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CHEMICAL KINETICS AND CATALYSIS

The Transformations of Toluene on Alumina and Bifunctional Catalysts

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Abstract—The activity of Pt, Rh, and Ni catalysts deposited on Al_2O_3 and tungsten-containing catalysts 20% $H_4SiW_{12}O_{40}/ZrO_2$ and 15% WO_x/ZrO_2 in the hydrogenation of toluene and toluene ring opening and isomerization in the presence of hydrogen was studied. Under experimental conditions (160–360°C, 2.2 MPa), the main reactions on Rh/Al_2O_3 were the hydrogenation of toluene into methylcyclohexane, hydrogenolysis into isoheptanes, and hydrocracking into alkanes C_1-C_6 . On Pt, Rh, and Ni catalysts on carriers with strong acid properties, the isomerization of the six-membered into five-membered ring followed by hydrogenolysis (hydrocracking) of alkylcyclopentanes occurred. The yield of heptane isomers, however, did not exceed 13%. The activity of Pt and Rh catalysts on a high-acidity carrier (WO_x/ZrO_2) in hydrocracking was much higher than that of catalysts based on deposited heteropoly acid. The yields of hydrogenolysis (hydrocracking) products on Ni/WO_x/ZrO_2 were much lower than on Pt(Rh)/WO_x/ZrO_2. The highest yield of ring opening products (isoheptanes and *n*-heptane) was obtained with layered loading of two catalysts; it reached 58 wt % at 300°C and a 2.2 MPa pressure, which was 4.5 and 2 times higher than the yield obtained on Ni-Pt/WO_x/ZrO_2 and 2% Rh/Al_2O_3 catalysts. Hydrodemethylation was not the main direction of toluene transformations on any of the catalysts studied.

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INTRODUCTION

Changes in the requirements imposed on the content of aromatic hydrocarbons in fuels have increased the interest of researchers in catalytic hydrodearomatization. Transformations of benzene on bifunctional catalysts in the presence of hydrogen are widely covered in the literature [1-5]. The hydrogenation of benzene or its deeper transformations with breaking ring C-C bonds occur depending on reaction conditions. The main reaction direction on Rh and Ir deposited on Al₂O₃ at elevated pressures is ring opening with the formation of *n*-hexane. The isomerization of the six- into five-membered ring followed by the hydrogenolysis into 2- and 3-methylpentanes and *n*-hexane occurs on Pt and Rh catalysts with strong acid centers [1, 5]. The following types of toluene transformations on metal oxide catalysts are discussed in the literature: hydrogenation, hydrodemethylation, and disproportionation. The hydrogenation of toluene on Pt and Rh was considered in [6, 7]. It was shown that the activity of aromatic hydrocarbons (benzene, toluene, and p-xylene) in hydrogenation decreased as the number of methyl substituents increased [6]. According to the thermodynamic data [8], an equilibrium mixture of toluene and methylcyclohexane (MCH) contains equal amounts $(\sim 50\%)$ of the components at atmospheric pressure and 280°C. At lower temperatures, MCH, and at higher, toluene, prevail. The hydrodemethylation of toluene into cyclohexane occurs on Pt catalysts at low temperatures of $50-100^{\circ}$ C [9]. The hydrodemethylation of toluene into benzene at temperatures above 380°C was studied in [10–12]. Group VIII metals form the series Ni > Rh > Ir > Ru > Pt > Pd in order of decreasing activity in hydrodemethylation [10]. The selectivity of C–C bond breaking between the methyl group and ring in toluene on Rh/Al₂O₃ is almost 20 times higher than the selectivity of breaking ring C–C bonds [11]. Ring opening with the formation of MCH occurs on Ir/Al₂O₃ along with hydrodemethylation of toluene into benzene [13].

The purpose of this work was to study the influence of the nature of metals (Pt, Rh, and Ni) and carrier acid properties (Al₂O₃, H₄SiW₁₂O₄₀/ZrO₂, and WO_x/ZrO₂) on the types of toluene transformations under the conditions that made six-membered ring opening possible.

