Activity of Palladium Sulfide Catalysts in the Reaction of Gas-Phase Hydrogenation of 2-Methylthiophene

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Abstract—In the interaction of hydrogen with 2-methylthiophene in the gas phase over palladium sulfide catalysts at 180–260°C and 0.1–0.8 MPa, the saturation of the thiophene ring resulting in 2-methylthiolane and the hydrogenolysis of 2-methylthiophene occurs. When the conversion is lower than 60%, these reactions occur independently; at higher conversions, methylthiolane also undergoes hydrogenolysis. The specific catalytic activity of PdS supported on γ -Al₂O₃, TiO₂, and carbon and without support is much lower in the hydrogenation of 2-methylthiophene than the activity of PdS supported on SiO₂, aluminosilicate, and zeolite HNaY having strong Brönsted acid surface sites.

INTRODUCTION

The gas-phase catalytic hydrogenation of thiophene and its derivatives is an essential stage in oil hydrotreating. Over hydrodesulfurization catalysts containing Mo, W, Ni, and Co sulfides, the hydrogenolysis of thiophene occurs in parallel to its hydrogenation into thiolane, although the yield is low [1-4].

In the gas-phase hydrogenation of thiophene over nickel-containing zeolites CaY and NaY (T = 250– 325° C, P = 0.1-2.5 MPa), the yield of thiolane may be as high as 70–98%; however, the catalysts are rapidly deactivated due to coke formation [5, 6]. The most active catalyst for the gas-phase hydrogenation of thiophenes is palladium sulfide [1, 2, 7].

In this work, we studied the effect of the nature of supports and the palladium sulfide content of catalysts on their activity and selectivity in the gas-phase hydrogenation of 2-methylthiophene (MT) into 2-methylthiolane (MTL).

EXPERIMENTAL

Palladium sulfide without support was obtained by precipitation with hydrogen sulfide from a hot aqueous solution of palladium chloride and hydrochloric acid. Pd black was obtained by reducing PdCl₂ with hydrazine hydrate at room temperature. Supported catalysts were prepared from ready-for-use materials: γ -Al₂O₃ ($S_{sp} = 200 \text{ m}^2/\text{g}$), SiO₂ ($S_{sp} = 300 \text{ m}^2/\text{g}$), amorphous aluminosilicate (AlSi) with an Al content of 10 wt % ($S_{sp} =$ 360 m²/g), Sibunit carbon ($S_{sp} = 560 \text{ m}^2/\text{s}$), TiO₂ as anatase ($S_{sp} = 220 \text{ m}^2/\text{g}$), and zeolite HNaY ($S_{sp} = 530 \text{ m}^2/\text{g}$). A PdS/HNaY catalyst was obtained by treating Pd/HNaY with hydrogen sulfide at 150°C for 1 h. A Pd/HNaY sample was obtained by the ion exchange of NaY in a [Pd(NH₃)₄Cl₂] aqueous solution followed by treating air and hydrogen at 350°C. Other catalysts were prepared by the incipient-wetness impregnation of supports by a PdCl₂–HCl aqueous solution or by a solution of palladium acetate in toluene followed by drying at 120°C and sulfurization with 15% H₂S in Ar at 150°C for 1 h. Metallic catalysts were obtained by the impregnation of supports with a solution of a Pd compound followed by the reduction with hydrogen at 290°C for 16 h. The Pd and S content of the catalysts was determined by elemental analysis.

The dispersity of metallic Pd was measured by chemisorption of oxygen, and the dispersity of PdS, using a JEM-100 CX electron microscope with a resolution of 5 Å. ¹H NMR spectra of 2-methylthiophene adsorbed on the catalysts were recorded on a Bruker CXP-300 instrument. IR spectra of adsorbed CO and pyridine were recorded on a Specord-751R spectrometer. All chemicals were reagent grade or chemically pure.

