Kinetics and Catalysis, Vol. 44, No. 2, 2003, pp. 277–282. Translated from Kinetika i Kataliz, Vol. 44, No. 2, 2003, pp. 300–306.
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Thiophene Hydrogenation to Tetrahydrothiophene over Tungsten Sulfide Catalysts

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Received June 3, 2002

Abstract—Independent reactions of thiophene reduction to tetrahydrothiophene and thiophene hydrogenolysis to form hydrogen sulfide and C_4 hydrocarbons are shown to occur over supported tungsten sulfide catalysts and unsupported tungsten sulfide at an elevated temperature and a high pressure. The highest rate of tetrahydrothiophene formation over the supported catalysts is observed when alumina was used as a support, and the lowest reaction rate is found when silica gel was used as a support. Both catalysts are less active than unsupported tungsten disulfide. The rate of thiophene hydrogenation over tungsten disulfide increases with increasing thiophene concentration and hydrogen pressure and is inhibited by tetrahydrothiophene. The selectivity to tetrahydrothiophene is constant (70–90%) in the whole range up to high thiophene conversions. The high selectivity over tungsten sulfide catalysts is suggested to be due to the reaction pathway through thiophene protonation mediated with the surface SH groups and to the inhibition of hydrogenolysis.

INTRODUCTION

Hydrogenation of various organic compounds, including sulfur-containing compounds, occurs over tungsten sulfide catalysts [1]. According to the authors of [2], thiophene undergoes hydrogenolysis over unsupported tungsten disulfide at $T = 272–305°C$ and $P = 0.1$ MPa and produces H_2S and hydrocarbons, and the reduction of a thiophene ring to form tetrahydrothiophene (THT) also occurs with a yield of at most 2 mol %. Over the sulfided Ni(Co)W catalysts at $T >$ 200°C, thiophene mainly participates in hydrogenolysis, and the yield of THT is low [3]. Gas-phase thiophene hydrogenation over supported WS_2 at $T =$ 300°C, $P = 0.5$ MPa, and a thiophene conversion of 20% has been studied [4]. The catalysts based on silica gel and carbon supports proved to be the most active and selective. The selectivity to THT was at most 50%, and the productivity of the process was 0.15 mmol THT (g Cat)$^{-1}$ h^{-1}. When alumina or zeolite NaY were used as supports, the catalysts were less efficient, and this fact was attributed to the low dispersion of tungsten disulfide on the surface.

Earlier [5, 6] we studied the activity of various sulfided catalysts in thiophene hydrogenation to THT at $T = 240°C$, $P = 2$ MPa, and $X = 20\%$. Tungsten disulfide supported on alumina, silica gel, or carbon has been shown to be much less active than most sulfided catalysts but highly selective toward THT. However, thiophene hydrogenation over tungsten sulfide catalysts has not been studied in detail. In particular, thiophene hydrogenation over unsupported WS_2, the activity and selectivity of supported catalysts as a function of the tungsten concentration, and the effect of reaction conditions on the process performance are of interest. In this work aimed at solving these problems, we studied thiophene hydrogenation over supported tungsten sulfide catalysts with various compositions and unsupported tungsten disulfide.

EXPERIMENTAL

The reagents and materials used in the work were of reagent grade and chemical purity grade. Supported catalysts were prepared by incipient-wetness impregnation of alumina ($S_{sp} = 250$ m^2/g), silica gel ($S_{sp} =$ 300 m^2/g), and carbon support Sibunit (C) ($S_{sp} =$ 560 m^2/g) with an aqueous solution of phosphotungstic acid. Samples were dried at $T = 110°C$ for 5 h. They were treated before reaction with a mixture of 15% H_2S + 85% H_2 at $T = 300–350°C$ for 1–2 h. Unsupported tungsten disulfide was prepared by the decomposition of ammonium thiotungstate according to the procedure described in [1]. The tungsten and sulfur concentrations in the catalysts were determined by elemental analysis.

The experimental procedures and analyses have been described earlier [5, 6]. The thiophene conversion (X, %), yield of products (Y, mol %), selectivity ($S = Y/X$, %), the thiophene hydrogenation rates per 1 g of the catalyst (ω, mmol (g Cat)$^{-1}$ h^{-1}) and per 1 g of tungsten (ω, mmol (g W)$^{-1}$ h^{-1}), and the THT formation rate (ω_{THT}, mmol (g Cat)$^{-1}$ h^{-1}) were determined.