EXPERIMENTAL

We used Pt, Rh, and Ni catalysts on the following carriers: γ -Al₂O₃ with specific surface area $S_{sp} =$ 250–300 m²/g, ZrO₂ (prepared from Zr(OH)₄ with $S_{sp} =$ 150 m²/g), and 15% WO_x/ZrO₂ and 20% H₄SiW₁₂O₄₀/ZrO₂ (WO_x/ZrO₂ and HSiWO/ZrO₂ in what follows). The preparation of WO_x/ZrO₂ and HSiWO/ZrO₂ was described in [5]. The metals (Pt, Rh, and Ni) were introduced in the form of dilute aqueous solutions of H₂PtCl₆, RhCl₃, and Ni(NO₃)₂. The sam-



Fig. 1. Temperature dependences of toluene conversion (*x*) and major product yields (*y*) on the 2% Rh/Al₂O₃ catalyst at a 2.2 MPa pressure: (*1*) methylcyclohexane, (*2*) isoheptanes and *n*-heptane, (*3*) cyclohexane, and (*4*) C₁–C₅ alkanes.

ples were dried at 130°C. Prior to experiments, catalysts on Al_2O_3 were reduced in a flow of H_2 at 450°C for 3 h, and catalysts on HSiWO/ZrO₂ and WO_x/ZrO₂ were calcined in a flow of air for 3 h at 350 and 500°C,

respectively. The concentrations of Pt and Rh in the catalysts were 1–2 wt %, and that of Ni, 6 wt %. Bimetallic Ni–Pt catalysts were prepared by successively impregnating carriers with solutions of Ni(NO₃)₂ and H₂PtCl₆. The bimetallic catalysts contained 6 wt % Ni and 0.2 wt % platinum.

Toluene transformations were studied in a flow reactor at 160–360°C and a 2.2 MPa pressure. The volume of catalyst loads was 3 cm³, the rate of supplying toluene was 2 h⁻¹, and the hydrogen : hydrocarbon molar ratio was 10 : 1. The products were analyzed by gas-liquid chromatography on a column 3 m long packed with 15% PFMS/Celite and a capillary column 25 m long with SE-30. The activity of the catalysts was estimated from the yield of ring opening products (isoheptanes and *n*-heptane) and selectivity of their formation. Selectivity was calculated as the ratio between the yield of ring opening products and the total yield of ring opening products, hydrocracking, and hydrodealkylation.

RESULTS AND DISCUSSION

On the basis of literature data, we suggest the following scheme of toluene transformations on bifunctional catalysts in the presence of hydrogen:



This scheme includes the isomerization of MCH into dimethyl- and ethylcyclopentanes on catalysts with strong acid properties such as $Pt/SO_4/ZrO_2$ [14]. The CH_2-CH_2 bonds in alkylcyclopentanes (AlkCP) preferably experience hydrogenolysis on Pt, Rh, Ni, Ru, and Ir catalysts [15]. The selective hydrogenolysis of CH_2-CH_2 bonds was also described for MCH [8].

As is known, Rh catalysts on Al_2O_3 and SiO_2 are active and selective in cyclohexane and benzene ring opening with the formation of *n*-hexane [5]. On the other hand, hydrodealkylation of toluene occurs on Rh/Al_2O_3 at high temperatures and atmospheric pressure [11].

The temperature dependences of the yields of the main toluene transformation products on 2% Rh/Al₂O₃ are shown in Fig. 1. The conversion of toluene over the temperature range studied (180–360°C) at a 2.2 MPa pressure was 98–100% (Fig. 1, Table 1). Figure 1 shows that toluene is only hydrogenated to MCH at low temperatures (up to 200°C). Above 200°C, we observe

t, °C	x, %	y(I)				y(II)		y(III)	y(IV)	<i>y</i> (V)
		CH ₄ -C ₅ H ₁₂	MP	<i>n</i> -C ₆ H ₁₄	DMP	MH	<i>n</i> -C ₇ H ₁₆	AlkCP	Cyclohex- ane	MCH
260	99.9	0.4	2.8	0.1	0.2	14.3	0.1	0.2	0.2	81.4
300	99.9	2.1	13.7	0.7	1.2	29.1	0.4	0.8	0.7	50.5
320	99.4	5.0	17.1	1.6	2.0	29.6	0.6	1.5	1.4	41.1

