



Catalytic activity and selectivity of Palladium and Nickel catalysts in hydrogenation reactions of nitro- and acetylene compounds

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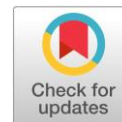
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Abstract

This paper presents the results of a study on the catalytic activity and selectivity of nickel and palladium catalysts in hydrogenation reactions of nitro- and acetylene compounds. It was shown that the activity and selectivity of nickel catalysts in the hydrogenation of phenylacetylene depend on the nature of modifying additives (Cu, Zn, Ti, Cr, Bi, Ti-Cu, Mn, Fe), and the activity and selectivity of palladium catalysts based on a polymer of metal complexes depends on the method of their preparation. It was found that for certain concentrations of the active phase of palladium (0.8 wt.%) and the polymer of potassium humate (1.0 wt.%) in the catalyst, where palladium and the polymer were deposited on bauxite-094 together, the catalyst exhibits the greatest activity and selectivity when hydrogenating phenylacetylene and potassium orthonitrophenolate.

Keywords

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Key findings

- New highly active and selective catalysts were synthesized based on nickel and palladium fixed to the carrier in various ways.
- It was shown that the activity and selectivity of nickel catalysts depends on the nature of modifying additives.
- It was established that the activity and stability of PMC-based catalysts depend on the method of their preparation.

1. Introduction

In industry, platinum group metals, Pt, Ph, Ru, and Pd, deposited on carriers, are commonly used as catalysts for selective hydrogenation of products of high-temperature pyrolysis. However, such catalysts are sensitive to catalytic poisons and expensive due to the high content of precious metals. In addition, carrying out the hydrogenation process in their presence under relatively harsh conditions (high temperature and partial pressure of H₂), caused by the need to obtain a product of acceptable quality, increases the energy intensity of the process, which, in turn, increases the cost of the final product.

The search for new cheap, highly active and selective hydrogenation catalysts for individual unsaturated hydrocarbons and their technical mixtures is a problem of great practical importance [1–7].

To increase the efficiency of selective hydrogenation of highly unsaturated impurities in hydrocarbon streams, a focused approach is required to select a catalyst system that must meet a certain set of requirements. These include: high activity of the catalyst in the hydrogenation process, which allows bringing the conversion of impurities to almost 100%, high selectivity of the catalyst for alkyne (not lower than 80%), stability of the

catalyst, insensitivity of the catalyst to poisoning by reaction products, ease of production, ease of regeneration and low cost of the catalyst. The most applicable for this purpose are palladium and nickel-based hydrogenation catalysts, which have high activity and relatively low cost compared to noble metal-based catalysts [1–9].

Among a large number of diverse catalysts, the deposited metal complex catalysts modified with polymers should be especially noted [10–17]. The advantages of polymer-metallic catalysts (PMC) are activity and stability under mild experimental conditions, which allows excluding undesirable side processes of isomerization or destruction. The main achievement in this area is the creation of new technologies based on multifunctional PMC on carriers and their introduction into industry.

Humic acids (HA) obtained from RK coals are environmentally safe and economically cheap, which determines the possibility of their use as a natural polymer-modifier in applied PMC. The study of the regularity of the composition, nature, structure and properties of HA contributes to the possibility of using them as a natural polymer-modifier in PMC, and to understanding of the dependence of the catalytic properties of these catalysts on the physicochemical properties of the polymer, which leads to an increase in the activity, stability and selectivity of the action of catalysts based on them. In this regard, the development of PMC-based catalysts with high activity and stability during long-term use is an urgent task today.

Multicomponent skeletal nickel catalysts, which have been successfully used in various hydrogenation processes, have also been found to be very industrially effective. This is due to high activity and selectivity, ease of preparation and regeneration, stability of operation in a long cycle, resistance to poisoning with catalytic poisons. It has been shown that the modification of skeletal nickel with various metals allows to regulate the properties of the catalyst in a wide range.

In this paper, we synthesized catalysts based on nickel and palladium, fixed on the carrier bauxite-094 (B-094) by various methods and studied their catalytic properties in the processes of hydrogenation of nitro- and acetylene compounds.

2. Experimental

2.1. Preparation of skeletal nickel catalysts

Weighed amount (0.8 g) of ground, powdered Ni-Al-alloy from 0.06–0.20 mm fractions (the compositions of alloys are given in Table 1) was treated with a 20% KOH solution at a temperature of 96 °C in a boiling water bath for 2 hours. The washing of the obtained products from alkali was carried out with distilled water by decanting 4–5 times, until a negative reaction to OH⁻ ions in washing water. The catalyst was then washed with a solvent in which hydrogenation was carried out.