RESULTS AND DISCUSSION

Thiophene hydrogenation was studied over tungsten disulfide supported in different amounts on alumina, silica gel, and a carbon support, as well as over unsup-

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[1] L.G. Sakhaltueva and V.N. Yakovleva participated in the experimental work.

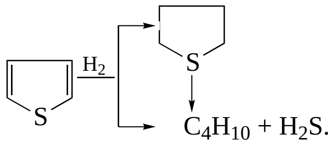
Table 1. Thiophene hydrogenation over the sulfided catalyst 20% WS_2/Al_2O_3 at $P = 2.0$ MPa and $C_0 = 1$ vol %

T, °C	τ, s	X, %	Y, mol %		S, %	
			THT	H_2S	THT	H_2S
220	5.0	31	25	6	81	19
	11.1	50	39	10	78	20
240	1.6	31	22	9	71	29
	6.5	66	47	18	71	27
	16.0	90	52	37	58	41
260	0.8	32	19	12	59	38
	2.5	61	34	25	56	41
	8.8	84	34	49	40	58
280	0.5	32	15	16	47	51
	1.2	64	28	34	44	54
	3.9	89	28	59	32	66
300	0.2	42	7	34	17	81
	0.6	72	12	58	17	80
	1.8	90	9	79	10	88

ported WS_2. The thiophene conversion, the yields of products, and the selectivity as a function of the contact time (τ) at a constant temperature, pressure, and initial thiophene concentration (C_0) were determined for each catalyst. In all cases, thiophene reduction to THT and hydrogenolysis to H_2S and C_4 hydrocarbons formed in an equimolar ratio occurred.

Over the supported sulfided catalysts, the thiophene conversion and the yield of the hydrogenolysis products[2] steadily increased with increasing contact time, other conditions being the same, whereas the THT yield increased with time to some limit and then did not change or somewhat decreased. The selectivity to THT and the hydrogenolysis products remained constant with an increase in the thiophene conversion up to ~70%, and then the selectivity to THT somewhat decreased and that to the hydrogenolysis products increased (Table 1, Fig. 1).

This allows one to conclude that THT and the hydrogenolysis products are simultaneously formed from thiophene at some thiophene conversions, while at high conversions, a secondary reaction occurred: the hydrogenolysis of the THT formed. The reactions occurred via the parallel-consecutive mechanism with the dominance of the parallel pathway:



An increase in temperature favored an increase in the conversion and reaction rate, but the selectivity to THT decreased (Tables 1, 2).

To compare catalysts with different concentrations of tungsten disulfide, we determined the contact time at which the thiophene conversion was 50% from the kinetic curves at $T = 240$°C and $P = 2.0$ MPa and then calculated the selectivity and the rates of thiophene transformation and THT formation. The results are presented in Table 3. As can be seen, the catalysts based on SiO_2 are less active than those on other supports. The catalysts containing 5 wt % of tungsten on all the supports studied are poorly active and unselective in THT formation. The thiophene hydrogenation rate increased with an increase in the tungsten concentration on the support up to 20 wt % WS_2 on Al_2O_3 and SiO_2 and up to 10 wt % WS_2 on C and then decreased. At a higher concentration of WS_2, the activity of the catalyst 10 wt % WS_2/C is ~3 times higher than that of the catalyst 10 wt % WS_2/Al_2O_3. The catalysts WS_2/C are two to three times less active than the catalysts based on alumina, whereas these catalysts show the same selectivity. Over the SiO_2-supported catalysts, the thiophene hydrogenation rate per 1 g of tungsten continuously decreased with an increase in the tungsten concentration. Over the Al_2O_3-supported catalysts, the rate increased with an increase in the tungsten concentration from 5 to 20 wt %. Over the C-supported catalysts, the rate increased with an increase in the tungsten concentration from 5 to 10 wt % and then decreased (Table 3), probably due to a change in the dispersion of the active component. The introduction of 2.5 wt % Ni in the catalyst 20 % WS_2/Al_2O_3 led to an increase in the thiophene hydrogenation rate and a sharp decrease in selectivity. As a result, the rate of THT formation decreased fivefold. Modification of the catalyst 20% WS_2/Al_2O_3 with palladium did not improve its catalytic performance either (Table 4).

