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Pd-BASED HYDROGEN DIFFUSION MEMBRANES AS CATALYSTS IN CARBON MONOXIDE HYDROGENATION

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Pd-23 at% Ag and Pd-7.8 at% Y hydrogen-diffusion membranes were prepared, characterised and examined as catalysts for CO hydrogenations with (1) hydrogen permeating through the membranes and (2) H_2/CO mixture, at 1 atm total pressure and in the temperature range of 140–400 ° C. C1–C4 hydrocarbons were produced with conversions of less than 1%. The Pd-Y membrane showed marginal Pd-enrichment on both sides but no change was indicated for the Pd-Ag alloy by XRD.

1. Introduction

The catalytic hydrogenation of carbon monoxide is an industrially important reaction because of the possibility of the production of numerous valuable chemicals such as methane and higher hydrocarbons and/or oxygenated products including methanol and higher alcohols.

Group VIII metals especially in the form of films, as single crystals or supported on a variety of materials (such as alumina, magnesia, silicon carbide, alumino-silicates, active and/or amorphous carbon, La_2O_3, CeO_2, TiO_2, ZrO_2, ThO_2 etc.), have been used in the hydrogenation of CO as active catalysts [1–19]. The performance of these catalysts can vary: some induce CO dissociation with subsequent C–C bond formation [20,21]. Hydrogen in these reactions can act as a typical reducing agent in the activation of the synthesis reaction and also as a reactant in the straightforward hydrogenation reaction. Therefore its adsorption

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kinetics and energetics as well as its interactions with CO and surface species strongly influence the catalyst activity and/or selectivity [22–24].

Pd-based catalysts have been used successfully as exceptionally active and selective catalysts in hydrogenation reactions. Palladium and palladium alloys, when used as membranes, are still the only effective single-phase metallic systems which permit hydrogen to permeate at an appreciable rate at moderate temperatures and differential pressures applied across the membranes [25,26]. However, only a few of these materials such as the Pd-Ag alloys have found extensive use as hydrogen permeating membranes in industry. They can be used as catalysts in hydrogenation, dehydrogenation and hydrogenation, and also for hydrogen transfer reactions. Their use as membrane catalysts supplying hydrogen to the reactants such as in the hydrogenation reactions has not yet been fully exploited industrially.

It is in this respect that we report our early results and observations obtained with two such alloy membranes in the hydrogenation of carbon monoxide at 1 atm total pressure, at a temperature in the range of 100–400 °C with permeate and/or molecular hydrogen in a membrane reactor operating in a semi-batch mode.

2. Experimental

Two membrane materials were chosen namely Pd-7.8 at% Y and Pd-23 at% Ag. The former was prepared from its constituent elements by argon arc-melting, followed by homogenizing in a vacuum furnace at 1223 K, 10^{-6} Torr for 2 weeks in tantalum foils. The Pd-7.8 at% Y alloy exhibits a larger hydrogen solubility, and thus higher hydrogen permeation rate coupled with a greater mechanical strength and a greater resistance to contamination than any other Pd-alloy reported [26]. The Pd-23 at% Ag alloy is used in industry hence is chosen as a reference material.

The resulting alloy buttons were then cold-rolled (with several intermediate anneals) to the required thickness of 0.01–0.005 cm. Discs of 2.47 cm in diameter were then cut from these sheets and given a final anneal at 900 K for 3 hours before use in the reactor. The Pd-23 at% Ag membrane material was kindly supplied by Johnson Matthey Technology Centre.

Optical microscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) were used for surface and bulk characterization during the production of the membranes and before and after the reaction studies.

The carbon monoxide hydrogenation studies were carried out in a stainless steel reactor shown in fig. 1, with the membranes clamped between two copper gaskets, which divided the reactor into two equal-volume compartments, i.e. a high pressure (upstream) and a low pressure (downstream) reaction side. The heating was achieved by means of a tubular electric furnace and the furnace and

