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# The Chemistry and Catalysis of the Water/Toluene Reaction

## 1. The Specific Activities and Selectivities of the Group VIII Metals Supported on $Al_2O_3$

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The reaction of steam with heavy hydrocarbons to produce liquids and light gases is an attractive alternative to hydrocracking in that expensive hydrogen is replaced by water. In this and the following paper, investigations of the chemistry and catalysis of the selective steam dealkylation reaction over the Group VIII metals are reported. The first paper will discuss the specific activities and selectivities of the Group VIII metals supported on alumina for the model reaction of water and toluene to produce benzene, carbon oxides, and hydrogen. The relative specific activities (rates per surface metal atom) for benzene formation of the Group VIII metals/$Al_2O_3$ are: Rh, 100; Ru, 52; Pd, 34; Pt, 21; Ir, 14; Ni, 9; Os, 3. The selectivities (molecules of benzene formed per molecule of toluene reacted) of the supported metals are: Pd, Pt, 0.95–1.00; Rh, Ir, 0.85–0.90; Ru, Os, 0.60–0.70; Ni, 0.40. Studies of the dependence of rate on the partial pressures of water and toluene over the Group VIII metals are reported for the first time. For toluene the dependence of rate on partial pressure varies from $-0.13$ to $+0.26$, whereas for water the variation is from 0.25 to 0.67. Where possible, these results are compared to those of other workers. For example, the specific activities of Rh, Pd, and Pt reported here show good agreement with values reported previously for these metals. In all cases, rhodium is found to be the most active metal for the water/toluene reaction.

### INTRODUCTION

In recent years, there has been a rapid increase in the costs of energy. A consequence of this increase has been a corresponding increase in the costs of chemical processes that either consume large amounts of energy or consume valuable clean petroleum feedstocks. Hydrogen production by the steam reforming of hydrocarbons is one process that is both energy intensive and dependent on the supply of light, clean (low-sulfur) hydrocarbon distillates or gases for feedstocks. The production of hydrogen and the use of processes (such as hydrocracking and hydrotreating) that consume hydrogen have significantly increased in costs. Processes utilizing water in lieu of hydrogen to alter the boiling point distribution of petroleum feedstocks are of increasing interest. One such process is the steam dealkylation of alkylaromatics to produce benzene, carbon oxides, and hydrogen—a process that produces rather than consumes hydrogen. This series of papers will discuss the chemistry and kinetics of the steam dealkylation of alkylaromatics.

The simplest steam dealkylation reaction is the reaction of toluene and water as

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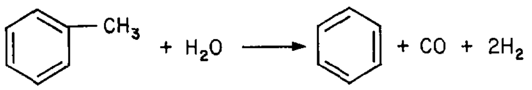
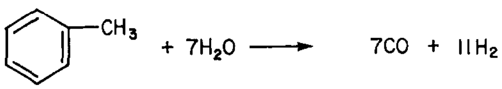
follows:



(1)



(2)

Reaction (1) will be referred to as either the *selective* steam reforming reaction or the steam dealkylation reaction, whereas reaction (2) will be referred to as the total steam reforming reaction of toluene. The relative rates of reactions (1) and (2) determine the overall selectivity of the dealkylation reaction. Because of their high selectivities to benzene, the catalysts of choice are the supported noble metals. Rabinovich and co-workers (*1–9*) in the Soviet Union have studied the steam dealkylation of simple alkylaromatics using supported Group VIII metal catalysts. Kochloefl (*10*) in Germany and several groups of workers in Japan (*11*, *12*) have also reported results on the steam dealkylation of toluene using a variety of noble metal catalysts. These studies have in general not compared the activities of the noble 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/$\gamma$-$Al_2O_3$ for the water/toluene reaction will be presented. Where possible these results will be compared to the results of other workers for the specific activities and selectivities of the noble metals. For the first time a study of the dependence of rate on the partial pressures of toluene and water over the Group VIII metals will be presented. In addition, a comparison of the results of steam dealkylation over Group VIII metals to paraffin steam reforming reactions will be made. In Part 2 of this series the effect of support on the kinetics of toluene dealkylation will be discussed. A reaction sequence will be presented that incorporates the role of metal and support in the overall reaction of water and toluene.