Table 1. Influence of reaction temperature on toluene transformation product yields (y, wt %) on 2% Rh/Al₂O₃ (molar ratio $H_2 : C_7H_8 = 10 : 1, p = 2.2$ MPa, $v_{vol} = 2$ h⁻¹)

Note: I, hydrocracking; II, ring opening; III, ring isomerization; IV, hydrodealkylation; V, hydrogenation; v_{vol} is the toluene volume feeding rate; *x* is the conversion of toluene; MP stands for 2- and 3-methylpentanes; DMP, for dimethylpentanes; MH, for 2- and 3-methylhexanes; MCP is methylcyclopentane; AlkCP denotes dimethylcyclopentanes and ethylcyclopentane; and MCH is methylcyclohexane. The yield of C₈₊ is 0.2–0.9 wt %.

the formation of six-membered ring opening products, 2- and 3-methylhexanes and *n*-heptane. Their total yield passes a maximum as the temperature increases and equals 29 wt % at 300°C. The yield of isohexanes increases at 250–340°C simultaneously with the yield of isoheptanes. Isohexanes are probably formed as a result of the splitting off of the CH₃ group from the corresponding methylheptanes (Table 1). At 360°C, toluene fully transforms into C_1 – C_3 alkanes. According to Table 1, the hydrodemethylation of toluene occurs to an insignificant extent at 260-300°C (the yields of cyclohexane and the product of its hydrogenolysis (n-hexane) are lower than 1.5%). Alkylcyclopentanes are also formed in insignificant amounts, and their yields do not exceed 1%. It follows that the predominant types of toluene transformations on 2% Rh/Al₂O₃ at temperatures up to 300°C are its hydrogenation to MCH and the hydrogenolysis of the latter to 2- and 3-methylhexanes. The yield of ring opening products from toluene is, however, approximately half that from benzene [5]. The contribution of secondary reactions such as hydrocracking to lower alkanes, the formation of C_{8+} hydrocarbons, and skeletal isomerization increases at 320-340°C.

It is known from the literature [1, 4] that the isomerization of six-membered into five-membered rings is only possible in the presence of Broensted acid centers, whereas, in the presence of only Lewis acid centers, cyclopentane hydrocarbons do not form. We showed [5] that methylcyclopentane and its hydrogenolysis products (isohexanes and *n*-hexane) were predominantly formed from benzene under certain conditions on Pt and Rh catalysts deposited on carriers with strong acid properties, WO_x/ZrO₂ and HSiWO/ZrO₂. We studied toluene transformations on these catalysts. The temperature dependences of the yields of the main toluene transformation products on 1% Pt/HSiWO/ZrO₂ and 1% Rh/HSiWO/ZrO₂ are presented in Fig. 2 and Table 2. The conversion of toluene on 1% Rh/HSiWO/ZrO₂ was close to 100% over the temperature range studied (160-340°C), and that on the Pt catalyst decreased to 95% as the temperature increased to 300°C (Fig. 2). The reason for this may be easy dehydrogenation of naphthene hydrocarbons to aromatic hydrocarbons on Pt catalysts [8]. On the other hand, Pt/HSiWO/ZrO₂ might be deactivated, because the yields of C₈₊ hydrocarbons likely formed as a result of disproportionation, transalkylation, and other secondary reactions increased on this catalyst at high temperatures (Table 2). The predominant reactions at 160–260°C on both catalysts were the hydrogenation of toluene to MCH and its isomerization into alkylcyclopentanes (AlkCP), including 1,1-, 1,2-, and 1.3-dimethylcyclopentanes and ethylcyclopentane. The highest yield of AlkCP was 37.5 wt % on Pt/HSiWO/ZrO₂ and 46 wt % on the Rh catalyst. Ring opening products (dimethylpentanes, methylhexanes, and *n*-heptane) are formed at 220°C and above. The yield of \overline{C}_1 - C_6 alkanes also increases substantially at these temperatures. A small yield of heptane isomers, 6.6 wt %, was observed on the Pt catalyst at 260°C; on the Rh catalyst, this yield was 11.3 wt % at 320°C. Hydrocracking reactions make a substantial contribution at these temperatures, and the yields of C_1-C_5



Fig. 2. Influence of the nature of metals on toluene conversion (*x*) and major product yields (*y*) on the catalysts (*1*–5) 1% Pt/HSiWO/ZrO₂) and (*1*'–5') 1% Rh/HSiWO/ZrO₂ at 2.2 MPa; (*1*, *1*') conversion, (*2*, *2*') MCH, (*3*, *3*') AlkCP, (*4*, *4*') isoheptanes and *n*-heptane, and (*5*, *5*') C₁–C₅ alkanes.