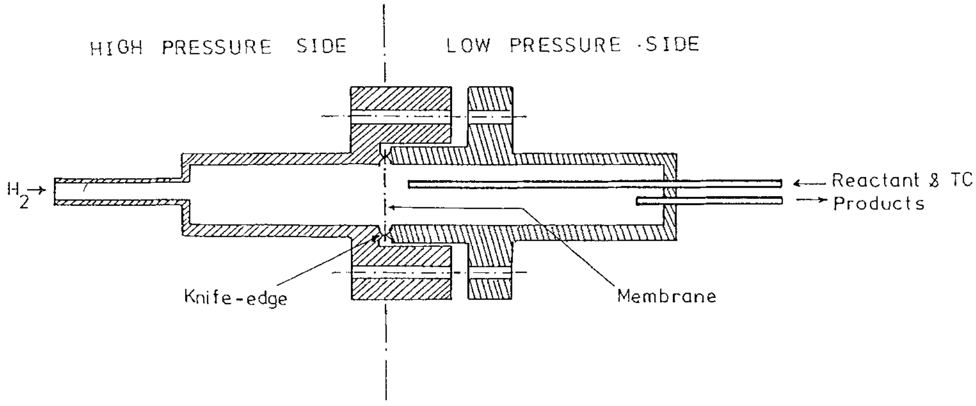

Fig. 1. Diffusion membrane reactor.

the reactor temperature was monitored by thermocouples and control units. The reactor temperature was read by a K-type thermocouple placed very near to the surface of the membrane on the reaction side. The reactant gases were introduced into the downstream side of the membrane by the inlet tubes placed about 3 mm away from the membrane surface.

The reactor was operated in a semi-batch mode. In the case of CO hydrogenation via permeate hydrogen, the low pressure side of the reactor was charged with 5

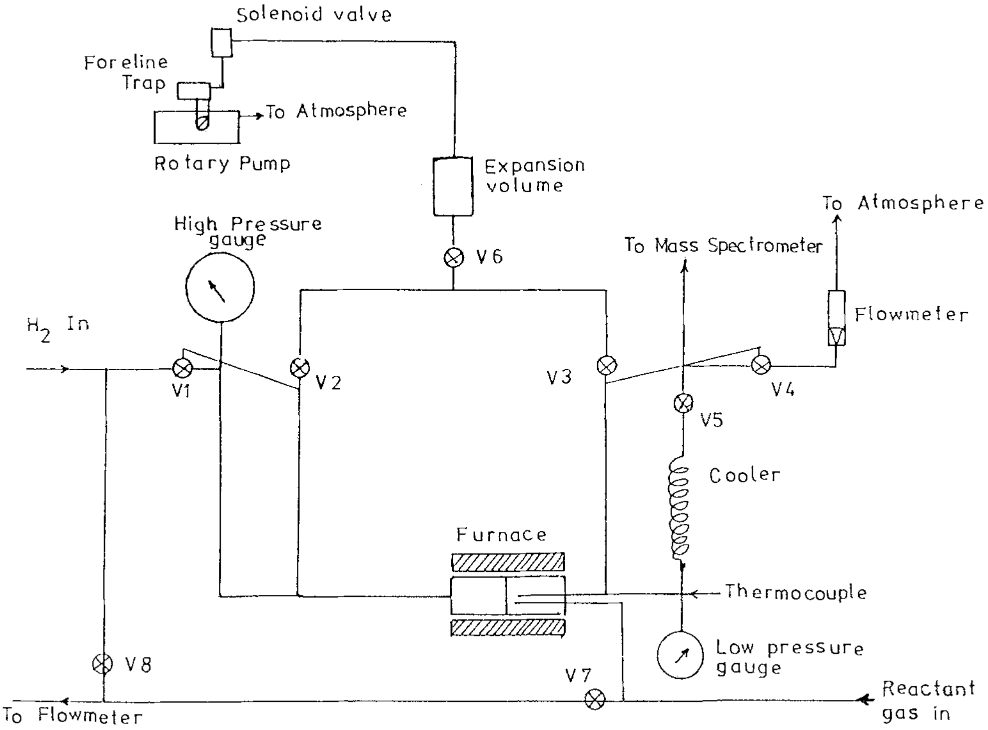

Fig. 2. Hydrogen permeation and hydrogenation reaction rig.

cm^3 CO with p_{CO} varying from 0.122 to 0.181 atm in helium to make a total pressure of 1 atm while hydrogen was supplied continuously from the high pressure side. For CO hydrogenation via molecular hydrogen, the low pressure side of the reactor was charged with 5 cm^3 CO, 10 cm^3 H_2 and helium to a total pressure of 1 atm whilst helium was the only gas admitted to the high pressure side of the membrane. The reaction was followed by gas chromatography and mass spectrometry. Figure 2 illustrates the experimental set-up for both permeability and hydrogenation studies.

