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# Enhancement of Efficiency of Pd/$Al_2O_3$Catalysts in Selective Hydrogenation of Sec-Butylbenzene by Modification with $H_2SO_4$ or $H_2WO_4$

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**Abstract:** Hydrogenation of bulky aromatic hydrocarbons is an important problem to be solved in order to improve the quality of fuels. Pd-containing catalysts modified by strong acids have been prepared and studied by diffuse-reflectance IR spectroscopy, and the catalytic activity of the materials has been determined. In studying the selective liquid-phase hydrogenation of sec-butylbenzene as a model substrate, it was shown that modification of Pd/$Al_2O_3$ catalysts with acid additives ($H_2SO_4$ or $H_2WO_4$) results in a significant increase in the hydrogenation activity and selectivity. IR spectroscopy of adsorbed CO and $d_3$-acetonitrile revealed that larger palladium metal particles are formed on the Pd-$H_2SO_4$($H_2WO_4$)/$Al_2O_3$ catalysts, with ionic states of palladium being present even in the samples reduced in $H_2$.

**Keywords:** hydrogenation; palladium; sulfated alumina; tungstated alumina; alkylaromatic hydrocarbons

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## 1. Introduction

Hydrogenation of aromatic compounds is discussed from several points of view: (a) to remove aromatic hydrocarbons from fuels, (b) to test the properties of model catalysts in order to find features in the behavior of metal particles with different morphology and dispersion. Recently, the need in the development of new effective catalysts for hydrogenation of heavy aromatics is significantly raised, since reducing the content of aromatic hydrocarbons in diesel fuels provides an increase in their cetane number. The number of publications on hydrogenation of aromatic compounds is enormous, but the studies in all available publications are mainly focused either on hydrogenation of simple aromatic molecules such as benzene, toluene, xylenes or on conversion of heavy hydrocarbons or their mixtures such as bi- and trinuclear-fused aromatic compounds, like biphenyl or anthracene [1–3].

As a rule, Pt- and/or Pd-supported catalysts (aluminosilicates, alumina, zeolites, etc.,) or nickel catalysts with a high Ni content (30–70 wt%) in combination with chromium, cobalt, copper, and other transition metals are considered as most effective in hydrogenating such substrates. It was shown [4] that Pd in the supported catalysts is electron-deficient, and as a result, toluene is more strongly adsorbed on metal than benzene. In addition, a stronger interaction of toluene with acid centers of the carrier, in comparison with benzene, leads to a decrease in the hydrogenationrate. A further increase in the density of electrons in the aromatic ring by introducing additional alkyl groups explains the even lower reactivity of xylenes and, especially, aromatic compounds with branched substituents. This behavior was discussed for hydrogenation of a number of substituted benzenes [5].

The use of metal-zeolite catalysts in selective hydrogenation of aromatic compounds is described [2], in particular, by the example of hydrogenation of monoalkylbenzenes on

Pt/ZSM-5 catalysts. Bulky alkylbenzenes, such as sec-butylbenzene, whose molecules are too large to penetrate the pores of zeolite catalysts, are hydrogenated at a low rate only on metal particles located at the outer surface of zeolites.

A few publications and patents are devoted to hydrogenation of aromatic hydrocarbons with bulky and branched alkyl substituents [6,7]. In most cases, the catalysts do not exhibit a high selectivity in hydrogenation. The hydrogenation reaction is usually accompanied by cracking, hydrogenolysis, isomerization, disproportionation, and other side reactions, which lead to the formation of tars and coke. The catalytic activity in hydrogenation of aromatic hydrocarbons decreases in the series: Pt > Ni > Pd [8]. However, Ni or Pd catalysts are more preferable because of the higher stability to sintering at elevated temperatures [9].

Thus, the development of new active and selective catalysts is of considerable interest from the viewpoint of improving the process of removal of aromatic compounds with branched and bulky substituents from fuels.

The purpose of this work is to compare the activity and selectivity of low-percentage $Pd/Al_2O_3$ catalysts and the $Pd/Al_2O_3$ catalysts modified with acidic ($H_2SO_4$ or $H_2WO_4$) additives in the selective hydrogenation of the model substrate (sec-butylbenzene).

