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The Chemistry and Catalysis of the Water/Toluene Reaction

2. The Role of Support and Kinetic Analysis

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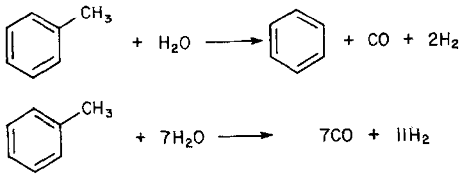
The influence of support on the activity of rhodium for the water/toluene reaction and the H_2/toluene reaction is investigated. It is shown that an effective catalyst for water/hydrocarbon reactions is bifunctional in the sense that both metal and support provide activation sites for reactants. In the selective steam dealkylation of toluene, as in total steam reforming reactions, the support significantly influences the catalyst's specific activity when based on the metal surface area. For example, in the steam dealkylation reaction the rate of benzene formation over a Rh/SiO_2 catalyst is only 1/37th the rate over a Rh/Al_2O_3 catalyst. The absence of support leads to an even further drop in the specific activity of rhodium, as a rhodium black catalyst is only 1/200th the activity of the Rh/Al_2O_3 catalyst. In contrast the support has no influence on the specific activity of rhodium for the H_2/toluene (hydrodealkylation) reaction. A Langmuir–Hinshelwood approach is used to describe the kinetics of the water/toluene reaction in terms of a surface reaction between activated water species (from support sites) and activated toluene (on metal sites for Rh and the other Group VIII metals investigated). This approach leads to a simple power-law rate expression of the form:

$$r = kP_{\mathrm{Tol}}{}^{n}P_{\mathrm{H_2O}}{}^{(1-n)/2}.$$

The observed kinetic parameters reported in Part I of this series of papers agree well with those predicted from this rate expression.

INTRODUCTION

With the rapid rise in hydrogen costs, petroleum conversion processes which utilize water in place of hydrogen will become increasingly attractive. The selective steam reforming or steam dealkylation of alkylaromatics to produce aromatics and hydrogen is an example of such a process. The simplest alkylaromatic/water reaction is that involving toluene. This reaction may occur by the selective steam reforming reaction (1) and/or the total steam reforming reaction (2) shown below.



(1)

(2)

In the first paper of this series (*1*) selectivities and kinetic parameters for the water/toluene reaction were presented for the Al_2O_3-supported Group VIII metals. Our results were compared to the work of other investigations for selective steam

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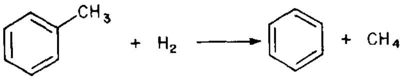
reforming and total steam reforming reactions.

It has been hypothesized (*2–6*) that the support is the principal site for water activation in total steam reforming reactions. Rostrup-Nielsen (*6*) studied the effect of support for total steam reforming of ethane. He concluded, based on activity measurements and partial-pressure dependencies, that the support was the activation site for water. Rabinovich and Mozhaiko (*7*) observed that changing the type of alumina altered the activity of rhodium for the steam dealkylation of toluene. In the present paper the effect of various supports on the activity of rhodium for the selective steam dealkylation of toluene is discussed.

A reaction similar to the selective steam dealkylation of toluene is the hydrodealkylation of toluene according to reaction (3).

 (3)

This reaction is also catalyzed by the Group VIII noble metals. In the present paper the effect of support on the activity of rhodium for this reaction is compared to the effect of support on the activity of rhodium for the water/toluene reaction. A future paper will discuss the kinetics of the H_2/toluene reaction over the Group VIII metals. In accordance with the observations discussed in the present paper, a reaction sequence is proposed which, with simplifying assumptions, leads to a simple power-rate law consistent with the kinetic results.

EXPERIMENTAL

The same experimental equipment and techniques described in Part 1 (*1*) were used to measure the metal surface areas and the kinetic parameters of the various catalysts studied.