The hydrogenation of 2-methylthiophene was carried out at an atmospheric or elevated pressure in a flow setup connected to a chromatograph. Hydrogen from a gas bottle was supplied to a constant-temperate bubbler filled with 2-methylthiophene and then to a reactor packed with a catalyst. The reactor was heated with an inertia-free oven. The reaction mixture was analyzed by chromatography (flame-ionization detector; $3 \text{ m} \times$ 3 mm column packed with 5% XE-60 on Chromaton N-AW-DMCS, 0.20–0.25 mm) at regular intervals. The hydrogenation product was usually sampled 30 min after the admission of the mixture to the reactor. All experiments were carried out in the kinetic regime on catalysts with a particle size of 0.10-0.16 mm at a gas flow rate of at least 0.9 cm³/s. The contact time (τ) was calculated as a ratio of the catalyst volume to the gas flow rate, both in cm³/s, at $T = 20^{\circ}$ C and P = 0.1 MPa. From analytical data, we calculated the conversion of 2-methylthiophene (x); the product yield, mol %; the

<i>T</i> , °C	τ, s	x, %	S, %	W, mmol MT/(g Cat) h	<i>T</i> , °C	t, s	x, %	S, %	W, mmol MT/(g Cat) h
	$2.4 \text{ PdS/Al}_2\text{O}_3, P = 0.1 \text{ MPa}$				3.6 PdS/AlSi, P = 0.1 MPa				
200	4.2	27	50	0.39	180	1.6	20	90	0.86
	16.0	36	47	0.14		30.0	31	87	0.71
	27.0	48	40	0.11			,		
240	2.9	45	48	0.94	220	1.0	48	80	3.3
	4.2	50	44	0.72		2.8	60	84	1.5
	6.1	56	39	0.56	240	0.25	50	67	13.7
	16.0	63	37	0.24		0.52	58	62	7.7
	4.2*	27	63	0.91		0.44**	19	86	5.9
	21.0*	42	60	0.28		1.6	73	56	3.1
		3.6PdS/A	lSi, P = 0	.8 MPa	3.6PdS/AlSi, $P = 0.8$ MPa				
200	0.06	10	94	95	220	0.25	48	85	11.0
	0.09	22	91	13.7		0.3	53	86	14.1
	1.2	51	87	3.5		0.4	56	87	8.0
	1.5	58	86	2.2		0.6	70	80	6.7
_	4.0	78	73	1.1		1.0	80	78	4.6

Table 1. Reduction of MT on palladium sulfide catalysts ($[MT]_0 = 1.0-1.2 \text{ mmol/l}$)

* [MT]₀ = 2.8 mmol/l.

** $[MT]_0 = 2.4 \text{ mmol/l}.$

selectivity with respect to the formation of 2-methylthiolane (S); and the average conversion rates of 2-methylthiophene for 1 g of the catalyst (W), for 1 g of Pd (W_{Pd}), and for 1 m² of PdS or Pd (W_{sp}).

RESULTS AND DISCUSSION

The hydrogenation products contained unreacted 2-methylthiophene, 2-methylthiolane, pentane, and H₂S. The carbon balance was generally $\pm 5\%$.



Fig. 1. Effect of the contact time on (1) the conversion of MT and the yields of (2) MTL and (3) pentane on the 3.6 PdS/AlSi catalyst at $T = 240^{\circ}$ C and $[MT]_0 = 1.4$ mmol/l.

At an atmospheric pressure, the reduction of 2-methylthiophene into 2-methylthiolane occurred only at elevated temperatures. The data on the hydrogenation of 2-methylthiophene over 2.4 PdS/Al₂O₃ and 3.6 PdS/AlSi¹ are presented in Table 1. It is seen that, on the alumina-palladium sulfide catalyst, 40–60% conversion of 2-methylthiophene is attained over a longer contact time because the hydrogenation rate is low. On Pd/AlSi, the hydrogenation rate is much higher. With either of the catalysts, the conversion of 2-methylthiophene increases with temperature and decreases with an increase in the initial concentration of 2-methylthiphene ([MT]₀). The higher [MT]₀, the higher the selectivity to 2-methylthiolane. PdS/AlSi is more active and more selective than PdS/Al₂O₃.

