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Membrane–catalyst systems for selectivity improvement in dehydrogenation and hydrogenation reactions

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Abstract

Variation in the selectivity of dehydrogenation and hydrogenation reactions was observed as a result of the conditions of hydrogen transfer from the zone of paraffin, olefin or cyclohexane dehydrogenation into the zone of diene hydrogenation through a hydrogen permeable membrane in the form of foil, thin-walled tube or a dense palladium alloy layer on the thermostable porous support. Industrial granular catalysts Pt-Re/Al_2O_3 and alumina-chromia were used for dehydrogenation, and hydrogenation was performed by palladium-containing membrane catalysts. The dependence of the selectivity of cyclopentadiene (CPD) hydrogenation into cyclopentene (CPE) was measured by an increase in the thickness from 20 to 80 nm of the palladium–ruthenium (Pd–Ru) alloy layer on the polydimethylsiloxane film which was inert towards CPD hydrogenation. Cyclopolyolefines C_7–C_{12} of different structure differ in the rate of their reaction with hydrogen diffused through the membrane catalysts or mixed with the polyolefin. © 2001 Published by Elsevier Science B.V.

Keywords: Pd-containing membrane catalysts; Selectivity of dehydrogenation and hydrogenation of different hydrocarbons

1. Introduction

A method for carrying out simultaneously the catalytic reactions involving hydrogen evolution and consumption was proposed 30 years ago [1]. Two reactions were conducted by means of hydrogen transfer through a partition permeable only to hydrogen which also served as a catalyst. The types and forsakes of systems of different catalysts and hydrogen permeable membranes were mentioned in [2–4]. It was found [5] that the thin-walled tube of palladium–nickel alloy dehydrogenates isoamylenes into isoprene swifter in the experiments with hydrogen/olefin mixtures, their partial pressure ratio being up to 1, than with pure olefin. A further increase in hydrogen share in the initial mixture depresses the dehydrogenation rate. A similar effect was found [6] with another catalyst for isobutane dehydrogenation. The authors [6] probably were not acquainted with [5].

The aim of this study is to elucidate the selectivity improvement by changing the conditions and increasing the share of hydrogen removal from the dehydrogenation zone and hydrogen introduction into the zone of hydrogenation through palladium alloy membranes of different content, composite membrane catalysts with different thickness of palladium layer and by use of membrane–catalyst systems.

2. Results and discussion

The simplest in preparation and the most reliable in operation palladium alloys — palladium–ruthenium

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(Pd–Ru; 9.8% Ru) and Pd–Ru–Sn (4.3% Ru, 0.9% Sn) foils 0.1 mm thick with 20.5 cm^2 surface — were used for hydrogen removal from the zone of butane dehydrogenation at 813 K and space velocity of 230 h^{-1}. The dehydrogenation reaction was carried out on the commercial alumina-chromia catalyst. The catalyst particles (1–2.5 mm in diameter) were placed as a monolayer onto palladium alloy foils. Along the other surface of the foil argon (curves 1 and 2 in Fig. 1) and the air (curves 1′ and 2′) was passed.

The tin-containing membrane is more efficient than the Pd–Ru membrane for increasing the selectivity of butane dehydrogenation and permits higher share of removed hydrogen (see the curves 1 and 2 or 1′ and 2′ of Fig. 1). The combination of hydrogen removal with its oxidation by air on the membrane is useful for maintaining the proper temperature of the dehydrogenation catalyst.

