

## Hydrogenation of Unsaturated Compounds to Irradiation-Quantum Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$ and Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$

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Received: Feb 03, 2017; Accepted: May 09, 2017; Published: May 16, 2017

### Abstract

In the present research, we have made a survey on the influence of  $\gamma$ -rays ( $^{60}\text{Co}$  sources) on the activity and selectivity of Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  (0, 5-5% Pd) in the reaction of liquid phase hydrogenation of cyclohexene, nitrobenzol and phenylacetylene. The samples Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  have been prepared by impregnating method  $\gamma$ - $\text{Al}_2\text{O}_3$ , previously calcined at 500°C for 4 hours with an aqueous solution of palladium chloride, followed by drying at 250°C. The resulting samples were recovered in a hydrogen stream for 2 hours at 500°C. The hydrogenation of unsaturated compounds was conducted in a thermo stated glass reactor-a catalyst "duck" in 96% ethanol at 10, 20, 30 and 40°C with simultaneous measuring of the catalyst potential during the reaction relative to the saturated calomel half-cell.

**Keywords:** Hydrogenation; Radiation; Catalyst; Radiation treatment; Concentration

### Introduction

$\text{Al}_2\text{O}_3$  is widely used as a carrier for various catalysts [1]. In their works Morterra and Magnacca [2] considered the alumina treated surface for distribution and condition of the active components and catalytic activity in various reactions; high thermal stability has been also investigated which characterizes aluminium oxide [3]. In the works [4,5] they pay much attention to the efficiency of the catalyst.  $\text{Al}_2\text{O}_3$  contains a certain proportion of cationic vacancies ( $\text{Al}_8[\text{Al}_{13}(1/3)2(2/3)]\text{O}_{32}$ ) [6]. The deposition of precious metals on  $\text{Al}_2\text{O}_3$  has determined its oxidation-reduction interaction. The precious metal in Pd(Pt)/ $\text{Al}_2\text{O}_3$ , according to the data, can exist in at least two different states. In the works of Otto and other authors they used XPS [7-9] and Raman spectroscopy [10], and showed that palladium has two different states on the surface of Pd/ $\text{Al}_2\text{O}_3$  samples.

With low concentrations of palladium, we have obtained similar results for the samples Pd/Al<sub>2</sub>O<sub>3</sub> Gigola [11,12]. Similar results [9,13] were obtained for Pt/Al<sub>2</sub>O<sub>3</sub> system. Al<sub>2</sub>O<sub>3</sub> supports the effect of the displacement of the phase transition temperature Pd-PDO. The carrier has a significant effect on the phase transformation, most likely due to the effects of the interaction between the metals (or metal oxide) [14,15].

The nature of the interaction of the metal-carrier in Pd/Al<sub>2</sub>O<sub>3</sub> and the catalysts / Al<sub>2</sub>O<sub>3</sub> Pt is still not well understood. Several constructions have been proposed for the interaction of Pd with the Al<sub>2</sub>O<sub>3</sub> surface. The formation of a two-dimensional surface complex [16] includes the formation of the palladium-aluminate phase due to the stabilization of active cations in EXAFS [17] and the stabilization of palladium in the form of PDO<sub>2</sub> [9]. In the Pt/Al<sub>2</sub>O<sub>3</sub> system, the interaction between Pt and Al<sub>2</sub>O<sub>3</sub> can result in dissolution of PtO<sub>2</sub> in Al<sub>2</sub>O<sub>3</sub> surface layers or formation of PtO<sub>2</sub>• Al<sub>2</sub>O<sub>3</sub> [13]. Until now, the nature of the interaction between the active component of Pd/Al<sub>2</sub>O<sub>3</sub> and the Pt/Al<sub>2</sub>O<sub>3</sub> systems and the action of CO+O<sub>2</sub> has not been studied in detail. Our investigation shows [18-23], that palladium can be re-dispersed or agglomerated under oxidizing treatments.

