

Liquid-Phase Hydrogenation of Thiophenes on Palladium Sulfide Catalysts

A. A. Zirka and A. V. Mashkina

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Received October 30, 1998

Abstract—Palladium sulfide catalysts are active for the hydrogenation of thiophenes of different structure in hydrocarbons at 220–300°C and 3.0–9.5 MPa. Thiophenes and benzothiophenes are close in reactivity. An increase in palladium sulfide concentration in the catalyst leads to an increase in the reaction rate per 1 g of the catalyst but has only a slight effect on the specific reaction rate of hydrogenation calculated per 1 g of Pd. The specific activity of palladium sulfide supported on aluminosilicate is one order of magnitude higher than that of PdS without a support and the catalysts supported on the aluminum oxide and carbon. The aluminosilicate-supported catalyst is also more selective.

INTRODUCTION

Thiolane and its derivatives are used in the production of biologically active substances, antioxidants, and polymers [1]. A promising method for thiolane synthesis is the catalytic hydrogenation of thiophenes [2]. Metallic palladium (1–10 wt %) supported on γ - Al_2O_3 , SiO_2 , activated carbon, or barium sulfate accelerates the hydrogenation of thiophenes to thiolanes in solutions at $T = 20$ – 80°C and $P = 0.1$ – 5.0 MPa; however, the catalysts are rapidly deactivated. Transition metal sulfides are more stable under the reaction conditions; however, they are active at $T > 100^\circ\text{C}$ and a high hydrogen pressure. The best results were obtained in the liquid-phase hydrogenation of thiophenes on alumina–palladium sulfide catalysts: over 1 g of 2.4% PdS/ Al_2O_3 at $T = 200^\circ\text{C}$ and $P = 24$ MPa, thiophene produced thiolane at a yield of 48% and a selectivity of 80% for 3 h; at the same temperature and $P = 5$ MPa, 2-methylthiophene produced 2-methylthiolane for 1 h with a yield of 40% and a selectivity of 100% [2–5]. The effect of the nature of the support and the palladium content on the activity of the catalysts was not investigated.

In this work, we studied the hydrogenation of thiophene, benzothiophene, and their alkyl derivatives over sulfide-containing catalysts of different compositions.

EXPERIMENTAL

PdS without a support was obtained by precipitation with hydrogen sulfide from a hot hydrochloric acid aqueous solution of PdCl_2 . We also used catalysts containing different amounts of palladium sulfide supported on the following supports: γ - Al_2O_3 ($S_{\text{sp}} = 200 \text{ m}^2/\text{g}$), amorphous aluminosilicate with an Al content of 12 wt % ($S_{\text{sp}} = 370 \text{ m}^2/\text{g}$), and Sibunit carbon support ($S_{\text{sp}} = 560 \text{ m}^2/\text{g}$). The catalysts were prepared by the impregnation with a

hydrochloric acid aqueous solution of PdCl_2 to incipient wetness, drying at 120°C , and treatment with 15–20 vol % H_2S in argon or hydrogen at 150°C for 1 h. Some samples were additionally reduced at 290°C for 1 h before or after sulfurization. Metallic palladium catalysts were obtained by reduction of supported PdCl_2 with hydrogen at 290°C for 16 h. The Pd and S concentrations in the catalysts were determined by elemental analysis. The state of Pd in the catalysts was investigated by IR spectra of CO adsorbed on the catalyst samples; the spectra were recorded on a Specord-75IR spectrometer. The dispersity of palladium sulfide on supports was estimated using a JEM-100 CX electron microscope with a resolution of 5 Å, and the dispersity of metallic Pd was found by oxygen chemisorption [6]. The amounts of coke in the deactivated catalysts were determined by ESR as described in [7].

All chemicals were reagent or chemically pure grade. 2-Methylthiolane (MTL) was obtained by the hydrogenation of 2-methylthiophene (MT) over an alumina–palladium catalyst.