High pressure is favorable for the hydrogenation reaction (compare the data of Table 1 to those in Fig. 2). At a constant temperature and pressure, an increase in the contact time leads to an increase in the conversion of 2-methythiophene and the yield of pentane. The yield of 2-methylthiolane also increases to a certain threshold value (Fig. 1). At x < 50-60%, the selectivities to 2-methylthiolane and pentane remain constant; at higher x, the selectivity to 2-methylthiolane decreases and the selectivity to pentane increases (Fig. 2). Analogous dependences were obtained for the other catalysts under investigation. These findings suggest that the

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

hydrogenation of 2-methylthiophene over palladium sulfide catalysts occurs according to the consecutiveparallel scheme:



The ratio of the specific rate of 2-methylthiophene conversion per unit catalyst weight and the concentration of 2-methylthiophene changes in the inverse proportion to the concentration of 2-methylthiolane in the reaction mixture (Table 2). At constant [MTL], the reaction rate is proportional to [MT]. For example, on the 1.2 PdS/SiO₂ catalyst ($T = 200^{\circ}$ C, P = 0.8 MPa, [MTL] = 0.045 mmol/l), we obtained the following results:

[MT], mmol/l	0.6	1.2	2.1
W, (mmol MT) (g Cat) ⁻¹ h ⁻¹	9.4	18.1	34.0

The reaction rate increases with pressure. For example, the hydration rate on 3.6 PdS/AlSi (240°C, [MT]₀ = 1 mmol/l, [MTL] = 0.2 mmol/l) at P = 0.1, 0.2, and 0.8 MPa is equal to 13.5, 26.3, and 47.0 (mmol MT) (g Cat)⁻¹ h⁻¹, respectively. The selectivity to MTL on this catalyst is 67% at an atmospheric pressure and 82% at higher temperatures.

The rate of MT hydrogenation increases with temperature; in this case, S decreases, and the selectivity to pentane increases (Table 3). The apparent activation energy of the reaction is equal to 80 ± 5 kJ/mol.

In the gas-phase hydrogenation, the palladium sulfide catalysts exhibit a high stability. For example, during the reaction at 240°C and an atmospheric pressure, the activity of the 5 PdS/AlSi catalyst remains constant for 90 h (the maximal duration of a run). Only the 2.5 PdS/HNaY catalyst was rather unstable: its activity decreased by 30% for 1 h, and polymeric deposits were found at the catalyst surface.

PdS catalysts on different supports exhibit different activities and selectivities to MTL (Table 4).

At higher temperatures, PdS can partially be reduced to Pd_2S (the sulfur-deficient phase) and metallic Pd [2]; however, this process is slow. For example, the degree of reduction of unsupported PdS at 200°C over 1 h was at most 2%. The catalytic conditions are unfavorable for the reduction of PdS due to the sulfurization of the catalyst with H_2S and the products of the dissociative chemisorption of components available in the reaction mixture. Moreover, palladium sulfide may be stabilized via the formation of a complex involving the sulfur atom of an undecomposed sulfurous compound [1]. Thermodynamic calculations show that the equilibrium of the reaction PdS + $H_2 == H_2S + Pd$ is shifted toward PdS. Under equilibrium conditions at



Fig. 2. Effect of the conversion of MT on the selectivities of the formation of (1) MTL and (2) pentane on the 3.6 PdS/AlSi catalyst at $T = 240^{\circ}$ C and [MT]₀ = 1.4 mmol/l.

