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The Chemistry and Catalysis of the Toluene Hydrodealkylation Reaction

I. The Specific Activities and Selectivities of Group VIIB and Group VIII Metals Supported on Alumina

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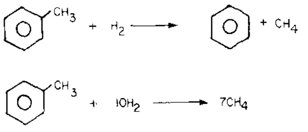
The catalytic hydrodealkylation of alkylaromatics is a reaction of continued industrial interest. In this and the following paper, investigations of the chemistry and catalysis of the hydrodealkylation reaction over supported metals are reported. The first paper will discuss the specific activities and selectivities of alumina-supported Group VIIB and Group VIII metals for the model reaction of toluene and hydrogen to produce benzene and methane. The relative specific activities (rates per surface metal atom) of the metals for benzene formation at 380°C are: Ni, 1000; Rh, 329; Ir, 177; Os, 69; Ru, 47; Pt, 9; Pd, 2; Re, 1. The selectivities (molecules benzene formed per toluene molecule reacted) of these metals are: Pd, 1.0; Rh, 0.98; Pt, 0.96; Ir, 0.95; Ni, 0.94; Os, 0.93; Re, 0.85; Ru, 0.82. The dependence of rate on the partial pressures of hydrogen and toluene over these metals are reported for the first time. For hydrogen the dependence of rate on partial pressure varies from -0.39 for Pd to 1.65 for Re. The dependence of rate on toluene partial pressure varies from -0.17 for Re to 0.47 for Pt and Pd. The magnitudes and periodic trends of these kinetic parameters are found to be substantially different from the periodic trends of these metals previously observed for other C–C bond breaking reactions such as ethane hydrogenolysis. Where possible the results of this present study are compared to those of other workers. For example, the specific activities of Rh and Pd reported here are in good agreement with results previously reported, but differ substantially for the specific activities of Ru and Pt. In agreement with this study, the previous studies point to rhodium as the most active noble metal for the toluene hydrodealkylation reaction.

INTRODUCTION

The production of benzene by dealkylation of alkylaromatics has been a reaction of industrial importance. The reaction can be carried out either thermally or catalytically. In the catalysis of hydrodealkylation reactions (dealkylation in the presence of H_2), both metal and oxide catalysts have been described (*1*). Recently, noble metal catalysts have been the focus of investigations for both hydrodealkylation (*2–5*) and steam dealkylation (*6*) reactions (dealkylation in the presence of steam). In this and the following paper the chemistry and catalysis of the simplest hydrodealkylation reaction, the reaction of toluene and H_2 to produce benzene and CH_4, over selected Group VIII metals is discussed.

Under hydrodealkylation conditions the reaction of toluene and H_2 can occur via two pathways as shown below.



(1)

(2)

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Reaction (1) is the desired reaction and will be referred to as the toluene hydrodealkylation reaction (THD). Reaction (2) is undesirable and represents the total hydrogenolysis of toluene. Equation (2) is written showing only CH_4 as the hydrogenolysis product since this was the only hydrocarbon product observed other than benzene. The relative rates of reactions (1) and (2) determine the selectivity of the overall toluene/H_2 reaction.

The catalysis of the THD reaction has not been extensively studied. Dydykina *et al.* (*2*) and Mozhaiko *et al.* (*3*) in the Soviet Union have studied the THD reaction over supported noble metals. Kochloefl (*4*) in Germany reported results for the THD reaction over several supported Rh catalysts. Kasoka and co-workers (*5*) in Japan compared the THD reaction over supported Rh, Pt, Pd, and Rh–Pt bimetallic catalyst systems. These studies have not compared the activities of the metals based on specific activities (rates per surface metal atom) as in the present study. In Part 1 of this study the specific activities and selectivities of the Group VIII metals/γ-Al_2O_3 for the THD reaction will be presented. Where possible, these results are compared to the results of other workers for this reaction. A study of the dependence of rate on the partial pressures of toluene and hydrogen over the Group VIII metals will be presented. A comparison of the activities of the Group VIII metals for THD to the activities of these same metals for paraffin hydrogenolysis reactions will also be made. In Part 2 of this study a reaction sequence will be presented that incorporates both carbon–carbon bond breaking and product desorption steps in the overall sequence.

