Reversible hydrogenation—dehydrogenation reactions of *meta*-terphenyl on catalysts with various supports

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For developing new composite systems (substrate—catalyst) for hydrogen storage, the activities of Pt and Pd catalysts on various supports were compared in reversible *meta*-terphenyl hydrogenation and perhydro-*meta*-terphenyl dehydrogenation. The microstructure of the catalysts was studied. Carbon-supported catalysts are more efficient in both reversible reactions than alumina-supported systems.

Key words: catalysis, hydrogenation, dehydrogenation, hydrogen storage, *meta*-terphenyl, perhydro-*meta*-terphenyl, platinum.

In recent years, increasing attention has been paid to hydrogen as a universal energy carrier. For successful development of the environmentally benign power engineering based on hydrogen fuel cells, it is important to design efficient methods for hydrogen storage and generation. Of considerable interest are aromatic hydrocarbons whose hydrogen capacity exceeds 7.5 wt.%, which is higher than that of any known storage systems.¹⁻³ Aromatic hydrocarbons are able to undergo repeated hydrogen saturation and evolution cycles in reversible hydrogenation—dehydrogenation reactions without formation of CO_x gases contaminating the atmosphere.⁴⁻⁶

The reversible hydrogenation-dehydrogenation reactions of aromatic compounds are usually conducted with supported catalysts based on noble metals. The rate of reactions is known^{7,8} to depend on the structure of the metal surface and the support used; therefore, selection of the optimal support is an important aspect of development of efficient catalysts for these reactions. It was found, for example, that multiphase catalysts on acidic supports are often characterized by enhanced activity and selectivity, in particular, due to hydrogen spillover.^{9,10} Meanwhile, acidic supports have a considerable drawback, namely, high catalytic activity towards cracking and ring opening reactions at dehydrogenation temperatures.^{11,12} One way to decrease these undesirable reactions is to use supports with higher intertness such as activated carbon or modern carbon materials,^{13,14} which bear much less functional groups on the surface than acidic supports.

Previously, 15-17 the terphenyl—perhydroterphenyl pair has been shown to be promising for hydrogen storage

in the catalytic composite systems. Here we compare the performances of Pt and Pd catalysts on different supports in reversible hydrogenation—dehydrogenation reactions of *meta*-terphenyl and perhydro-*meta*-terphenyl.

Experimental

Determination of the catalytic activity. Commercial γ -alumina-supported catalysts for benzene hydrogenation were used: 5% Pt/Al₂O₃, 2.5% Pd/Al₂O₃, and 0.12% Pd-3.8% Ni-4.3% Cr/Al₂O₃. The carbon-supported catalysts represented commercial 3% Pt/C (Aldrich) on the activated carbon (lot No. HI06523BT) and 3% Pt/Sibunit. Platinum was deposited on Sibunit (Institute of Hydrocarbon Processing, Siberian Branch of the Russian Academy of Sciences, Omsk) by impregnating the support to incipient wetness with an aqueous solution of [H₂PtCl₆] according to the previously reported procedure.¹⁸ The catalyst characteristics are summarized in Table 1.

meta-Terphenyl (Aldrich, 99%) (m.p. 84 °C, b.p. 379 °C, $\rho = 0.98 \text{ g cm}^{-3}$) served as the starting reactant for hydrogenation. *meta*-Terphenyl was hydrogenated in an R-201 high pressure autoclave (Korea) with 100 mL inner volume at 180 °C and 70 atm. In all experiments, the substrate (50 cm³) and the catalyst (5 cm³) were placed into the autoclave and the reaction was carried out with stirring of the reaction mixture at 600 rpm. The time (*t*/h) of complete conversion of *meta*-terphenyl to perhydro-*meta*-terphenyl served as the key criterion for comparison of the catalysts in hydrogenation. Additionally, the catalyst activity (A_g) was evaluated using the ratio of the number of moles of the perhydro-*meta*terphenyl ($C_{18}H_{32}$) formed to the number of moles of the active metal M_{ac} (Pt, Pd), which was reduced to the hydrogenation time.

