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A Study of the Toluene Hydrogenation Reaction in the Presence of Polymer/Nickel-Based Nanocatalysts

Abstract

The hydrogenation of aromatic compounds is widely utilized in modern industrial catalytic processes, which form the basis of motor fuel refining technologies. Researchers have determined that catalysts containing metals such as Ni, Co, Rh, and Ru ensure the selective progression of hydrogenation processes. Several Ni-containing synthetic polymer-based complex compounds have been synthesized. The identification of the obtained complexes was performed using various physicochemical analysis methods (XRD, SEM, EDS). Additionally, the catalytic properties of these complexes were studied in the hydrogenation of toluene. The catalytic properties of the synthetic polymer-based Ni-containing complex based on poly-N-vinylpyrrolidone (PVP) were investigated under mild conditions, with varying molar ratios of reagents.

Keywords: *unsaturated alcohols, oxidation, hydrogenation, toluene*

Introduction

Hydrogenation of aromatics is an important precursor for the production of cyclohexane, which is an important reaction in the production of nylon-6,6 (Suleymanova, Zeynalov, Qulubayova, Guliyeva, Mammadova, Babayev, 2022; Shikhverdieva, Mammedova, Zeynalov, 2023; Alexey V.,et al.,2021). Hydrogen serves as a clean energy carrier and can be produced from renewable sources such as solar and wind energy. The toluene/methylcyclohexane (MCH) pair is a promising cyclic hydrocarbon system for the safe and efficient storage of hydrogen. In this approach, hydrogen is added to toluene (C_7H_8) through a hydrogenation reaction, converting it into MCH (C_7H_{14}), which can be transported using chemical tankers just like toluene. At the point of demand, hydrogen is released from MCH via a dehydrogenation reaction, with toluene being recovered for reuse. As a liquid organic hydrogen carrier (LOHC), this system is well-suited for large-scale storage and long-distance transportation, offering stability under ambient conditions and minimizing potential risks. The toluene/methylcyclohexane (MCH) system is not only reversible and highly selective but also free from carcinogenic by products. Additionally, it offers a relatively high hydrogen storage capacity (6.2 wt.%, 46.5 kg-H_2/m^3), and the volatility range of its components allows for seamless integration with existing transportation infrastructure, including storage tanks and refueling stations. This advantage makes it more suitable for hydrogen storage and transport compared to other solid hydrocarbons. However, the hydrogenation of aromatic compounds, such as toluene, traditionally requires high temperatures and pressures, often exceeding 100°C and 50 atm H_2. Therefore, achieving hydrogenation under milder conditions remains a critical challenge, both for energy efficiency and environmental sustainability (Wang, 2021; Guliyeva, Suleymanova, Zeynalov, Qulubayova, Shikhverdiyeva 2023).

Research

The storage of hydrogen (H_2) using liquid organic hydrides plays a crucial role in harnessing renewable electricity from sources such as wind, solar, and hydropower (Bourane, Elanany, Pham, Katikaneni, 2016, Preuster, Papp, Wasserscheid, 2016). Methylcyclohexane (C_7H_{14}, MCH) is a promising candidate for chemical hydrogen storage. It enables hydrogen storage through the hydrogenation of toluene (C_7H_8), making it an efficient and viable option for energy applications.

$$\mathbf{C_7H_8 + 3H_2 = C_7H_{14} – 205\ kJ\ mol^{-1}}$$

This reaction has been widely studied in the petrochemical industry, with established infrastructure for the synthesis and transportation of MCH. Additionally, MCH offers a relatively high hydrogen storage capacity, with volumetric and gravimetric densities of 47 kg-H_2/m^3 and 6.1 wt%, respectively. It also possesses good transportability and relatively low toxicity, making it a promising option for hydrogen storage and distribution (Bourane, Elanany, Pham, Katikaneni, 2016).