Unsupported tungsten disulfide exhibits a higher activity and selectivity than the supported catalysts. For example, the rate of THT formation over WS_2 at $T = 240$°C, $P = 2.0$ MPa, $C_0 = 1$ vol %, and $X = 50$% was 6–30 times higher than that over the most active supported catalysts, and the selectivity was 1.1–1.4 times higher. Unsupported tungsten disulfide was also more active and selective than the supported catalysts at other

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[2] The yield of only one hydrogenolysis product, H_2S, which coincides with the yield of C_4 hydrocarbons, is presented in the tables and figures.

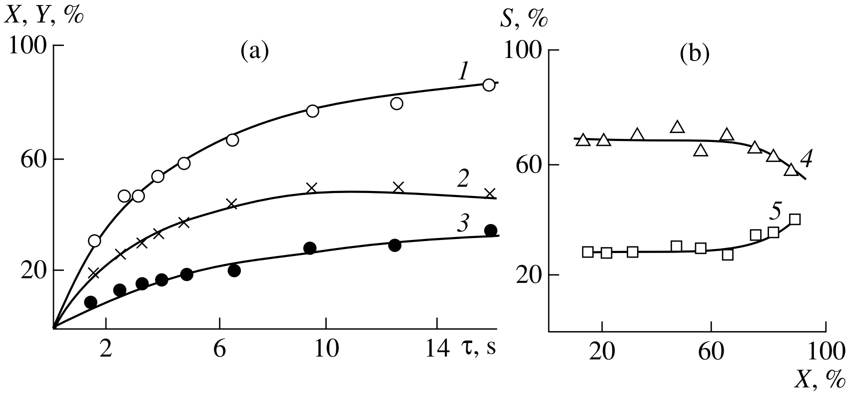

Fig. 1. (a) Effect of the contact time on (*1*) thiophene conversion and the yields of (*2*) THT and (*3*) H_2S. (b) Effect of thiophene conversion on selectivity to (*4*) THT and (*5*) H_2S. Catalyst 20% WS_2/Al_2O_3, $T = 240°C$, $P = 2.0$ MPa, $C_0 = 1$ vol %.

temperatures (Tables 2, 3). It follows from the above findings that the catalysts under study can be arranged in the following series according to their activity in THT formation:

$$WS_2 > WS_2/Al_2O_3 > WS_2/C > WS_2/SiO_2.$$

We studied the effect of conditions of thiophene hydrogenation on the process performance. Experiments were performed at $T = 200–300°C$, $P = 0.4–3.1$ MPa, $C_0 = 0.8–10.3$ vol %, and different contact times. Some results are shown in Table 5 and Figs. 2–4.

Table 2. Effect of temperature on the activity and selectivity of the tungsten sulfide catalysts at $P = 2.0$ MPa, $C_0 = 1$ vol %, and $X = 50\%$

T, °C	WS_2			20% WS_2/Al_2O_3		
	w_{THT}, μmol h^{-1} (g Cat)$^{-1}$	S, %	w, mmol h^{-1} (g W)$^{-1}$	w_{THT}, μmol h^{-1} (g Cat)$^{-1}$	S, %	w, mmol h^{-1} (g W)$^{-1}$
200	129	92	0.2	–	–	–
220	496	84	0.8	58	78	0.4
240	1200	80	2.0	189	70	1.3
260	1980	60	4.5	226	55	2.0
280	2058	49	5.7	422	44	4.8
300	1440	30	6.5	460	25	11.5

Table 3. Activity and selectivity of the WS_2-containing catalysts on different carriers at $T = 240°C$, $P = 2.0$ MPa, $C_0 = 1$ vol %, and $X = 50\%$