3. Results and discussion

The hydrogen permeability results obtained for the two membrane systems are given in fig. 3 and are in good agreement with published data [27]. Table 1 shows the products obtained in the first 15 minutes (initial) and at the end of 2 hours (final) of the reaction. In the case of the permeate-hydrogen reactions, both membranes give rise to C4-hydrocarbons as the initial products and most commonly buta-1,3-diene appears to be the primary reaction product. However butenes and butane are formed, but these appear to be derived from the buta-1,3-diene following hydrogenation of the latter. It is presumed also that C3- to C1-hydrocarbons (alkanes) were derived via hydrogenolysis of the C4-hydro-

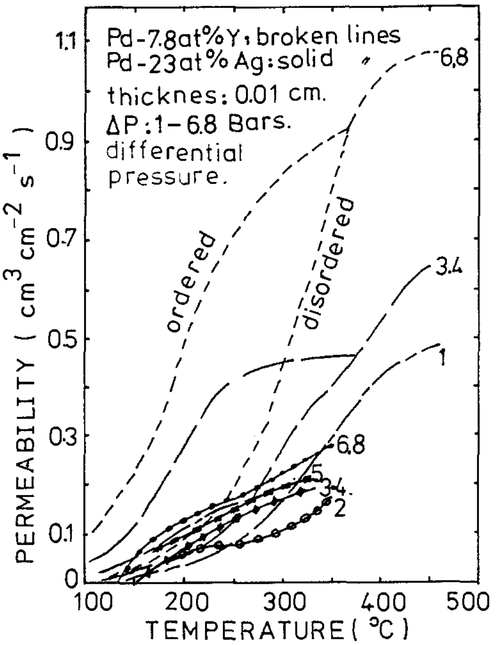

Fig. 3. Hydrogen permeability versus temperature, for Pd-23 at% Ag and Pd-7.8 at% Y membranes at various differential pressures, ($\Delta P = 1 - 6.8$ Bars).

Table 1
Product distribution in $CO+H_2$ reaction with Pd-23 at% Ag and/or Pd-7.8 at% Y membrane via permeate and/or molecular hydrogen at 1 atm total reaction pressure

Membrane Material	H_2-mode	T, °C	P atm	time	% products			
					C1	C2	C3	C4
Pd-23 at% Ag	P	154	1	I	–	–	–	100.00
				F	12.01	87.98	–	–
	P	292	1	I	–	–	–	100.00
				F	–	–	73.45	26.53
	P	374	1	I	–	–	94.40	5.60
				F	–	–	100.00	–
	M	154	0	I	42.39	–	–	57.61
				F	–	100.00	–	–
	M	292	0	I	–	–	78.48	21.51
				F	–	–	100.00	–
	M	374	0	I	–	96.74	2.36	0.90
				F	18.03	77.73	1.45	1.25
Pd-7.8 at% Y	P	141	1	I	–	1.91	30.62	67.47
				F	–	2.16	74.40	23.44
	P	285	1	I	18.00	21.00	50.00	8.54
				F	+	+	–	–
	P	366	1	I	4.00	–	2.6	93.40
				F	57.00	9.00	34.00	–
	M	141	0	I	89.5	10.5	–	–
				F	83.0	16.9	–	–
	M	280	0	I	85.77	14.22	–	–
				F	95.19	4.81	–	–
	M	359	0	I	81.73	3.67	14.59	0.01
				F	+	+	–	–

P = Permeate, M = molecular hydrogen, I = initial, F = final.

carbons in the form of n-butane. There are interesting differences between the two membrane systems. The Pd-Ag system gives C2, C3 hydrocarbons at low temperatures but mostly C3, C4 hydrocarbons at higher temperatures.

