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Silver and Palladium Nanoparticles–Containing Products of the Low-Temperature Wave Conversion of an Energetic Material: Catalytic Activity in Piperylene Hydrogenation

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Abstract—The hydrogenation of 1,3-pentadiene into pentenes over the commercial 0.5% Pd/Al_2O_3 catalyst and over a new catalyst containing 1.0% Pd and 3.7% Ag (μ-catalyst) has been investigated. The new catalyst has been prepared via the flameless wave conversion of cyclotrimethylenetrinitramine in a porous composite. The catalytic properties of the new composite in the hydrogenation reaction depend on the hydrogen/1,3-pentadiene ratio and on the catalyst activation temperature. The reaction conditions for selective 1,3-pentadiene hydrogenation have been optimized. The pentenes yield as a function of temperature passes through a maximum at any H_2/C_5H_8 ratio between 1 and 2. The 2-pentene/1-pentene ratio in the reaction products increases as the temperature is raised.

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It was discovered earlier that the exothermic decomposition of some energetic compounds in ballasted condensed systems (containing an inert filler) can take place in the frontal low-temperature flameless combustion mode [1–3]. The resulting condensed products, depending on the stock composition and process conditions, are usable in the production of a wide variety of functional materials [4]. In particular, it is possible to obtain reaction products containing nanoparticles of *d* metals and their derivatives [5]. A specific feature of the synthesis of these new composites is that, in the self-propagating low-temperature combustion zone, the formation of a high-porosity polymer matrix and the filling of this matrix by metal particles take place in a single step. By purposefully varying the proportions of some of the initial components, it is possible to alter the physical and chemical properties, internal structure, and morphology of the resulting material and the particle size of metals and their derivatives in wide ranges.

A possible application of these materials is catalysis in various chemical processes, including hydrogenation. For example, a challenging problem in the production of olefins for polymerization and basic organic synthesis is that of removing dienes and acetylenic hydrocarbons from the olefins, which are usually obtained by the pyrolysis of petroleum products and other hydrocarbon feedstocks. Ethylene typically contains up to 1% acetylene, which has to be reduced to 10–20 ppm.

Olefinic C_3–C_5 fractions also contain dienes, including allenes, and acetylenic impurities. For example, pentenes usually contain up to 2–5% piperylene (1,3-pentadiene), which markedly complicates polymerization and alkylation and poisons the catalyst. The polymer resulting from piperylene can clog pipelines and cause a failure of the polymerization unit.

A perfect catalyst should selectively hydrogenate the diene or acetylene into an olefin, not into a saturated compound. A drawback of many of the conventional hydrogenation catalysts, such as Pd/Al_2O_3, is that they cause simultaneous dimerization or oligomerization of dienes or acetylenic hydrocarbons, yielding so-called green oil [6]. In addition, because the conventional palladium-containing catalysts work unstably [7], piperylene hydrogenation needs Pd-rich ones.

The causes of the instability of the conventional alumina-supported catalysts were investigated by IR spectroscopy of adsorbed CO, X-ray diffraction, and thermogravimetry [8]. It was demonstrated that, during the reaction and catalyst regeneration, the total percentage of supported metals—Pd and Ag—changes insignificantly; however, the silver atoms become less accessible to adsorbing CO molecules and their number in the closest environment of the palladium atoms decreases, which enhances the acetylene-to-ethane hydrogenation selectivity. The decrease in the accessibility of silver is due to the rehydration-induced change in the phase composition of the alumina support. It was hypothesized that the resulting aluminum hydroxide with boehmite morphology is the source of the strong Lewis sites that catalyze oligo-

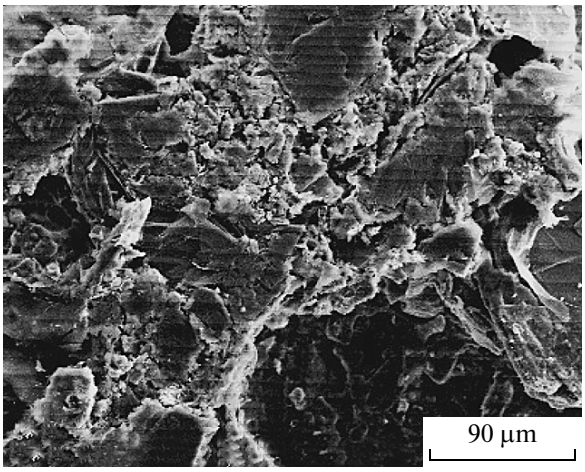

Fig. 1. Macrostructure of μ-(3.7% Ag–1% Pd): SEM data.