The system of the industrial Pt-Re/Al_2O_3 granular catalyst for cyclohexane dehydrogenation with Pd–Ru foil for hydrogenation of 1,3-pentadiene by hydrogen removed from the zone of cyclohexane dehydrogenation allows enhancing the rates of both reactions and using 99% of formed hydrogen for selective 1,3-pentadiene transformation into pentenes. Fig. 2 depicts that the amount of hydrogen removed from the zone of cyclohexane dehydrogenation during the coupling of this reaction with 1,3-pentadiene hydrogenation (upper curve) is much more pronounced than the one for the experiments with the diffused hydrogen removal by the argon flow (lower curve). The feed flow of cyclohexane does not influence the amount of removed hydrogen. The data obtained with cyclohexane vapour flows of 0.7; 1.3 and 2.6 × 10^{-6} mol s^{-1} are shown in Fig. 2 by triangles, squares, and circles, respectively. The argon flow rate in the zone of 1,3-pentadiene hydrogenation is plotted on the abscissa in Fig. 2. The partial pressure 1,3-pentadiene

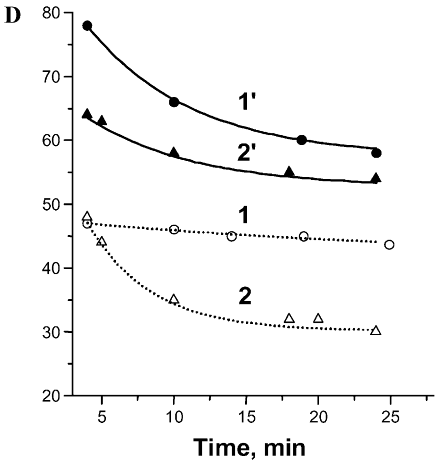

Fig. 1. The share (D) of hydrogen removed from the zone of butane dehydrogenation by Ar flow (curves 1 and 2) or air flow (curves 1′ and 2′); 1,1′-Pd–Ru–Sn foil membrane; 2,2′-Pd–Ru foil membrane.

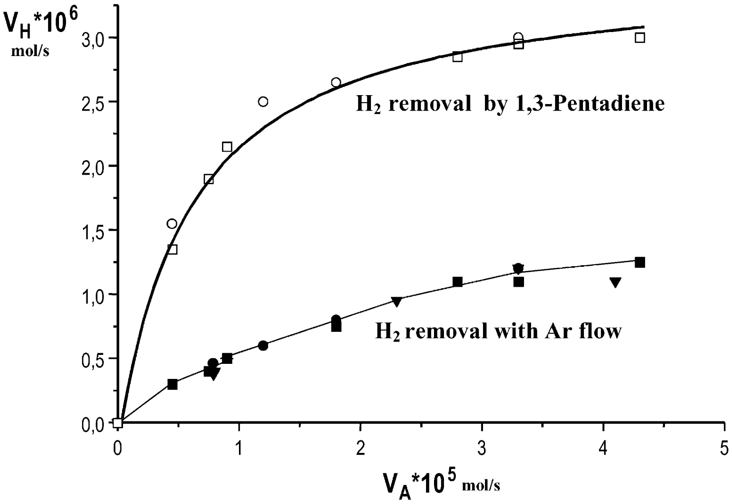

Fig. 2. The dependence of the removed hydrogen amount on the argon flow rate in 1,3-pentadiene hydrogenation zone.

on the input of hydrogenation zone was constant in all experiments.

The thermoconductivity of Pd–Ru foil membrane catalyst is sufficiently high, for using the heat evolved during 1,3-pentadiene hydrogenation to stimulate the endothermic cyclohexane dehydrogenation without extra heating.

Composite membrane catalysts prepared by covering the polydimethylsiloxane film with Pd–Ru alloy layers of different thickness from 20 to 80 nm have the higher selectivity of cyclopentadiene (CPD) hydrogenation into cyclopentene (CPE) the thicker is the palladium alloy layer (see Fig. 3). The reason is the formation of a dense metallic layer which is responsible for atomic hydrogen supply to the hydrogenatable substance. Any fouling of the dense palladiumbased layer of the composite membrane–catalyst depresses the selectivity of hydrogenation as a result of molecular hydrogen penetration. The upper curve in Fig. 3 coincides with the data obtained with the palladium foil as the membrane catalyst.

The polymer support is catalytically inert in the CPD hydrogenation reaction.