2.2. Preparation of applied palladium catalysts

A 500 cm³ beaker was filled with 100 cm³ of distilled water, carrier and Na₂CO₃ to pH 9–10 and stirred at room temperature on a magnetic stirrer. The suspension was stirred for 10–15 minutes until the carrier was completely wetted. Bauxite-094 (B-94) was used as the carrier. The calculated amount of Na₂PdCl₄ was adjusted with distilled water to 50 mL and then this solution was transferred by impregnation to a beaker with the stirred carrier suspension. In order to achieve complete palladium precipitation, the slurry is stirred for one hour. The completeness of palladium precipitation was tested by a negative reaction with potassium rhodanide. The catalyst was washed with distilled water until neutral, filtered, dried in a vacuum oven at 363 K for three hours.

2.3. Potassium humate-modified (PtH) palladium catalysts deposited on bauxite-094

The chemical composition of bauxite-094 was Al₂O₃ – 35.1%; SiO₂ – 15.1%; Fe₂O₃ – 23.7%. Applied on bauxite-094 modified PtH, from the coal of the "Oi-Karagai" deposit, palladium catalysts were prepared as follows: a weighed amount of bauxite (3g) was added to 150 ml of distilled water, then a solution of PtH (0.8 wt.% relative to the weight of the carrier) and an aqueous solution of palladium chloride (1.0 wt.%) were added while stirring. The resulting catalysts were stirred for 3 hours and then washed, filtered and dried at 383 K for two hours.

2.4. Methods of experiments.

Hydrogenation was carried out in a thermostatted catalytic "filling" at atmospheric pressure and temperature of 20 °C. Simultaneously, reaction rates (amount of hydrogen absorbed per unit time, cm³/min) and catalyst potential (mV) relative to the calomel reference electrode were recorded. Prior to the reaction, the catalyst was treated with hydrogen in a solvent ($V = 25 \text{ cm}^3$) until a reversible hydrogen potential was established. Hydrogenation was carried out in a kinetic mode (700–800 rpm).

Chromatographic analysis was carried out on a Chromos GC-1000 chromatograph with a flame ionization detector in isothermal mode using a VR21 capillary column (FFAP) with a polar phase (Polyethylene Glycol modified with nitro terephthalate) of 50 m in length and an internal diameter of 0.32 mm. The column was maintained at 90 °C, the temperature in the evaporation chamber was 200 °C, the carrier gas was helium, the volume of the injected sample was 0.2 µl. During the experiment, 2–3 samples of the liquid reaction mixture were taken for analysis.

3. Results and Discussion

The obtained results of the study of the process of hydrogenation of phenylacetylene on a modified (Cu, Zn, Ti, Cr, Bi, Ti-Cu, Mn, Fe) skeletal nickel catalyst are shown in Table 1.

Table 1 Hydrogenation of phenylacetylene on multicomponent skeletal nickel catalysts ($P_{atm}, q_{cat} = 0.8 \text{ g}, V_{H_2} = 100 \text{ cm}^3$).

No.	Composition of alloys	Content of Ni-Al-Me, wt. %	Phenylacetylene (plant / ethanol)			
			$W_{C=C}$	$W_{C=C}$	ΔE_{start}	K_s
1	Ni-Al	50-50	68	82	330	0.82
2	Ni-Al-Cu	40-55-5	100	210	180	0.89
3	Ni-Al-Zn	43-44-13	117	258	170	0.89
4	Ni-Al-Ti	47-50-3	97	134	350	0.87
5	Ni-Al-Cr	47-50-3	70	84	290	0.84
6	Ni-Al-Bi	45-50-5	69	128	320	0.90
7	Ni-Al-Ti-Cu	42-50-3-5	72	83	320	0.81
8	Ni-Al-Mn	40-50-10	34	50	290	0.83
9	Ni-Al-Fe	45-50-5	25	47	260	0.85

* W is the activity of the catalyst, $\text{cm}^3/\text{min}\cdot\text{g Ni}$; ΔE_{start} is the initial displacement of the catalyst potential, mV; K_s is the selectivity factor.