## Methods

The hydrogenation of unsaturated compounds was conducted in a thermo stated glass reactor known as catalyst "urinal" in 96% ethanol at 10°C, 20°C, 30°C and 40°C with the simultaneous measuring of catalyst's potential during the reaction of the relatively saturated calomel semi element [3].

In order to analyze the influence of  $\gamma$ -quantas on the activity of catalyst we used the following four samples of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: unirradiated (1st method); irradiated system of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (2<sup>nd</sup> method); catalyst previously irradiated with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (3<sup>rd</sup> method) and Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared from the solution of palladium chloride pre-irradiated with  $\gamma$ -quantas.

## Research Procedure

FIG. 1 illustrates the kinetic and potentiometric curves of cyclohexene and nitrobenzene's hydrogenation at Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (5% Pd), prepared with the usage of various methods at a 20°C.

In accordance with FIG. 1, the hydrogenation of cyclohexene and nitrobenzene on the unirradiated (curves 1 and 4) and irradiated (curves 2, 3, 5, 6 and 7) samples of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are carried out according to the zero order. This is also supported by the fact that the speed of hydrogenation of these compounds does not depend on the change in their concentration (within the limits equivalent to the absorption of 50-200 ml H<sub>2</sub>). The speed rate of cyclohexene's reduction on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> irradiated by method 3 (curve 2) is 1.8 times higher, and by method 2 (Curve 3) is 2.5 times higher in comparison with the speed rate observed on the unirradiated catalyst (Curve 1).

In case of the nitrobenzene's hydrogenation, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> irradiated according to the methods 2 and 4, also shows a higher activity (2-2.2-fold) than the unirradiated sample [24]. It can be noted here that higher speed of the process corresponds to a more anodic displacement of the catalyst's potential (curves 3 and 6), which in its turn indicates to the more reactive nature of hydrogen sorbed on irradiated  $\gamma$ -quanta Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

FIG. 2 illustrates the kinetic and potentiometric curves of hydrogenation of unsaturated connections on 5% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples unirradiated and irradiated with a dose of 33 krad at 20°C. As the figure suggests, the speed rate of hydrogenation in the irradiated catalysts is 1.5 to 2.2 times higher than in the unirradiated ones, depending on the nature of the connections to be hydrogenated, wherein the shape of the kinetic and potentiometric curves is not replaced.

Selectivity of irradiated catalyst constitutes 74% and this value is lower in comparison with the unirradiated sample by 10%. It should be noted that, when the temperature of hydrogenation is raised up to 40°C the reaction proceeds at a faster rate, but due to some annealing of active centers the effect of radiation is reduced. Since annealing is an activation process, then with an increase of the reaction's temperature, steady-state concentration of the active centers, arising under the influence of radiation on the surface of the catalyst, will accordingly decrease. The correlation between 5% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> activity and dose of radiation remains constant at a dosage range of 30 to 100 krad, then the activity of the catalyst declines with an increase of the irradiation dose almost to its initial value.