Hydrogenation of thiophenes in dodecane or cyclohexane was carried out in a batch setup with a shaken stainless steel reactor (100-ml) equipped with an electric oven. The reactor was charged with 20–30 ml of a reaction solution and shaken 800 times per minute in one direction. To determine the catalyst activity, each run lasted 0.5–1 h. All measurements were carried out on the catalysts with a particle size of 0.16–0.25 mm. When the particle size was decreased to 0.06–0.1 mm, the rate of MT conversion at 260°C and $P = 8$ MPa did not increase, pointing to the absence of diffusion control. In the determination of the catalyst activity, all experiments were carried out on fresh catalyst samples.

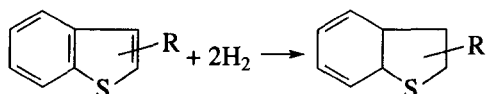
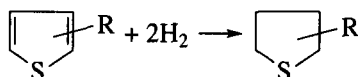
Thiophene, alkyl thiophenes, and benzothiophene were determined by GLC (flame-ionization detector; 3 m \times 3 mm column packed with 5% XE-60 on Chro-

maton, and 0.20–0.25 mm). The total sulfur content and sulfidic sulfur content in the products of 3-methyl- and 3,5-dimethylbenzothiophene hydrogenation were determined according to [8]. To identify the products containing thiolane rings, they were isolated from the hydrogenation products as complexes with AgNO_3 [9]; oxidized to sulfoxides; and analyzed for sulfoxide sulfur and for total C, H, and S contents using elemental analysis.

From these analyses, we calculated the conversion of initial thiophenes (x), the product yield (in mol %), and the selectivity (S). We determined the rate of consumption of the initial substrate or the rate of the product formation at a given conversion; the rates were calculated for 1 g of the catalyst (W , $\text{mmol (g Cat)}^{-1} \text{ h}^{-1}$) or for 1 g of Pd (W_{sp} , $\text{mol (g Pd)}^{-1} \text{ h}^{-1}$). The stability of catalysts during the hydrogenation of MT was studied as follows. The reaction was carried out on a catalyst sample for 1 h to determine x and S values, the solution was decanted, and the hydrogenation reaction was carried out with a fresh portion of the solution for 1 h. The procedure was repeated several times. The stability of the catalyst was taken to be the amount of MTL (in mmol/g Cat) formed until the conversion x decreased to a given value.

RESULTS AND DISCUSSION

The hydrogenation of thiophene, benzothiophene, and their alkyl derivatives in the presence of $2.5\text{PdS}/\text{Al}_2\text{O}_3$ ¹ was carried out in cyclohexane solutions at an initial concentration of $\sim 0.1 \text{ mol/l}$, $T = 200^\circ\text{C}$, $P = 5 \text{ MPa}$, and different contact times. Under these conditions, the hydrogenation of the thiophene ring yielded thiolanes or 2,3-dihydrobenzothiophene:



where $R = \text{H}$ or alkyl. H_2S and aliphatic or aromatic hydrocarbons were also present in the products. The contact times corresponding to $x = 35\text{--}40\%$ were determined from kinetic curves; the values obtained were used to calculate the reaction rates and selectivities at this conversion. A comparison of the results (Table 1) shows that thiophenes with different structures are close in their reactivity with respect in thiophene ring hydrogenation.

The effect of the reaction conditions on the hydrogenation rate and the dependence of the activity and selectivity of catalysts on their composition were inves-

Table 1. Hydrogenation of thiophenes in cyclohexane on the $2.5\text{PdS}/\text{Al}_2\text{O}_3$ ($T = 200^\circ\text{C}$, $P = 5 \text{ MPa}$, $x = 35\text{--}40\%$)

Hydrogenation substrate	W^* , $\text{mmol g}^{-1} \text{ h}^{-1}$	S^{**} , %
Thiophene	1.6	94
2-Methylthiophene	1.9	97
2-Propylthiophene	2.2	90
2-Hexylthiophene	2.7	91
2-Octylthiophene	2.5	88
2-Butyl-5-methylthiophene	1.9	90
Benzothiophene	2.8	98
3-Methylbenzothiophene	2.2	96
3,5-Dimethylbenzothiophene	3.1	85

* The overall conversion rate.