## EXPERIMENTAL METHODS

The kinetic studies were conducted in a down-flow microreactor using oil-filled U-tube manometers to monitor flow rates of gases. The catalyst (100- to 150-$\mu$m particles) was supported by a quartz frit in a quartz tube and was maintained at reaction temperature by a Lindberg tube furnace controlled with a West Model JP proportional controller. The $H_2O$ and toluene were added to the reactor by saturation of inert gas streams. To assure complete saturation at known conditions, the water and toluene were placed in 75-ml metal gas sampling bombs to which standard fritted glass tubes were attached by means of metal to glass joints. These bombs were maintained at constant temperature by immersion in separate Lauda constant-temperature baths (Model NB). The exit lines from the constant-temperature baths to the reactor were heated with electrical heating tapes to temperatures well above the saturation temperatures of the water and toluene. The exit line from the reactor to the heated in-line gas sampling valve was also maintained at temperatures high enough to assure that the products and unreacted feed remained in the vapor phase. Product distributions of the total reactor effluent were measured by means of a heated in-line gas sampling valve connected to a Hewlett–Packard 7620 chromatograph with Poropak Q columns and subambient temperature programming capabilities. A Hewlett–Packard 3370B electronic integrator was used to determine sample peak areas. Total gas space velocities of about 20,000 v/v/hr were typically used in order to maintain toluene conversions of 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. For the most active catalyst system, $Rh/Al_2O_3$, the turnover number was found (*13*) to be constant for a metal loading range of 0.3 to 1.2 wt% Rh on $Al_2O_3$, thereby satisfying the Koros–Nowak criterion (*14*) for absence of diffusion effects.

For all the catalysts studied, there was a continued slow decline in activity over the course of the run. In order to be consistent, the activities and selectivities of the catalysts are reported as their value after 1 hr on stream. During the determinations of activation energies and partial pressure dependencies, the activity measurement at any given set of conditions was always bracketed with activity measurements at standard conditions of temperature (appropriate to catalyst studied) and partial pressures of toluene and water of 0.08 and 0.26 atm, respectively. This method assured that the kinetic parameters were unbiased by the continual catalyst deactivation with time on stream.

All the catalysts used in this study were prepared by incipient wetness techniques using a wettability factor of 0.5 ml $g^{-1}$ $\gamma$-$Al_2O_3$. The $\gamma$-$Al_2O_3$ support obtained from Engelhard Chemical Division had a BET surface area of about 175 $m^2$ $g^{-1}$. Aqueous solutions of the following metal salts were used: $RhCl_3 \cdot 3H_2O$, $RuCl_3 \cdot xH_2O$, $H_2PtCl_6 \cdot 6H_2O$, $(NH_4)_2PdCl_4$, $H_2IrCl_6 \cdot 6H_2O$, $H_2OsCl_6 \cdot 2H_2O$, and $NiNO_3 \cdot 6H_2O$. After impregnation the samples were dried overnight at 120°C.

Hydrogen chemisorption measurements, used to determine the metal surface area, were made in a glass apparatus similar to one described by Vannice (*15*). For the determination of Pd surface area by $H_2$ chemisorption, the method described by Boudart and Hwang (*16*) was employed. For the other metals, the zero-pressure intercept value of the $H_2$ isotherm was taken as the monolayer coverage.

The hydrogen (99.5% purity) used in both the chemisorption measurements and catalyst reductions was obtained from Linde Company and was further purified by passage through a Deoxo unit followed by a molecular sieve drying trap. The water used in the kinetic experiments was distilled and deionized. The toluene (reagent and spectrophotometry grade) supplied by Matheson Coleman & Bell Manufacturing Chemists was used as received.

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 measurements. Kinetic measurements were made after the catalysts were reduced for 1 hr at 500°C and then cooled under $H_2$ to the operating temperature. Hydrogen was subsequently purged from the reactor with helium and the flow rates of water and toluene over the catalyst were set at the desired values.