## 2. Materials and Methods

### 2.1. Catalysts Preparation

$\gamma$-$Al_2O_3$ (A-64, Ryazan Refinery, Ryazan, Russia, 170 $m^2/g$) was used as the carrier. A 0.5%$Pd/Al_2O_3$ catalyst was prepared by impregnating the carrier to incipient wetness with an aqueous solution of $H_2PdCl_4$ at pH = 1 followed by air drying at 90 °C and calcination at 500 °C for 2 h.

0.5%Pd-$H_2SO_4$($H_2WO_4$)/$Al_2O_3$ catalysts were obtained in two steps. In the first step, the carrier was impregnated with 0.2 M aqueous solutions of $H_2SO_4$ or $(NH_4)_2WO_4$ followed by drying at 90 °C for 3 h. In the second step, impregnation was repeated with a 1 M aqueous solution of $H_2PdCl_4$ at pH = 1 followed by drying at 90 °C for 3 h and calcination at 500 °C for 2 h.

Prior to hydrogenation tests, catalyst samples were reduced in $H_2$ (50 mL/$g_{cat}$ min) at 300 °C for 1 h and then transferred to an autoclave in $N_2$.

### 2.2. Catalytic Measurements

Sec-Butylbenzene (s-BB) (Aldrich, USA, 99.9%) was used as a model substrate containing a bulky alkyl substituent. A PARR-300 (300 mL) autoclave was charged with 2 g of a catalyst and 40 $cm^3$ of s-BB. The autoclave was then purged with hydrogen, and the hydrogen pressure was increased to 20 atm. The autoclave was heated to 90 °C or up to 140 °C for 0.3–0.5 h. Then the mixture was kept in the reactor for 4 h with vigorous stirring at a speed of 500 rpm. Analysis of reaction mixtures was performed using a "Crystallux" gas chromatograph (Chromatek, Yoshkar-Ola, Russia) with a SE-54 capillary column (50 m) in a programmable mode: 60 °C (4 min) and then raising the temperature at 20 °C/min to 180 °C. The specific activity was calculated by two methods: as the amount of sec-butylbenzene (in grams) converted per 1 g of the catalyst per 1 h or (2) as the amount of hydrogen (in moles) consumed for hydrogenation per 1 g of palladium per 1 h.

### 2.3. Study of Catalysts by DRIFTS

Diffuse-reflectance FTIR spectra (DRIFTS) were recorded at room temperature using a Nicolet "Protege" 460 spectrometer (Nicolet, USA) equipped with a diffuse-reflection attachment [10] in an interval 6000–400 $cm^{-1}$ in 4 $cm^{-1}$ increments. For a satisfactory signal-to-noise ratio, 500 spectra were collected. $CaF_2$ powder was used as the standard. The intensity of absorption bands in spectra was expressed in Kubelka-Munk units [11]. Spectra were processed using the OMNIC program (Nicolet, USA). Carbon monoxide was used as a test molecule for the electronic state of supported metals, and deuterated acetonitrile was used to test low-coordinated metal ions. Adsorption was carried out at room temperature at an equilibrium pressure of 15 Torr of CO and saturated vapor pressure of $CD_3CN$ (96 Torr). Before measurements, the samples were subjected to alternating treatment in a vacuum and $H_2$ at a temperature of 300 °C for 2 h (heating rate 4 °C/min) to remove adsorbed gases and water and to reduce palladium.

## 3. Results

The results of hydrogenation of s-BB in an autoclave at 90 °C and a pressure of 20 atm on the initial 0.5%Pd/$Al_2O_3$ catalyst and the modified catalysts are shown in Table 1.