EXPERIMENTAL METHODS

The experimental apparatus and techniques used for the determination of the THD reaction kinetics are identical to those employed for the toluene steam dealkylation studies described in detail previously (*6*). Briefly, the kinetic studies were carried out in a down-flow quartz microreactor using oil-filled U-tube manometers to monitor the flow rates of gases. The toluene was added to the reactor by saturation of an inert gas stream. Both the exit line from the toluene saturator and the exit line from the reactor were continually heated with electrical heating tapes to temperatures well above the saturation temperature of the toluene. Total gas space velocities of about 20,000 V/V/hr were typically used in order to maintain toluene conversion less than 5%, thus assuring reactor operation in a differential conversion mode. The use of a differential reactor minimizes heat and mass transfer effects, eliminates significant effects due to product inhibition, and provides information on initial rates and initial product distributions.

All the catalysts used in this study were prepared by incipient wetness techniques using aqueous solutions of the following metal salts: $RuCl_3 \cdot xH_2O$, $RhCl_3 \cdot 3H_2O$, $(NH_4)_2PdCl_4$, $NiNO_3 \cdot 6H_2O$, $H_2OsCl_6 \cdot 2H_2O$, $H_2IrCl_6 \cdot 6H_2O$, $H_2PtCl_6 \cdot 6H_2O$, and $HReO_4$. The support (obtained from Englehard Chemical Division) used for all catalyst preparations was γ-Al_2O_3 with a BET surface area of about 175 m^2 g^{-1}.

Hydrogen chemisorption measurements used to determine the metal surface area were made in a glass apparatus similar to one described by Vannice (*7*). For the determination of Pd surface area by H_2 chemisorption, the method described by Boudart and Hwang (*8*) was employed. For the other metals, the zero pressure intercept value of the H_2 isotherm was taken as the monolayer coverage.

Prior to H_2 chemisorption measurements, the catalysts were reduced for 1 hr at 450°C, then evacuated at 400°C for 1 hr, and finally cooled to room temperature prior to H_2 uptake determinations. Kinetic measurements were made after the catalysts were reduced for 1 hr at 500°C and then

TABLE 1

Dispersion of Metal Catalysts Used in This Study

Catalysts (% M/γ-Al_2O_3)	H_2 uptake (μmol/g of catalyst)	Fraction exposed
1% Ru	10.2	0.21
1% Rh	47.7	0.98
1% Pd	13.2	0.28
2% Os	12.3	0.23
2% Ir	94.1	1.0
2% Pt	60.1	1.0
5% Ni	77.3	0.18
10% Re	23.1	0.08

cooled under H_2 to the operating temperature. The hydrogen (99.5% purity) used in both chemisorption and kinetic measurements was supplied by Linde Company and was further purified by passage through a Deoxo unit followed by a molecular sieve drying trap. The toluene (reagent grade) supplied by Matheson Coleman and Bell Manufacturing Chemists was used as received.

As is the case with most catalytic hydrocarbon conversions, there was some catalyst activity loss during the runs. In general the activity decrease was greatest during the first hour on stream. This activity loss was largest for Re which lost 40% of its initial activity during the first hour. The loss of activity for the other metals varied from 25% for Os to only a 10% loss for Ir. The rate of activity loss after 1 hr was much less than that which occurred during the first hour on stream. Therefore, all the kinetic parameters were determined after 1 hr on stream using the bracketing techniques previously described (*6*).

RESULTS

The results of the hydrogen chemisorption studies on freshly reduced catalysts are presented in Table 1 for the catalysts discussed within this paper. Also listed are the calculated metal dispersion or fraction-exposed values, where fraction-exposed $= m_s/m_t$ with m_s representing the number of surface metal atoms and m_t representing the total number of metal atoms in the catalyst. For the Pt catalyst, and particularly the Ir catalyst, the H_2 uptake was greater than one H atom per metal atom. The H/Pt ratio was 1.17, and the H/Ir ratio was 1.81. This chemisorption behavior for Ir has also been observed by McVicker