Metal surfaces facilitate the hydrogenation of aromatic rings in arenes (Ari F.,2024). Catalysts containing metals such as Ni, Co, Rh, and Ru have been employed by researchers as promoters that ensure selective hydrogenation processes (Atsumi, Kobayashi, Xieli, Nanba, Matsumoto, Matsuda, Tsujimura, 2020) Nickel is widely recognized as a cost-effective metal for hydrogenation, delivering desirable results. Its significance in the industry stems from its electronic structure, which closely resembles that of platinum and palladium. Ni-based catalysts exhibit high activity when the $C_6H_5CH_3$:H_2 ratio is greater than 3. In contrast, the activity decreases sharply when the ratio is lower than 3, which is not considered a favorable condition for the hydrogenation of toluene. According to the results of the analysis of literature, in recent years, nickel metal, which has a low economic cost, has been widely used in the production of selective catalysts for the effective implementation of catalytic hydrogenation processes of hydrocarbons (Atsumi, Kobayashi, Xieli, Nanba, Matsumoto, Matsuda, Tsujimura, 2020, Cui, Ishii, Tsujimura, Ttaniguchi, Hashimoto, Nanba, 2019). Catalyst tests using toluene as a model compound showed that the surface properties of the modifier, especially surface area, pore volume, and pore diameter, affect the performance of the catalysts (Shuwa, Jibril, Al-Hajri, 2017).

Experimental section

Description of the device used for the hydrogenation process of Toluene

A flow laboratory apparatus was used to carry out the hydrogenation reaction of toluene. The operating principle of this apparatus can be divided into three stages (Ari, 2024):

1)Preparatory section 2)Catalytic section 3)Chromatographic section

The first section consists of a system designed for hydrogen delivery:

The required hydrogen flow was supplied from a suitable cylinder (1) and regulated by a two-chamber reducer (3). Gas pressure stability was ensured using a low-pressure regulator (2). Columns (4) filled with activated carbon, silica gel and molecular sieves were used to purify the hydrogen used as a hydrogenating agent from other impurities. Precise regulation of gas flows was carried out using sensitive regulating valves (5) calibrated with a capillary rheometer (7). The specified amounts of H_2, catalyst and toluene are mixed in the reactor (8) by means of a magnetic stirrer (11, 12) with a furnace. The reaction products and unreacted toluene leaving the reactor pass through a counter cooler (9), a certain part of which condenses and returns to the reactor, while a part of the steam is collected in a cooled trap, and finally the unreacted hydrogen passes through the trap and is released into the atmosphere. After the start of the reaction, a sample of the reaction products is taken from the sampling loop every 60 minutes for analysis (Bykov, Demidenko, Nikoshvili, Sulman, Kiwi-Minsker, 2021).