The activity of the multicomponent skeletal nickel catalysts (Table 1, Figures 1 and 2) depends on the nature of the modifying additives. The introduction of Ti, Cu, Zn into the alloy leads to an increase in the activity of skeletal nickel ($W_{C=C} = 97\text{--}117 \text{ cm}^3/\text{min}\cdot\text{g Ni}$). The Mn and Fe additives reduce it ($W_{C=C} = 25\text{--}34 \text{ cm}^3/\text{min}\cdot\text{g Ni}$). Cr, Bi and Ti-Cu have no significant effect on the catalyst activity ($W_{C=C} = 69\text{--}72 \text{ cm}^3/\text{min}\cdot\text{g Ni}$).

The introduction of most modifying additives is associated with an increase in selectivity with the exception of Bi, Cr, Mn and Ti-Cu ($K_s = 0.81\text{--}0.90$, $W_{C=C}/W_{C=C} = 1.2\text{--}1.4$). The greatest effect falls on Cu, Zn, Ti ($K_s = 0.88\text{--}0.91$, $W_{C=C}/W_{C=C} = 1.5\text{--}2.4$). The displacement of the potential $\Delta E_{C=C}$, depending on the nature of the additives, ranges from 170 to 360 mV. On Cu and Zn modified catalysts, $\Delta E_{C=C}$ is 170–180 mV, while Ti increases the adsorption strength ($\Delta E = 350 \text{ mV}$).

On nickel catalysts, the addition of the first mole of hydrogen to phenylacetylene is predominantly via a triple bond. The "stepwise" form of kinetic curves and a sharp decrease in the potential shift of catalysts (ΔE) in the second half of the processes when hydrogenating phenylacetylene on multicomponent skeletal nickel catalysts (Figure 1) show greater adsorbability of alkynes compared to intermediate alkenes on the surface of the catalysts. This is probably due to the high selectivity of alkyne hydrogenation: $K_{Sphenylacetylene} = 0.81\text{--}0.90$ depending on the nature of the modifying additive (Table 1).

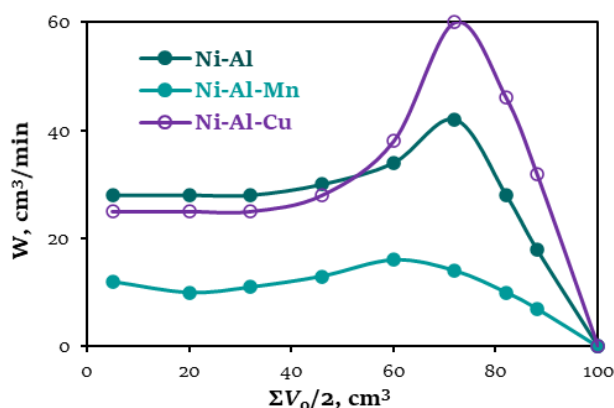


Figure 1 Hydrogenation curves of phenylacetylene ($A_{H_2} = 100 \text{ cm}^3 \text{ H}_2$) in ethanol on multicomponent skeletal nickel catalysts from alloys: 1 - Ni-Al (50-50%), 2 - Ni-Al-Mn (40-50-10%), 3 - Ni-Al-Cu (40-55-5%). Weighed amount of alloys 0.8 g.

Further, we conducted a study of the process of hydrogenation of nitro compounds and phenylacetylene on modified palladium catalysts. The dependence of the activity and selectivity of the Pd-humate potassium/B-94 catalyst on the method of its preparation was studied. Potassium humate (PtH) acts as a natural polymer in the formation of polymer-metal complexes (PMC). The optimal concentration of palladium in the catalyst of 0.8 wt.% was selected experimentally, and that of PtH was 1.0 wt.% [12].

Preparation of modified PtH palladium catalysts deposited on bauxite-094. The chemical composition of bauxite-094 is $\text{SiO}_2 - 15.1\%$; $\text{Al}_2\text{O}_3 - 35.1\%$; $\text{Fe}_2\text{O}_3 - 23.7\%$. Modified PtH palladium catalysts applied to bauxite-094 were prepared in the following 5 ways:

1. Potassium bauxite-094 and Na_2PdCl_4 were applied simultaneously. The carrier (3 g) was poured with 150 ml water, then while stirring, the solutions of PtH (1.0 wt.%) and Na_2PdCl_4 (0.8 wt.%). The mixture was stirred for 2 h, then washed, filtered and dried at 383 K for 2h.
2. The polymer and Na_2PdCl_4 were applied alternately to the support. Bauxite-094 was stirred with PtH solution for 2 hours, then palladium chloride solution was added by dripping. The mixture was stirred for 2 hours, after which the catalyst was washed, filtered and dried.
3. Bauxite-094 was stirred with Na_2PdCl_4 solution for 2 hours, then added by dropping with PtH solution. The mixture was stirred for 2 hours, after which the catalyst was washed, filtered and dried.
4. The catalyst was prepared similarly to the previous one, but after stirring the support with both components, the mixture was left in the mother liquor for 10 hours.