## RESULTS

The results of hydrogen chemisorption studies on the freshly reduced catalysts are listed in Table 1. Also listed are the calculated metal dispersion or fraction exposed[1] values, where fraction exposed = $m_s/m_t$, with $m_s$ representing the number of surface metal atoms and $m_t$ the total number of metal atoms in the catalyst sample. For the Pt catalyst and particularly the Ir catalyst, the $H_2$ uptake was significantly greater than one H atom per metal atom. The high hydrogen uptake on Ir has also been observed by McVicker *et al.* (*17*). The high hydrogen uptake is indicative of a highly dispersed metal component. This coupled with CO chemisorption results,

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[1] The IUPAC Commission on Colloid and Surface Chemistry has recently recommended the use of the term *fraction exposed,* in lieu of the more commonly used term *dispersion,* to signify the number of surface metal atoms in a catalyst sample.

TABLE 1

Dispersion of Metal Catalysts Used in this Study

| Catalyst (% M/$\gamma$-$Al_2O_3$) | $H_2$ uptake ($\mu$mol/g of catalyst) | Fraction exposed |
|---|---|---|
| 1% Ru | 10.2 | 0.21 |
| 1% Rh | 47.7 | 0.98 |
| 1% Pd | 17.2 | 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 |

which also indicate 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 parameters for the water/toluene reaction. Selectivities (molecules of benzene formed per molecule of toluene reacted) were calculated according to the expression:

$$S = \frac{X_{\mathrm{Ben}}}{\left(X_{\mathrm{Ben}} + \dfrac{\sum X_{\mathrm{C}_1} - X_{\mathrm{Ben}}}{7}\right)}, \quad (3)$$

where $X_{\mathrm{Ben}}$ = mole fraction benzene in product and $X_{\mathrm{C}_1}$ = mole fraction $C_1$ species in product. The activities listed are the activities after 1 hr on stream and are expressed as turnover rates. When activities were not specifically measured at 440°C, the activities were adjusted to 440°C using the equation $r_0 = r_0' \exp(-E_A/RT)$, where $E_A$ is the apparent activation energy and $r_0'$ is the preexponential factor. In all cases the activities were measured within 50°C of 440°C, thus minimizing extrapolation errors. Figure 1 compares the specific activities (Fig. 1A) and selectivities (Fig. 1B) of the various Group VIII metals supported on $\gamma$-$Al_2O_3$ according to the metal's position in the periodic table. With the second-period metals there is a sharp maximum in the activity at the Group $VIII_2$ metal, rhodium. In the third period there is a gradual rise in activity with increasing atomic number. As seen in Fig. 1B, the selectivities of the second- and third-period Group VIII metals increase with increasing atomic number. It is interesting to note that the trend for increasing selectivity for benzene formation 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 (*18*). It is clear from Fig. 1 that the metal of choice for the $H_2O$/toluene reaction is rhodium, since it has the highest activity and reasonable selectivity for benzene formation. For this reason the majority of previously reported work for the toluene steam dealkylation reaction has focused on rhodium catalysts.

The relative order of specific activity of the metals for steam dealkylation is: Rh, 100; Ru, 52; Pd, 34; Pt, 21; Ir, 14; Ni, 9; Os, 3. Using the selectivity value for each catalyst reported in Table 2, it is possible to calculate the activity for total toluene reacted by both reactions (1) and (2). In this case, the order of activities changes only moderately, with the biggest change occurring for the very unselective Ni catalyst. Thus the relative order of activities for total toluene reacted is: Rh, 100; Ru, 72; Pd, 29; Pt, 18; Ni, 17; Ir, 13; Os, 4.

Of the metals studied, Ni is the most easily oxidized. In the absence of a counterbalancing reducing component, $H_2O$ at 440°C will oxidize Ni metal. However, in the presence of both hydrocarbons and the water/hydrocarbon reaction products, CO and $H_2$, Ni metal is thermodynamically favored and is therefore assumed to be the active component in the supported Ni catalyst discussed above.