 $T = 327^{\circ}$ C and P = 0.1 MPa, even very small amounts of H₂S will suffice to stabilize the PdS phase [2]. After experiments, the sulfur content of the sulfide samples was lower than stoichiometric. The adsorption of CO on the catalysts containing 2 wt % of metallic palla-

 Table 2. Effect of the MTL concentration in the reaction

 mixture on the rate of MT hydrogenation on palladium sulfide catalysts

[MTL], mmol/l	$\frac{W/[MT],}{(mmol MT)}$ (g Cat) h [MTL], mmol/l		$\frac{W/[MT],}{(mmol MT)}$ (g Cat) h			
3.6 PdS/AIS	i, $T = 240^{\circ}$ C,	$1.2 \text{ PdS/SiO}_2, T = 200^{\circ}\text{C},$				
P=0.	.1 MPa	P = 0.8 MPa				
0.07	21.5	0.03	21.0			
0.10	13.1	0.04	16.1			
0.21	6.9	0.11	6.4			
P=0.	8 MPa	0.12	5.6			
0.01	100	0.15	4.5			
0.02	52	0.22	2.5			
0.10	12	0.31	2.3			

Table 3. Effect of the temperature on the rate of MT hydrogenation on palladium sulfide catalysts at P = 0.8 MPa, $[MT]_0 = 1.2$ mmol/l, and x = 50%

<i>T</i> , °C	<i>W</i> /[MT], (mmol MT) (g Cat) h	S, %	$\frac{W/[MT],}{(mmol MT)}$ (g Cat) h	S, %	
	3.6 PdS/.	AlSi	1.2 PdS/SiO ₂		
200	3.5	91	2.9	93	
220	15.6	86	8.2	90	
240	30.0	80	15.0	83	
260	95.6	68	33.6	72	

Support	Pd, wt %	W, (mmol MT) (g Cat) h	$\frac{W_{\rm Pd}}{(\rm mmol \ MT)}$ (g Pd) h	S, %	Support	Pd, wt %	W, (mmol MT) (g Cat) h	W _{Pd} , (mmol MT) (g Pd) h	S, %
Without	77	1.5	0.002	64	HNaY	2.5	35	1.40	83
support					AlSi	0.50	2.2	0.44	80
γ-Al ₂ O ₃	0.5	0.65	0.13	53		1.1	6.2	0.56	83
	1.1	1.3	0.12	54		2.0	10.8	0.54	79
	2.0	2.4	0.12	56		3.6	28.4	0.79	80
	2.0*	0.56	0.03	35		7.1	46.9	0.66	83
	2.4	5.3	0.22	60		13.0	45.5	0.35	80
	5.3	6.4	0.12	62	SiO ₂	0.54	7.2	1.33	82
	10.0	14.0	0.14	53		1.2	12.4	1.03	83
TiO ₂	2.5	1.5	0.06	58		2.0	18.0	0.90	85
Sibunit	0.37	0.3	0.09	43		2.7	29.7	1.10	83
	0.77	2.5	0.32	45		5.1	31.6	0.62	71
	2.2	7.0	0.32	40		9.7	34.9	0.36	78
	4.6	12.9	0.28	41					

Table 4. Activity and selectivity of palladium sulfide catalysts in MT hydrogenation at $T = 240^{\circ}$ C, P = 0.8 MPa, $[MT]_0 = 1.2$ mmol/l, and x = 50%

* The catalyst obtained from a solution of palladium acetate in toluene.

dium on γ -Al₂O₃, SiO₂, AlSi, and HNaY was responsible for IR bands at 2060–2080 cm⁻¹ characteristic of Pd⁰CO. These bands were also found in the IR spectra of CO adsorbed on the corresponding sulfide samples before and after the reaction; however, the intensity of the bands was lower. In addition, the spectra contained absorption bands at 2122–2125 cm⁻¹, which are characteristic of Pd⁺CO and Pd²⁺CO [8]. These IR bands suggest that normal coordinatively unsaturated PdS is present at the surface.