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t, °C	x, %	y(I)			y(II)			y(III)		y(IV)	<i>y</i> (V)		
		CH ₄ C ₅ H ₁₂	DMB + MP	<i>n</i> -C ₆ H ₁₄	DMP	MH	<i>n</i> -C ₇ H ₁₆	МСР	AlkCP	Cyclo- hexane	MCH	y"(C ₈₊)	
1% Pt/HSiWé/ZrO ₂													
200	100	2.8	0.1 + 0.3	0.1	0.2	1.3	0.3	0.7	37.5	0.2	54.9	1.6	
260	100	20.7	0.9 + 2.4	0.6	1.0	4.6	1.0	4.2	29.5	1.2	28.2	5.7	
1% Rh/HSiWO/ZrO ₂													
200	100	0.2	traces	traces	traces	0.2	0.1	0.1	33.8	traces	65.2	0.4	
260	100	2.3	0.1 + 0.3	0.1	0.8	3.0	0.7	0.7	46.0	0.2	44.4	1.4	
320	99.8	22.6	0.7 + 2.1	0.8	1.8	7.5	2.0	3.4	33.0	0.6	21.9	3.4	
$1\% \text{ Pt/WO}_x/\text{ZrO}_2$													
200	100	5.9	0.2 + 0.6	0.2	2.2	5.9	1.1	1.0	31.4	0.4	49.3	1.8	
220	100	15.7	0.5 + 1.2	0.3	3.2	8.1	1.7	1.7	27.4	0.7	36.8	2.7	
260	100	68.0	1.9 + 3.4	1.1	1.6	4.2	0.9	2.0	7.7	0.6	7.5	1.1	
1% Rh/WO _x /ZrO ₂													
200	100	0.5	0.1	traces	0.4	1.7	0.3	0.1	38.0	0.1	58.3	0.5	
260	100	13.2	0.4 + 1.0	0.3	3.0	8.8	2.0	1.2	34.0	0.3	33.4	2.4	

Table 2. Influence of the acidic properties of carriers on the yields of the major toluene transformation products (y, wt %) on Pt and Rh catalysts (molar ratio $H_2 : C_7 H_8 = 10 : 1, p = 2.2$ MPa, $v_{vol} = 2$ h⁻¹)

Note: See Table 1 for notation.

alkanes amount to 21-23 wt % (Fig. 2). Hydrodealkylation product yields are insignificant (Table 2). A comparison of Pt and Rh catalysts showed that the same toluene hydroconversion reactions occur on them, but the temperature is lower by 50–60°C on the Pt catalyst (Fig. 2).

The results obtained for toluene transformations on 1% Rh/WO_x/ZrO₂ and 1% Pt/WO_x/ZrO₂ are presented in Fig. 3 and Table 2. The main toluene transformation



Fig. 3. Influence of the nature of metals on the yields of major toluene transformation products (*y*) on the catalysts (*1*-4) 1% Pt/WO_x/ZrO₂ and (*I*'-4') 1% Rh/WO_x/ZrO₂ at a 2.2 MPa pressure; (*1*, *I*') MCH, (*2*, *2*') AlkCP, (*3*, *3*') C₁-C₅ alkanes, and (*4*, *4*') isoheptanes and *n*-heptane.

patterns on catalysts deposited on WO_x/ZrO₂ are similar to those observed for catalysts HSiWO/ZrO₂. As with the heteropoly acid catalysts, all reactions on Pt/WO_x/ZrO₂ occur at lower temperatures than on Rh/WO_x/ZrO₂. As distinct from heteropoly acid catalysts, the hydrogenolysis and hydrocracking of MCH and AlkCP on Pt and Rh catalysts deposited on WO_x/ZrO₂, which is characterized by stronger acid properties [16], occur at temperatures lower by 40–60°C and to deeper transformation degrees. The highest yield of ring opening products on Pt/WO_x/ZrO₂ is higher than that on Pt/HSiWO/ZrO₂ and equals 13 wt %. The maximum yield on Rh/WO_x/ZrO₂ is 13.8 wt %, which is commensurate with the yield obtained on Rh/HSiWO/ZrO₂.