Except for Ir and Os, the apparent activation energies were determined by bracketing the sample with measurements at standard conditions as described above.

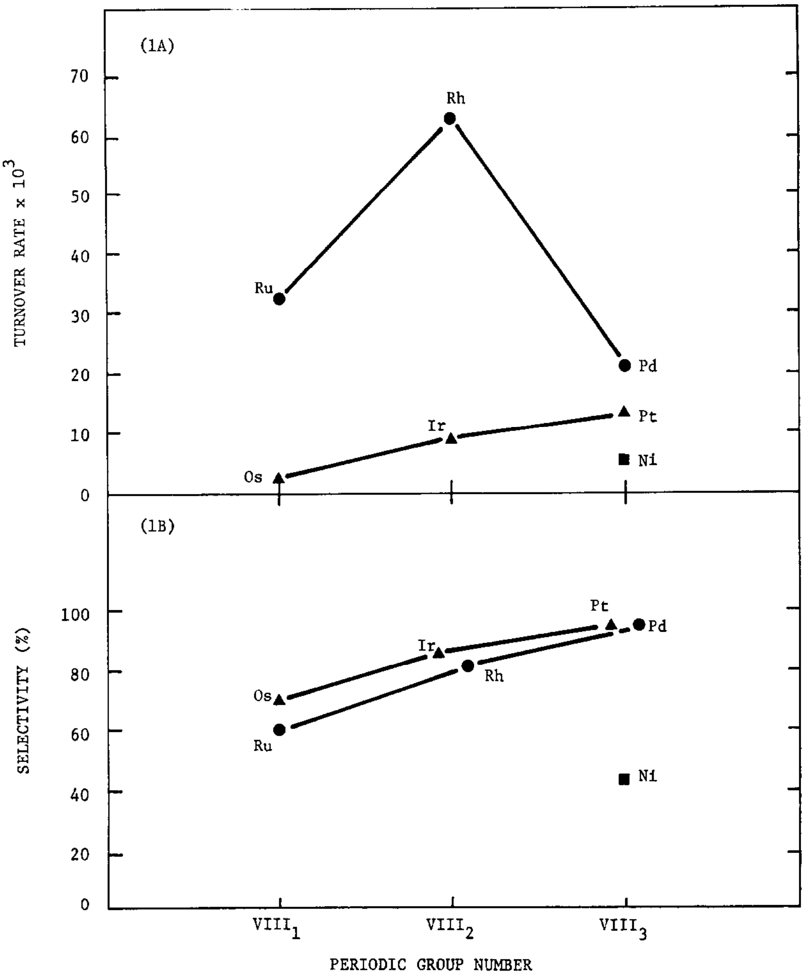

FIG. 1. Activities and selectivities of Group VIII metals/$\gamma$-$Al_2O_3$. Activities are turnover rates at 440°C, $P_{tol} = 0.08$ atm, and $P_{H_2O} = 0.26$ atm. Selectivities were determined at the temperatures listed in Table 2.

For Os and Ir the activity decline during reaction was much more rapid than for the other catalysts. With these two metals the apparent activation energy increased as a function of time on oil, probably because of the rapid coking of the catalyst surface. This was not the case for the other metals. In order to overcome this activity decline and corresponding bias in activity measurements, the bracketing technique discussed above was modified to include a 15-min steam treatment at the standard temperature to aid in removal of carbonaceous deposits. This technique slowed the rate of activity decline sufficiently to allow the determination of the apparent activation energy without the perturbing influence of carbonaceous deposits. The partial-pressure dependencies were determined for all metals except Os by bracketing activity measurements with activity measurements at standard conditions. With the exception of Os, the partial-pressure dependencies did not vary significantly as a function of run length. The technique employed for determination of the apparent activation energy