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Catalyst	BulkSurfacedensityarea, $/g \mathrm{cm}^{-3}$ $S_{\mathrm{BET}}/\mathrm{m}^2$		Metal particle size, <i>R</i> /nm	Metal dispersion, D(%)	
5% Pt/Al ₂ O ₃ *	0.72	230	1.5-2	67	
2.5%Pd/Al ₂ O ₃ *	0.72	215	4.5-5	25	
0.12%Pd-3.8%Ni-4.3%Cr/Al ₂ O ₃ *	0.74	130	25-27	4	
3%Pt/C («Aldrich»)	0.32	760	5-5.5	22	
3%Pt/Sibunit	0.65	300	2-2.5	49	

Table 1. Data on the morphology for the catalysts of *meta*-terphenyl hydrogenation and perhydro-*meta*-terphenyl dehydrogenation

* Commercial catalysts (Redkino catalyst plant).

The product formed after hydrogenation was separated from the catalyst and analyzed. The product containing \geq 99% of the target perhydro-meta-terphenyl was introduced into the back dehydrogenation reaction. A catalyst sample (6 cm³) was placed at the center of a steel reactor of 10 mm diameter and 230 mm length. Liquid perhydro-meta-terphenyl was fed into the reactor with a HPP 5001 high-pressure pump and dehydrogenation was carried out in the flow mode at 320 °C and feed flow rate of 6 mL h⁻¹. All piping of the flow catalytic setup was maintained at 90 °C. At the reactor outlet, hydrogen and the reaction products were separated. In order to obtain pure hydrogen without other gas impurities at the outlet, a substrate cooling system was used comprising saturators and filters, including membrane filters.¹⁹ The conversion of perhydro-*meta*-terphenyl and selectivity to meta-terphenyl in the sample accumulated after the reaction in the flow setup during 1 h served as the major criteria for comparison of the catalysts in dehydrogenation. In view of the possible catalyst deactivation, samples obtained after dehydrogenation for 4 h were compared. Since hydrogen is the target reaction product, the catalyst activity in dehydrogenation (A_d) was calculated as the ratio of the total number of moles of hydrogen evolved upon dehydrogenation of perhydrometa-terphenyl for 4 h to the number of moles of the active metal M_{ac} (Pt, Pd), which was reduced to the time.

Prior to hydrogenation and dehydrogenation, the catalysts containing Pt and Pd were activated for 2 h at 320 °C in a hydrogen flow (30 mL min⁻¹) and Ni-containing catalysts were activated for 2 h at 500 °C.

Chromatographic analysis. The products of hydrogenation and dehydrogenation were analyzed on a Kristalux-4000M chromatograph equipped with a flame ionization detector with a ZB-5 capillary column (ZEBRON, US). Analysis was carried out in a programmed mode at 70 to 220 °C at a heating rate of 6 °C min⁻¹. The partly hydrogenated and side reaction products were identified on a FOCUS DSQ II GC/MS spectrometer (Thermo Fisher Scientific, USA) with a TR-5MS capillary column (Thermo, USA). The purity of the hydrogen formed was determined by gas chromatography with a heat conductivity detector on a Porapak Q packed column.

The conversion for both hydrogenation and dehydrogenation (X) were calculated by the formula

 $X = (c_0 - c)/c_0 \cdot 100\%$

where c_0 and c are the initial and final concentrations of the substrate being converted. The selectivity (S) was calculated by the equation

 $S(i) = \sum c(i) / \sum c(k) \cdot 100\%,$

where $\Sigma c(i)$ and $\Sigma c(k)$ is the sum of concentrations of a group of products and all reaction products, respectively.

Study of the catalyst structure. The specific surface area (S_{BET}) of the catalysts was calculated from measurements of low-temperature nitrogen sorption by the BET model.²⁰ The particle size R and dispersion D of active noble metals (Pt, Pd) were determined from CO chemisorption measurements conducted at 35 °C on an ASAP-2020 plus Micromeritics microanalyzer (USA).²¹ In the calculation of R, the catalyst particles were assumed to be spherical. The dispersion of the multicomponent system was estimated using the stoichiometric coefficient K = 1.5, where K is the number of CO molecules per metal atom. This coefficient takes into account different forms of CO adsorption. The catalyst morphology was studied by field emission scanning electron microscopy (SEM) using a Hitachi SU8000 microscope for alumina-supported catalysts and a JEOL JSM-6390 microscope for carbon-supported catalysts. The images were recorded in the secondary electron mode at an accelerating voltage of 2-30 kV and a working distance of 8-10 mm. EDS study of the samples was carried out using an Oxford Instruments X-max energy dispersive spectrometer. The sample microstructure was examined by transmission electron microscopy (TEM) on a Hitachi HT7700 electron microscope. The images were recorded in the light field mode at an accelerating voltage of 100 kV.22

Results and Discussion

The composition and morphological data for the catalysts used in reversible *meta*-terphenyl hydrogenation and perhydro-*meta*-terphenyl dehydrogenation reactions are summarized in Table 1.