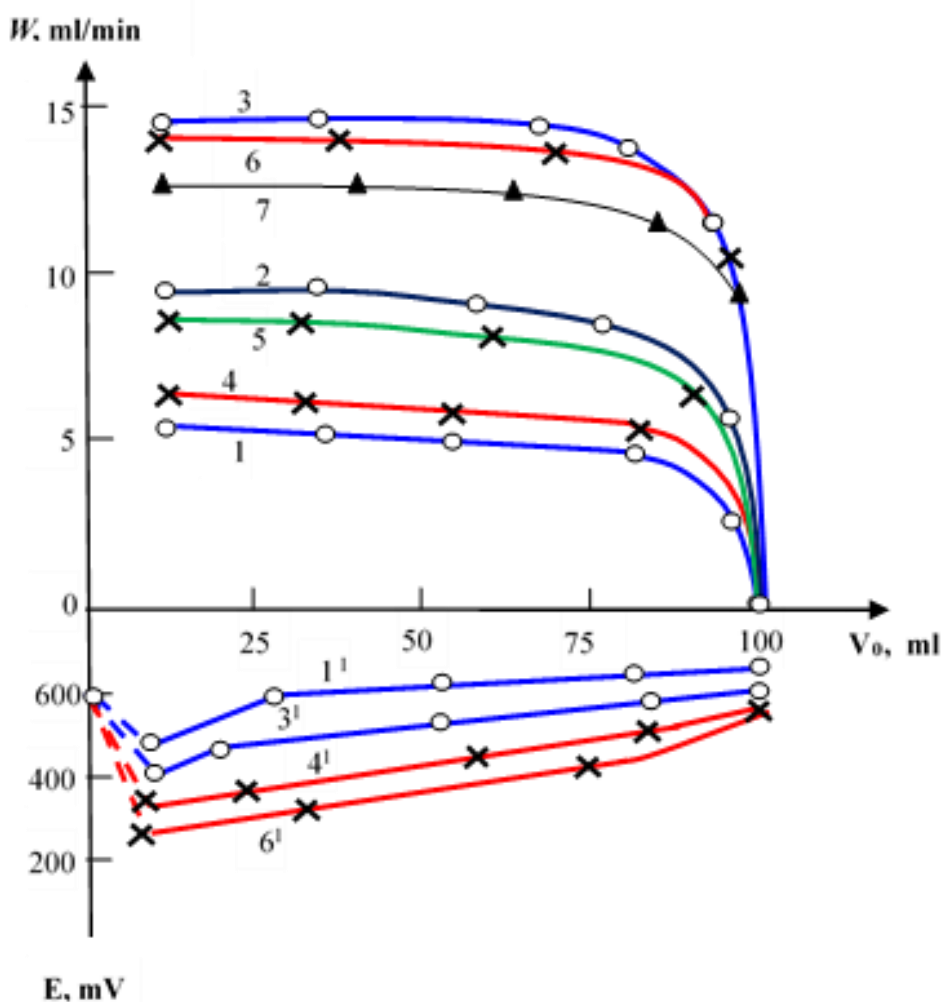


FIG. 1. Kinetic and potentiometric curves of hydrogenation of cyclohexene (1, 2, 3 and 1', 3') and nitrobenzene (4, 5, 6, 7 and 4', 6') respectively in the unirradiated (1 and 4), the radiation dose 58 krad (3 and 6) 5% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 2 and 5-a catalyst prepared on previously irradiated medium dose of 66 krad, 7-catalyst prepared from previously irradiated palladium chloride dose of 66 krad.

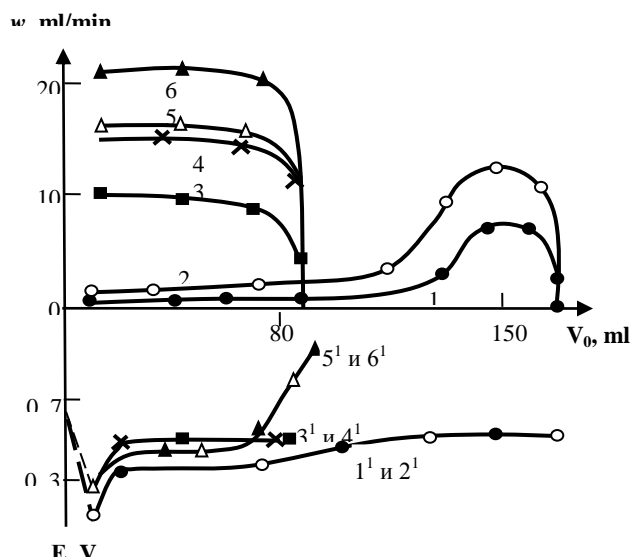


FIG. 2. Kinetic and potentiometric curves of hydrogenation of phenylacetylene (1,2), cyclohexene (3,4), nitrobenzene (5,6) on 5% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples unirradiated (1, 3, 5) and irradiated (2, 4, 6) with a dose of 33 krad at a 20°C.

However, the selectivity of the process in the case of the hydrogenation of phenylacetylene irradiated at a dose of 11 krad catalyst is higher than the unirradiated and constitutes 96%.