TABLE 2

Kinetic Parameters for Steam Dealkylation of Toluene

| Catalyst (% M/$\gamma$-$Al_2O_3$) | Temp.[a] (°C) | $n$[b] | $m$[c] | $E$[d] | $A$[e] | $N$[f] | $S$[g] |
|---|---|---|---|---|---|---|---|
| 1% Ru | 440 | $-0.07 \pm 0.07$ | $0.47 \pm 0.06$ | $42.5 \pm 2.8$ | $3.48 \times 10^{11}$ | 0.0326 | 0.60 |
| 1% Rh | 390 | $0.08 \pm 0.05$ | $0.41 \pm 0.08$ | $33.0 \pm 1.9$ | $8.22 \times 10^{8}$ | 0.0629 | 0.83 |
| 1% Pd | 440 | $0.28 \pm 0.12$ | $0.25 \pm 0.06$ | $33.8 \pm 1.4$ | $4.87 \times 10^{8}$ | 0.0212 | 0.95 |
| 2% Os | 490 | $-0.13 \pm 0.04$ | $0.62 \pm 0.08$ | $33.4 \pm 2.1$ | $3.40 \times 10^{7}$ | 0.0020 | 0.70 |
| 2% Ir | 430 | $-0.16 \pm 0.05$ | $0.73 \pm 0.12$ | $31.9 \pm 0.9$ | $4.49 \times 10^{7}$ | 0.0086 | 0.85 |
| 2% Pt | 440 | $0.05 \pm 0.08$ | $0.40 \pm 0.06$ | $32.8 \pm 0.4$ | $1.5 \times 10^{8}$ | 0.0133 | 0.95 |
| 5% Ni | 440 | $-0.06 \pm 0.06$ | $0.67 \pm 0.08$ | $26.7 \pm 3.4$ | $8.42 \times 10^{5}$ | 0.0055 | 0.43 |

[a] Temperature at which reaction orders were determined (°C).
[b] Order with respect to toluene.
[c] Order with respect to $H_2O$.
[d] Apparent activation energy (kcal/mol).
[e] Preexponential factor (molecules per second per metal site), in the equation $N = A \exp(-E/RT)$.
[f] Turnover rate at 1 hr on stream. $T = 440°C$, $P_{tol} = 0.08$ atm, and $P_{H_2O} = 0.26$ atm.
[g] Selectivity for benzene formation (molecules of benzene formed per molecule of toluene reacted).

of the Os and Ir catalysts was again used for determining the partial-pressure dependencies for the Os catalyst.

## DISCUSSION

In this section the results of the present study of the steam dealkylation of toluene will first be compared to the results of others for the steam reforming reaction over similar catalysts. Next the water/toluene reaction which has been investigated by several groups of workers (*1–12*) using a variety of catalysts will be discussed in relation to the present studies.

The catalytic steam reforming of hydrocarbons is used commercially to produce either hydrogen, synthesis gas (CO-$H_2$ mixtures), or $CH_4$, according to the following reactions:

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right) H_2, \quad (4)$$

$$CO + H_2O \rightarrow CO_2 + H_2, \quad (5)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O. \quad (6)$$

The overall reaction is characterized by the complete destruction of the hydrocarbon feeds according to reaction (4). The only hydrocarbons normally seen in the reactor effluent are aromatics such as benzene—illustrative of the inherent stability of the aromatic nucleus. The gaseous products normally attain equilibrium according to reactions (5) and (6). Catalysts commonly used for steam reforming contain nickel supported on a variety of supports (*19*).

The literature on steam reforming is voluminous and frequently contradictory. A recent book by Rostrup-Nielsen (*20*) provides an excellent up-to-date review of steam reforming catalysts. It is not the purpose of this paper to review steam reforming in general, but instead to incorporate into the discussion of the steam dealkylation reaction the general features of steam reforming applicable to *selective* steam reforming or steam dealkylation. A review of the literature on steam reforming provides one important conclusion. The conflicting results in the literature suggest on the one hand the complexity of the reaction and on the other hand the danger of extrapolating kinetic results much beyond the experimental conditions employed for the kinetic measurements. Thus the experimental results discussed in this paper should only be considered valid for the experimental conditions employed and the particular metal/support combinations described.