The specific surface areas (S_{BET}) of the 5%Pt/Al₂O₃ and 2.5%Pd/Al₂O₃ catalysts are close. According to SEM data, the particles of these catalysts are ~4 µm aggregates with a disordered structure. The S_{BET} surface area of the 0.12%Pd-3.8%Ni-4.3%Cr/Al₂O₃ catalyst is smaller and the particles are shaped like corals with tightly interlaced arms of up to 0.4 µm length.

The morphology of the 3%Pt/C catalyst (Aldrich) is typical of activated carbon-supported catalysts. The SEM image demonstrates the >2 µm-large grown-together



Fig. 1. TEM image of the 0.12%Pd-3.8%Ni-4.3%Cr /Al₂O₃ catalyst.

particles of various shape. Among the studied catalysts, the activated carbon-supported sample has the largest surface area. The surface of the 3% Pt/Sibunit catalyst is more homogeneous than that of the activated carbon-supported catalyst and the surface morphology is similar to that of 5% Pt/Al₂O₃.

For microstructure analysis, thin sections of the catalyst were studied by TEM. Considering the TEM image of the 0.12%Pd-3.8%Ni-4.3%Cr/Al₂O₃ sample (Fig. 1), one can see that the microstructure of alumina comprises needle-like crystallites with an average size of $\sim 20-30$ nm. On the surface of some of them, particles of the active component are located. The gaps between the microblocks of needle crystals form micropores (0.6-1.5 nm) and mesopores (<45 nm).²³

The TEM images of the carbon-based catalysts (Fig. 2) show that the microstructure of the 3%Pt/C catalyst supported on activated carbon consists of irregularly shaped aggregates, whereas the 3%Pt/Sibunit catalyst has a globular microstructure. The porous structure of activated carbon mainly consists of micro- and macropores. The Sibunit carbon support is mainly a mesoporous material.²³ It follows from comparison of the TEM images that the Pt particles in the 3%Pt/C catalyst on activated carbon are distributed homogeneously, whereas in the Sibunit-supported catalyst, they are mainly located on the surface of globules. It can be seen that the average Pt particle size



Fig. 2. TEM images of the 3%Pt/C (Aldrich) (*a*) and 3%Pt/Sibunit (*b*) catalysts.

in the catalyst on activated carbon is greater than that for the catalyst on Sibunit, which is correlated with the CO chemisorption data (see Table 1).

Data on the *meta*-terphenyl hydrogenation and perhydro-*meta*-terphenyl dehydrogenation are summarized in Table 2.

The reversible hydrogenation of *meta*-terphenyl (1,3diphenylbenzene, $C_{18}H_{14}$) and dehydrogenation of perhydro-*meta*-terphenyl (1,3-dicyclohexylcyclohexane, $C_{18}H_{32}$) can be represented as general Scheme 1.

The target product of *meta*-terphenyl hydrogenation is perhydro-*meta*-terphenyl and the reverse reaction of

Table 2. Catalyst activity in meta-terphenyl hydrogenation and perhydro-meta-terphenyl dehydrogenation

Catalyst	$S_{\rm BET}/{ m m^2g^{-1}}$	Hydrogenation			Dehydrogenation		
		X(%)	<i>t</i> /h	Ag	X(%)	S(%)	Ad
5% Pt/Al ₂ O ₃	230	99	15	0.06	43	38	0.5
2.5% Pd/Al ₂ O ₃	215	73	20	0.04	35	90	0.9
0.12%Pd-3.8%Ni-4.3%Cr/Al ₂ O ₃	130	86	16	1.10	26	85	17.2
3%Pt/C («Aldrich»)	760	100	4	0.80	92	94	2.8
3%Pt/Sibunit	300	99	5	0.32	91	95	1.4





perhydro-*meta*-terphenyl dehydrogenation gives, on the contrary, *meta*-terphenyl. 3-Cyclohexylbiphenyl and 1,3-diphenylcyclohexane with one saturated ring $(C_{18}H_{20})$ and phenyl-1,3-bicyclohexane and 3-phenylbicyclohexane with two saturated rings $(C_{18}H_{26})$, respectively, are formed as intermediate products.^{15,17}