** The selectivity to thiolanes or 2,3-dihydrobenzothiophenes.

tigated in the hydrogenation of MT in dodecane. The hydrogenation products contained unreacted MT, MTL, pentane, and in some cases isopentane (on PdS/AlSi).

By varying the time of hydrogenation (t) and the catalyst weight (g), all other parameters being constant, we found that the rate of MT conversion and the selectivity to MTL were about the same when the value tg was kept constant. For example, at $T = 260^\circ\text{C}$ and $P = 5 \text{ MPa}$, we obtained the following results:

Catalyst	4.4PdS/ Al_2O_3	3.6PdS/ AlSi
tg , h g	0.2×2.5	0.5×1.0
W , ($\text{mmol MT}) \times (\text{g Cat})^{-1} \text{ h}^{-1}$	10.5	11.0
S , %	85	84

These data suggest that the surface coverage of the catalyst with hydrogen was proportional to the pressure.

It is seen from Table 2 that the reaction rate increased with temperature. When the temperature was increased from 220 to 300°C , the rate MT conversion (at $x = 50\%$) on the $4.4\text{PdS}/\text{Al}_2\text{O}_3$ catalyst at $P = 5 \text{ MPa}$ and the initial concentration $[\text{MT}]_0 = 0.31 \text{ mol/l}$ increased from 2.5 to $52 \text{ mmol (g Cat)}^{-1} \text{ h}^{-1}$. In this case, the rate of MTL formation also increased from 2.3 to $42 \text{ (mmol MTL) (g Cat)}^{-1} \text{ h}^{-1}$. The apparent activation energy for the overall reaction of MT conversion was $\sim 80 \text{ kJ/mol}$.

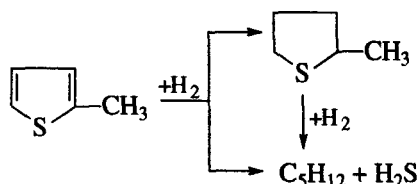
As a value of tg was increased, all other conditions being the same, the conversion of MT and the yield of pentane increased, whereas the yield of MTL first increased to some limit and then decreased (Tables 2 and 3; Fig. 1). In all experiments, the selectivity to MTL was higher than the selectivity to pentane. As the conversion of MT increased, the selectivities to MTL

¹ Henceforth, the number preceding PdS indicates the Pd concentration in the catalyst in wt %.

Table 2. Hydrogenation of 2-methylthiophene in dodecane on the 4.4PdS/Al₂O₃ catalyst ($P = 5$ MPa, $[MT]_0 = 0.31$ mol/l)

t_g , h g	x , %	S , %	W , mmol MT/(g Cat h)	t_g , h g	x , %	S , %	W , mmol MT/(g Cat h)
220°C				260°C			
0.5	30	92	5.6	0.033	16	94	45.1
1.4	45	91	3.0	0.170	37	92	20.2
2.0	52	89	2.4	0.330	48	90	13.5
4.0	63	86	1.5	0.500	56	84	10.4
8.0	72	76	0.8	1.500	78	69	4.8
240°C				300°C			
0.25	30	94	11.2	0.03	30	90	96.2
0.50	45	91	8.4	0.05	41	83	76.3
0.92	57	91	5.8	0.09	50	82	51.7
1.33	61	88	4.3	0.11	54	81	45.7
2.00	72	76	3.4	0.28	70	69	22.5

and pentane remained virtually constant until some point. Then, the selectivity to MTL decreased and the selectivity to pentane increased (Tables 2, 3; Fig. 2). This suggests that thiophene ring hydrogenation and MT hydrogenolysis occur independently until $x = 50$ –60%, and MTL also undergoes hydrogenolysis at higher conversions:



It was found that the conversion product MTL decelerates the hydrogenation of MT. For example, when 0.03–0.1 mol/l MTL was added to the reaction solution, the conversion of MT on 4.4PdS/Al₂O₃ ($T = 260^\circ\text{C}$, $P = 5$ MPa, $[MT]_0 = 0.11$ mol/l, and $t_g = 0.07$ h g) decreased by a factor of 1.5–2.2. The reaction rate divided by the MTL concentration increases with an increase in the MT concentration; in this case, the reac-

tion is close to first-order with respect to MT (Fig. 3). As $[MTL]$ is increased, the hydrogenation rate divided by $[MT]$ linearly decreases (Fig. 4).