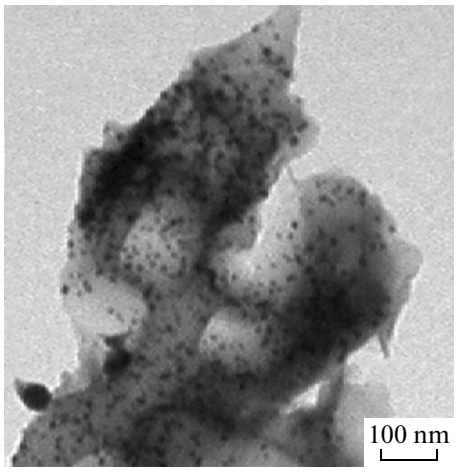

Fig. 2. Metal nanoparticles in μ-(3.7% Ag–1% Pd): TEM data.

merization on the catalyst surface. It was anticipated that the new, carbon-supported, high-porosity composites (which differ radically in acid and adsorption properties from the conventional alumina-based hydrogenation catalysts) would be free of these drawbacks. In order to verify this hypothesis, we chose to study piperylene hydrogenation into 1-pentene and 2-pentene for the reason that this reaction allows one to estimate both the catalytic activity and the pentene isomer selectivities—important data for new, unconventional catalysts.

Here, we report the catalytic properties of a new composite containing palladium and silver nanoparticles in selective piperylene hydrogenation.

EXPERIMENTAL

Catalyst Preparation

μ-(Ag–Pd) catalyst. The high-porosity composite (HPC) was obtained by the low-temperature combustion of a mixture of cyclotrimethylenetrinitramine, 1,6-hexamethylene diisocyanate (HDI) oligoisocyanurate containing 40 wt % NCO groups, and graphite as the inert filler. The precursors of the metal nanoparticles were silver carbonate and palladium chloride.

The stock components—35% cyclotrimethylenetrinitramine, 1% palladium chloride, 3% silver carbonate, 46% graphite, and 15% HDI—were mixed by hand in a mortar at room temperature. The resulting mixture was compacted into cylindrical samples 15.1 mm in diameter (~4.9 g). The samples were baked by heating them to 600°C over 2 h. The baked samples were placed in a combustion reactor ~310 cm^3 in volume. Low-temperature combustion was initiated by giving a heat pulse to an end of the sample from an electrically heated nichrome coil. Combustion was monitored as the evolution of gaseous combustion products and as the propagation of the black color of the reaction products over the light gray surface of the initial sample. The combustion zone temperature was up to 900°C.

The resulting catalyst contained 3.7% silver and 1.0% palladium. The bulk density of the catalyst was 0.6 g/cm^3. According to scanning electron microscopy data, the internal structure of the material is made up of a porous polymer matrix filled with graphite particles (Fig. 1). The nanometer-scale size of the metal particle in this material was evidenced by transmission electron microscopy (Fig. 2).

Conventional 0.5% Pd/Al_2O_3 catalyst. Commercial 0.5% Pd/Al_2O_3 catalyst (Ryazan Catalyst Plant, MA-15 brand, bulk density of 0.75 g/cm^3) was calcined in air at 350°C for 5 h before being introduced into the reaction because, according to its technical specifications, it is produced in sulfided form.

Immediately before the reaction, catalyst samples were activated with flowing hydrogen (20 ml/min) in the reactor at various temperatures for 3 h.