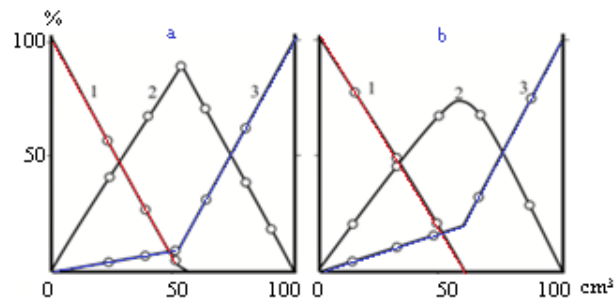


Figure 2 Diagrams of the catalyst composition (a) Ni-Al-Bi (45-50-5%), (b) Ni-Al-Ti-Cu (42-50-3-5%): 1 - phenylacetylene, 2 - styrene, 3 - ethylbenzene.

5. Application of pre-mixed solutions of PtH and Na_2PdCl_4 to the carrier. With the calculated concentration, the solutions of PtH and PdCl_2 were pre-mixed with each other, then this mixture was added by dropping while stirring onto the carrier. The mixture was stirred for 2 hours and then the catalyst was washed, filtered and dried at 383 K.

The catalysts prepared by these methods were tested for activity and selectivity in the hydrogenation reactions of ortho-nitrophenolate potassium (ONPP) and phenylacetylene. The results are presented in Table 2.

From Table 2, it can be seen that jointly, separately and alternately (with settling) precipitated Pd and PtH catalysts reduce ONPP and phenylacetylene at a rate higher than the 0.8% Pd/B-094 catalyst and precipitated alternately and pre-mixed Pd and PtH catalysts are less active and selective than the initial catalyst. The most active and selective ($K_s = 0.98$) turned out to be the catalyst where Pd and PtH were applied together, whose activity is also twice higher than the activity of the catalyst 0.8% Pd/B-094; the least active and selective ($K_s = 0.79$) turned out to be the catalyst prepared according to method 5.

So, the activity of the catalyst based on PMC, developed by us, depends on the method of its preparation. When palladium and potassium humate are deposited on the support in parallel, the stereoregular orientation of the active phase particles acquires an optimal structure and, thereby, the activity of the catalyst prepared in this way is explained.

Micrographs of the 0.8% Pd - PtH (1%)/B-094 catalyst samples were taken; the samples differed in the methods of applying palladium and potassium humate to bauxite-094 (Figure 3). Agglomerates consist of loosely bonded particles, with the sizes of the primary particles and agglomerates depending on the method of preparation.

Thus, the catalyst obtained by co-deposition of Pd and PtH (Table 2, method 1) is dispersed and has a more conformational structure. Presumably, in the catalyst prepared in this way, the polymer (PtH) binds to the surface of the support mainly in the form of "loops" and in the form of "tails", and palladium is distributed, binding to the functional groups of the polymer matrix and forming a polymer metal

complex, as well as partially adsorbing on the surface of the support itself. This contributes to the formation of dispersed nanoparticles (2–3 nm) of palladium and its uniform distribution on the surface of the carrier (Figure 3).

In the catalysts prepared by other application methods (methods 2), it is likely that the surface of the support is coated with a thin layer of polymer, and then the palladium is bound to the surface functional groups of the polymer. In the catalyst prepared according to method 5, palladium and PtH form a polymer-metallic complex, and then, when applying this complex to the surface of the support, the surface conformational construction of the active phase may turn out to be such that some part of it is a closed polymer layer inaccessible to the reagents.