The kinetics of MT hydration over the metallic palladium catalysts on different supports (Table 5) was similar to that on palladium sulfide catalysts. With an increase in τ , the conversion of MT and the yield of pentane increased, whereas the yield of MTL increased only to a certain limit and then decreased. In the region below x = 50-60%, the selectivity remained constant; at higher conversions, the proportion of MTL decreased, whereas that of pentane increased. Within the limits of experimental error, the conversion, product yield, and selectivity obtained for the reaction over the catalysts originally containing metallic palladium agreed with those for the palladium sulfide catalysts (Fig. 3). It is probable that the metal was sulfurized to yield the sulfide during the reaction. With an increase in the concentration of Pd, the activity of the metallic catalysts per 1 g of the catalyst increases, and the activity per 1 g of Pd remains constant. The specific activity of palladium supported on SiO_2 , AlSi, and HNaY is an order of magnitude higher than for Pd black and the catalysts on the other supports; these catalysts also exhibit an increased selectivity to MTL (Table 5).

An analogous pattern was observed for the supported PdS catalysts (Table 4). For palladium sulfide on SiO₂, AlSi, and HNaY, the activity per 1 g of Pd (W_{Pd}) is much higher than that of PdS without a support and PdS supported on γ -Al₂O₃, TiO₂, and carbon. At x =50%, the selectivity to MTL over the SiO₂-, AlSi-, and HNaY-supported catalysts is 82–85%, whereas it is equal to 35–64% for the other supported catalysts.

The influence of the catalyst composition on the rate of MT hydrogenation of MT may be due to different PdS dispersities. The dispersities of palladium on different supports are about the same. It is unlikely that the sulfurization of Pd will substantially change the dispersity. According to electron microscopic data, the average size of PdS particles on the carbon and TiO₂ supports is equal to 15 and 40 Å, respectively; on the other supports, it is equal to ~30 Å. However, these catalysts

Catalyst	[Pd], wt %	$S_{\rm sp},{\rm m^2/g}$	$W, \ \frac{(\text{mmol MT})}{(\text{g Cat}) \text{ h}}$	$W_{\rm Pd}, \ \frac{(\rm mmol \ MT)}{(\rm g \ Pd) \ h}$	$W_{\rm sp}, \frac{(\rm mmol \ MT)}{(\rm m^2 \ Pd) \ h}$	S, %
Pd black	100	5	0.004	0.004	0.80	42
Pd/Al ₂ O ₃	1.1	217	1.0	0.09	0.41	40
	2.0	204	3.4	0.17	0.83	38
	2.0*	217	0.6	0.03	0.14	38
Pd/C	4.0	167	1.6	0.04	0.24	54
Pd/AlSi	4.0	110	38.4	0.96	8.7	79
Pd/HNaY	2.5	300	45.0	1.80	6.0	80
Pd/SiO ₂	0.5	163	2.2	0.44	2.7	84
	1.1	68	7.0	0.64	9.4	82
	2.7	102	23.2	0.86	8.4	82
	5.3	58	29.7	0.56	9.7	76
	13.0	59	63.7	0.49	8.3	78

Table 5. Effect of support on the activity and selectivity of metallic palladium in the hydrogenation of MT at $T = 240^{\circ}$ C, P = 0.8 MPa, $[MT]_0 = 1.2$ mmol/l, and x = 50%

* The catalyst obtained from a solution of palladium acetate in toluene.

differ dramatically in their activities. For example, at x = 50%, we obtained the following results:

Support	SiO ₂	HNaY	AlSi	С	Al_2O_3	TiO ₂	Without support
$W_{\rm sp}$, (mmol MT) m ⁻² h ⁻¹	4.5	4.0	3.0	1.2	0.4	0.3	0.25
<i>S</i> , %	85	83	82	38	56	60	64

Here, W_{sp} is calculated per 1 m² of PdS; S_{sp} of the palladium sulfide catalysts with a palladium concentration of 2.0–3.6 wt % was calculated from the data on the average size of PdS particles.

Thus, it may be concluded that different activities of the catalysts are not due to different dispersities of PdS on different supports. It is more likely that the differences in the catalytic activities are determined by the acidic properties of the surface. This is supported by the following facts.