TABLE 2

Kinetic Parameters for Hydrodealkylation of Toluene

Catalyst (% M/γ-Al_2O_3)	Temperature[a]	n[b]	m[c]	E[d]	A[e]	N[f]	S[g]
1% Ru	380	0.16 ± 0.06	1.03 ± 0.09	32.8 ± 2.0	1.62×10^9	0.0170	0.82
1% Rh	320	0.23 ± 0.03	0.20 ± 0.05	32.4 ± 1.1	8.32×10^9	0.1191	0.98
1% Pd	450	0.47 ± 0.10	−0.39 ± 0.15	38.7 ± 1.8	6.47×10^9	0.0007	1.00
2% Os	380	0.01 ± 0.06	1.23 ± 0.05	25.3 ± 1.6	7.35×10^6	0.0250	0.93
2% Ir	340	0.15 ± 0.04	0.49 ± 0.11	27.9 ± 1.3	1.40×10^8	0.0642	0.95
2% Pt	380	0.47 ± 0.03	−0.06 ± 0.04	33.7 ± 2.8	5.90×10^8	0.0031	0.96
5% Ni	290	0.34 ± 0.07	−0.15 ± 0.06	31.1 ± 1.9	9.09×10^9	0.3621	0.94
10% Re	450	−0.17 ± 0.03	1.65 ± 0.06	33.0 ± 3.5	3.21×10^7	0.0003	0.85

[a] Temperature at which reaction orders were determined, degrees centigrade.

[b] Order with respect to toluene.

[c] Order with respect to hydrogen.

[d] Apparent activation energy, kilocalories per mole.

[e] Preexponential factor, molecules per second per metal site, in the equation $N = A \exp(-E/RT)$.

[f] Turnover rate after 1 hr on stream. $T = 380°C$, $P_{Tol} = 10.1$ kPa, $P_{H_2} = 36.5$ kPa.

[g] Selectivity for benzene formation, molecules of benzene formed per molecule of toluene reacted.

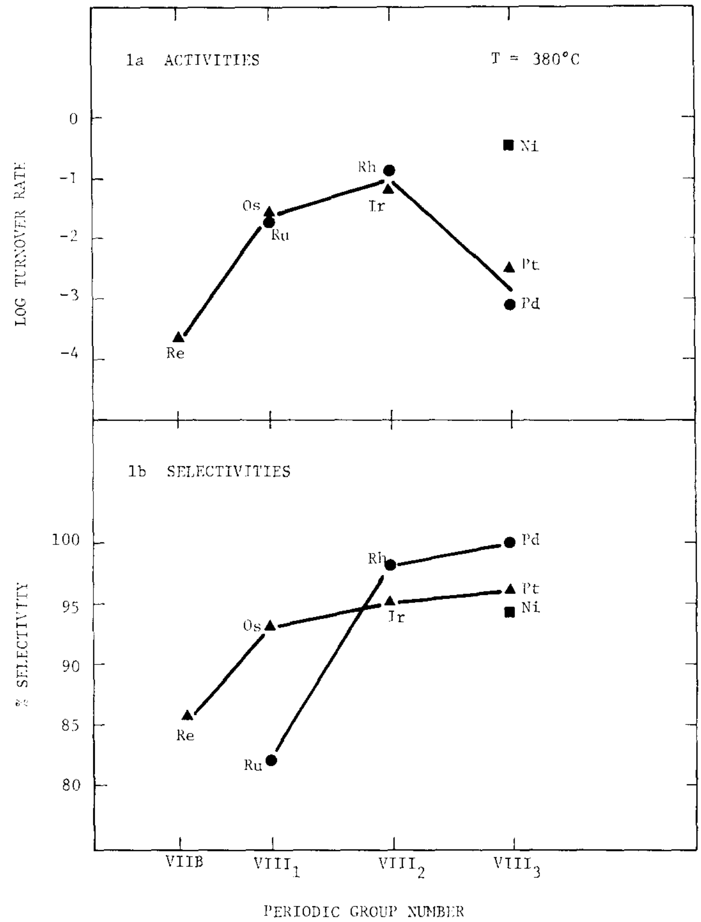

FIG. 1. (a) Activities and (b) selectivities of alumina-supported metals. Activities are turnover rates at 380°C and partial pressures of H_2 and toluene of 36.5 and 10.1 kPa, respectively. Selectivities were determined at the reaction temperatures reported in Table 2.

et al. (*9*). The high H_2 uptake is indicative of a highly dispersed metal component. This, coupled with CO chemisorption results, which also indicates high dispersion, justifies the assumption that Pt and Ir have fraction-exposed values of 1.0. For the other metals one chemisorbed H atom was assumed to represent one surface metal atom.

