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CATALYSIS

An Effect of a Support Nature and Active Phase Morphology on Catalytic Properties of Ni-Containing Catalysts in Hydrogenation of Biphenyl

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Abstract—Ni/Sup catalysts were prepared, where SBA-15, γ -Al₂O₃, SiO₂ were used as supports (Sup). The synthesized catalysts were investigated by the methods of low-temperature nitrogen adsorption, temperature-programmed reduction (TPR), and high-resolution transmission electron microscopy. The catalytic properties of the prepared catalysts were tested in liquid phase hydrogenation of biphenyl under conditions of a flow installation at temperatures of 60–100°C, pressure of 4 MPa, volumetric feed rate of 4–10 h⁻¹ and H₂: feed ratio of 1500 nM.. A 1 wt % solution of biphenyl in heptane, , as a model mixture, was used. It has been established that the activity of nickel hydrogenation catalysts depends on the nickel content and the type of support. The activity of supported nickel catalysts decreases in the series Ni-12/SBA-15 > Ni-12/SiO₂ >> Ni-12/Al₂O₃. The kinetic characteristics of the biphenyl hydrogenation reaction were determined: the rate constants and activation energy for the hydrogenation of the first and second aromatic rings of the substrate molecule.

Keywords: biphenyl, hydrogenation, Ni-containing catalysts, SBA-15, Al₂O₃, SiO₂

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In recent decades, there has been a trend to tighten the requirements for energy efficiency and emissions of pollutants into the environment. In this regard, energy sources based on alternative fuels, including hydrogen, are in great demand. The use of such fuel cells is impossible without the development of efficient hydrogen storage methods that will ensure its safe storage and transportation. The use of liquid organic hydrogen carriers (LOHCs) can be one of such methods, which is based on the use of reversible hydrogenation–dehydrogenation reactions of organic compounds, for example, aromatic and polycyclic aromatic hydrocarbons [1, 2].

There are a number of requirements for LOHC systems: high hydrogen capacity (> 5.0 wt %), thermal stability, suitable boiling points and melting points, favorable thermodynamic conditions for hydrogenation—

dehydrogenation, availability, low toxicity, and reasonable price [3]. At the first stage, benzene–cyclohexane and toluene–methylcyclohexane pairs were considered as the most promising among hydrogen carriers, the conditions of hydrogenation and dehydrogenation of which were well studied [4]. However, a common drawback of these compounds is the low boiling point, which makes them highly volatile and causes a loss of the substrate. Recently, the attention of researchers has increasingly been attracted to systems based on polycyclic aromatic compounds, and biphenyl is one of the promising candidates as a hydrogen carrier because it meets most of the requirements for LOHC.

Considerable attention is also paid to the selection of catalysts for the processes of hydrogenation and dehydrogenation. The catalyst, besides the fact that it must exhibit high activity and selectivity, must be stable and minimize the possibility of side cracking reactions. Selective hydrogenation of biphenyl was studied in the presence of supported catalysts based on Pt [5, 6], Rh, Ru [7], Pt–Pd [8], CoO–MoO₃ [9]. Data on the hydrogenation of biphenyl on Ni-containing catalysts are practically absent, despite the fact that the hydrogenation of other aromatic hydrocarbons on nickel catalysts has been well studied [10, 11]. Data on the reduction of phenol, naphthalenes, biphenyls, acenaphthenes, and other compounds are reported to the corresponding hydrocarbon derivatives on the Raney Ni-Al alloy in a dilute aqueousalkaline solution at 90°C and atmospheric pressure. There is also evidence of the selective hydrogenation of biphenyl to cyclohexylbenzene on skeletal Ni (Raney Ni) [13]. According to the literature, nickel catalysts are less active than platinum, but they are much cheaper, which makes them attractive for research and potential use. Changing the type of carrier and the content of the active phase allows varying the properties of the catalyst and choosing a system that will ensure efficient operation of the LOHC system based on biphenyl.

The purpose of this work was the synthesis and experimental study of the catalytic activity of nickel catalysts on various supports in the liquid-phase hydrogenation of biphenyl.