The penetration of atomic hydrogen through the membrane catalyst provides higher selectivity (curve 1 in Fig. 4) than the introduction of the mixtures of the CPD vapour and hydrogen (curve 2 in Fig. 4).

Investigation of hydrogenation of cyclic polyolefines C_7–C_{12} shows that this reaction rate is higher in the case of hydrogen diffusion through the membrane–catalyst (W_1) than the one for the introduction of a mixture of the polyolefin vapour with hydrogen (W_2). The corresponding data for several polyolefins are presented in the Table 1. It depicts that this effect is more pronounced for more strongly adsorbed polyolefin molecules. An increase in the number of double bonds causes a rise in the amount of hydrogen transferred through the membrane catalyst during hydrogenation.

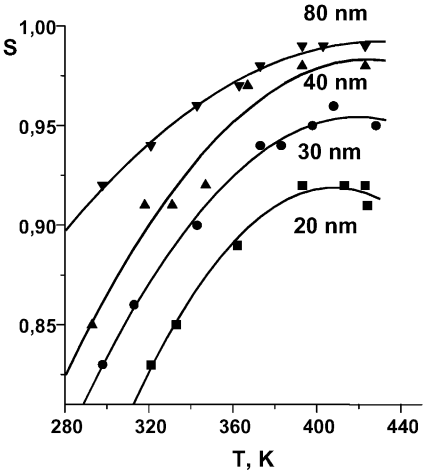

Fig. 3. Temperature dependence of the selectivity of CPD hydrogenation into CPE by the composite membrane catalyst with Pd–Ru alloy layer of different thickness.

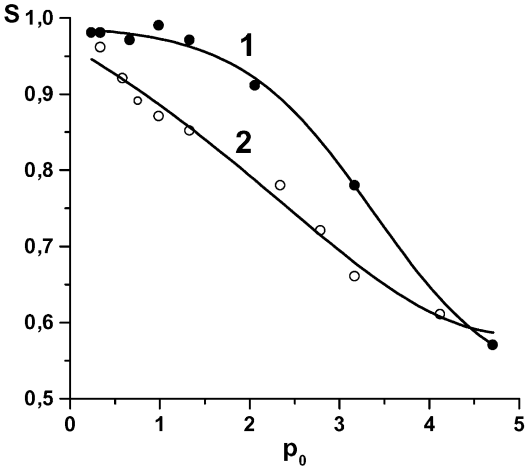

Fig. 4. The influence of the CPD/H ratio (p_0) on the selectivity of the conversion to CPE by hydrogen introduction through the membrane (1) or in mixture with CPD vapour (2).

Table 1
Influence the polyolefin structure on the rate of its hydrogenation by the diffused or mixed hydrogen

Hydrocarbon	W_1/W_2
Cycloheptatriene	3.0
Cyclooctene	1.7
Cyclooctadiene-1,3	1.8
Cyclooctadiene-1,5	2.0
Cyclooctatetraene	1.3
Cyclododecatriene	7.5

3. Conclusions

It is found that oxidation of hydrogen removed through certain membranes from the zone of butane dehydrogenation by the alumina-chromia industrial catalyst increased the yield of butadiene about twice. Olefin dehydrogenation into dienes may be improved by hydrogen introduction into the olefin stream through the walls of the palladium–nickel alloy tube with hydrogen–olefin partial pressure ratio up to 1. Selective hydrogenation of 1,3-pentadiene into pentenes by Pd–Ru foil with hydrogen diffused through this membrane from the zone of cyclohexane dehydrogenation by the industrial Pt-Re/Al_2O_3 granular catalyst increased three times the amount of hydrogen removed from the zone of dehydrogenation in comparison with its removal by the argon flow. The CPD hydrogenation into CPE by a dense Pd–Ru alloy layer on the inert support increased up to 0.98 with increasing layer thickness from 20 to 80 nm. The mentioned selectivity was observed for Pd–Ru foil 0.1 mm thick which contains several thousands more Pd and Ru on the unit surface of membrane catalyst.

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