Comparison of the experimental data (see Table 2) indicates that complete saturation of *meta*-terphenyl with hydrogen during hydrogenation is markedly faster with Pt/C catalysts than with alumina-supported catalysts. The differences can be attributed to the diffusion restrictions caused by pore clogging with coke, which is typical of reactions involving large molecules and catalyzed by alumina-based catalysts.²⁴ Hydrogenation time is virtually the same for both Pt/C catalysts, despite the fact that the 3% Pt/Sibunit surface area is almost twice smaller than that of the 3% Pt/C catalyst on activated carbon. Possibly, in the activated carbon-based catalyst, some Pt is blocked in micropores, which reduces the fraction of the accessible surface of the active metal.

While comparing Pd-containing catalysts, one can see that the modified 0.12% Pd-3.8%Ni-4.3%Cr/Al₂O₃ catalyst exhibits higher activity towards hydrogenation of *meta*-terphenyl than the 2.5% Pd/Al₂O₃ catalyst containing more Pd. The mechanical grinding of the initial 0.12% Pd-3.8%Ni-4.3%Cr/Al₂O₃ catalyst granules leads to increase in the conversion up to 99% with hydrogenation time decreasing to 12 h, whereas similar mechanical treatment of the 2.5% Pd/Al₂O₃ catalyst does not change the activity towards *meta*-terphenyl hydrogenation. Apparently, the forced disconnection of the coral arms in the modified Pd catalyst promotes an increase in the active surface area, whereas in the case of extensive surface of the 2.5% Pd/Al₂O₃ catalyst, the mechanical decrease in the initial granules does not have a noticeable effect.

In the reverse dehydrogenation of perhydro-meta-terphenyl carried out with three alumina-supported catalysts, the conversion increases with increasing content of the active metal (see Table 2). The conversion in the dehydrogenation catalyzed by 5% Pt/Al₂O₃ is markedly lower than the conversions on either of the 3% Pt/C catalysts. The 2.5%Pd/Al₂O₃ and 0.12%Pd-3.8%Ni-4.3%Cr/Al₂O₃ catalysts show higher selectivities to metaterphenyl than the 5% Pt/Al₂O₃ platinum catalyst. The conversions of perhydro-meta-terphenyl and the selectivities to meta-terphenyl obtained on both Pt/C catalysts are similar, although the surface areas (S_{BET}) , dispersions (D), and active component particle sizes (R) differ for these catalysts. In both cases, the evolved hydrogen was of high purity, as shown by chromatography. In the dehydrogenation, the longest continuous operation without deactivation was found for the 3%Pt/C catalyst with activated carbon.¹⁹

Examination of the data of Table 2 converted to the amount of noble metal (Pt, Pd) indicates that the highest A_g and A_d values in both reversible reactions were shown by the modified 0.12% Pd-3.8% Ni-4.3% Cr/Al₂O₃ catalyst. However, for hydrogen storage applications, most important is the system capacity for saturation and evolution of the highest amount of hydrogen rather than the activity per unit metal. From this standpoint, the best conversion and activity balance for hydrogenation and dehydrogenation reactions is attained with both Pt/C catalysts. Meanwhile, both these values are higher for the catalyst with activated carbon, but the Sibunit catalyst is more processable, especially for dehydrogenation carried out in a flow reactor.

Thus, the obtained experimental data on *meta*-terphenyl hydrogenation and perhydro-*meta*-terphenyl dehydrogenation in the presence of various Pt and Pd catalysts demonstrate that the catalysts on carbon supports are more efficient in both reversible reactions than alumina-supported systems. It was also found that Pt catalysts provide higher conversion in both reactions than the Pd catalysts. It was demonstrated that the content of the noble metal can be reduced by modifying the noble metal by other metals, which is important for the design of less expensive hydrogen storage catalytic composite systems.

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