At a constant temperature, the hydrogenation rate is proportional to the hydrogen pressure (Fig. 3); that is, the reaction is first-order with respect to hydrogen. Thus, the rate of hydrogenation of MT on the supported palladium sulfide catalysts is proportional to the MT concentration and the hydrogen pressure and inversely proportional to the MTL concentration.

The prolonged hydrogenation of MT (for 46 h, $T = 260^\circ\text{C}$, $P = 5$ MPa, $[MT]_0 = 0.11$ mol/l, and $g = 0.3$ g) yielded ~250 mmol of MTL. The surface of the deactivated catalyst 4.6PdS/Al₂O₃ contained 6 wt % of carbon in the form of coke with a low degree of condensation (calculated from ESR spectra [7]). The heating of the solvent in the presence of PdS/Al₂O₃ to 260°C also resulted in coke formation on the catalyst surface. It is not improbable that coke is the product of deep decomposition of MT and MTL or the product of their polymerization on the support surface. When 2.5 mol/l of

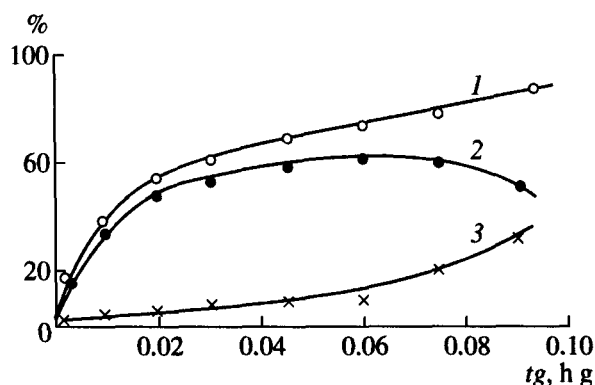


Fig. 1. The plots of (1) the conversion of MT and the yields of (2) MTL and (3) pentane on the 3.6 PdS/AlSi catalyst vs. product t_g ($T = 260^\circ\text{C}$, $P = 5$ MPa, $[MT]_0 = 0.31$ mol/l).

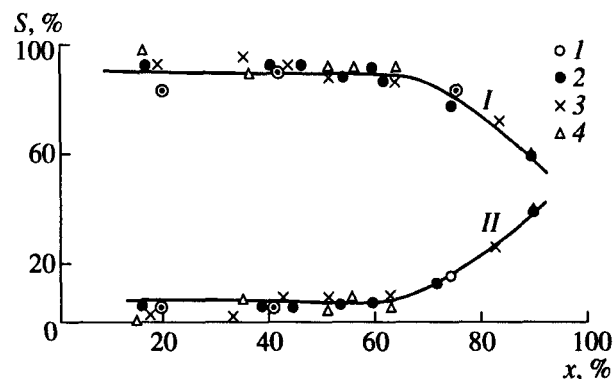


Fig. 2. The effect of the conversion of MT on the selectivities of the formation of (I) MTL and (II) pentane on the 3.6 PdS/AlSi catalyst at $T = 260^\circ\text{C}$, $P = 5$ MPa, and the initial MT concentrations (1) 0.11, (2) 0.31, (3) 0.52, and (4) 1.0 mol/l.