Table 2 presents the kinetic parameter for the H_2–toluene reaction. Selectivities (molecules benzene formed per molecule toluene reacted) were calculated according to the following expression:

$$S = \frac{X_{\mathrm{Ben}}}{(X_{\mathrm{Ben}} + [\{X_{\mathrm{CH_4}} - X_{\mathrm{Ben}}\}/7])}, \quad (3)$$

where X_{Ben} = mole fraction of benzene in the product, and $X_{\mathrm{CH_4}}$ = mole fraction of CH_4 in the product. Activities listed were determined after 1 hr on stream and are expressed as turnover rates. When activities were not specifically measured at 380°C, they were adjusted to 380°C using the equation $N = A\exp(-E_a/RT)$ where E_a is the measured apparent activation energy and A is the preexponential factor. Both these parameters are included in Table 2. The activities were all determined at constant partial pressures of H_2 and toluene of approximately 36.5 and 10.1 kPa, respectively. Figure 1 compares the periodic trends of the specific activities (Fig. 1a) and selectivities (Fig. 1b) of the various metals supported on Al_2O_3. With both the second and third period metals there is a maximum in activity at the Group $VIII_2$ metals, Rh and Ir. From Fig. 1b it is seen that the selectivities increase with increasing atomic number. This trend within the Group VIII metals is opposite to the tendency of these metals to catalyze C–C bond-breaking reactions such as the ethane hydrogenolysis reaction studied by Sinfelt (*10*). It is clear from Fig. 1 that the metal of choice for toluene hydrodealkylation is Rh since it has both high activity and selectivity. It is also interesting to note that Rh is the preferred metal for the toluene steam dealkylation reaction (*6*) because of its high activity and selectivity to benzene for that reaction. The relative order of specific activities of the metals for toluene hydrodealkylation is: Ni, 1000; Rh, 329; Ir, 177; Os, 69; Ru, 47; Pt, 9; Pd, 2; Re, 1.

The partial pressure dependencies of H_2 and toluene over Group VIII metals, which have not been previously reported, are presented in Table 2 for the THD reaction. As can be seen from Table 2, the partial pressure dependencies vary systematically according to the metal's periodic position. The toluene order of reaction varies from near zero order to about $\frac{1}{2}$ order. The H_2 order varies from strongly positive over Ru, Os, and Re to negative over Pt, Pd and Ni.

DISCUSSION

In this section the results of the present study will be discussed in relation to what is known about these metals as catalysts for general carbon–carbon bond-breaking reactions. Next, the results of other workers for THD reaction studies will be compared to the present results.

The metal-catalyzed reaction of hydrogen with hydrocarbons in which C–C bonds are broken is termed hydrogenolysis. The H_2/toluene reaction may thus be considered a selective cleavage of the alkyl carbon atom bond with the aromatic nucleus. The simplest hydrogenolysis reaction is the reaction of ethane and hydrogen as follows:

$$C_2H_6 + H_2 \rightarrow 2CH_4 \qquad (4)$$

This reaction has been one of the most extensively studied metal-catalyzed reactions. Sinfelt and co-workers have reported detailed studies of the kinetics of this reaction as catalyzed by the Group VIIB, VIII, and IB metals on a variety of supports, principally SiO_2. These results are summarized in a review by Sinfelt (*10*) and in an updated kinetic analysis (*11*).

It will be useful to compare the periodic trends of the kinetic parameters of ethane hydrogenolysis with those found for the THD reaction. For this purpose the results reported by Sinfelt (*10*) for the various metals supported on SiO_2 will be used. As was previously shown (*12*), the specific activity of rhodium is virtually independent of support with the difference in activity varying by about a factor of 2 between Rh/Al_2O_3, Rh/SiO_2, Rh/C, and unsupported Rh black. These results also indicate that the THD is structure insensitive since the fraction-exposed of rhodium varied from 0.01 for Rh black to 1 for Rh/Al_2O_3. Thus it is reasonable to compare the specific activities of the various metals supported on Al_2O_3 for the THD reaction to the specific activities of the metals supported on SiO_2 reported by Sinfelt for ethane hydrogenolysis.

For ethane hydrogenolysis, the activities of the Group VIII metals vary over an extremely wide range. At a temperature of 205°C, Sinfelt observed a range of activities of seven to eight orders of magnitude from the least active metals, Pt and Pd, to the most active metals, Os and Ru. In Fig. 2 the periodic trends of the specific activities at 205°C of various metals for ethane hydrogenolysis, using the data of Sinfelt (*10*), are compared to the periodic trends of the activities of those metals for the THD reaction at 380°C. It is quite clear that ethane hydrogenolysis activity is much more specific to the particular metal chosen than is the THD reaction. The kinetic parameters of Pt and Pd for ethane hydrogenolysis were determined by Sinfelt in approximately the same temperature range as employed in this current study of the THD reaction. It is thus reasonable to compare the specific activities of these two metals for the H_2/C_2H_6 reaction and the THD reaction. At 380°C, Pd is 140 times more active and Pt is 10 times more active for ethane hydrogenolysis than for THD. Therefore, for all Group VIII metals the specific activity is one too many orders of magnitude higher for ethane hydrogenolysis than for toluene hydrodealkylation.