The Pd-Y membranes generally give C3, C4 hydrocarbons initially in the reaction but finally, at all temperatures, lower hydrocarbons especially C1, C2 alkanes were observed. Mass spectroscopic analysis did indicate the presence of H_2O and CO_2 and possibly methanol in the products, but more extensive MS/GC analyses are required to confirm these observations. The two systems also show significant differences in their behaviour with respect to each other and also their permeate-hydrogen behaviour when they were subjected to studies as outlined earlier on with molecular hydrogen.

The Pd-23 at% Ag system gives rise initially to C3 and C4 hydrocarbons which later on resulted in the formation of methane and ethane except at 292 °C which favoured more C3-hydrocarbon formation. With the Pd-7.8 at% Y at 141 and

Table 2
SEM analysis for CO hydrogenation

Membranes		Hydrogen side		Reaction side	
		Pd	Y	Pd	Y
Pd-7.8 at% Y	Before reaction	93.0	7.0	93.0	7.0
	After reaction	93.2	6.8	94.1	5.9
		Pd	Ag	Pd	Ag
Pd-23 at% Ag	Before reaction	78.2	21.8	78.2	21.8
	After reaction *	not yet determined			

* XRD analysis indicates no change. The diffraction lines were sharp, material was single phase.

280 ° C, the only products from the start of the reaction were methane and ethane. At 359 ° C, apart from methane and ethane a little C4-hydrocarbon was also detected. If the latter results are compared with those obtained with the permeate hydrogen for the Pd-7.8 at% Y membrane at 1 atm pressure, it can be seen that at 141° C, no methane existed and at higher temperatures, it was the initially formed C4 hydrocarbons which in turn were converted into methane and ethane. However, conversions were low, less than 1% based on carbon conversion but this is not surprising given the low metal surface area of the membranes.

Palladium and palladium based alloy membranes are known to suffer from surface contamination which may result either from chemical reactions with gas-borne reactive species and/or from chemisorption of active unsaturated hydrocarbons such as acetylene, ethylene, propylene etc. at high concentrations thus blocking catalytically active sites on the alloy surface and retarding the dissociation of hydrogen, consequently reducing permeability. Carbon can also occupy interstitial sites with the same effects. If carbon residues were formed, as is thought to occur in Fischer-Tropsch synthesis, they did not lead to the gross carbon deposition and eventual failure of the membrane as observed in ethylene hydrogenation [28] especially with the Pd-Y system.

Table 2 shows some of the SEM and XRD results for these membranes before and after the CO-hydrogenation. There is a marginal enrichment of Pd on both sides of the membrane in the case of the Pd-7.8 at% Y system and this small increase is more apparent on the reaction side. The XRD analysis indicates no change in the case of the Pd-23 at% Ag system, the diffraction lines being sharp and the material being single phase.

As yet, it is not possible to explain the observed differences in the product distributions but it is likely that the oxygen derived from carbon monoxide may well become associated with yttrium whereas this will not occur with silver. The apparent formation of buta-1,3-diene as an initial product is very significant and it would be of interest to examine the state of the surface when CO is interacted with it. It was not possible to study the nature, orientation and association of CO on these surfaces and this would be a more instructive exercise. H_2/CO mixtures

(2 : 1 ratio by volume) was passed over pure copper turnings in the same temperature range (140–385 ° C) at 20 ml/min flow rate and no activity for the production of hydrocarbons were detected so that the presence of copper gaskets in the reaction is not thought to contribute to the observed products [29].

4. Conclusions

The two systems give interesting and different product distributions with permeate and/or molecular hydrogen. In the former case, the Pd-Ag membranes gave C2, C3-hydrocarbons at low temperatures but mostly C3 and C4 hydrocarbons at high temperatures whereas the Pd-Y membranes generally favoured C3, C4-hydrocarbon formation initially and finally at all temperatures. Reactions of CO with molecular hydrogen on the Pd-Ag, membrane gave rise to methane and ethane formation at low temperatures and at 374 ° C methane and ethane are formed with appreciable quantities. In the case of the Pd-Y membrane, methane and ethane formation was favoured from the very beginning of the reaction at all temperatures and their concentrations were far greater than those for the Pd-Ag membrane. Neither membrane showed signs of gross carbon deposition and did not rupture due to excessive use during the reaction studies. There was a marginal enrichment of Pd on both sides of the Pd-Y membrane but XRD indicated no change in Pd-Ag case; this is probably due to the greater affinity of yttrium for oxygen.

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