**Table 1.** Results of s-BB hydrogenation in an autoclave at 90 °C and 20 atm.

| Catalyst | Specific Activity, $g_{s\text{-}BB}/g_{cat}$ h | Specific Activity, Mole $H_2/g_{Pd}$ h |
|---|---|---|
| 0.5%Pd/$Al_2O_3$ | 3.5 | 15.6 |
| 0.5%Pd-4.5%$SO_4$/$Al_2O_3$ | 4.8 | 21.3 |
| 0.5%Pd-9%$SO_4$/$Al_2O_3$ | 5.95 | 26.6 |
| 0.5%Pd-15%$WO_4$/$Al_2O_3$ | 6.05 | 27.0 |
| $Al_2O_3$ | 0 | - |
| 9%$SO_4$/$Al_2O_3$ | 0.3 | - |
| 15%$WO_4$/$Al_2O_3$ | 0.2 | - |

The results presented in Table 1 show that the modification of the support with acidic additives such as tungstic and sulfuric acids results in a significant increase in the activity of the catalysts in hydrogenation of the branched aromatic substrate as compared to the starting 0.5%Pd/$Al_2O_3$ catalyst. The selectivity of all catalysts for sec-butylcyclohexane (s-BCH) was higher than 99%.

It was of interest to investigate the hydrogenation of s-BB at a higher temperature, when the contribution of side reactions, such as cracking and isomerization, increases. The results are shown in Table 2.

**Table 2.** Results of s-BB hydrogenation in an autoclave at 140 °C and 20 atm.

| Catalyst | Composition of Products, wt% | | | | | | Conversion of s-BB, % | Selectivity for s-BCH, % |
|---|---|---|---|---|---|---|---|---|
| | $C_6$ | $C_7$ | $C_8$ | $C_9$ | s-BB | s-BCH | | |
| 0.5%Pd/$Al_2O_3$ | 0.2 | 4.8 | 7 | 12.9 | 49.6 | 25.5 | 50.4 | 50.6 |
| 0.5%Pd-4.5%$SO_4$/$Al_2O_3$ | 0.1 | 0.4 | 2,1 | 0.5 | 12.5 | 84.4 | 87.5 | 96.5 |
| 0.5%Pd-9%$SO_4$/$Al_2O_3$ | 0,2 | 0.9 | 3.4 | 0.9 | 3.5 | 91.1 | 96.5 | 94.4 |
| 0.5%Pd-15%$WO_4$/$Al_2O_3$ | 0.4 | 1.4 | 4 | 5.6 | 0.2 | 88.4 | 99.8 | 88.6 |
| $Al_2O_3$ | nd | nd | nd | nd | nd | nd | 0 | nd |
| 9%$SO_4$/$Al_2O_3$ | 79.4 | 17.2 | <2 | <2 | 97.7 | 0 | 2.3 | 0 |
| 15%$WO_4$/$Al_2O_3$ | 82.6 | 15.5 | <1 | <1 | 98.6 | 0 | 1.4 | 0 |

It follows from Table 2 that the modified catalysts show a higher s-BB conversion at elevated temperatures as well, while the selectivity to s-BCH is also significantly higher on the modified catalysts compared to the unmodified system. The modified catalysts, as well as the initial one, can be regenerated using conventional treatment with hydrogen or oxygen-containing gas.

It was of interest to understand the nature of the increased activity and selectivity of the acid-modified catalysts in the selective hydrogenation of aromatic substrates with bulky substituents, like s-BB. For this purpose, the catalysts were investigated by DRIFT spectroscopy using adsorbed CO and $d_3$-acetonitrile. Carbon monoxide is a probe molecule that is very sensitive to both the presence and strength of low-coordinated metal ions (Lewis acid sites) and the electronic state of the supported metal. Also, in the case of palladium nanoparticles forming linear and bridged CO complexes, the IR spectra of adsorbed CO provide indirect information about the dispersion of the supported metal, as can be judged by the ratio of the bridged and linear complexes. Therefore, we have chosen this probe molecule that can be studied by IR spectroscopy to reveal some properties of the catalyst, including both acid–base properties and metal state/dispersion.

The DRIFT spectra during CO adsorption–desorption on 0.5%Pd/$Al_2O_3$ and modified catalysts are shown in Figures 1–3. It should be noted that the alumina modified with sulfuric acid was studied earlier by one of the authors (L.M. Kustov) and the results have been published [12,13]. Therefore, there was no reason to reproduce the published data. Also, it should be noted that modified alumina ($SO_4/Al_2O_3$ or $WO_4/Al_2O_3$) shows almost a zero activity in hydrogenation of sec-butylbenzene (Tables 1 and 2). Mainly cracking products are formed on the acidic carriers, however, as the reaction temperatures are low, the conversions are poor.