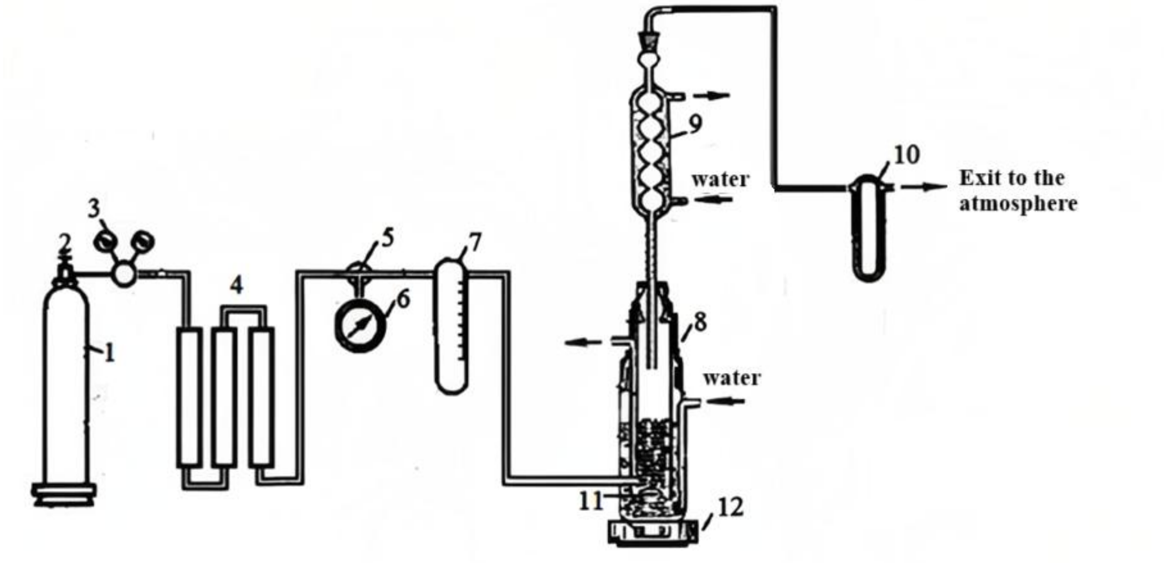

Figure 1. Schematic diagram of the assembled device for the hydrogenation reaction of toluene

1.Hydrogen cylinder
2.Low-pressure regulator
3.Two-chamber reducer
4.Gas purification columns
5.Gas sensitive regulating valve
6.Manometer
7. Capillary rheometer
8. Reactor
9. Condenser
10. Reaction products collector
11 and
12. Magnetic stirrer with stove

The hydrogen and nitrogen consumption entering the measuring column of the chromatograph (Agilent 7890B HP-5 column), at a gas carrier rate (N_2 and N_2) of 1.2 ml/min and a pressure of 5.41 psi (pounds-force per square inch), is determined. Before carrying out the reaction, the chromatograph is adjusted according to the procedure to be carried out. After determining the normal operating mode of the chromatograph and the required gas flow rate (N_2, H_2), the sample taken from the holder is manually introduced. The reaction products and unreacted toluene leaving the reactor are collected in a cooled reaction products collector, while the unreacted hydrogen and gases produced as a result of the reaction pass through the trap and are released into the atmosphere. After the start of the reaction, a sample of the reaction products from the sampling loop is fed to the chromatograph for analysis every 60 minutes.

Results and Discussion

In the research work, polymer complexes containing nickel as a catalyst in the hydrogenation reaction of toluene were synthesized. To obtain a nickel-polymer-based nanocomposite, nickel salts were immobilized into the polymer matrix by a chemical method. A synthetic polymer PVP and various percentages of Nickel metal (5,10,15%) were used as carriers. It has been found that, depending on the structure of the carrier and the amount of metal, it is possible to obtain small-sized nanoparticles (10-60 nm) in immobilized complexes. The sizes of the nanoparticles were determined by the Dynamic Light Scattering (DLS) method. The successful implementation of the metal immobilization process into the polymer was proven by the X-ray Diffraction (XRD) and Scanning electron microscope (SEM) analysis methods (Rahimli, Mammadova, Tagiyev, Zeynalov, Ismayılova, Babyev, 2025).

The hydrogenation reaction of toluene was carried out under mild conditions, with different molar ratios of $C_6H_5CH_3:H_2$. The products obtained from the reaction were analyzed on an Agilent 7890 B gas chromatograph. The effect of reaction time on the selectivity (relative to methylcyclohexane) of the hydrogenation reaction of toluene in the presence of a Ni-poly-N-vinylpyrrolidone catalyst was also studied. Thus, in the initial stage of the hydrogenation reaction (1.5-2 hours), a mixture containing methylcyclohexadiene, methylcyclohexene, methylcyclohexane, and toluene is obtained. It was found that the yield of methylcyclohexane was 11.3% as a result of the hydrogenation of toluene for 6 hours (40^0C) in the presence of PVP/Ni (10%) nanocatalysts (Parsafard, Peyrovi, Mohammadian, 2019).

Conclusion

In recent years, the acquisition of selective catalysts for the effective implementation of catalytic hydrogenation processes of aromatic hydrocarbons has attracted great interest. For this purpose, economically inexpensive nickel metal is widely used. In the presented work, a PVP/Ni-based catalyst was synthesized and it was determined that the yield of the target product was 11.3% at a temperature of 40^0C and a molar ratio of $C_6H_5CH_3:H_2$ of 1:3. Thus, the immobilized polymer-based nickel nanocatalyst shows high activity in the toluene hydrogenation reaction and maintains it over repeated cycles.

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