The activities of alumina-palladium sulfide catalysts depend on the nature of their precursors. For example, the activity of the 2.0 PdS/Al₂O₃ catalyst obtained by depositing palladium from a PdCl₂-HCl aqueous solution is about four times that for a similar catalyst obtained from a solution of palladium acetate in toluene (Table 4). An increase in the HCl concentration in the impregnating solution from 0.7 to 6 wt % leads to an increase in the activity by a factor of 3. Hydrogen chloride that evolved during catalyst preparation from PdCl₂ can be adsorbed by the support to yield strong acid sites. A favorable effect of a chlorinecontaining precursor on the activity of a supported metallic catalyst for the gas-phase hydrogenation of benzene was noted in [9].

The proton affinity of Brönsted acid sited (BASs) on the surface of the catalysts for hydrogenation of MT to MTL was calculated from the data on pyridine adsorption [10]. It was found that the most active catalysts (PdS supported on SiO₂, aluminosilicate, and zeolite HNaY) contain a larger amount of strong BASs.

The acidity of the support can affect the electron state of the active component of the catalyst. However, in the palladium sulfide catalysts studied, this effect should not to be substantial because of the large sizes of PdS particles leading to a weakening of their interaction with the support [9]. Chou and Vannice [9] showed that metallic palladium supported on AlSi is more active than unsupported Pd and Pd supported on SiO₂, Al₂O₃, or carbon in the gas-phase hydrogenation of benzene. It was suggested that BASs located near the metal–support interface are the adsorption sites for benzene reacting with active hydrogen on palladium. BASs are probably involved in the activation of MT. It is known that, in the adsorption of thiophene on a hydroxylated surface, hydrogen bonds are formed at



Fig. 3. (a) The effect of the contact time on (1) the conversion of MT and the yields of (2) MTL and (3) pentane and (b) the effect of the conversion of MT on the selectivities of the formation of (4) MTL and (5) pentane. Catalysts: 2.7 PdS/SiO₂ (open circles) and 2.7 Pd/SiO₂ (solid circles). Reaction conditions: $T = 240^{\circ}$ C, P = 0.8 MPa, and [MT]₀ = 1.2 mmol/l.

the α -position of the thiophene ring because of an increased electron density on carbon atoms in this position [1]. In the case of acceptor sites, the adsorption via sulfur atoms favors the destruction of the thiophene ring.

In the ¹H NMR spectra of the 2.0 PdS/SiO₂ and 2.0 Pd/SiO₂ samples, we find the lines characteristic of hydrated silica gel: the narrow line with the chemical shift $\delta = 1.56$ ppm corresponding to the isolated OH groups and a broader shoulder of a lower intensity with $\delta \cong 3$ ppm corresponding to hydrogen-bonded OH groups. Upon the admission of MT, the intensity of the signals from OH groups decreases, and the additional narrow line with $\delta = 6.7$ ppm corresponding to hydrogen-bonded MT occurs in the spectra. The small width of this signal is explained by a high mobility of the adsorbed molecule.

Hydrogen adsorbed on palladium sulfide may undergo heterolytic decomposition. For example, the adsorption of hydrogen on ruthenium sulfide is accompanied by the formation of the SH groups and hydride ions [11]. The protonation of thiophene in the α -position enables its subsequent interaction with hydride ion to yield a thiolane ring [12]. We can suggest that the hydrogenation of 2-methylthiophene into 2-methylthiolane occurs via this pathway. Some fraction of MT molecules can be adsorbed to form the >S-Pd bonds and thus break the aromatic conjugation. This process is favorable for the decomposition of the thiophene ring and the formation of hydrogenolysis products in the hydrogen medium. The chemisorption of 2-methylthiolane (the product of hydrogenation of 2-methylthiophene) via its sulfur atom also favors hydrogenolysis. We further plan to elucidate the mechanism of MT hydrogenation to MTL.

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