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> CHEMICAL KINETICS AND CATALYSIS =

Using Ceramic Membranes for the Separation of Hydrogen Produced by Dehydrogenation of Perhydro-*m*-terphenyl

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Abstract—The efficiency of a variety of ceramic membranes for the purification of hydrogen obtained by dehydrogenation of perhydro-*m*-terphenyl in a catalytic flow reactor from vapors of initial hydrocarbons and dehydrogenation products is investigated.

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INTRODUCTION

The current trend toward the decentralization of electric and heat supply networks based on compact, highly efficient electric power sources is of great interest worldwide. Hydrogen fuel elements, which produce pure water and no hazardous substances during operation, are considered a priority area of power source development; however, there are very strict requirements for the purity of their fuel. As is well known, it is neither convenient nor safe to store and transport pure hydrogen under the conditions of a modern metropolis.

The technique for storing hydrogen described in [1-3], based on reversible cycles of the hydrationdehydrogenation of organic chemical compounds and characterized by high hydrogen absorbing capacity (7-7.5 wt %), is completely explosion proof, since hydrogen is stored in the chemically bonded state and is separated only under the specific conditions of the dehydrogenation reaction.

The aim of this work was to study the possibility of separating hydrogen from hydrocarbon vapors in the dehydrogenation reaction of perhydro-*m*-terphenyl (PHMT) in a flow catalytic system using hydrogen permeable ceramic membranes.

EXPERIMENTAL

To study the possibility of separating hydrogen from hydrocarbon vapors in dehydrogenation process, we used two types of hydrogen permeable membranes based on closed at one end tubular ceramic carriers (α -Al₂O₃, 120 mm long, 8 mm o.d., 6 mm i.d.) with an average pore size of up to 0.2 µm. Membranes (I) with and (II) without carbonized coating ~100 µm thick on the outer surface were provided by the National Research Center Kurchatov Institute. Resole phenolformaldehyde resin, LBS-1 grade (GOST 901-78, mod. 1–6; 58–60 wt % resin, up to 9.0 wt % free phenol, and no more than 10 wt % water; gelling time, up to 100 s) was used as a precursor of the carbonized layer. The carbonized coating was formed by increasing the resin's capability to adhere to the substrate under various conditions of drying, thermal stabilization, and substrate surface modification, without penetrating the structure of the near-surface layer.

Catalytic Experiment

The capability of membranes to separate hydrogen from hydrocarbon vapors in the dehydrogenation reaction of perhydro-*m*-terphenyl was investigated in a flow catalytic system [4]. The PHMT dehydrogenation was conducted continuously for 8 and 25 h in three different ways: (a) without ceramic membranes; (b) using ceramic membrane (I) with the carbonized coating on its external surface; and (c) using membrane (II) without carbonized coating.

The basic criterion for evaluating the capability of membranes to separate hydrogen was the quantity of dissolved hydrocarbons in the solvents mixture at the separator's outlet.

Each catalyst sample (6 cm³) was charged into a steel reactor 10 mm in diameter and 230 mm long. The catalyst bed was fixed in the center of the reactor with a quartz wool. The reactor was placed in an oven and heated to the reaction temperature. Liquid perhydro-*m*-terphenyl was supplied to the reactor using an HPP 5001 high-pressure pump at 90–95°C and a volume rate of 1 h⁻¹. The substrate for the dehydrogenation reaction (i.e., perhydro-*m*-terphenyl) was obtained via the full hydration of commercial *m*-terphenyl (99%, Aldrich) in an R-201 chemical reactor (Reaction

Content of gas products from the PHMT dehydrogenation reaction, %

| τ, h | А | В | С |
|------|------|------|------|
| 8 | 0.29 | 0.01 | 0.12 |
| 25 | 0.37 | 0.03 | 0.14 |

 τ is length of the experiment, (A) no membrane, (B) membrane (I), and (C) membrane (II).

Engineering, Inc.). All supply lines were thermostatted at $90-95^{\circ}$ C.