It is also of interest to note in Fig. 2 that the maximum activity for THD over the noble metals is at the Group $VIII_2$ metals (Rh, Ir) whereas the maximum in activity for ethane hydrogenolysis is at the Group $VIII_1$ metals (Ru, Os). It may be pointed out that the weak specificity of the metals coupled with the maximum activity at the Group $VIII_2$ metals is more typical of hydrogenation reactions over Group VIII metals rather than hydrogenolysis reactions. This point will be discussed in more detail in the second paper of this present study.

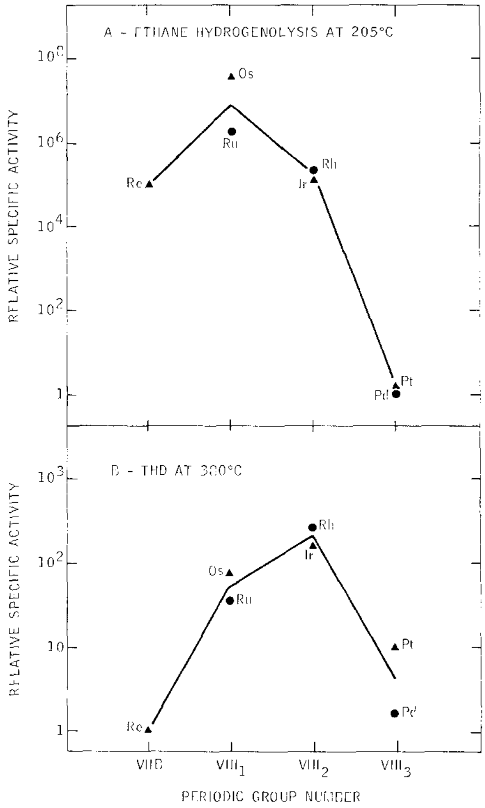

FIG. 2. Comparison of the periodic trends of the relative activities of metals for (A) the ethane hydrogenolysis reaction and (B) the THD reaction. For each reaction the specific activities of the metals are made relative to the lowest activity metal at the temperature listed. The ethane hydrogenolysis data is from reference (*10*).

Another significant difference between ethane hydrogenolysis and THD is the large differences in reaction orders for the two reactions. Sinfelt (*10*) has determined that the ethane partial pressure dependence increases from about $\frac{1}{2}$ order to first order when moving across the periodic table from Group VIIB through the Group $VIII_3$ metals. For THD, the toluene order of reaction varies from slightly negative for Re to about $\frac{1}{2}$ order for Pt and Pd as shown in Table 2. The H_2 orders are even more different for these two reactions. For ethane hydrogenolysis, according to Sinfelt (*10*), the H_2 orders are strongly *negative* for all the metals studied except Fe and Re. On the other hand only Pt, Pd, and Ni have negative hydrogen orders of reaction for THD. As shown in Table 2, Group $VIII_1$ and Group $VIII_2$ metals have H_2 orders varying from about 0.2 for Ir to about first order for Ru and Os. Re has a H_2 order of reaction substantially above 1. Clearly then there are major differences between the kinetics observed for typical hydrogenolysis reactions such as ethane hydrogenolysis and the kinetics reported here for toluene hydrodealkylation. These differences will be discussed in more detail in Part 2 of this present study. A reaction sequence will be proposed for THD that incorporates both hydrogenolysis (C–C bond breaking) and hydrogenation (product desorption) steps in the overall reaction sequence.