For the Rh/SiO_2 catalyst, Cab-O-Sil, purchased from Cabot Corp. and having a surface area of 300 m^2 g^{-1}, was impregnated by incipient wetness techniques with an aqueous solution of $RhCl_3 \cdot 3H_2O$. For the Rh/C catalyst, Carbolac, obtained from Cabot Corp. and having a surface area of 950 m^2 g^{-1}, was also impregnated by incipient wetness techniques with an aqueous solution of $RhCl_3 \cdot 3H_2O$. Rhodium black was purchased from Engelhard Chemical Corp. and was used as received.

Prior to kinetic measurements the supported rhodium catalysts were all reduced for 1 hr in flowing H_2 at 500°C. The rhodium black catalyst was reduced at 420°C for 1 hr prior to kinetic measurements. For H_2 chemisorption measurements, the supported rhodium catalysts were reduced at 450°C in flowing H_2 for 1 hr and then evacuated at 400°C for 1 hr before cooling to room temperature and measuring the H_2 uptake. The rhodium black catalyst was reduced in flowing H_2 by heating in stages to 420°C and then held for 1 hr at 420°C before evacuating for 1 hr at 400°C. The catalyst was then cooled in vacuum to room temperature and the H_2 uptake was measured.

The same experimental apparatus as used for the water/toluene reaction studies was used to measure the kinetics of the reaction of hydrogen and toluene. For this reaction no water was added to the feed system. The kinetic parameters were all obtained in an analogous manner to those described in Part 1 of this study of the water/toluene reaction. The turnover numbers were determined at standard partial pressures of 0.36 and 0.10 atm of hydrogen and toluene, respectively.

RESULTS

The hydrogen chemisorption results for fresh rhodium catalysts are presented in Table 1. Also listed are the calculated metal dispersion values, fraction exposed[1]

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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

Dispersions of Metal Catalysts

Catalyst	H_2 uptake (μmol/g of catalyst)	Fraction exposed
1% Rh/Al_2O_3	47.7	0.98
2% Rh/Cab-O-Sil	69.7	0.72
4% Rh/C	81.2	0.42
Rh black	57.0	0.012

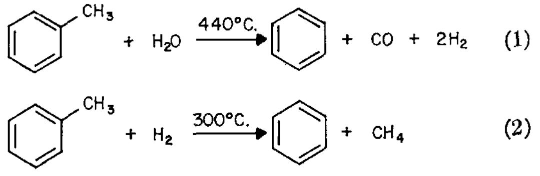
$= m_s/m_t$, where m_s is the number of surface metal atoms and m_t is the total number of metal atoms in the catalyst sample. The fraction exposed of rhodium atoms varies from 1 for Rh/Al_2O_3 to only 0.01 for rhodium black.

In Table 2 the effect of support on the turnover rate of rhodium for benzene formation by steam dealkylation [reaction (1)] and by hydrodealkylation [reaction (3)] is shown. For the steam dealkylation reaction there is a nearly two orders of magnitude difference between the Rh/Al_2O_3 and the Rh/C catalysts. The difference is even greater when comparing the Rh/Al_2O_3 catalyst to the rhodium black catalyst. In contrast, the hydrodealkylation activity of rhodium is virtually independent of support.

The selectivities to benzene for the catalysts are included in Table 2. For the steam dealkylation reaction the selectivities for the nonalumina-supported catalysts are all lower. In particular, the rhodium black catalyst has a very low selectivity of only 23% compared to 83% for the Rh/Al_2O_3 catalyst. For the hydrodealkylation reaction the selectivities of the supported metal catalysts are all greater than 90%, whereas the rhodium black catalyst has a selectivity of 85%. A series of nonalumina-supported and unsupported rhodium catalysts was mixed with equal parts of Al_2O_3 by light

TABLE 2

Effect of Support on Specific Activity and Selectivity of Rhodium for the Water/Toluene and Hydrogen/Toluene Reactions