EXPERIMENTAL

Aluminum oxide γ -Al₂O₃, mesoporous aluminosilicate SBA-15, and silicon oxide SiO₂ (Sigma-Aldrich) with textural characteristics (Table 2) were used as supports. To synthesize a support based on γ -Al6₂O₃, peptization of TH-60 pseudoboehmite powder (SASOL firm) with nitric acid was carried out, then it was molded by extrusion (length and diameter of cylinders were 6 and 1.5 mm, respectively), dried in air at 60, 80, 120°C (for 2 h) and calcined at 550°C for 2 h (the rate of temperature rise to 550°C was 1 deg min⁻¹).

SBA-15 was prepared according to the method [14] using the following reagents: tetraorthosilicate (TEOS) as a source of silicon, Pluronic 123 as a surfactant, 2 M HCl solution and distilled water. With stirring, a solution of Pluronic 123 in distilled water was prepared, then a solution of HCl was added dropwise to it, and at last TEOS was added dropwise. The resulting mixture was kept under static conditions at 80°C for 48 h. The white precipitate formed was filtered, washed several times with water, dried at 60, 80, 120°C (5, 2, 5 h, respectively) and calcined at 240 and 550°C (4 and 6 h, respectively). The calcined precipitate was tableted under a press (5 tons). The molded supports were crushed and a fraction of 0.25–0.50 mm was sieved out, which was later used to prepare catalysts.

A commercial sample (Sigma-Aldrich), fraction 0.25–0.50 mm, was used as silicon oxide.

The active component was applied to the prepared fraction of the support by the method of single impregnation by capacity with an aqueous solution of nickel(II) nitrate hexahydrate. The impregnated samples were kept for 1 day at room temperature, and then dried (at 60°C for 2 h, at 120°C for 6 h) and calcined at 450°C in air for 1 h. Recovery of the catalysts was carried out in an excess of hydrogen at 400°C for 2 h in the reactor, in which then the catalytic activity of the prepared sample was studied. The synthesized nickel catalysts had the abbreviation Ni-*x*/Sup, where *x* is the nickel content in the sample (wt %), Sup is the type of support (γ -Al₂O₃, SiO₂, SBA-15).

The textural characteristics of the synthesized carriers were investigated by the method of low-temperature nitrogen adsorption on a Quantochrome Autosorb-1 porosimeter. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) model. The total pore volume and pore size distribution were calculated from the desorption branch of the nitrogen adsorption isotherm using the Barrett–Joyner–Handenda model (BJH).

The synthesized catalysts were investigated by the methods of thermoprogrammed recovery and high resolution transmission electron microscopy.

Thermoprogrammed recovery of nickel catalysts was carried out on TPDRO 1100 using a thermal conductivity detector. Immediately prior to analysis, the samples were dried under argon at different temperatures. Thermoprogrammed recovery was carried out in a 5 vol % hydrogen mixture in nitrogen with the following parameters: a volumetric feed rate of 50 mL min⁻¹, a temperature range from room temperature to 400°C, a heating rate of 10 deg min⁻¹. Recovery was carried out for 1 h.

The reconstructed samples of the catalysts were examined by TEM-BP using a Tecnai G2 20 electron microscope with a LaB6 cathode with a resolution of 0.14 nm and an accelerating voltage of 200 kV in order to determine the average sizes of the metal particles on the surface. High resolution images were analyzed using the Fourier method. Samples for TEM BP were placed on a perforated carbon film on a copper grid, then 10–15 micrographs were obtained for each catalyst.

Testing of the synthesized catalysts was carried out in a laboratory flow-through installation with a plug flow reactor. A 1 cm³ catalyst (fraction 0.25–0.5 mm) in a 1 : 1 mixture with silicon carbide (of the same size) was loaded into the isothermal zone of the reactor. The hydrogenation of biphenyl was carried out under the following conditions: temperature in the range of 60– 100°C, pressure of 4 MPa, volumetric feed rate (VFR) of raw materials 4–10 h⁻¹, and the hydrogen circulation ratio of 1500 nm³ m⁻³. A model mixture, 1 wt % solution of biphenyl in heptane, was used as a raw material. Samples were taken at least 1 time per hour and analyzed by gasliquid chromatography on a Kristall-2000M instrument (FID) with a quartz capillary column ZB-35 with a grafted phenyl (35%)–polydimethylsiloxane phase, helium carrier gas. Chromatec Analyst software, version 2.6, was used for recording and processing chromatograms. Identification of the components of the reaction mixture was performed by the method of gas chromatography/ mass spectrometry using the device GMS-QP2010 Ultra (Shimadzu).