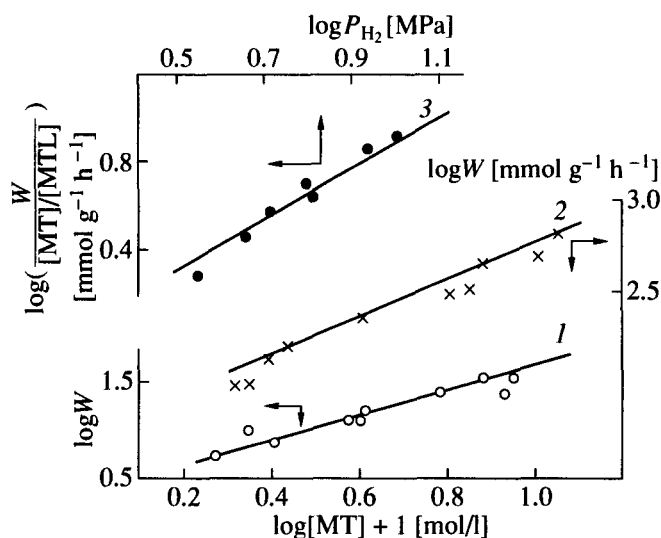


Fig. 3. The logarithmic plots of the rate of hydrogenation of MT on (1) 4.4 PdS/Al₂O₃ and (2) 3.6 PdS/AlSi vs. [MT] ($T = 260^\circ\text{C}$, $P = 5$ MPa) and (3) the logarithmic plot of the hydrogenation rate divided by [MT]/[MTL] on 4.4 PdS/Al₂O₃ vs. hydrogen pressure.

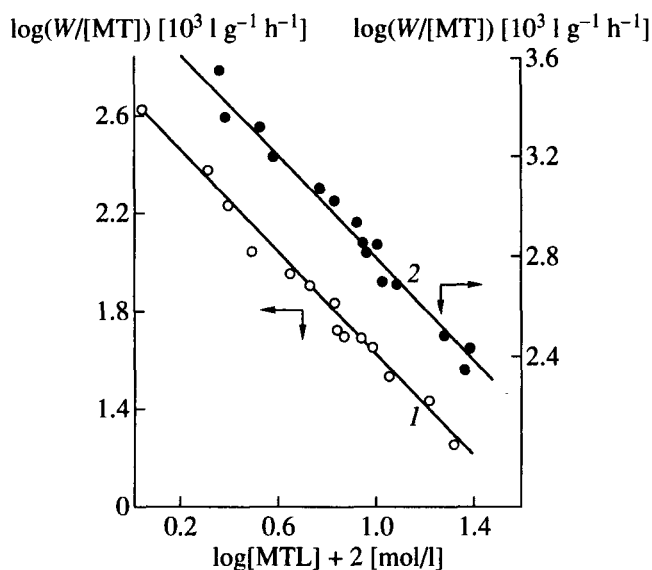


Fig. 4. The logarithmic plots of the rate of hydrogenation of MT divided by the average concentration of MT vs. average concentration of MTL on the (1) 4.4 PdS/Al₂O₃ and (2) 3.6 PdS/AlSi catalysts at $T = 260^\circ\text{C}$ and $P = 5$ MPa.

pentadiene, which is one of the products of MT decomposition, was added to the reaction solution, the catalyst remained active.

IR spectra of CO adsorbed on the deactivated catalysts did not reveal substantial changes in the electron state of Pd; as in the spectrum of the initial sample, we find the absorption band at 2140 cm^{-1} assigned to Pd⁺CO or Pd²⁺CO. This band is characteristic of coordinatively unsaturated palladium sulfide. The absorption band at $\sim 2077\text{ cm}^{-1}$ corresponding to Pd⁰CO was absent.

To reveal the effect of the composition of catalysts on their activity and selectivity, we investigated the

hydrogenation of MT in dodecane in the presence of PdS and PdS supported (in different amounts) on $\gamma\text{-Al}_2\text{O}_3$, carbon, and aluminosilicate (AlSi). The characteristics of the process were studied depending on the catalyst weight and reaction time at $T = 260^\circ\text{C}$, $P = 5$ MPa, and $[\text{MT}]_0 = 0.31\text{ mol/l}$. The catalysts were compared in activity measured by the average rate of MT conversion at $x = 50\text{--}60\%$.