Hydrogen and the other reaction products outgoing from the reactor entered a standard metallic saturator designed for the basic separation of liquid reaction products from gases. The saturator's outlet for liquid products was tightly connected to a receptacle. The saturator's gas outlet was connected to one neck of a two-necked flask. The investigated membrane was placed inside the flask and gas-tightly glued to the hydrogen inlet tube at its open end. The hydrogen was then passed from the output neck of the flask to a bubbler filled with a mixture of equal volumes of cyclohexane and benzene with a total volume of 100 mL. The outlet of the bubbler was connected directly to a purified gas volume meter (an RG7000 drum gas counter) via a glass tube. So, after passing through the membrane, the gas mixture of hydrogen and possible byproducts formed during the dehydrogenation went first to the flask and then to the bubbler with the solvent mixture, where possible organic impurities were dissolved, and finally to the meter for measuring the volume of separated gas. For better condensation of the possible gas products of reaction entering the bubbler, it was cooled in water.

Catalyst Preparation

A heterogeneous Pt/C catalyst based on platinum as the active component in amounts of 3 wt % dispersed on the surface of a sibunit carbon carrier was used both for the hydration of *m*-terphenyl and the dehydrogenation of perhydro-*m*-terphenyl. The catalyst was prepared by impregnation with metal precursors aqueous solutions (chloride complexes), followed by hydrogen reduction. The initial reagents for platinum-based catalysts were an H₂PtCl₆ solution $(\omega(Pt) = 36.3 \text{ wt }\%)$ of pure grade, prepared from calculated amount of hexachloroplatinic acid $[H_2PtCl_6 \cdot 6H_2O]$ and a 30% formalin solution (2.5 parts per one part of hexachloroplatinic acid). It was applied at 10°C, and the coated sample was then impregnated with a 50% KOH solution (300% sample weight) at 5°C. The resulting mass was heated on a water bath at 55-65°C for 1 h, then rinsed with distilled water to a neutral pH, and then placed in a drying oven at 105–110°C for 2.5 h [5]. Finally, samples of the catalyst were reduced at 320° C in a hydrogen flow (30 mL/min) for 2 h.

Chromatographic Analysis

The analysis of hydrocarbon reaction products and of the solvents mixture from the bubbler was performed using a Kristalux-4000M chromatograph with ZB-5 capillary column (ZEBRON, United States), equipped with a flame ionization detector (FID). The programmed temperature profile was 70–220°C with a heating rate of 6 K/min. Some samples of the reaction products were analyzed on a FOCUS DSQ II GC-MS instrument equipped with a TR-5ms capillary column for detailed identification of partial hydrogenation products and byproducts of substrate dehydrogenation. The purity of the obtained hydrogen was additionaly controlled by gas chromatography with thermal conductivity detector on a Porapak Q column.

RESULTS AND DISCUSSION

The main products of the full dehydrogenation of PHMT cycloalkane are *m*-terphenyl and hydrogen. The partially hydrated *m*-terphenyls (cyclohexyl-diphenyl, diphenylcyclohexane and dicyclohexylben-zene) are byproducts of perhydro-*m*-terphenyl dehydrogenation. The structural features of a flow catalytic system ensured an output of hydrogen without byproduct gases. Trace amounts of *m*-terphenyl cracking products such as diphenyl and benzene were observed under more hard reaction conditions (higher temperature, minimal substrate flow rate).

The amount of impurities in the gas mixture at the separator outlet was estimated chromatographically under the assumption that all boiling phases could be removed from the reactor zone along with the hydrogen. A sample of partially hydrated *m*-terphenyl with a 94% degree of conversion and 92% selectivity toward perhydro-*m*-terphenyl was used. A 0.0003 g sample composed of perhydro-*m*-terphenyl (more than 90%), *m*-terphenyl (6%), and a mixture of partialy hydrogenated forms of PHMT with traces of diphenvl (total, $\sim 4\%$) was added to 1 mL of a 50 : 50 cyclohexanebenzene (both solvents of analytical grade) mixture giving the 300 ppm (0.03%) solution. In a similar manner, samples with concentrations of 1500, 1000, 500, 150, and 50 ppm were prepared and analyzed on a chromatograph.