Reaction Procedure

A catalyst sample (1 cm^3, 0.10–0.15 size fraction) was placed in a quartz reactor (tube 7 mm in diameter) having a well for a control thermocouple. The thermocouple was positioned inside the catalyst bed. The reactor was heated to a preset temperature while passing hydrogen through the catalyst. Piperylene was fed into the reactor at atmospheric pressure using a syringe pump. The VHSV of piperylene was varied in the 1–4 h^{-1} range. Piperylene and hydrogen (which was supplied from a cylinder through a metering valve) were mixed in a gas blender placed immediately before the reactor inlet. The H_2/C_5H_8 molar ratio was varied between 0.7 and 4.0. The products leaving the reactor were collected in a cold receiver over 1 h under given process conditions, and then the process conditions were changed.

Table 1. Effect of the H_2/C_5H_8 molar ratio on the activity and selectivity of piperylene hydrogenation catalysts*

Catalyst	T, °C	H_2/C_5H_8, mol/mol	Conversion, %	C_5H_{10} selectivity, %	Specific activity, (mol C_5H_8)(g Pd)$^{-1}$ h^{-1}
0.5% Pd/Al_2O_3 (commercial brand MA-15)	40	0.75	25.1	89.0	0.7
	40	1.5	46.9	76.3	1.3
	40	2.5	72.0	39.0	2.0
	40	4.0	99.8	5.2	2.8
	80	1.5	100.0	0.2	–
μ-(3.7 %Ag–1% Pd)	40	0.75	67.2	99.2	1.1
	40	1.5	95.4	98.0	1.5
	40	2.5	99.7	58.2	1.6
	40	4.0	100	45.2	–
	80	1.5	100	19.1	–

* Atmospheric pressure, C_5H_8 VHSV of 1 h^{-1}.

The reaction products were analyzed on a Model 3700 chromatograph using an SE-54 capillary column (50 m) under isothermal conditions at 60°C.

RESULTS AND DISCUSSION

In the selective hydrogenation of acetylene mixed with ethylene (5 and 95%, respectively), the ethane selectivity of the $Pd–Ag/Al_2O_3$ catalyst increases from 10% to nearly 100% as the H_2/C_2H_2 ratio is raised from 1 to 2 [9]. A similar situation was expected to take place in piperylene hydrogenation. It was of interest to verify this supposition using the new high-porosity composite catalyst containing silver and palladium nanoparticles.

Effect of the H_2/C_5H_8 Molar Ratio

Table 1 present the results of comparative tests of two catalyst samples at different H_2/C_5H_8 molar ratios and atmospheric pressure.

Both catalysts are highly active even at 40°C; however, the pentene selectivity of the μ-(3.7% Ag–1% Pd) catalyst is higher than that of the commercial catalyst. At small H_2/C_5H_8 molar ratios of 1.5 and below, the specific activity of the HPC-based catalyst containing silver and palladium particles is somewhat higher.

At 40°C, the selectivity of both catalysts toward total 1,3-pentadiene hydrogenation into *n*-pentane increases as the H_2/C_5H_8 ratio is raised. A similar effect is observed as the reaction temperature is elevated to 80°C. Note, however, that this effect for the μ-(Ag–Pd) catalyst is not so fatal as in the case of Pd/Al_2O_3.

Thus, the catalytic tests demonstrated that, with the μ-(Ag–Pd) catalyst, the selective hydrogenation of piperylene into pentenes can be carried out successfully in wider ranges of temperature and H_2/C_5H_8 (1.0–1.5 mol/mol). This is essential for practical use of the composite catalyst.