We first investigated the effect of the catalyst preparation conditions on the activity of PdS supported on $\gamma\text{-Al}_2\text{O}_3$ and AlSi. The activity did not depend on the time of drying the samples (1–9 h) after the deposition of PdCl₂ onto the supports nor on the treatment of the catalysts (with H₂S in hydrogen or argon at 150°C for

Table 3. Hydrogenation of 2-methylthiophene in dodecane on the 3.6 PdS/AlSi catalyst ($T = 260^\circ\text{C}$, $P = 5$ MPa)

$t_g, \text{ h g}$	$x, \%$	$S, \%$	$W, \text{ mmol MT}/(\text{g Cat h})$	$t_g, \text{ h g}$	$x, \%$	$S, \%$	$W, \text{ mmol MT}/(\text{g Cat h})$
[MT] ₀ = 0.11 mol/l				[MT] ₀ = 0.69 mol/l			
0.0006	19	84	965	0.0044	18	93	847
0.0034	42	93	408	0.0220	35	93	329
0.0100	60	90	198	0.0650	52	92	166
0.0200	75	85	124	0.1300	64	91	101
[MT] ₀ = 0.31 mol/l				[MT] ₀ = 1.0 mol/l			
0.002	16	94	744	0.007	16	95	738
0.010	39	95	363	0.036	36	92	300
0.020	55	91	256	0.065	44	95	203
0.030	61	90	189	0.100	52	94	156
0.040	59	92	183	0.200	55	93	83
0.060	74	82	115	0.400	64	94	48

Table 4. The activity of metallic palladium sulfide catalysts in the hydrogenation of 2-methylthiophene at $T = 260^\circ\text{C}$, $P = 5\text{ MPa}$, and $[\text{MT}]_0 = 0.31\text{ mol/l}$ ($x = 50\text{--}65\%$)

Catalyst	Pd, wt %	t_g , h g	x , %	Yield, mol %		S , %	W_{sp} , mol MT/(g Pd h)
				MT	pentane		
PdS/ Al_2O_3	2.4	0.500	62	49	9	79	0.33
Pd/ Al_2O_3	2.6	0.500	62	46	13	74	0.30
PdS/C	4.6	0.250	53	46	7	87	0.29
Pd/C	4.0	0.250	51	44	8	86	0.32
PdS/AlSi	3.9	0.025	53	48	6	91	3.8
Pd/AlSi	3.9	0.025	52	47	5	90	3.4

Table 5. The activity and selectivity of palladium sulfide catalysts of different composition in the hydrogenation of 2-methylthiophene at $T = 260^\circ\text{C}$, $P = 5\text{ MPa}$, and $[\text{MT}]_0 = 0.31\text{ mol/l}$ ($x = 50\text{--}60\%$)

Catalyst	Pd, wt %	x , %	S , %	W , mmol MT/(g Cat h)	W_{sp} , mol MT/(g Pd h)
PdS	77	51	84	69.3	0.09
PdS/ Al_2O_3	0.4	50	72	0.6	0.15
	0.7	51	76	1.4	0.20
	1.1	62	70	2.0	0.18
	2.4	62	79	7.9	0.33
	4.4	56	84	10.4	0.24
	5.3	57	84	14.3	0.27
PdS/C	0.4	56	82	1.0	0.26
	0.8	55	78	3.0	0.38
	2.2	57	79	7.3	0.33
	4.0	55	85	10.8	0.27
	4.6	53	87	13.3	0.29
PdS/AlSi	0.5	40	72	12.0	2.4
	1.1	55	91	32	2.9
	2.0	58	91	58	2.9
	3.5	58	91	147	4.2
	4.0	58	90	148	3.7
	4.7	54	91	136	2.9
	7.1	57	93	178	2.5
	13.0	56	91	260	2.0