Catalyst		Reaction 1		Reaction 2	
		TR[a]	Selectivity[b]	TR[c]	Selectivity[b]
1% Rh/Al_2O_3		0.0629	0.83	0.0036	0.95
2% Rh/Cab-O-Sil		0.0017	0.54	0.0036	0.94
4% Rh/C		0.0009	0.76	0.0047	0.99
Rh black		0.0003	0.23	0.0029	0.85
Rh black-Al_2O_3	(1:1)	0.0004	0.54	—	—
Rh/C-Al_2O_3	(1:1)	0.0008	0.90	—	—
Rh/Cab-O-Sil-Al_2O_3	(1:1)	0.0071	0.64	—	—

[a] Turnover rate at 1 hr on stream (molecules of benzene formed per second per metal site) at 440°C, $P_{Tol} = 0.08$ atm, and $P_{H_2O} = 0.26$ atm.

[b] Selectivity for benzene formation (molecules of benzene formed per molecule of toluene reacted).

[c] Turnover rate at 1 hr on stream (molecules of benzene formed per second per metal site) at 300°C, $P_{Tol} = 0.10$ atm, and $P_{H_2} = 0.36$ atm.

grinding with mortar and pestle. The activities and selectivities of these mixed catalyst systems for the water/toluene reaction are included in Table 2. With the exception of the Rh/SiO_2–Al_2O_3 mixed system there was little change in activity by inclusion of the Al_2O_3 component. In all cases, however, the selectivity to benzene increased with addition of alumina. The reasons for this increase are unclear at this time.

The kinetic parameters of the Group VIII metals supported on Al_2O_3 for the water/toluene reaction were presented in Part 1 of this series. For all the metals studied, the reaction orders with respect to toluene and water were near zero and one-half, respectively. For Rh/SiO_2 the orders of reaction for toluene and water are -0.05 and 0.5, respectively. For the Rh/C catalyst the orders of reaction for toluene and water are about 0.2 and 0.5, respectively. With both of these catalysts the activity and selectivity decreased markedly as a function of time on steam. The orders of reaction were therefore determined in the same manner as the method used for the Os/Al_2O_3 catalyst described in Part 1 of this study.

DISCUSSION

As discussed in Part 1 of this series, the steam dealkylation reaction can be considered a special type of steam reforming reaction. It is thus instructive to review the general steam reforming literature in order to gain some insight on the effect of support for H_2O/hydrocarbon reactions. Balashova *et al.* (*3*) studied the steam reforming of cyclohexane over Ni–C and Ni–SiO_2 catalysts. They found that the Ni–C catalyst was inactive for the reaction of cyclohexane with water, while the two catalysts had comparable activities for cyclohexane dehydrogenation. They attributed this to the failure of the carbon support to activate water. Bhatta and Dixon (*4*) observed substantially different kinetics for the steam reforming of *n*-butane over Ni–alumina and Ni–urania catalysts. They attributed the differences to be due to the support being the site for water activation on each catalyst, but with the rate of transport of "oxygenated species" being different for the two supports. Phillips *et al.* (*5*) studied the kinetics of *n*-heptane and *n*-hexane steam reforming and concluded that the support was the principle site for water activation. Rostrup-Nielsen (*6*) has made a comprehensive study of the steam reforming of ethane over Ni on a wide variety of supports. He found that Ni on carbon had substantially lower activity than Ni supported on either SiO_2 or Al_2O_3. The noble metals supported on carbon were also reported by him to be much lower in activity than when supported on Al_2O_3. Rostrup-Nielsen also made the point that the order of reaction for H_2O was sensitive to the support material, which he again attributed to the support's playing a major role in the water activation process.

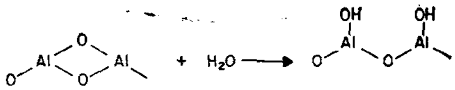
Rostrup-Nielsen (*6*) found a ratio of specific activities of about 25 for Ni/MgO compared to Ni/C. Depending on the type of alumina used, he found the ratio of Ni/Al_2O_3 to Ni/C to be somewhat larger or smaller than 25. The results presented in Table 2 for various rhodium catalysts also clearly indicate that the support plays a significant role in the water/toluene reaction. The difference in specific activity of Rh/Al_2O_3 compared to Rh/C for the toluene steam dealkylation reaction is about 70. For Rh black, the activity for steam dealkylation drops even further, being only 1/200th the activity of Rh/Al_2O_3. As shown in Table 2, the support does not affect the hydrogen/toluene reaction where only the metal sites are expected to be important.