Note that the specific activity of the commercial Pd/Al_2O_3 catalyst grows almost linearly with an increasing H_2/C_5H_8, molar ratio owing to the specific kinetic features of the reaction. The specific activity of the μ-(Ag–Pd) catalyst is less dependent on the H_2/C_5H_8 ratio (in our case, on the linear velocity of the gaseous feed). This is likely due to the specific features of the morphology and active metal distribution in the catalyst pellet. The conventional Pd/Al_2O_3 catalysts for selective diene and acetylene hydrogenation [9] are eggshell-type: the active metal is localized on the pellet surface. By contrast, the new HPC-based catalyst has an internal porous structure in which palladium metal particles, which are the active sites of hydrogenation, are distributed fairly uniformly. In view of this, it is possible that there are internal diffusion limitations for the reaction in the μ-(Ag–Pd) catalyst. However, these limitations are counterbalanced by the high degree of dispersion of the active metal. It is clear from Fig. 2 that the particle size of palladium in μ-(Ag–Pd) does not exceed 3–5 nm.

Effect of the Temperature of Catalyst Activation with H_2

It was of interest to elucidate the activation temperature effect on the catalytic properties of the μ-(Ag–Pd) catalyst. Figure 3 plots the activity and selectivity of the catalysts at large VHSV values versus the temperature at which the catalysts were prereduced with flowing hydrogen. For the conventional Pd/Al_2O_3 catalyst, a significant decrease in the piperylene conversion is observed as the prereduction temperature is raised above 300°C, and this is accompanied by an increase in the pentene selectivity. This is likely due to the sintering of palladium metal particles. This assumption is in agreement with the report that, in the selective hydrogenation of acetylene into ethylene, a similar reaction, the high ethane selectivity of Pd catalysts is due to the high degree of dispersion of palladium [10]. A different situation is observed for μ-(Ag–Pd): the activity and selectivity of this catalyst depends

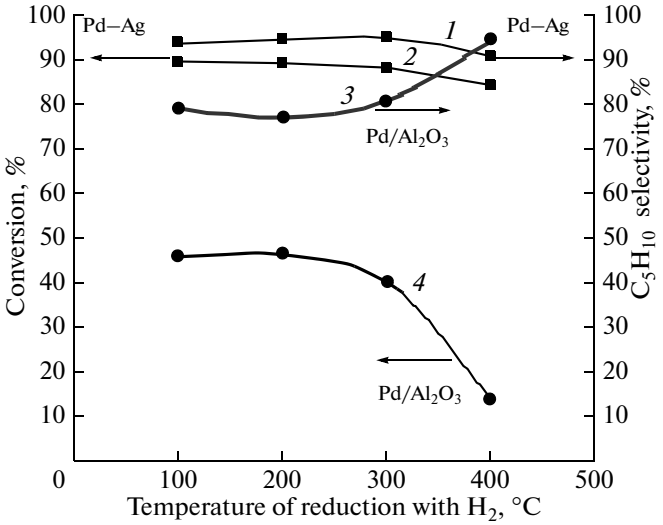

Fig. 3. Effect of the temperature of preactivation with hydrogen on the selectivity (*1*, *3*) and (*2*, *4*) activity of (*1*, *2*) μ-(3.7% Ag–1% Pd) and (*3*, *4*) Pd/Al_2O_3 in piperylene hydrogenation at 60°C, H_2/C_5H_8 = 1.5 mol/mol, and a piperylene VHSV of 2 h^{-1}

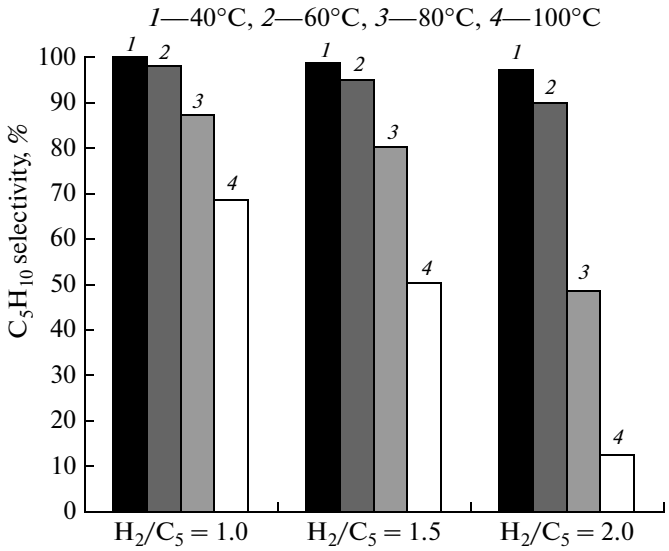

Fig. 4. C_5H_{10} selectivity as a function of the reaction temperature at a 1,3-pentadiene VHSV of 2 h^{-1} and different H_2/C_5H_8 ratios for the μ-(3.7% Ag–1% Pd) catalyst prereduced with H_2 at 200°C.