1 h or with hydrogen at 290°C for 1 h before or after the sulfurization). The initial metallic palladium on the supports and the supported palladium sulfide catalysts exhibited the same activity in MT hydrogenation (Table 4). Upon the reaction, the samples with a Pd content lower than 3 wt % were stoichiometric in sulfur, whereas the atomic ratio $S : \text{Pd}$ was equal to 0.6–0.8 at higher Pd contents. The hydrogenolysis of MT and MTL was accompanied with the formation of hydrogen sulfide; in this case, the $\text{H}_2\text{S} : \text{Pd}$ ratio was at least (20–50) : 1, which was enough for the conversion of Pd into PdS [3].

Table 5 presents the data on the activity and the selectivity of palladium sulfide catalysts depending on their composition. PdS without a support exhibits a low specific activity (W_{sp}); the specific activity of the supported PdS catalysts is higher. As the PdS concentration in the supported catalysts is increased, the activity per 1 g of the catalyst increases, but the activity per 1 g of Pd remains of the same order of magnitude. The specific activities (per 1 g of Pd) palladium sulfide without a support and PdS on the $\gamma\text{-Al}_2\text{O}_3$ and carbon supports are about an order of magnitude lower than that of the PdS/AlSi catalyst. The PdS/AlSi catalyst provides a

Table 6. The specific surface area of supported catalysts containing 2 wt % Pd

Support	Specific surface area of		
	palladium sulfide, m ² /g PdS		metallic palladium**, m ² /g Pd
	from data of electron microscopy*	by the Boreskov rule	
γ -Al ₂ O ₃	220	180	204
Carbon	280	130	167
AlSi	220	1174	93

* Calculated from electron microscopic data on the average size of PdS particles [6].

** Measured by the chemisorption of oxygen.

higher selectivity: 88–91% (at $x = 50$ –60%) versus 78–85% for the other catalysts.

The higher activity of PdS/AlSi compared with the catalysts on the other supports cannot be explained in terms of the dispersity of PdS. According to electron-microscopic data, particles with the mean diameter $d = 30$ Å dominate in all the samples except PdS/C, for which $d = 15$ Å and the activity is low. The specific surface areas of metallic palladium supported on AlSi and other supports are of the same order of magnitude. As was mentioned above, the activities of the supported catalysts originally containing Pd are approximately the same as those of the catalysts originally containing PdS. The activity of Pd/AlSi is much higher than those of the catalysts on the other supports (Table 3). It is unlikely that the interaction of metallic Pd with H₂S evolved during the reaction will dramatically change the dispersity of the active component. The calculation of the specific surface areas (S_{sp}) of the supported catalysts from S_{sp} of PdS without a support (35 m²/g) and its activity in the liquid-phase hydrogenation of MT, on the assumption of the constant specific catalytic activity (the Boreskov rule [10]), shows that S_{sp} values of 2.0–2.7 PdS on the Al₂O₃ and carbon supports are close to each other and are about the same as the specific surface area of metallic palladium on the same supports (Table 6 [2]). At the same time, S_{sp} of the PdS/AlSi catalyst calculated by the Boreskov rule is an order of magnitude higher than the specific surface area of metallic Pd on AlSi (Table 6).

The aluminosilicate surface contains strong proton sites in substantial amounts with a proton affinity (mea-

sured by pyridine adsorption) of 1180 kJ/mol, but γ -Al₂O₃ and the carbon support have a low proton acidity [3]. The acidity of the support can affect the electron state of the active component of the catalyst [11]. However, it is more probable that proton sites favor the activation of MT similarly to that occurred in the gas-phase hydrogenation of benzene on metallic palladium supported on aluminosilicate [12]. The elucidation of the effect of the support acidity on the catalytic activity for the liquid-phase hydrogenation of MT is the subject of further research.

ACKNOWLEDGMENTS

We are grateful to A.L. Chuvilin, V.Yu. Gavrilov, E.A. Paukshtis, and V.F. Anufrienko (Department of Physicochemical Investigation Methods, Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences) for their help in this study.

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