The positive effects resulting from irradiation with  $\gamma$ -quanta are achieved by hydrogenation of phenylacetylene to Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as well. (FIG. 3). As the FIG shows, the change in the course of the kinetic (1 and 2) and potentiometric curves (1', 2') comes after one Mole of hydrogen absorption, which indicates to the selectivity of the process. The reduction speed of C $\equiv$ C and C=C ties irradiated by catalyst of method 2 is 1.7 times higher, but, as shown by the results of the chromatographic analysis, the selectivity of the process is lower (S=76%) than in the unirradiated ones (S=88 %).

The observed radiation effect depends on the radiation dose of the catalyst (FIG. 4). The greatest effect is shown by Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, irradiated with a dose of 40-70 krad, depending on the nature of these hydrogenated compounds. It should be noted that the rate of hydrogenation of nitrobenzene and phenylacetylene by the catalyst irradiated with a dose of 8 Mrad, is greater than the unirradiated sample, while reduction speed of C=C ties decreases rapidly to the initial value [25].

This pattern makes it possible to adjust the selectivity of the process by varying the dose of the catalyst. Thus, the selectivity of the process for the hydrogenation of phenylacetylene on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> irradiated with a dose of 8 Mrad increases from 76 to 96%. TABLE 1 shows the results of calculations of the amount of adsorbed and dissolved forms of hydrogen in accordance with the data of the charging curves unirradiated and irradiated with various doses of  $\gamma$ -quanta Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 20°C.

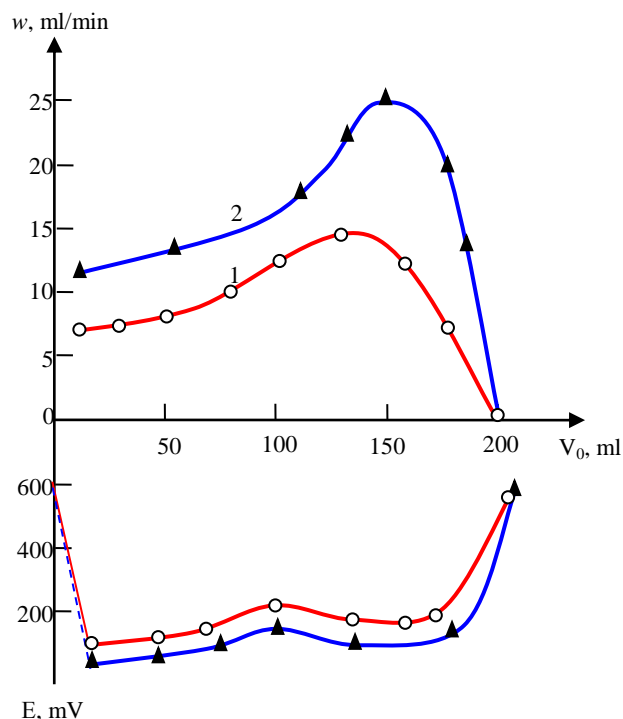


FIG. 3. Kinetic and potentiometric curves of hydrogenation of phenylacetylene on 5% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples unirradiated (1) and irradiated (2) with a dose of 33 krad.

From the data of TABLE 1 follows that the total amount of hydrogen adsorbed on the irradiated catalyst increases, and when irradiated with a dose of 58 krad constitutes 23 ml of H<sub>2</sub> per 1 g of Pd, i.e., which is almost twice as much as on the unirradiated catalyst. It can also be noted that as the radiation dose of the catalyst is increased by  $\gamma$ -quanta, the amount of dissolved hydrogen increases, the fraction of which determines the selectivity of the process.