There has not been extensive research on THD reported in the literature. The most comprehensive studies have been those by Rabinovich and co-workers in the Soviet Union. Mozhaiko *et al.* (*3*) report the activities, selectivities, and activation energies of the Group VIII noble metals supported on γ-Al_2O_3 as determined in a flow reactor. They report the relative order of activities of the Group VIII metals at 490°C as follows: Rh, 100; Ir, 75; Os, 11; Pd, 9; Ru, 4; Pt, 1.5. The percentage selectivities of the various metals for benzene formation were reported to be: Pd, 99–100; Pt, 98–99; Rh, 96–98; Os, 95–96; Ir, 90–92; Ru, 80–85. In an earlier study Dydykina *et al.* (*2*) reported the following results from a pulse reactor study: Rh > Ir > Os > Ru > Pt > Pd. Using the present results from Table 2 the relative specific activities of the noble metals at 380°C are: Rh, 100; Ir, 54; Os, 21; Ru, 14; Pt, 3; Pd, 1. The sequence of activities reported by Dydykina *et al.* (*2*) is identical to the activity sequence reported here. However, the activity sequence from the flow reactor studies reported by Mozhaiko, Rabinovich *et al.* (*3*) differs significantly from the present results for the less active metals.

In contrast to the present study, the studies of Dydykina and Mozhaiko do not report activities as specific rates relative to the metal surface area of the catalyst. Mozhaiko *et al.* (*3*) did report, however, metal surface areas for several of the metals. Using their results it is possible to calculate turnover rates for several of the metals based on their reported conversion, flow rate, and activation energy results. If this is done, Table 3 can be constructed comparing the present results to those reported by Mozhaiko *et al.* The turnover rates for Rh and Pd agree quite well (within a factor of 2) whereas the results for Ru and Pt disagree substantially. The present results for turnover rates of Ru and Pt are more than an order of magnitude higher than those reported by Mozhaiko. The author has no explanation for these large discrepancies although differences in catalyst preparations and experimental conditions may in part account for the differences.

Kochloefl (*4*) has also reported the activity of Rh/Al_2O_3 for THD. Using his results it is possible to calculate a turnover rate for Rh which is also included in Table 3. Kochloefl reports a much lower value for the turnover rate of Rh than those of the other workers. Also included in Table 3 are a comparison of the selectivities and activation energies. The present results agree quite well with those reported by Mozhaiko *et al.* The activation energy reported by Kochloefl for Rh is quite low compared to the other results. This is suggestive of possible diffusional constraints in Kochloefl's experiments and may in part account for his lower turnover rate. All studies, however, report Rh as the most active noble metal for THD.

Neither Mozhaiko *et al.* nor Kochloefl report partial pressure dependencies for any of metals studied. Dydykina *et al.* (*2*) report (based on pulse reactor studies) that Rh, Ru, Os, and Ir respond positively to the presence of hydrogen indicating a possible positive order with respect to hydrogen, whereas they report that Pt and Pd respond negatively to the presence of hydrogen, suggesting a negative order of reaction with respect to hydrogen. These qualitative observations agree directionally with the quantitative results presented in Table 2. Mozhaiko *et al.* (*3*) noted that the dealkylation rate appeared to be independent of the toluene partial pressure, thus suggesting a near zero order of reaction with respect to toluene. Kasaoka *et al.* (*5*) have studied a Rh–Pt/Al_2O_3 alloy catalyst for THD. They report orders of reaction with respect to toluene and hydrogen to be 0.15 and 1.0, respectively. As shown in Table 2,

TABLE 3

Comparison of Present Results for THD to Published Results

Metal	T.R. × 10^{3a} (at ca. 380°C)	Selectivity[b]	Activation energy[c]	Source
Rh	119	98	32.4	This study
Rh	77	96–98	30.3	Mozhaiko *et al.* (*3*)
Rh	18	—	12.8	Kochloefl (*4*)
Ru	17	82	32.8	This study
Ru	1.1	80–85	28.6	Mozhaiko *et al.* (*3*)
Pd	0.7	100	38.7	This study
Pd	1.2	99–100	37.0	Mozhaiko *et al.* (*3*)
Pt	3.1	96	33.7	This study
Pt	0.2	98–99	33.1	Mozhaiko *et al.* (*3*)
Ir	64	95	27.9	This study
Ir	—	90–92	25.8	Mozhaiko *et al.* (*3*)
Os	25	93	25.3	This study
Os	—	95–96	17.3	Mozhaiko *et al.* (*3*)

[a] Turnover rate, molecues of benzene formed per second per metal site.
[b] Selectivity, molecules of benzene formed per molecule of toluene reacted.
[c] Apparent activation energy, kilocalories per mole.

the present results indicate a near zero- to ½-order dependence on toluene partial pressure. In Part 2 of this study a kinetic analysis of the THD reaction is presented that fits these kinetic parameters to a power rate law expression derived from an assumed reaction sequence.

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