Kochloefl (*8*) studied the effect of support on the activity of Rh supported on a variety of oxide supports. Although he did not directly compare the activities of the various catalysts based on specific metal surface areas, it is possible to calculate this comparison based on his reported metal surface areas for each of the catalysts. When making the comparison in this manner, his results show a range of specific activities of about one order of magnitude. He found Rh/Al_2O_3 to be 4.5 times the activity of Rh/SiO_2. These results differ substantially with the results presented in the present work. Once again this points out the difficulty of making direct comparisons of results by different workers for water/hydrocarbon reactions. It is quite possible that differences in experimental conditions and catalyst preparations and compositions could account for the observed differences in results.

Rabinovich and Mozhaiko (*7*) have studied the effect of support on the activity of rhodium for the steam dealkylation of toluene and the steam reforming of *n*-heptane. They performed these experiments by preparing a $Rh/\alpha\text{-}Al_2O_3$ catalyst and diluting this preparation with either $\alpha\text{-}Al_2O_3$, $\theta\text{-}Al_2O_3$, or $\gamma\text{-}Al_2O_3$, having surface areas of 1.3, 60, and 180 $m^2\ g^{-1}$, respectively. The activity of Rh increased by about a factor of 2.5 when comparing the $Rh/\alpha\text{-}Al_2O_3$ catalyst diluted with γ-alumina to the $Rh/\alpha\text{-}Al_2O_3$ catalyst diluted with α-alumina. The authors concluded that the water was being activated on the hydrophylic surface of the alumina.

Included in Table 2 are our measured activities for the water/toluene reaction over Rh black, Rh/C, and Rh/SiO_2 catalysts, each of which was diluted with equal parts of $\gamma\text{-}Al_2O_3$. In comparing the activities of these catalysts with the respective undiluted catalysts, only the Rh/SiO_2 catalyst diluted with $\gamma\text{-}Al_2O_3$ showed any significant difference in activity. For this catalyst the activity for benzene formation increased by a factor of 4. It is clear from the results in Table 2 that the support has a significant influence on the activities of supported metals for the water/toluene reaction. The results of the diluted catalysts suggest that this influence is complicated and must require a high degree of intimate mixing of metal and support. The mild mixing employed in the preparation of these mixed-support catalysts apparently precluded the intimate mixing of Al_2O_3 with the Rh/C catalyst and the relatively large particles of the Rh black catalyst.

Dydykina *et al.* (*9*) have proposed for the steam dealkylation of toluene over noble metal on alumina catalysts that the hydroxyl groups on the alumina support are the source of oxygenated species for the formation of CO in water/hydrocarbon reactions. They based their conclusion on the fact that the infrared stretching frequency of the hydroxyl groups decreased during reaction of toluene on the metal supported on alumina catalysts in the absence of added water. Concomitant with the disappearance of the hydroxyl groups' infrared spectra was the observance of CO in the product gas stream. Addition of water after the reaction completely restored the original infrared spectra of the hydroxyl ions. They proposed a scheme for water activation as follows:



(4)

The results of this present study are consistent with the support's being the principal site for water activation. Supports that readily and reversibly interact with water, such as alumina, are superior to supports such as SiO_2 which have only tightly bound hydroxyl groups or carbons and metal blacks which probably have only a few sites that might accommodate the type of dissociative water adsorption envisioned above.

In Part 1 of this study the total steam reforming reaction was briefly discussed. It is generally accepted that under steam reforming conditions hydrocarbons react irreversibly to form an equilibrium mixture of carbon oxides, hydrogen, methane, and water. The only hydrocarbons other than methane normally seen in the product effluent are basic aromatic structures such as benzene, which is indicative of the stability of the aromatic nucleus.