It follows that the hydrogenation of toluene into MCH and isomerization of MCH into AlkCP followed by the hydrogenolysis (hydrocracking) of cyclic structures largely occur in the presence of Pt and Rh deposited on acid carriers under the conditions studied. The direction of toluene transformations strongly depends on the strength of the acid properties of carriers.

The shortcoming of catalysts containing noble metals is their irreversible poisoning with small amounts of sulfur [3]. The hydrodearomatization of oil fractions is performed using Ni–W catalysts [17] more stable toward the action of sulfur and cheaper than Pt and Rh catalysts. The temperature dependences of the yields of the main toluene transformation products on 6% Ni/WO_x/ZrO₂ are shown in Fig. 4. We see that tol-



Fig. 4. Temperature dependences of toluene conversion (*x*) and major product yields (*y*) on the catalysts (1-5) 6% Ni/WO_x/ZrO₂ and (1'-5') 0.2% Pt–6% Ni/WO_x/ZrO₂ at a 2.2 MPa pressure; (a) (1, 1') conversion, (2, 2') MCH, and (3, 3') AlkCP and (b) (4, 4') C₁–C₅ alkanes and (5, 5') isoheptanes and *n*-heptane.

uene conversion on this catalyst is 100% at temperatures up to 300°C and rapidly decreases at higher temperatures. This can be related to the deactivation of the catalyst by compaction products, as follows from the presence of C₈₊ hydrocarbons in reaction products. The yield of C_{8+} hydrocarbons reaches 4–5 wt % at 300– 340°C (Table 3). Platinum (0.2 wt %) was introduced into the Ni catalyst to increase its stability. The major toluene transformation products on Ni and Ni-Pt catalysts are MCH and AlkCP (Fig. 4, Table 3). The highest yield of AlkCP is 47-48 wt % (260-300°C); this is higher than the yields obtained on the Pt and Rh catalysts. As distinct from the Pt and Rh catalysts, ring opening occurs on Ni-Pt/WO₁/ZrO₂ at higher temperatures, and the yield of isoheptanes does not exceed 11 wt %. The yield of hydrocracking products on $Ni-Pt/WO_{y}/ZrO_{2}$ is much lower compared with Pt(Rh)/WO_x/ZrO₂.

As is shown in [5, 18], aromatic and naphthene hydrocarbons can transform into branched alkanes with the number of carbon atoms equal to that in the initial substance when two catalysts are used simultaneously. In order to increase the yield of ring opening products (isoheptanes) from the hydrogenolysis of toluene, we tested combined catalysts comprising two fractions, 6% Ni-0.2% Pt/WO_x/ZrO₂ and 2% Rh/Al₂O₃ (Table 3). The volume of catalyst loads remained the same as previously (3 cm^3) , and the volume ratio between the two fractions was 1:1. Close results were obtained no matter whether catalysts were loaded in layers or mixed (Fig. 5). The hydrogenation of toluene and isomerization of the six- into five-membered ring occurred on the acid component of combined catalysts (6% Ni-0.2% Pt/WO_x/ZrO₂), and MCH and AlkCP underwent hydrogenolysis with the formation of methylhexanes and dimethylpentanes on the metal oxide component (Table 3). The total yield of heptanes reaches 52-58 wt % at 300-320°C, which is 4.5 times larger compared with individual Ni–Pt/WO_x/ZrO₂ and two times larger than on 2% Rh/Al₂O₃. Simultaneously, a fairly high yield of isohexanes is obtained at 300–320°C. The yield of C₁– C₅ alkanes does not exceed 18 wt % even at 320°C. It follows that joint use of two catalysts may provide the highest yield of ring opening products and a high ratio between disubstituted and monosubstituted heptane isomers.

Using the data on toluene transformations on metal oxide and bifunctional catalysts and the scheme of toluene transformations given above, the following main toluene reactions can be specified: (1) hydrogenation into methylcyclohexane, (2) isomerization of the sixinto five-membered ring, (3) ring opening with the formation of mono- and disubstituted heptane isomers, and (4) hydrocracking of naphthene hydrocarbons and C_7H_{16} into C_1-C_6 alkanes.