In spite of the wide use of the steam reforming process there has not been any extensive research into the kinetics of this reaction. Those studies that have been reported, in general, vary widely in their conclusions, principally because of the varied conditions and nature of the catalysts employed. The majority of the kinetic studies reported has used nickel catalysts [see Ref. (*19*)]. There are only a few investigations using noble metal catalysts (*20–24*), the most comprehensive study being that of Rostrup-Nielsen (*20*). He reported that the Group VIII metals (0.5 wt% noble metal/$Al_2O_3$) have the following relative specific activities for the steam reforming of ethane at 500°C and 1-atm total pressure: Rh, 100; Ru, 82; Pd, Pt, 9. Various nickel catalysts were reported by him to have activities comparable to those of the Pt and Pd catalysts. While rhodium and ruthenium catalysts have substantially higher activities than nickel catalysts, the greater costs of the noble metal catalysts preclude their practical use. The steam dealkylation of toluene is technically a selective steam reforming reaction. Depending on the noble metal chosen, the selectivity to benzene based on toluene reacted varies between 60 and 100%, as shown in Fig. 1B. The relative order of metal activity for total toluene reacted, as discussed in the Results section, is similar to that observed by Rostrup-Nielsen for ethane steam reforming.

The selective steam reforming or steam dealkylation of toluene converts toluene into the more valuable liquid, benzene. In addition to high yields of benzene, the steam dealkylation reaction produces a gas product similar in composition to that produced in steam reforming. The catalytic dealkylation of toluene to produce benzene is usually carried out in the presence of hydrogen and is a net consumer of increasingly expensive hydrogen. The potential value of using water in place of hydrogen to convert toluene into benzene in high yield and selectivity has led to extensive studies of this reaction principally in the Soviet Union, but also by workers in Japan and Germany.

Rabinovich and co-workers have extensively studied the activity of the noble metals for the steam dealkylation of toluene. The original experiments (*7*) were carried out in a pulse reactor and the following results were obtained for the activities of the various noble metals supported on $Al_2O_3$:

$$Rh > Pt > Pd > Ir, Ru > Os.$$

The comparisons in this series are not based on specific activities. More recently, Rabinovich and Mozhaiko (*9*) have reported kinetic results for the reaction of water and toluene in a flow reactor. Their results from the flow reactor studies are:

| | Rh | Ir | Pd | Pt | Ru | Os |
|---|---|---|---|---|---|---|
| Relative activity (430°C) | 100 | 13 | 11 | 5 | 3 | 1 |
| Percentage selectivity | 85–87 | 88–93 | 96–98 | 96–98 | 60–70 | 88–93 |

These relative activities are not based on specific catalytic activities (rates per surface metal atom) as in the present work. In their work they reported metal surface areas for several of their catalysts. From these data it is possible to calculate turnover rates which are compared in Table 3 to the results of this study. Also included in Table 3 is a comparison of their apparent activation energies to the apparent activation energies determined in this study. Kochloefl (*10*) has recently reported specific activities for the steam dealkylation of toluene over Rh, Pt, and Pd on alumina

TABLE 3

Comparison of Published Results to Present Results

| Catalyst | Turnover rate[a] $\times 10^3$ | Selectivity[b] | $E$[c] | Source |
|---|---|---|---|---|
| $Rh/Al_2O_3$ | 91.6 | 0.85–0.87 | 33 | Rabinovich and Mozhaiko (*9*) |
| $Rh/Al_2O_3$ | 27.1 | — | 24.3 | Kochloefl (*10*) |
| $Rh/Al_2O_3$ | 62.9 | 0.83 | 33.0 | This study |
| $Pd/Al_2O_3$ | 8.4 | 0.96–0.98 | 34 | Rabinovich and Mozhaiko (*9*) |
| $Pd/Al_2O_3$ | 4.8 | — | 18.8 | Kochloefl (*10*) |
| $Pd/Al_2O_3$ | 21.2 | 0.95 | 33.8 | This study |
| $Pt/Al_2O_3$ | 6.9 | 0.96–0.98 | 40 | Rabinovich and Mozhaiko (*9*) |
| $Pt/Al_2O_3$ | 10.4 | — | 15.5 | Kochloefl (*10*) |
| $Pt/Al_2O_3$ | 13.3 | 0.95 | 32.8 | This study |
| $Ru/Al_2O_3$ | 2.8 | 0.60–0.70 | 40 | Rabinovich and Mozhaiko (*9*) |
| $Ru/Al_2O_3$ | 32.6 | 0.60 | 42.5 | This study |