much less strongly on the temperature at which it was pretreated with H_2. However, the high-temperature activation with hydrogen (above 300°C) again impairs the performance of the catalyst (Fig. 3).

Optimization of the Reaction Conditions

An essential step of our work was optimization of the selective 1,3-pentadiene hydrogenation conditions for the new catalyst μ-(Ag–Pd). We optimized the reaction temperature, diene VHSV, and H_2/C_5H_8 molar ratio. It was most interesting to study the reaction at a high VHSV of 2 h^{-1}, i.e., at a gas load close to that in the industrial selective acetylene hydrogenation process [9].

It is clear from Fig. 4 that, as the reaction temperature is raised, the C_5H_{10} selectivity decreases at any H_2/C_5H_8 ratio. The most dramatic drop of the selectivity is observed at large H_2/C_5H_8 ratios. The pentenes yield (Table 2) at H_2/C_5H_8 = 1–2 passes through a maximum in the temperature range of 40–100°C, and the highest yield is attained at a low 1,3-pentadene VHSV and H_2/C_5H_8 = 1.5 mol/mol. The 2-pentene/1-pentene ratio in the reaction products var-

Table 2. Testing data for the μ-(3.7% Ag–1% Pd) catalyst in 1,3-pentadiene hydrogenation

Entry	C_5H_8 VHSV, ml $(cm^3\ Cat)^{-1}\ h^{-1}$	H_2/C_5H_8, mol/mol	GHSV, h^{-1}	*T*, °C	Conversion, %	C_5H_{10} yield, %	C_5H_8-2/C_5H_8-1
1	1.0	1	450	40	80.8	79.8	8.9
2	″	1.5	560	″	95.4	95.2	5.0
3	″	2	675	″	97.4	78.0	2.8
4	2.0	1	900	40	48.1	48.1	4.8
5	″	″		60	70.2	68.9	6.0
6	″	″		80	96.0	83.7	7.4
7	″	″		100	100.0	68.8	9.2
8	″	1.5	1125	40	58.6	58.0	3.6
9	″	″		60	89.2	84.8	4.9
10	″	″		80	99.2	79.5	6.0
11	″	″		100	100.0	50.4	7.1
12	″	2	1350	40	64.0	62.4	3.0
13	″	″		60	86.1	77.5	4.2
14	″	″		80	99.8	48.1	4.9
15	″	″		100	100.0	12.4	6.0

ies between 3 and 10. For any H_2/C_5H_8 ratio, it increases with an increasing reaction temperature. This is evidence of a high rate of the double bond shift reaction (1-pentene isomerization into 2-pentene).

Thus, the new composite containing silver and palladium nanoparticles, obtained by the low-temperature wave conversion of the energetic component, is more active and more selective in 1,3-pentadiene hydrogenation into pentenes than the commercial 0.5% Pd/Al_2O_3 catalyst employed in similar acetylene hydrogenation into ethylene.

As compared to the conventional catalyst, the new catalyst is less sensitive to variations in the prereduction conditions and hydrogenation parameters, including the H_2/diene ratio in the feed. With the new catalyst, selective 1,3-pentadiene hydrogenation into pentenes is possible in wider ranges of temperature and H_2/C_5H_8 molar ratio (1.0–1.5). This is essential for applications of the new catalyst.

The pentenes yield as a function of the reaction temperature passes through a maximum at any H_2/C_5H_8 ratio between 1 and 2, and the 2-pentene/1-pentene ratio increases as the temperature is raised.

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