W, wt %	Carrier								
	Al_2O_3			C			SiO_2		
	w_{THT}, μmol h^{-1} (g Cat)$^{-1}$	S, %	w, mmol h^{-1} (g W)$^{-1}$	w_{THT}, μmol h^{-1} (g Cat)$^{-1}$	S, %	w, mmol h^{-1} (g W)$^{-1}$	w_{THT}, μmol h^{-1} (g Cat)$^{-1}$	S, %	w, mmol h^{-1} (g W)$^{-1}$
5	9	45	0.40	16	40	0.80	11	45	0.50
10	36	60	0.60	106	66	1.60	26	66	0.40
20	189	70	1.35	56	70	0.40	39	56	0.33
30	156	68	0.76	68	68	0.34	36	55	0.22
40	127	67	0.48	–	–	–	–	–	–

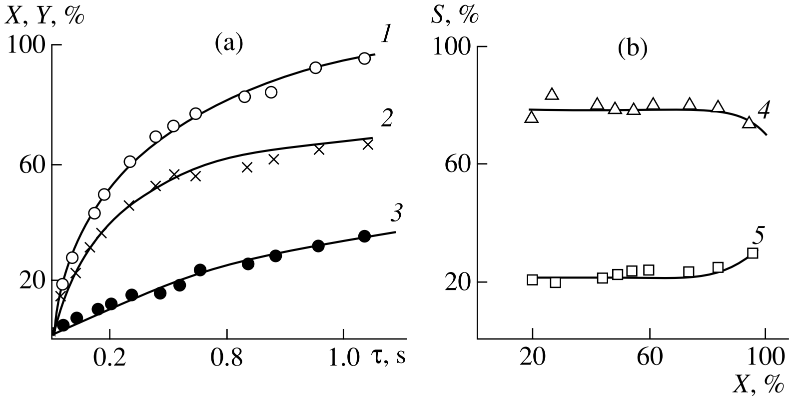

Fig. 2. (a) Effect of contact time on (*1*) thiophene conversion and the yields of (*2*) THT and (*3*) H_2S. (b) Effect of thiophene conversion on selectivity to (*4*) THT and (*5*) H_2S. Catalyst 20% WS_2/Al_2O_3, $T = 240°C$, $P = 2.0$ MPa, $C_0 = 1$ vol %.

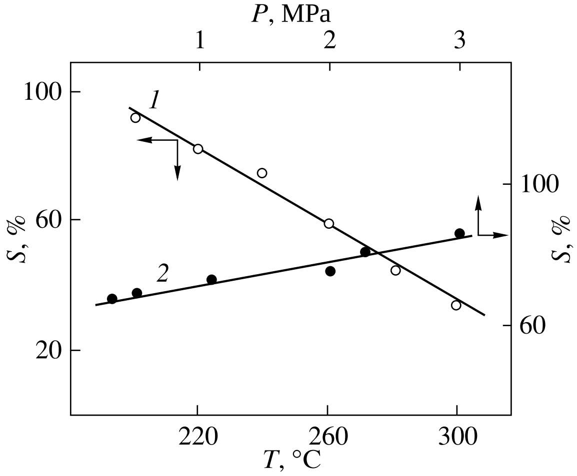

Fig. 3. Selectivity to THT over WS_2 at $X = 50\%$, $C_0 = 1$ vol %, and $P = 2.0$ MPa vs. (*1*) temperature of thiophene hydrogenation and (*2*) hydrogen pressure at $T = 240°C$.

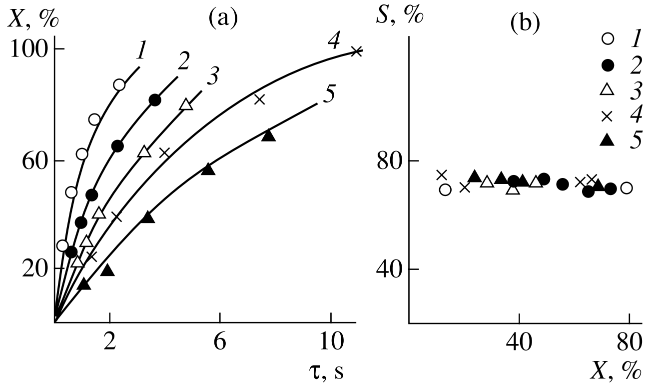

Fig. 4. (a) Thiophene conversion vs. contact time and (b) selectivity to THT vs. conversion at different C_0 (vol %): (*1*) 1.0, (*2*) 2.5, (*3*) 3.4, (*4*) 5.5, and (*5*) 9.6. Catalyst WS_2, $T = 240°C$, $P = 0.5$ MPa.