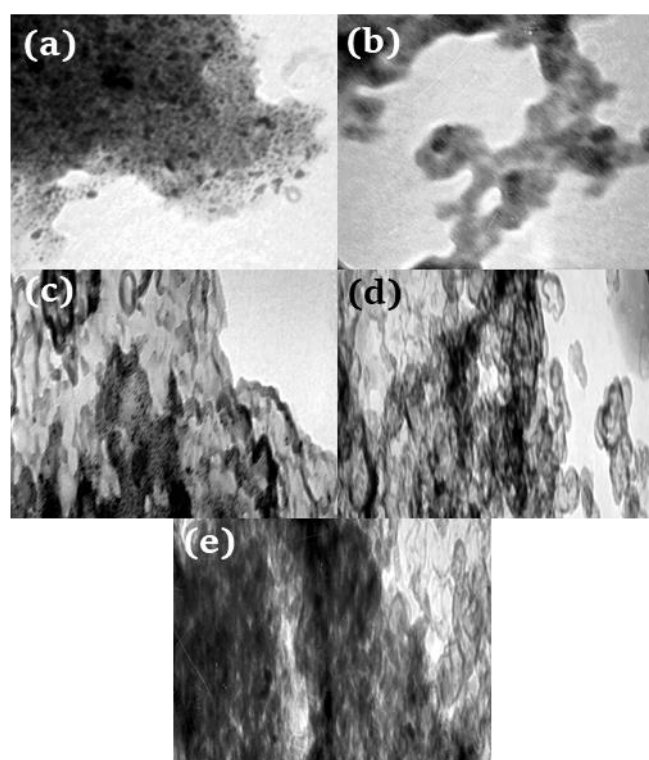


Figure 3 Micrographs of 0.8 Pd- PtH (1%)/B-094: Pd and PtH are applied together (a); Pd and PtH were applied separately (1 - PtH; 2 - Pd) (b); Pd and PtH were applied alternately (1 - PtH; 2 - Pd) (c); Pd and PtH were applied alternately (1 - PtH; 2 - Pd) with settling of in stock solution >10 h (d); preapplied mixed Pd and PtH (e).

Table 2 Activity of 0.8% Pd-PtH (1%) /B-094 catalysts in the reduction reactions of ONPP in 0.1 N KOH at $T = 313$ K and phenylacetylene in 96% ethanol at 313 K (P_{atm} , $q_{\text{cat}} = 0.1$ g, $V_{\text{H}_2} = 100$ cm³).

No.	Preparation methods	Recovery rate, cm ³ N ₂ /min					
		ONPP			Phenylacetylene		
		W, cm ³ /min	ΔE , mV	C=C	C=C	ΔE , mV	K_s
-	0.8% Pd/B-094	16.0	290	25.0	31.3	230	0.67
1	Pd and PtH were coapplied	31.0	340	58.0	62.8	260	0.98
2	Pd and PtH were applied separately: 1 - PtH; 2 - Pd	25.2	320	35.3	37.7	250	0.93
3	Pd and PtH were applied alternately: 1 - Pd; 2 - PtH;	14.6	270	23.5	22.4	240	0.86
4	Pd and PtH were applied alternately (1 - PtH; 2 - Pd) with settling >10 h	17.6	270	28.4	27.2	230	0.85
5	Pre-applied mixed Pd and PtH	11.2	330	20.6	18.5	230	0.79

Thus, the most active and stable catalyst is characterized by the presence of palladium particles uniformly distributed on the surface of the support, which are fixed to the support through a polymer (PtH) to form a complex. Potassium humate, binding to palladium by chemical bond, prevents agglomeration of active centers into larger particles, which explains the high activity and selectivity of the 0.8% Pd – PtH /B-094 catalyst, in which Pd and PtH are co-deposited.

4. Conclusions

The obtained results allow us to draw the following conclusions:

1. New highly active and selective catalysts on the basis of nickel and palladium attached to the medium by various techniques were synthesized, and the optimal process conditions were determined. It was demonstrated that the synthesized catalysts are especially active ($W = 68\text{--}258\text{ cm}^3/\text{min}\cdot\text{g}$) and selective ($K_s = 0.90\text{--}0.98$) in case of hydrogenation of potassium o-nitrophenolate and phenylacetylene.
2. It was shown that the activity and selectivity of multicomponent skeletal nickel catalysts in the hydrogenation of phenylacetylene depends on the nature of the modifying additives.
3. It was established that the activity and stability of PMC-based catalysts depends on the method of their preparation. In the best catalyst, palladium and polymer were applied to bauxite-094 together. The optimal concentrations of the active phase and polymer in the catalyst were determined: palladium – 0.8 wt.%; potassium humate – 1.0 wt.%.

Supplementary materials

No supplementary materials are available.

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Conflict of interest

The authors declare no conflict of interest.

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