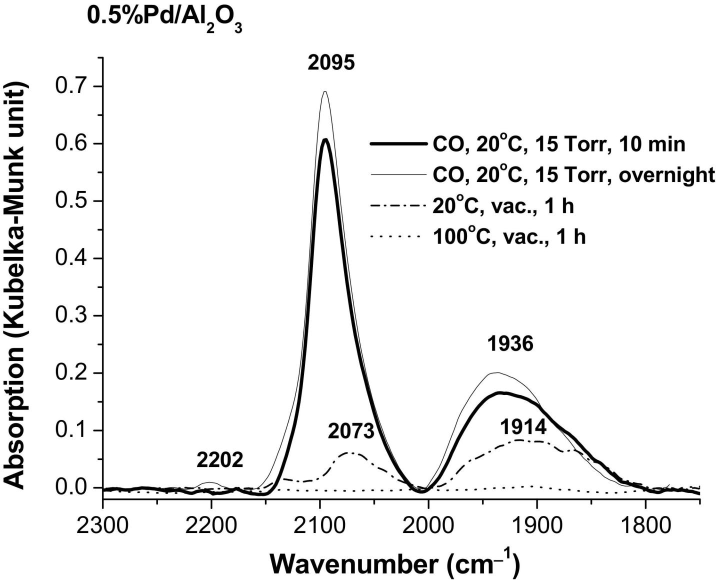

**Figure 1.** DRIFTS-CO adsorbed on 0.5%Pd/$Al_2O_3$.

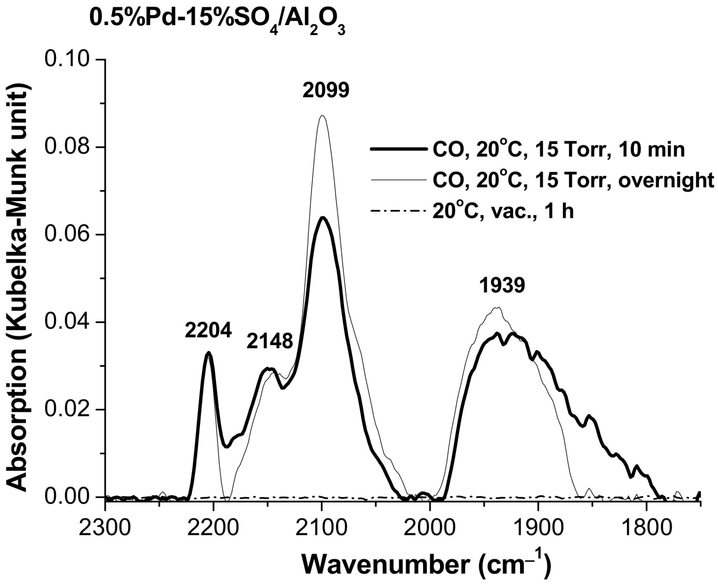

**Figure 2.** DRIFTS-CO adsorbed on 0.5%Pd-9%$H_2SO_4/Al_2O_3$.

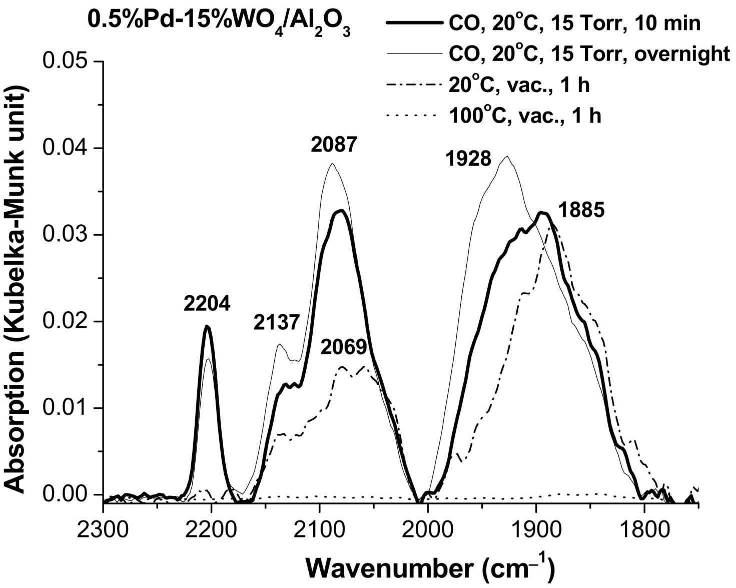

**Figure 3.** DRIFTS-CO adsorbed on 0.5%Pd-15%$H_2WO_4/Al_2O_3$.

Upon CO adsorption on 0.5%Pd/$Al_2O_3$, a narrow absorption band at 2095 $cm^{-1}$ appears in the spectrum together with a broad band at about 1936 $cm^{-1}$. CO adsorption on 0.5%Pd-9%$H_2SO_4/Al_2O_3$ is accompanied by the appearance of broad bands at 2099 and 2148 $cm^{-1}$, with another broad band at 1939 $cm^{-1}$. In the case of CO adsorption on 0.5%Pd-15%$H_2WO_4/Al_2O_3$, broad bands appear at 2087 and 2137 $cm^{-1}$, while another broad band has a maximum at 1928 $cm^{-1}$. In the spectra of all three catalysts, a low-intensity band at 2204 $cm^{-1}$ is observed characterizing CO complexes with low-coordinated aluminum [14,15]. In addition to the bands belonging to CO adsorbed on metallic palladium, the bands at 2148 and 2137 $cm^{-1}$ are observed for the 0.5%Pd-9%$H_2SO_4/Al_2O_3$ and 0.5%Pd-15%$H_2WO_4/Al_2O_3$ catalysts. Both bands are attributed to CO adsorbed on $Pd^{\delta+}$ species or $Pd^{2+}$ cations, probably linked to sulfate and tungstate [14,15].

The spectra of CO adsorbed on modified catalysts differ in the intensity and shape from the spectrum of CO on the unmodified catalyst. Comparing the intensity ratio of linear carbonyl bands (2099, 2095, and 2087 $cm^{-1}$) and bridging ones (1939, 1936, and 1928 $cm^{-1}$), it can be seen that metallic palladium in the 0.5%Pd/$Al_2O_3$ catalyst is fairly well dispersed. The ratio of the heights of the bands in the spectrum for 0.5%Pd/$Al_2O_3$ is 3.45; for 0.5%Pd-9%$H_2SO_4/Al_2O_3$—1.98; for 0.5%Pd-15%$H_2WO_4/Al_2O_3$—1.0. Thus, larger metal particles are formed on the surface of the Pd-$H_2SO_4$($H_2WO_4$)/$Al_2O_3$ catalysts modified by acids. The largest metal palladium particles are found on the catalyst modified with $H_2WO_4$.