Consistent with the observation that water is activated on sites associated with the support according to a reaction scheme such as that in Eq. (4) and with the observation that hydrocarbon species other than benzene irreversibly react on metal sites, the following reaction sequences can be proposed for the water/toluene reaction:

$$H_2O + S - O - S \overset{k_w}{\rightleftarrows} 2\,OH - S, \qquad (5)$$

$$\mathrm{Tol} + M \xrightarrow{k_1} \mathrm{Tol} - M, \qquad (6)$$

$$\mathrm{Tol} - M \xrightarrow{k_2} CH_x - M + \text{benzene}, \qquad (7)$$

$$CH_x - M + OH - S \xrightarrow{k_3} \text{products}. \qquad (8)$$

In the above equations S refers to sites associated with the support and M refers to metal sites. Assuming a Langmuir model for adsorption of H_2O onto the support, the following expression can be written for the concentration of $OH - S$ species:

$$(OH - S) = \frac{(k_w P_{H_2O})^{\frac{1}{2}}}{1 + (k_w P_{H_2O})^{\frac{1}{2}}}, \qquad (9)$$

where k_w is the equilibrium constant for water adsorption. If the steady-state approximation is assumed and if $CH_x - M$ is assumed to be the most abundant surface intermediate, the following expression can be written for $CH_x - M$:

$$(CH_x - M) = \frac{[k_1 P_{\mathrm{Tol}}/k_3(OH - S)]}{[1 + (k_1 P_{\mathrm{Tol}}/k_3(OH - S))]}. \qquad (10)$$

With the use of the well-known approximation of the expression $ax/(1 + ax)$ by the expression bx^α, over a moderate range of pressures Eq. (10) can be replaced by the simpler expression:

$$(CH_x - M) = b\left(\frac{P_{\mathrm{Tol}}}{OH - S}\right)^n, \qquad (11)$$

where $0 < n < 1$, and b = constant. The rate of reaction can be written as

$$r = k_3(CH_x - M)(OH - S), \qquad (12)$$

and by substitution from Eqs. (9) and (11), the rate becomes

$$r = bk_3 P_{\mathrm{Tol}}{}^n \left[\frac{(k_w P_{H_2O})^{\frac{1}{2}}}{1 + (k_w P_{H_2O})^{\frac{1}{2}}}\right]^{1-n}. \qquad (13)$$

If the equilibrium constant, k_w, for water adsorption onto the support is small and/or the partial pressure of water, P_{H_2O}, is small, it can be assumed that $1 \gg (k_w P_{H_2O})^{\frac{1}{2}}$. If this assumption is made, the rate of reaction can then be simplified to

$$r = bk_3 P_{\mathrm{Tol}}{}^n (k_w P_{H_2O})^{(1-n)/2}. \qquad (14)$$

Equation (14) represents the rate of benzene formation as a power-law expression involving the partial pressures of the reactants toluene and water. The derivation of Eq. (14) constrains the value of n to be in the interval $0 < n < 1$. At the upper extreme of n near to 1, the rate of benzene formation becomes proportional to the partial pressure of toluene and independent of the water partial pressure. At the lower extreme of n near to 0, the rate of benzene formation is independent of toluene partial pressure and is one-half order with respect to the water partial pressure. In Part 1 of this series, the kinetic parameters for the water/toluene reaction over the alumina-supported Group VIII metals (except Fe and Co) were given (Table 2 in Part 1). Figure 1 shows as a function of periodic position the partial-pressure dependencies for water and toluene