The table presents the results from quantitative estimates of the content of gas products from the PHMT dehydrogenation reaction after they were passed through a 1 : 1 mixture of cyclohexane and benzene with and without membranes (I) and (II). Unfortunately, the sensitivity of the Kristalux-4000M chromatograph did not allow us to determine with sufficient accuracy any concentrations below 50 ppm, so the concentrations for the product peaks registered experimentally on the chromatograms with areas of lower values were calculated by extrapolation. On the other hand, since benzene and cyclohexane are used as solvents in this work, only C_{12} and higher hydrocarbons were determined to estimate the ability of membranes to separate hydrogen from hydrocarbons.

Analysis of samples of the gas products from the PHMT dehydrogenation reaction showed that after they were passed through the mixture of solvents without membranes (A), an additional five peaks belonging to *cis*- and *trans*-perhydro-*m*-terphenyl, *m*-terphenyl, and two intermediate products of their transformation into one another appeared on the chromatograms along with the peaks of the solvents. The total amount of dissolved substances in the analyzed samples was ~0.29% (~1000 ppm) after 8 h (sample 1) and ~0.37 after 25 h. The rates of hydrogen evolution were 5.0, 4.7, and 4.0 L/h after 2, 8, and 25 h, respectively, with >90% PHMT conversion and >90% selectivity toward *m*-terphenyl for the first two points. A drop in these figures and a rise in the content of partially hydrated reaction products was unfortunately observed at the end of 25 h, due apparently to decrease of catalyst activity.

The volumes of the produced hydrogen did not change during PHMT dehydrogenation reaction (B) using membrane (I) with a carbonized layer; however, no C_{18} hydrocarbons are seen on the chromatograms, while they are present for samples 1 and 2 in experiment (A). Instead, four other peaks are seen that belong to PMHT and MT cracking products (dicyclohexyl, diphenyl, and intermediate products of their mutual transformation), and the total amount of dissolved substances in each analyzed sample did not exceed 0.03% even after 25 h (sample 4).

In experiment (C) using membrane (II) without carbonized layer, analysis of the samples of hydrogen after the dehydrogenation reaction showed that *cis*-and *trans*-perhydro-*m*-terphenyl and *m*-terphenyl (sample 5) accompanied the solvent peaks on the chromatograms in a total amount of 0.12% after 8 h, while *cis*- and *trans*-perhydro-*m*-terphenyl, *m*-terphenyl, and two intermediate products of their transformation into one other (sample 6) were present in a total amount of 0.14% after 25 h.

CONCLUSIONS

Based on a comparison of the results from experiments on the PHMT reaction without ceramic membranes (A), using membrane (I) with a carbonized coating on its outer surface (B), and a membrane (II) without carbonized layer (C), it was established that at the estimated volumes of hydrogen separated in PHMT dehydrogenation, using membrane (I) drastically reduced the passing of byproducts vapors from the PHMT dehydrogenation reaction along with hydrogen. At the same time, the concentration of impurities in the hydrogen produced by the dehydrogenation of the organic compound was even lower than in the technical grade hydrogen used for hydrogenation.

Using membrane (II) without carbonized coating also reduced the concentration of byproducts of PHMT dehydrogenation reaction in the mixture of solvents, but to a lesser degree than membrane (I) with the carbonized layer. At the same time, there was a progressive increase in the concentration of dissolved products of the PHMT dehydrogenation reaction over time. It should be noted that no trace amounts of C_{12} were observed while analysis for C_{18} hydrocarbons by chromatography.

The progress in using chemical composite systems of hydrogen storage can be attributed to the increased efficiency of catalyst operation and improvements in flow catalytic systems that use selective hydrogen-permeable membranes.

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