Thus, when comparing the catalytic data (Tables 1 and 2) and IR spectra of adsorbed CO, it can be seen that the increased activity in the hydrogenation reaction of sec-butylbenzene is achieved on palladium catalysts modified with acidic additives with a lower dispersion of metallic palladium. There are examplesin the literature [16,17] of the growth of the activity of palladium catalysts in hydrogenation of unsaturated compounds with a decrease in the Pd dispersion. This is explained by a number of factors, for example, by changing the electronic properties of nanoparticles, as well as by the strong interaction of unsaturated molecules with highly unsaturated palladium atoms, whose number is different depending on the palladium particle size [18]. The presence of palladium cationic centers on the surface of anion-modified catalysts can also increase their adsorption ability and the catalytic activity.

The relation between the acidity of the catalyst and its catalytic activity in sec-butylbenzene hydrogenation is not straightforward. On the one hand, the presence of any types of acid sites at the catalyst surface is beneficial for adsorption of the aromatic hydrocarbon substrate, which is a weakly basic molecule, thereby potentially leading to some enhancement of the conversion because of the increase of the concentration of the substrate near the metal nanoparticles. On the other hand, and this effect should be considered as even more important than the adsorption effect, the partial electron transfer from the metal nanoparticle to the acid sites of the modified support (mostly Bronsted acid sites) occurs, which is supported by the data on IR spectra of adsorbed CO and corresponding frequency shifts of C-O stretching vibration bands towards higher frequencies. Such an electron transfer provides a partial positive charge on a metal nanoparticle, thus further enhancing the adsorption of the aromatic hydrocarbon (but this time on the metal particle, not on the acid site), which will again result in an enhancement of the activity in hydrogenation. Also, the partially positively charged metal particles are sometimes considered to be more active in the reactions involving hydrogen.