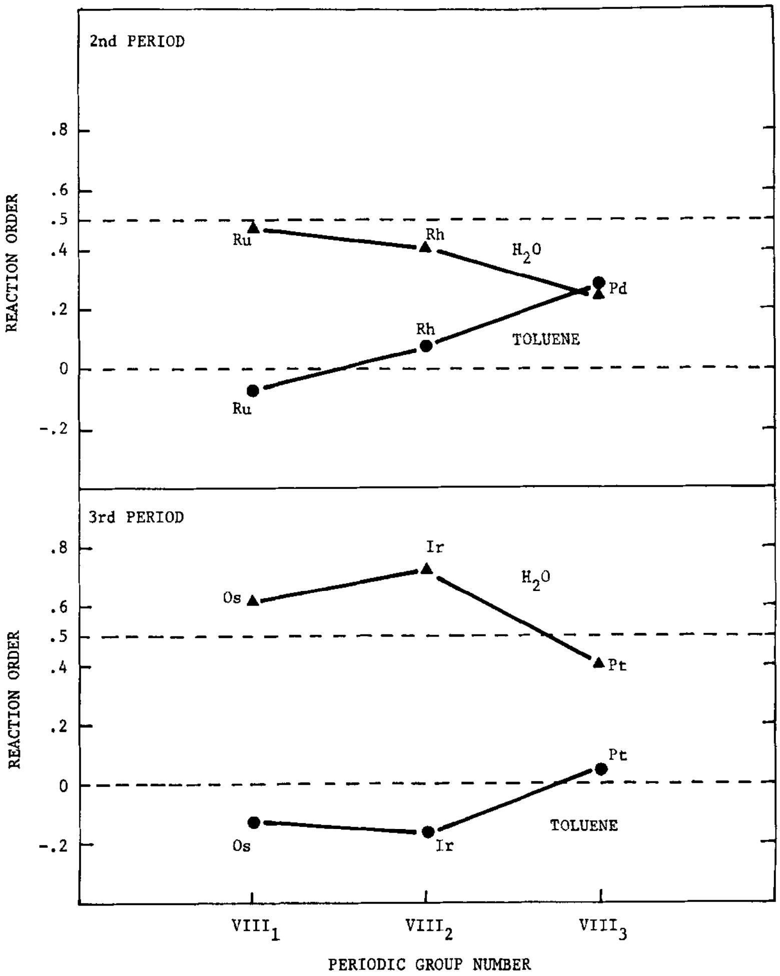


FIG. 1. Water and toluene reaction orders for Group VIII noble metals/γ-Al_2O_3.

for each of the metal/Al_2O_3 catalysts studied. As can be seen from Fig. 1, the values for the order of reaction with respect to toluene [parameter n in Eq. (14)] lie in the range of -0.2 to $+0.3$. That is, they all lie near to zero. The order of reaction with respect to water for all the catalysts is in the range of 0.3 to 0.7. That is, all values are near to $\frac{1}{2}$. The orders of reaction for the Rh/SiO_2 catalyst and Rh/C catalyst are also in the same range as the alumina-supported catalysts. It thus appears that if the lower limiting case of n approximately zero in Eq. (14) is assumed, then the experimental results agree reasonably well with the form of Eq. (14).

The values of the order of reaction with respect to toluene from Fig. 1 for Ru, Rh, Pt, and Ni are all quite close to zero. However, the values for Pd at 0.28 and Os and Ir at -0.13 and -0.16 are significantly far from zero. From Eq. (14) a positive value of the toluene order of reaction [parameter n in Eq. (14)] would predict a value for the water order of reaction to be less than $\frac{1}{2}$. As seen in Fig. 1, this is the case for Pd, although the calculated value from the expression $(1 - n)/2$ is only 0.35 compared to the experimental value of 0.25. The derivation of Eq. (14) constrains the value of n to be in the range $0 < n < 1$. Thus the theoretical derivation of Eq. (14) does not account for negative orders of reaction with respect to toluene as is observed experimentally for the Os and Ir catalysts. Nevertheless these values are not far from zero and therefore do not seriously invalidate the form of Eq. (14). More importantly, the form of Eq. (14) predicts an inverse relationship between the toluene exponent and the water exponent. As seen in Fig. 1, this is clearly observed experimentally. In general, n increases with increasing atomic number and the water order correspondingly decreases. Thus Eq. (14) directionally predicts the experimentally determined values for the water order of reaction. The good agreement of the interrelation of the toluene and water exponents in no way validates the assumed kinetic sequence, but at least provides some measure of success for the assumed reaction sequence. Inherent in the derivation of the rate expression given in Eq. (14) are the well-known limitations associated with the use of Langmuir isotherms to represent the surface coverage of adsorbed species. The spirit of the proposed reaction sequence was to develop the simplest reaction model leading to a power-law rate expression for comparison to observed kinetic parameters. Other more complicated sequences could be proposed. Nevertheless, the simple sequence proposed here gives a rate expression capable of duplicating the observed partial-pressure dependencies. More importantly, the reaction sequence provides insight into the importance of both metal and support in the overall water/hydrocarbon reaction sequence.