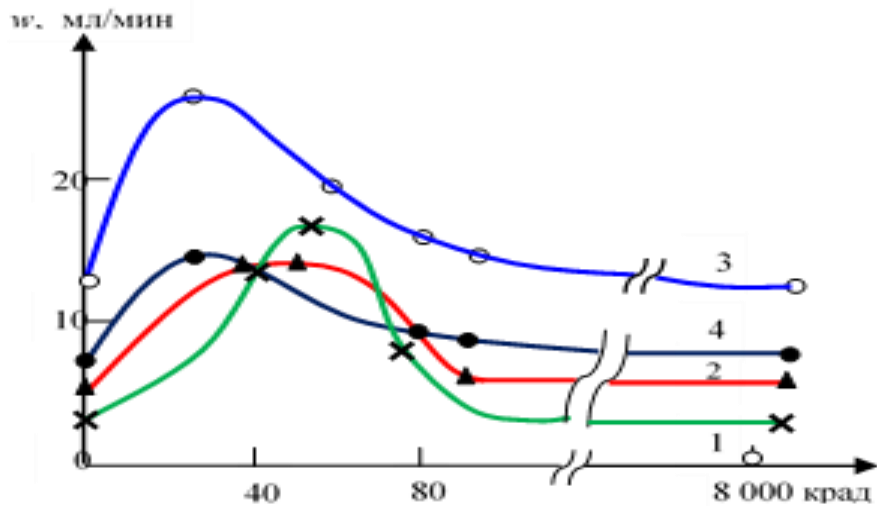


FIG. 4. The hydrogenation of cyclohexene (1), nitrobenzene (2) of styrene (3) and phenylacetylene (4) 5% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, irradiated with different doses of  $\gamma$ -quanta.

With an increase of the radiation's dose, probably occurs a partial annealing of morphological and catalytic active centers, emerging under the influence of radiation and responsible for the adsorption and activation of loosely tied form of hydrogen with a catalyst's surface, with is so necessary to saturate the C=C ties. Therefore, there is a sharp fluctuation in the selectivity of the process as a function of the radiation dose, although we can observe a correlation between the speed rate of hydrogenation of unsaturated compounds and the amount of hydrogen adsorbed by the catalyst [26].

TABLE 1. The amount of dissolved and adsorbed forms of hydrogen in the unirradiated and irradiated Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 20°C.

Radiation dose, krad	Amount of H <sub>2</sub> , ml/g Pd			Solution of hydrogen
	Total	Solution	Adsorption	Adsorbed hydrogen
0	12.0	6.5	5.5	1.18
33	16.0	8.4	7.6	1.10
58	23.0	14.0	9.0	1.55
8000	20.0	12.5	7.5	1.66

It should be noted that the hydrogenation of unsaturated compounds on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> unlike Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> the radiation effect is declined with a decrease of the active phase's concentration (TABLES 2 and 3).

TABLE 2. The hydrogenation of cyclohexene on Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 20°C.

Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> %	$\omega$ , ml/min		$\frac{\omega_{irr}}{\omega_{uni}}$
	Unirradiated	Irradiated with the dose of 58 krad	
5	5.2	13.2	2.5
3	4.8	10.5	2.2
1	3.4	6.2	1.18
0.5	2.2	4.0	1.7

TABLE 3. The hydrogenation of unsaturated compounds on the Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 20°C.

Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> %	Nitrobenzene			Cyclohexene		
	* $\omega_{ini}$ , ml/min	* $\omega_{irr}$ , ml/min	$\frac{\omega_{irr}}{\omega_{uni}}$	* $\omega_{uni}$ , ml/min	* $\omega_{irr}$ , ml/min	$\frac{\omega_{irr}}{\omega_{uni}}$
5	14.4	21.2	1.5	9.9	14.4	1.5
3	9.9	14.3	1.4	5.6	7.8	1.4
1	4.5	8.4	1.9	3.4	6.1	1.8
0.5	2.5	4.9	2.0	1.7	3.4	2.0

\* $\omega$ -Reaction rate to the absorption of 1/3 mole of H<sub>2</sub>.

## Conclusion

Overall, the observed radiation effect in the hydrogenation of unsaturated compounds depends on the dose and method of radiation with  $\gamma$ -quanta, the concentration of the active phase and nature of substances to be recovered as well as on the temperature of the reaction. By irradiating the catalyst with different doses, it is possible to stimulate and regulate the selectivity of the process.

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