

Energy matryoshka. Hydrogen storage in liquid organic hydrogen carrier

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The transition of the global energy system to the use of non-fossil energy sources is inevitable. Such a change will require the use of alternative ways to store the generated energy. By analogy with organic petroleum products, such energy storage can be hydrogen. Hydrogen can be produced from water and electricity. And as a result of its conversion into energy, the same amount of water will be returned as was spent on obtaining hydrogen. Such an energy carrier turns out to be cyclical in raw materials and does not lead to depleting the planet's material reserves. An additional advantage is that hydrogen energy capacity is significantly higher than that of a hydrocarbon fuel, therefore storing energy with hydrogen is more efficient.

However, one of the critical problems is its storage when using hydrogen, especially if it is necessary to stock large quantities. One of the options for the safe storage of hydrogen and its transportation is liquid organic carriers (LOHC). When hydrogen accumulates in the LOHC, it is chemically bound by a hydrogenation reaction. Hydrogen is extracted by a dehydrogenation reaction. The "discharged" LOHC is returned to hydrogenation, and the hydrogen is used as an energy carrier. Thus, it turns out a kind of matryoshka doll – hydrogen stores energy and LOHC stores hydrogen.

The most critical factor determining the efficiency of using LOHC is the thermal effect of the dehydrogenation reaction. If this effect is too significant, the system's efficiency as a whole will not be sufficient for practical use. Therefore, determining the thermal impacts of dehydrogenation reactions for potential LOHC is the first task is determining the potential of organic molecules to be hydrogen carriers.

In this work, we used the chemical equilibrium method to determine the thermal effects of hydrogenation-dehydrogenation reactions on the example of biphenyl and diphenylmethane. An experiment to study the chemical equilibrium of hydrogenation-dehydrogenation reactions was carried out in an autoclave with a stirrer on Pt and Pd catalysts with varying temperature, pressure, and the hydrogen ratio: raw materials. GC and GCMS determined the compositions of the reaction mixtures. The equilibrium state's achievement was confirmed by the constancy of the corresponding reactions' equilibrium constants, with varying reaction time, the ratio of reagents, and the catalyst amount.

The experimental chemical equilibrium constants of the hydrogenation-dehydrogenation reactions served as the basis for calculating the enthalpies and changes in the reactions' entropies. The paper also presents the dependences of the equilibrium compositions on the temperature, the ratio of hydrogen: substrate, and contact time. A model is proposed to describe the conditions of exhaustive hydrogenation and dehydrogenation of the studied substances. The dependence of the selectivity and the degree of conversion of the substrates on the process conditions were evaluated. The results of the experiment are compared with the data of combustion calorimetry and quantum chemical calculations.

Conclusions are drawn about the convenience of using chemical equilibrium as a method for determining the thermal effects of hydrogen accumulation and extraction reactions in LOHC.

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