for Fischer–Tropsch synthesis reported earlier [18]. After the impregnation operation the catalysts were hydrogen-treated at 450°C for 1 h at a flow rate 3000 h^{-1}. The reaction was carried out in a flow-type catalytic installation under the following conditions: pressure 0.1 MPa, temperature range 200–400°C, $CO : H_2 = 1 : 3$ (vol), flow rate 200 h^{-1}.

The results of CO hydrogenation using the carbon membranes which were carbonized in an inert atmosphere are given in table 2. Almost complete conversion of CO was observed on catalyst 1, with a maximum at 280°C. As in the case of the carbon membranes impregnated with cobalt before the carbonization operation, more CO_2 than CH_4 was formed on this catalyst. The yield of CH_4 reached 67.8 g/m^3 at 280°C when the reaction selectivity was 35%. Although an increase in the reaction temperature resulted in the slight improvement in selectivity, which reached its maximum at 360°C, both the conversion of CO and the yield of CO_2 decreased at higher temperatures. Catalyst 2 was less active in the reaction in terms

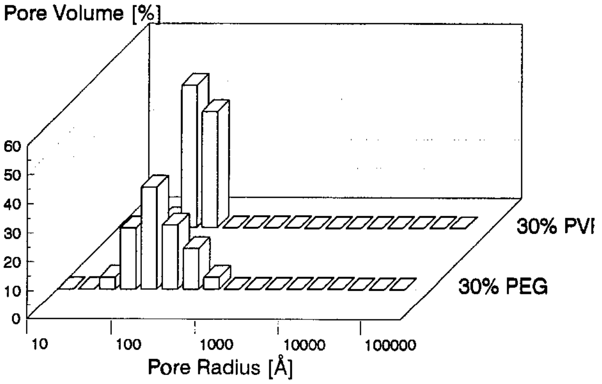

Fig. 1. Results of mercury-intrusion analysis of hollow-fibre carbon membranes produced from precursors containing low-carbon residual polymers.

Table 2
Results of CO hydrogenation on catalysts 1 and 2

Reaction temp. (°C)	Catalyst 1			Catalyst 2		
	CO conv. (%)	CH_4 select. (%)	CH_4 yield (g/m^3)	CO conv. (%)	CH_4 select. (%)	CH_4 yield (g/m^3)
200	26.8	30	12.8	–	–	–
240	52.7	37	31.7	–	–	–
280	97.6	35	67.8	13.7	67	13.6
320	95.0	38	60.1	34.9	53	25.0
360	93.8	41	54.3	77.5	56	50.0
400	93.8	34	65.6	75.7	53	41.4

of CO conversion and CH_4 yield, but the selectivity for CH_4 was remarkably higher in this case. The maximum conversion was registered at 360°C when CH_4 selectivity was 56%.

Since catalysts 1 and 2 differed only in their low-carbon residual additives, it can be assumed that uniform pores with the radii close to 100 Å, formed by PVP molecules, are more effective for the formation of methane in the Fischer–Tropsch synthesis than bigger pores with wider size distributions, resulting from PEG additives. This assumption is in good agreement with the earlier reported results of the hydrogenation of CO on the ordinary carbon fiber-based catalysts [18].

The synthesis of CH_4 was best accomplished on catalyst 4, where a complete conversion of CO occurred at 320°C and retained over the temperature range up to 400°C. The selectivity grew with the temperature increase and reached 88% at 400°C when the yield of CH_4 was 135 g/m^3. Membrane 4, activated in CO_2 prior to the carbonization operation, was used as a support for this catalyst. The effect of the activation on the parameters of the pore structure of the membranes were studied, using the mercury intrusion porosimetry. The specific surface area increased from 42 m^2/g for unactivated membrane 2 to 285 m^2/g for activated membrane 4.

Table 3
Results of CO hydrogenation on catalysts 3 and 4

Reaction temp. (°C)	Catalyst 3			Catalyst 4		
	CO conv. (%)	CH_4 select. (%)	CH_4 yield (g/m^3)	CO conv. (%)	CH_4 select. (%)	CH_4 yield (g/m^3)
200	7.1	–	–	2.6	60	2.1
240	5.8	27	2.1	35.4	80	25.7
280	15.3	67	17.8	93.7	80	102.1
320	52.6	60	52.1	99.5	85	128.6
360	50.7	58	44.3	99.6	86	123.6
400	33.9	63	41.4	99.1	88	135.0

It is noteworthy that the results obtained for catalyst 3, which was activated by the same method, were poorer than those for unactivated catalyst 2. A highest CO conversion was only 52.6% and CH_4 yield 52.1 g/m^3. Apparently, a lower molecular mass of PAN-based polymer used for the spinning of the membrane precursor was responsible for this. It has been shown earlier [12] that with a decrease in the intrinsic viscosity of the precursor material the number of pores per unit of surface area of hollow-fibre carbon membrane decreased and the pore dimensions increased drastically. As a consequence the void-forming effect of PVP was diminished during the casting procedure and the uniform porous system did not occur in membrane 3.

In conclusion, the catalysts active in CO hydrogenation with the formation of CH_4 were obtained by the impregnation of the hollow-fibre carbon membranes with cobalt. The addition of PVP to the casting solutions in combination with the high intrinsic viscosity of the membrane precursor material resulted in higher selectivity of the catalysts. The most effective catalysts were produced from the membranes activated prior to the impregnation operation. The study of the effect of gas separating properties of carbon membranes on the hydrogenation reaction is continuing.

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