Part 1 of this study (*1*) reviewed the results of other researchers' studies of the catalysis of the water/toluene reaction. In the comprehensive studies by Rabinovich and co-workers [see Refs. *1–9* in Part 1] and by Kochloefl (*9*), neither group published any information on the orders of reaction for the various catalysts studied. Kochloefl (*9*) reported that his results for $Rh/\gamma\text{-}Al_2O_3$ and $Rh/\alpha\text{-}Cr_2O_3$ could be fit by a Langmuir–Hinshelwood expression for a bimolecular surface reaction having the following form:

$$r = \frac{kK_TK_{H_2O}P_TP_{H_2O}}{(1 + K_TP_T + K_{H_2O}P_{H_2O})^2}. \qquad (15)$$

The general derivation of an expression of this form assumes that both water and toluene compete for similar sites. The results discussed in this present paper suggest, on the other hand, that under the experimental conditions employed in this study water and toluene do not compete for identical sites. Water is activated on sites associated with the support and toluene is activated on metal sites, which are then followed by a surface reaction of the independently activated species. As stated previously, Rabinovich and Mozhaiko (*7*) have proposed a mechanism for water activation similar to the one employed in this paper. Kasaoka and co-workers (*10*) have studied the water/toluene reaction over a $Rh\text{-}Pt/Al_2O_3$ catalyst. They report that the orders of reaction for toluene and water are 0.25 and 0.35, respectively. It is possible to use their experimental value of $n = 0.25$ to calculate a value for the water order of reaction according to Eq. (14). This calculation gives a calculated value of 0.38 for the water order of reaction, which compares well with their experimental value of 0.35. Kasaoka and co-workers did not speculate on a mechanism for the water/toluene reaction.

The results discussed in this paper and observations of others for steam reforming and steam dealkylation reactions in general support the thesis that the support is the primary activation site for water with supports such as Al_2O_3. The reaction sequence discussed above uses this notion along with the assumption that in the absence of large amounts of hydrogen the sequence of hydrocarbon reactions occurring at metal sites is irreversible. The reaction sequence and analysis chosen are the simplest possible given the above observations. The general success at correlating the experimental results lends credence to the simple model chosen but does not unequivocally verify it. Undoubtedly more complicated models consistent with more realistic assumptions such as heterogeneous surfaces, as proposed by Boudart (*11*), could lead to different expressions. However, the simple Langmuir–Hinshelwood approach taken here still provides insight into the nature and importance of the surface reactions taking place.

CONCLUSIONS

The steam dealkylation of toluene can be considered to be a special type of steam reforming reaction. The results presented in this paper clearly show that the efficient catalysis of this reaction must involve effective activation of water on sites associated with the support. A Langmuir–Hinshelwood approach was used to describe the kinetics of the water/toluene reaction in terms of a surface reaction between activated water species (from support sites) and activated toluene species (on metal sites). This approach leads to a simple power-law rate expression of the form:

$$r = kP_{\mathrm{Tol}}{}^{n}P_{\mathrm{H_2O}}{}^{(1-n)/2}. \qquad (17)$$

The observed kinetic parameters agree well with those predicted from Eq. (17). The conclusions presented here are generally consistent with the results of Rabinovich and co-workers for their studies of the water/toluene reaction.

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