As can be seen, the thiophene conversion, the yield of products, and the selectivity depend on the contact time and temperature in the same way as in the case of the supported catalysts. An increase in the hydrogen pressure results in an increase in the thiophene conversion and selectivity to THT. The thiophene conversion and the yields of products drop with an increase in the thiophene initial concentration, whereas the selectivity to THT remains unchanged.

Table 4. Comparison of the activity and selectivity of the catalysts at $T = 240°C$, $P = 2.0$ MPa, $C_0 = 1$ vol %, and $X = 50\%$

Catalyst	w, mmol h^{-1} (g Cat)$^{-1}$	S, %	w_{THT}, mmol h^{-1} (g Cat)$^{-1}$
20% WS_2/Al_2O_3	0.27	70	189
2.5% Ni/Al_2O_3	0.04	2	0.8
5% Pd/Al_2O_3	1.34	30	402
2.5% Ni, 20% WS_2/Al_2O_3	0.46	8	37
5% Pd, 20% WS_2/Al_2O_3	0.28	50	140
1% Pd, 20% WS_2/Al_2O_3	0.10	60	60

To estimate the effect of process parameters on the reaction rate, we used kinetic curves to determine the contact time corresponding to 50% thiophene conversion and calculated the rate of thiophene transformation and the average variable parameters. It was found (Table 6) that the rate of thiophene transformation based on its current concentration (C), ω/C, decreases with an increase in the current thiophene concentration and the value ω [THT] increases with thiophene concentration. The thiophene hydrogenation rate based on the thiophene concentration and multiplied by [THT] increases with hydrogen pressure. An increase in temperature caused an increase in the reaction rate, but the selectivity to THT dropped, especially at $T > 240°C$ (Tables 2, 5; Fig. 3). The apparent activation energy

Table 5. Thiophene hydrogenation over unsupported WS_2. $C_0 = 1 \pm 0.1$ vol %

τ, s	X, %	Y, mol %		S, %		τ, s	X, %	Y, mol %		S, %	
		THT	H_2S	THT	H_2S			THT	H_2S	THT	H_2S
P = 2.0 MPa						T = 240°C					
T = 200°C						P = 0.5 MPa					
0.77	37	33	4	89	11	0.52	49	36	12	71	25
2.80	56	52	3	93	5	0.84	64	46	17	72	26
5.50	84	75	8	89	10	2.28	87	56	29	65	33
T = 220°C						2.2[a]	66	47	17	71	26
0.26	33	26	5	79	15	3.7[b]	66	48	16	73	24
0.49	49	39	7	80	14	7.6[c]	72	55	19	76	26
1.44	88	67	22	76	25	P = 1.1 MPa					
T = 240°C						0.24	40	29	11	72	27
0.16	44	35	10	80	23	0.48	66	46	20	70	30
0.37	61	48	13	79	21	0.86	80	51	26	64	33
1.10	95	69	28	73	29	P = 3.1 MPa					
T = 260°C						0.14	22	19	3	86	14
0.03	20	11	11	56	45	0.30	48	42	5	88	10
0.08	42	24	17	57	41	0.47	65	53	11	82	17
0.25	79	31	47	39	60	0.89	78	61	16	78	20

Note: Initial thiophene concentration, vol %: [a], 2.5; [b], 5.7; [c], 9.6.

Table 6. Effect of the conditions of thiophene hydrogenation on the reaction rate at X = 50% over unsupported WS_2. T = 240°C

P = 0.5 MPa				C_0 = 1 vol %	
[THT], vol %	C, vol %	w/C, mmol h^{-1} (g Cat)$^{-1}$	w [THT], mmol vol % h^{-1} (g Cat)$^{-1}$	P, MPa	w [THT]/C, mmol h^{-1} (g Cat)$^{-1}$
0.16	0.62	0.76	0.08	0.4	0.16
0.26	1.74	0.54	0.22	0.5	0.19
0.34	2.52	0.41	0.29	1.1	0.35
0.47	4.40	0.31	0.43	2.0	0.53
1.08	5.60	0.13	0.55	2.2	0.57
1.57	8.18	0.08	1.00	3.1	0.73

was determined from the logarithmic plot of the normalized reaction rates versus the $1/T$ value and proved to be 100 ± 4 kJ/mol.