The hydrogenation of biphenyl (BP) is consistent with the formation of cyclohexylbenzene (TsGB) as an intermediate product and bicyclohexyl (BCG) as the final hydrogenation product:



The activity of the synthesized catalysts was estimated by the total rate constant for the hydrogenation of aromatic nuclei in the molecules of biphenyl and cyclohexylbenzene k, which was calculated in the approximation of the irreversible pseudo-first order reaction (a large excess of hydrogen was used in the experiments, which allowed to neglect the change in its concentration):

$$k_{\rm hyd} = -\frac{F_{\rm BP}}{m} \ln\left(1 - \frac{X}{100}\right),\tag{1}$$

where k_{hyd} is the rate constant for the reaction of biphenyl hydrogenation (s⁻¹); F_{BP} , consumption of biphenyl (g s⁻¹); *m* is the mass of the catalyst (g); *X* is the conversion of aromatic nuclei to cyclohexane, calculated by the formula

$$X = 100 - \left(c_{\rm BP} + \frac{1}{2} c_{\rm CHB}\right),$$
 (2)

100 is the initial concentration of aromatic nuclei (mol %); $c_{\rm BP}$ is the concentration of biphenyl in the reaction mixture (mol %); $c_{\rm CHB}$, the concentration of cyclohexylbenzene in the reaction mixture (mol %).

The reaction rate constant, normalized to 1 g of nickel (k_{Ni}) , was calculated based on the nickel content in the

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catalyst according to the formula

$$k_{\rm Ni} = -\frac{F_{\rm BP}}{m_{\rm Ni}} \ln\left(1 - \frac{X}{100}\right),\tag{3}$$

where k_{Ni} is the reaction rate constant over nickel (s⁻¹), m_{Ni} is the mass of nickel in the catalyst (g).

The conversion of biphenyl was calculated by the formula

$$X_{\rm BP} = \frac{c_{0,\rm BP} - c_{\rm BP}}{c_{0,\rm BP}} \times 100,$$
 (4)

where $c_{0,\text{BP}}$ and c_{BP} are the initial and current concentrations of biphenyl in the reaction mass, respectively (wt. fraction).

The conversion of cyclohexylbenzene was calculated by the formula

$$X_{\rm CHB} = \frac{c_{0,\rm BP} X_{\rm BP} - c_{\rm CHB}}{c_{0,\rm BP} X_{\rm BP}} \times 100,$$
 (5)

where X_{CHB} is the conversion of cyclohexylbenzene (%); $c_{0,\text{BF}}$, c_{CHB} , the initial concentration of biphenyl and the current concentration of cyclohexylbenzene (mol %), respectively.



Fig. 1. Adsorption–desorption isotherms of the obtained supports. (1) SBA-15, (2) SiO₂, (3) γ -Al₂O₃; the same for Figs. 2, 5.



Fig. 2. The distribution of pores along the radius.

The rate constants of the first k_1 and second k_2 reactions were calculated similarly by the formulas

$$k_1 = -\frac{F_{\rm BP}}{m} \ln\left(1 - \frac{X_{\rm BP}}{100}\right),\tag{6}$$

$$k_{1} = -\frac{F_{\rm BP} X_{\rm BP}}{m} \ln \left(1 - \frac{X_{\rm CHB}}{100} \right), \tag{7}$$

Table 1.	Textural	characteristics	of the	supports
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where $k_{1(2)}$ is the rate constant for the hydrogenation of biphenyl (cyclohexylbenzene) (s⁻¹); F_{BP} , consumption of biphenyl (g s⁻¹); *m* is the mass of the catalyst (g); X_{BP} , X_{CHB} , biphenyl and cyclohexylbenzene conversion calculated by formulas (4) and (5), respectively.