The hydrogenation of toluene into MCH is observed on all catalysts under the conditions studied (160-360°C, 2.2 MPa). At temperatures up to 180°C, MCH is the major product. The isomerization of the six- into five-membered ring only occurs on catalysts with Broensted acid sites (Pt, Rh, and Ni on WO₁/ZrO₂ or HSiWO/ZrO₂). A comparison of the Pt, Rh, and Ni catalysts shows that the isomerization of toluene into alkylcyclopentanes occurs on Pt catalysts at temperatures 50-60°C lower than those characteristic of the Rh and Ni catalysts. The yield of AlkCP increases as the temperature grows and passes a maximum. Both the nature of the metal and the acidity of the carrier play important roles in ring opening reactions with the formation of isoheptanes. The contribution of the ring opening reaction increases as the temperature grows. The hydrogenolysis of the six-membered ring gives monosubstituted isoheptanes, and five-membered ring opening largely results in the formation of disubstituted isomers. The yield of isoheptanes decreases in the series $Pt \cong Rh > Ni$ for catalysts deposited on WO_y/ZrO₂. The

t, °C	x, %	y(I)			y(II)			y(III)		y(IV)	y(V)	
		CH ₄ C ₅ H ₁₂	DMB + MP	<i>n</i> -C ₆ H ₁₄	DMP	MH	<i>n</i> -C ₇ H ₁₆	МСР	AlkCP	Cyclo- hexane	MCH	y(C ₈₊)
6% Ni/WO _x /ZrO ₂												
260	100	2.2	0.1 + 0.3	0.1	0.2	1.3	0.3	0.7	47.7	0.1	44.9	2.1
300	99.8	5.2	0.2 + 0.6	0.2	0.5	3.2	0.9	1.8	48.3	0.3	34.6	4.0
6% Ni–0.2% Pt/WO _x /ZrO ₂												
260	100	0.6	0.1	Traces	0.2	1.1	0.3	0.3	47.7	0.1	49.1	0.5
300	99.9	3.8	0.3 + 0.8	0.3	1.3	4.9	1.2	1.9	47.8	0.4	35.9	1.3
320	99.7	10.4	0.8 + 1.9	0.7	1.8	7.2	1.9	3.6	40.9	0.7	27.3	2.5
6% Ni-0.2% Pt/WO _x /ZrO ₂ + 2% Rh/Al ₂ O ₃ *												
260	100	0.9	0.1 + 0.6	0.1	6.4	10.5	0.7	0.2	36.5	0.1	43.3	0.6
300	99.9	9.4	0.7 + 8.1	1.2	20.5	35.4	2.4	0	7.7	0.3	12.8	1.4
320	99.8	17.9	1.6 + 14.6	2.0	18.1	31.6	1.8	0	4.7	0.3	5.5	1.7

Table 3. Yields of the major toluene transformation products (*y*, wt %) on Ni-containing catalysts (molar ratio $H_2 : C_7 H_8 = 10 : 1, p = 2.2$ MPa, $v_{vol} = 2$ h⁻¹, catalyst load volume 3 cm³)

* Two-layer catalyst loading, layer volumes 1.5 cm³. See Table 1 for notation.

activity of Pt/HSiWO/ZrO₂ in ring opening is half that of Pt/WO_x/ZrO₂ with stronger carrier acidity. The yield of isoheptanes on acid catalysts does not exceed 13 wt %. Cracking to C₁–C₆ alkanes becomes predominant on all catalysts studied at high temperatures. The yield of hydrocracking products may be as high as 100% on the Rh/Al₂O₃ and Me/WO_x/ZrO₂ (Me is Pt or Rh) catalysts. Hydrodemethylation is not the main direction of toluene transformations on any of the catalysts studied.



Fig. 5. Yields of major toluene transformation products on catalysts loaded in layers and as a mixture; I, Ni–Pt/WO_x/ZrO₂ + Rh/Al₂O₅ (layered loading); II, Ni–Pt/WO_x/ZrO₂ (mixture); III, Ni–Pt/WO_x/ZrO₂; and IV, Rh/Al₂O₃.

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