[a] Turnover rate = molecules of benzene formed per second per site at 440°C.

[b] Molecules of benzene formed per molecule of toluene reacted.

[c] Apparent activation energy (kcal/mol).

catalysts. His results are also compared in Table 3 to those of this study. The turnover rates of Rabinovich and Mozhaiko were calculated using their reported conversion data at 430°C and then were corrected to 440°C using their reported apparent activation energies. Kochloefl reported his activities at 450°C. His results were also corrected to 440°C using his reported apparent activation energies. It should be pointed out that the various activities were determined at different partial pressures of reactants (unspecified), which may account in part for the differences in reported values. However, as determined in this study, the effect of toluene partial pressure is near zero and the effect of $H_2O$ partial pressure is about one-half order for the various metals compared in Table 3; thus the corrections for partial pressure should be small. Mori and Uchiyma (*12*) have recently presented an activity sequence for the noble metal catalyzed steam dealkylation of toluene as follows:

$$Rh > Pt > Pd, Ir \gg Ru$$

Unfortunately, the authors did not state if this comparison was based on specific activities of the metal. All studies, however, point to Rh as the most active Group VIII element in the $H_2O$/toluene reaction.

With the exception of ruthenium, the results of the various researchers for specific activities of the noble metals agree quite well (within a factor of 4). Variations in the techniques used to prepare and characterize the ruthenium catalysts may in part account for the large difference in activity observed between Rabinovich *et al.* and this present study. The activity ranking of Ru determined in this study is consistent with the activity ranking reported by Rostrup-Nielsen (*20*) for ethane steam reforming. The range of selectivities and apparent activation energies reported by Rabinovich and co-workers agrees well with the results reported here. The apparent activation energies reported by Kochloefl are all substantially lower than either the results of Rabinovich *et al.* or the present results. These low values suggest the possibility of diffusional constraints in Kochloefl's experimental determination of activation energies.

There have not been any reports in the literature on the partial-pressure dependencies of the reactants in the water/toluene reaction. Table 2 presents the results of this present study for partial-pressure dependence of water and toluene. For all the metals studied, the partial-pressure dependence of toluene is near zero. For $H_2O$ the order of reaction varies from 0.3 to 0.7 for the catalysts studied. In Part 2 of this study a kinetic analysis is presented that fits these kinetic parameters to a power-law rate expression derived from an assumed reaction sequence.

## CONCLUSIONS

The specific activities, selectivities, and kinetic parameters of the supported Group VIII noble metals are presented for the steam dealkylation of toluene to produce benzene and light gases. The order and range of activities for benzene formation of the Group VIII metals studied are as follows: Rh, 100; Ru, 52; Pt, 34; Pd, 21; Ir, 14; Ni, 9; Os, 3. The percentage selectivities for benzene formation of the metals are: Pd, Pt, 95–100; Rh, Ir, 83–90; Ru, Os, 60–70; Ni, 40. These results qualitatively agree with results previously reported (*20*) for the order of activity of the noble metals for steam reforming of ethane. Where possible, the specific activities of the various metals for the water/toluene reaction have been compared to results previously reported for the same reaction. The present activity and selectivity results are in good agreement with the results presented in the literature. For the first time, the effect of reactant partial pressure on rates has been determined for the $H_2O$/toluene reaction. The order of reaction with respect to toluene is near zero for all the catalysts studied, while the order of reaction with respect to water is near one-half.

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