RESULTS AND DISCUSSION

Physicochemical properties of supports and catalysts. The obtained nitrogen adsorption–desorption curves for the synthesized supports (Fig. 1) refer to type IV isotherms. The nitrogen adsorption isotherm for SBA-15 (Fig. 1, curve *I*) is characterized by a clearly pronounced H1 hysteresis loop according to the IUPAC classification [15]. This type of hysteresis loop with symmetric curves of adsorption and desorption corresponds to capillary condensation and desorption in open cylindrical pores. The nearly vertical boundaries of the hysteresis loop (in the region of partial pressures $p/p_0 = 0.6-0.75$) indicate a narrow pore size distribution (Fig. 2), which is typical of micromesoporous silicates with an ordered porous structure [16].

The hysteresis loop on the adsorption isotherm SiO₂ also belongs to the H1 type, however, it is located in a much wider range of partial pressures ($p/p_0 = 0.6-0.9$) and has an elongated S-shape (Fig. 1, curve 2), which corresponds to spherical pores forms with a wide pore size distribution (Fig. 2).

The nitrogen adsorption isotherm obtained for the sample of the γ -Al₂O₃ support (Fig. 1, curve 3) has an asymmetric H3 hysteresis loop, localized in the region of partial pressures $p/p_0 = 0.7-0.9$, and indicates the presence of slit-like pores on the support surface formed by the microcrystalline structure of alumina.

At the same relative pressure p/p_0 (Fig. 1), the largest amount of adsorbate corresponds to the SBA-15 support, which indicates a more developed specific surface area than the other two carriers. The hysteresis loop of the

Cumport	Textural characteristics					
Support	$S_{\rm BET}$, m ² g ⁻¹	V_{P} , cm ³ g ⁻¹	$R_{\rm ef}$, Å			
SBA-15	706	0.84	27			
SiO ₂	360	0.99	45			
γ -Al ₂ O ₃	203	0.73	58			



Fig. 3. TPV curves of nickel catalysts supported on SiO₂. (1) Temperature change profile (°C); (2) Ni-24/SiO₂, (3) Ni-12/SiO₂, (4) Ni-6/SiO₂.

nitrogen adsorption isotherm for SBA-15 is shifted to a region of relatively low partial pressures, which indicates the predominance of pores with a smaller diameter in this support compared to SiO₂ and γ -Al₂O₃.

As can be seen from Fig. 2 the sample of γ -Al₂O₃ has the largest pore diameter of 116 Å, SiO₂ has a diameter of 90 Å, and a mesoporous material SBA-15 is of the smallest diameter (54 Å). Among the synthesized supports, the mesoporous aluminosilicate SBA-15 has the highest specific surface area (Table 1).

Analysis of the TPR data of Ni-catalysts showed that the Ni-*x*/Sup catalysts are completely reduced at 400°C. It was this temperature that was used when activating (reducing) the samples before testing the catalytic activity.

Thermograms (Fig. 3) allow conclusion that the intensity and temperature of the maximum of the absorption peak of hydrogen increase with increasing content of the metal precursor in the sample. Thus, for the sample of Ni-6/SiO₂ catalyst, the hydrogen absorption maximum occurs at a temperature of 360°C, with an increase in nickel concentration to 12 wt % (sample Ni-12/SiO₂) the maximum shifts to 373°C, and with an increase in Ni content to 24 wt % maximum occurs at 386°C. The observed facts indicate that with increasing precursor concentration (nickel nitrate), the nature of its distribution on the surface of the support changes. Probably, at relatively high concentrations, interactions of the precursor molecules with each other over the interactions of the precursor with the support surface begin to prevail (formally, this may correspond to the transition from monolayer filling the support surface to the multilayer one).

Conclusions about the size of the particles of the reduced metal and the nature of their distribution on the surface of the catalysts were made on the basis of the analysis of TEM images (Fig. 4).

As a result of statistical processing of electronic images of reduced catalysts, the dependence of the size distribution of nickel particles on the surface of catalysts was obtained (Fig. 5).

Nickel deposited on γ -Al₂O₃, had a high dispersion, the average particle size of 4 nm. The Ni-12/SiO₂ catalyst is characterized by a uniform distribution of particles on the surface; the average size of the metal clusters is 7.4 nm. The metal active phase of the Ni-12/SBA-15 sample is of two types of particles: nickel particles inside the carrier channels and particles located on the outer surface, whereby the distribution of Ni particles in the Ni-12/SBA-15 sample is bimodal. About 63% of all visible metal particles are located in the pores of SBA-15.