The productivity to THT over WS_2 at T = 240–260°C and P = 2 MPa reached 1.8–3.8 mmol (g Cat)$^{-1}$ h^{-1}, that is, was more than an order of magnitude higher than that to THT over the WS_2/SiO_2 and WS_2/C catalysts [4] and over tungsten carbide supported on zeolite Y, which is a selective catalyst for thiophene hydrogenation [7]. It follows from a comparison of the findings of this work with data on thiophene hydrogenation over an efficient palladium sulfide catalyst, 5% Pd/AlSi [5, 6], that, for example, the rate of total thiophene transformation at different conversions over unsupported tungsten disulfide at T = 240°C and P = 2 MPa is two to four times lower than that over the palladium sulfide catalyst (Table 7). The selectivity to THT at $X \approx 50\%$ over both catalysts is nearly the same but decreases much more slowly over tungsten disulfide with an increase in conversion than over the palladium catalyst. As a result, the rate of THT formation at high thiophene conversions over WS_2 (which is important for practical purposes) is somewhat higher than that over the palladium catalyst and the high selectivity remains.

The bond between tungsten and sulfur in WS_2 is strong [1, 8]. Therefore, the interaction of hydrogen

Table 7. Comparison of the catalysts WS_2 and PdS/AlSi [5]. $T = 240°C$, $P = 2.0$ MPa, and $C_0 = 1$ vol %

X, %	WS_2			5% Pd/AlSi		
	w, mmol h^{-1} (g Cat)$^{-1}$	S, %	w_{THT}, μmol h^{-1} (g Cat)$^{-1}$	w, mmol h^{-1} (g Cat)$^{-1}$	S, %	w_{THT}, μmol h^{-1} (g Cat)$^{-1}$
20	2.0	80	1600	8.54	86	7344
50	1.5	80	1200	4.45	75	3337
85	0.73	80	584	1.59	30	477
90	0.63	78	491	1.48	24	355

with sulfur on the catalyst surface results in the formation of the SH groups, which substantially cover the surface [9]. Tungsten disulfide is slowly reduced by hydrogen to some extent to form anionic vacancies on the surface [9, 10]. When thiophene adsorbs on the catalyst surface, the π-system of the thiophene ring interacts with the hydrogen atoms of the SH groups and thiophene is protonated at the α-carbon atom, forming a surface-bound thiophenium cation. The latter can transform into THT in the presence of activated hydrogen [11]. A portion of the thiophene molecules and THT formed can either be protonated at the sulfur atom or form the donor-acceptor bonds with the participation of the sulfur atom and coordinatively unsaturated cations on the surface. These complexes possibly contain a fragment of a thiophene molecule formed by C–S bond rupture, and its reaction with the activated hydrogen leads to the formation of hydrogenolysis products, H_2S and C_4 hydrocarbons [12]. Hydrogen is probably activated by the coordinatively unsaturated cations on the surface. Theoretical calculations for some sulfided catalysts, for example, MoS_2 [13], and experimental findings, for example, for RuS_2 [14, 15], show that not only homolytic but also heterolytic hydrogen decomposition are possible over sulfided catalysts. We discussed in [5] how the reaction between thiophenium cation and hydride ion is necessary for THT formation. The fact that WS_2 is barely reduced to form sulfur explains the low amount of coordinatively unsaturated sites on the surface and hence why hydrogen activation is difficult. This is the reason for the low activity of WS_2 in thiophene hydrogenation. The high selectivity over tungsten disulfide is due to the predominance of the protonated thiophene species on the surface, as was observed for thiophene hydrogenation over palladium sulfide supported on aluminosilicate [5, 6]. However, the process selectivity over palladium sulfide, which is high at low conversions, decreases at long contact times. This can be explained by the easiness of palladium sulfide reduction with hydrogen to form Pd^0 or Pd^+, which are the sites for THT adsorption, on which hydrogenolysis occurs with the participation of sulfur atoms. The high selectivity to THT is due to the fact that it is difficult to run this process over tungsten sulfide catalysts.

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