TheDRIFTspectrarecordeduponCD$_3$CN adsorption on the 0.5%Pd/Al$_2$O$_3$, 0.5%Pd-9%H$_2$SO$_4$/Al$_2$O$_3$, and 0.5%Pd-15%H$_2$WO$_4$/Al$_2$O$_3$ catalysts are shown in Figure 4.

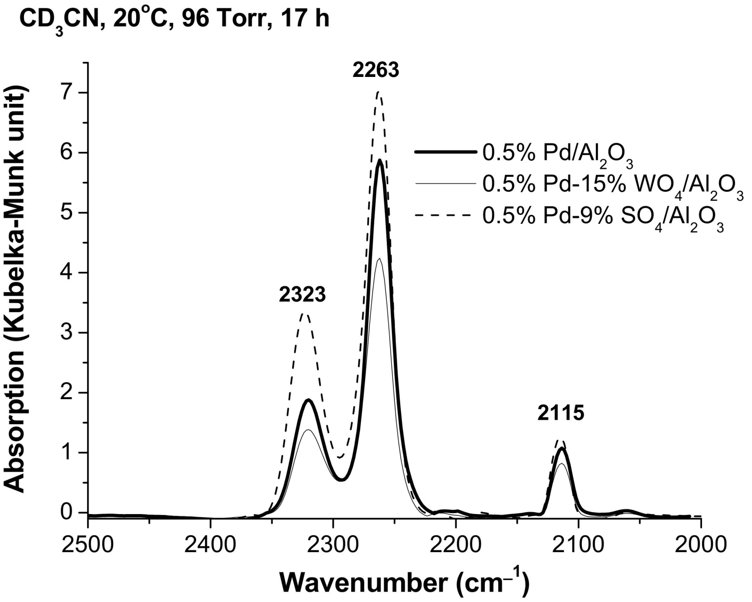

**Figure 4.** DRIFT spectra of CD$_3$CN adsorbed on three catalysts.

Three intense bands appear at 2323, 2263, and 2115 cm$^{-1}$ in the spectra of all the catalysts after adsorption of deuterated acetonitrile. The first two bands belong to the C≡N stretching vibrations in acetonitrile, the third band is assigned to the C-D stretching vibrations. The band at 2323 cm$^{-1}$ characterizes the vibrations in acetonitrile adsorbed on strong Lewis acid sites [19]. The blue frequency shift of the stretching vibrations of the C≡N bond relative to the frequency in the gas phase (2253 cm$^{-1}$) during adsorption of acetonitrile on these centers is equal to 67–70 cm$^{-1}$.

Comparison of the intensities of the absorption bands attributed to complexes with acid sites and their behavior in the course of evacuation at 100 °C allows us to rank the samples in terms of the increasing acidity according to the intensity of the corresponding bands measured after evacuation at 100 °C: 0.5%Pd/Al$_2$O$_3$ < 0.5%Pd-15%H$_2$WO$_4$/Al$_2$O$_3$ < 0.5%Pd-9%H$_2$SO$_4$/Al$_2$O$_3$.

The higher activity of the acid-modified catalysts in sec-butylbenzene hydrogenation can be explained by stronger adsorption of the substrate and increasing residence time of the adsorbed molecule to be hydrogenated on electron-deficient metal sites.

## 4. Conclusions

Thus, using the example of the selective liquid-phase hydrogenation of a model substrate (sec-butylbenzene), it was shown that modification of Pd/Al$_2$O$_3$ catalysts with acidic additives ($H_2SO_4$ or $H_2WO_4$) leads to a significant increase in activity and selectivity in hydrogenation of aromatic compounds with branched alkyl substituents, which can be used to reduce the content of aromatic hydrocarbons in fuels.IR spectroscopy of adsorbed probe molecules (CO and acetonitrile) demonstrated that the increased activity and selectivity of the acid-modified $Pd/Al_2O_3$ catalysts was observed due to the different dispersion and electronic state of the supported palladium.

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