The catalytic activity of Ni-x/SiO₂ in hydrogenation of biphenyl. Samples with a nickel content of 6, 12, and 24 wt% were synthesized and tested to determine the optimal nickel content in the catalyst. Commercial SiO₂ was used as a support. The test results for Ni-6/SiO₂, Ni-12/SiO₂, and Ni-24/SiO₂ in the biphenyl hydrogenation reaction are shown in Table 2.

From the data presented, it follows that the total rate constant for the reaction of hydrogenation of biphenyl increases with increasing nickel content in the sample. The sample Ni-24/SiO₂ exhibits the highest catalytic activity in the hydrogenation of biphenyl.





Fig. 4. TEM images of synthesized catalysts. (a) Ni-6/SiO₂, (b) Ni-12/SiO₂, (c) Ni-24/SiO₂, (d) Ni-12/Al₂O₃, (e) Ni-12/SBA-15.

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Catalyst	T °C	VFR of raw material, h ⁻¹	$c_{ m BCH}$	c_{CHB}	$c_{ m BP}$	Conversion,	$k \times 10^4$	$k_{ m Ni} imes 10^4$
	<i>I</i> , C		%		%	mol g ⁻¹ h ⁻¹		
Ni-6/SiO ₂	70	2	2	47	51	26	0.30	5.08
	80	2	3	57	40	32	0.39	6.51
	00	2	7	77	16	46	0.58	9.70
	90	4	1	44	55	23		9.70
	100	2	13	75	12	51	0.73	12.18
	100	4	3	56	42	30 ∫		12.10
Ni-12/SiO ₂	60	2	27	66	7	60	0.45	3 75
		4	2	40	58	22 ∫	0.15	5.75
	70	2	23	75	2	61	0.81	6.72
		4	3	63	34	35 ∫	0.01	0.72
:	80	2	65	35	0	82	1 40	11 60
		6	5	67	28	38	1.10	11.00
	90	4	51	49	0	75	1.90	16.00
		8	7	70	24	41 ∫		
	100 8	8	24	69	7	59	} 2.54	21.20
		12	6	64	30	38		
Ni-24/SiO ₂	60	2	36	63	1	67	0.65	2.69
		4	4	57	39	32		
	70	4	15	79	6	54		
		6	3	63	34	34	1.05	4.34
		8	2	50	48	27		
	80	8	6	73	21	42	1 (0	7.02

Table 2.

The dependences of the rate constant for the reaction of hydrogenation of biphenyl on nickel catalysts on silicon oxide were constructed based on the experimental results (Figs. 6, 7). Figure 7 shows that the specific rate constants for the Ni-12/SiO₂ catalyst are higher than $k_{\rm Ni}$ obtained for the other two samples over the entire temperature range studied. This suggests a more efficient operation of the active sites of the catalyst with an active component content of 12 wt %. Therefore, for further research, Ni-12/Sup catalysts were synthesized (where Sup is γ -Al₂O₃ and SBA-15) with the same concentration of the active component as in the Ni-12/SiO₂ sample.

10

10

12

14

90

3

13

10

8

57

73

54

53

41

14

36

39

31

49

37

34

The catalytic activity of Ni-12/Sup in hydrogenation of biphenyl. Figure 8 shows the results of determining the rate constant for the reaction of hydrogenation of biphenyl [Eq. (2)] at various temperatures in the presence of synthesized Ni-12/Sup catalysts. Under the same conditions Ni-12/SBA-15 showed the greatest activity. The activity of the studied catalysts decreased in the series Ni-12/SBA-15 > Ni-12/SiO₂ >> Ni-12/Al₂O₃. The rate constants of the hydrogenation reaction calculated at 80°C for Ni-12/SBA-15 and Ni-12/SiO₂ turned out to be 1.68 and 1.39 s⁻¹, respectively. The Ni-12/Al₂O₃ catalyst showed the least activity, the rate constant of the

1.68

2.37

7.03

9.89



Fig. 5. The size distribution of metal particles on the surface of catalysts.



Fig. 6. The observed rate constant of biphenyl hydrogenation reaction vs. temperature for Ni-*x*/SiO₂ catalysts. (*1*) Ni-24/SiO₂, (*2*) Ni-12/SiO₂, (*3*) Ni-6/SiO₂.



Fig. 7. The rate constant for the reaction of hydrogenation of biphenyl normalized to nickel vs. temperature. (1) Ni-6/SiO₂, (2) Ni-12/SiO₂, (3) Ni-24/SiO₂.



Fig. 8. The rate constant of the reaction of biphenyl hydrogenation vs. temperature for nickel catalysts. (*1*) Ni-12/SBA-15, (*2*) Ni-12/SiO₂, (*3*) Ni-12/Al₂O₃.

hydrogenation reaction at 80°C was close to zero. Even at temperatures above 100°C, the conversion of biphenyl on this catalyst did not exceed 35%.

Probably, the hydrogenation reaction of biphenyl on nickel catalysts is structurally sensitive and proceeds at the highest rate on particles of a certain size. Three synthesized samples of catalysts with the same nickel content (12 wt %) had a different size of metal particles on the surface. The Ni-12/Al₂O₃ sample was characterized by a highly dispersed active phase-an average particle size of 4 nm. The average particle size of the Ni-12/SiO₂ catalyst was 7.4 nm. According to the TEM BP data, in addition to fine metal particles inside the SBA-15 channels (particle size approximately equal to 6 nm), particles of 30 nm were present on the outer surface on the Ni-12/ SBA-15 surface of the sample. From the data obtained it follows that it is the large Ni particles formed on the surface of the SBA-15 crystallites that are responsible for the increase in the catalytic activity of the catalyst in the hydrogenation of biphenyl. The high dispersion of the active phase, achieved on the γ -Al₂O support, on the contrary, led to a loss of the catalytic activity of the synthesized sample Ni-12/Al₂O₃.

Determination of the activation energy of hydrogenation reaction of biphenyl on a Ni-12/SiO₂ catalyst. For the Ni-12/SiO₂ catalyst sample, which showed a high specific activity, the kinetic characteristics of the biphenyl hydrogenation reaction were determined in more detail (Fig. 9). When processing the obtained data in the Arrhenius coordinates (Fig. 10), the activation energy values were determined for the first and second



Fig. 9. The rate constants of the reaction of the first and second stages of biphenyl hydrogenation vs. temperature. (1) k_1 , (2) k_{hvd} , (3) k_2 .

stages of hydrogenation of biphenyl, which were 48 and 61 kJ mol⁻¹, respectively. The obtained values are in good agreement with the literature data, according to which the activation energy of aromatic hydrocarbons on Ni-containing catalysts averages 50–57 kJ mol⁻¹ [4].

CONCLUSIONS

The activity of the synthesized nickel hydrogenation catalysts increases with increasing nickel content in the sample, however, the specific catalytic activity of the metal phase formed on the surface passes through a maximum. The specific rate constants for the hydrogenation reaction of biphenyl were significantly higher for a catalyst with a metal content of 12 wt % as compared with samples of Ni-6/SiO₂ and Ni-24/SiO₂ over the entire temperature range studied.

When studying the catalytic activity of nickel catalysts on various supports in the hydrogenation reaction of biphenyl, it was found that the activity of the catalysts decreases in the series Ni-12/SBA-15 > Ni-12/SiO₂ >> Ni-12/Al₂O₃. Apparently, the hydrogenation of biphenyl is structurally sensitive: rather large particles exhibit a large catalytic activity, an increase in the dispersion of Ni leads to a decrease in the activity of such catalysts.

The sample of Ni-12/SBA-15 is the most effective of the studied nickel catalysts in hydrogenation of biphenyl. It provides almost complete hydrogenation of the substrate at a temperature of 100° C, a pressure of 4 MPa and a bulk flow rate of feed 10 h⁻¹ and less; at



Fig. 10. ln k_i vs. the inverse temperature. (1) k_1 , (2) k_2 .

80°C and a bulk flow rate of feed 4 h⁻¹, the conversion of aromatic nuclei reaches 90%. This sample can be recommended as a potential catalyst for the hydrogenation of aromatic compounds from the LOHC class to create a technology for preserving free energy into chemically bound hydrogen.

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