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Noble Metal-Catalyzed Water–Hydrocarbon Reaction Paths

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An investigation of water–hydrocarbon reactions showed vanadium to be a strong promoter for the Rh/Al_2O_3-catalyzed reaction of water and toluene to produce benzene. Studies with $Rh/VO_x/Al_2O_3$ were extended to other structurally different hydrocarbons to determine major reaction pathways. A nonaromatic hydrocarbon that cannot aromatize by simple dehydrogenation undergoes random carbon–carbon bond scissions and the resulting fragments react with water to give gaseous products. Cleavage of aromatic carbon–carbon bonds is much slower. This along with the selective adsorption of high molecular weight compounds results in an accumulation of low molecular weight aromatics in the product mixture. Phenanthrene is converted to naphthalene and benzene with no evidence for initial cracking of the central C–C bonds.

INTRODUCTION

Water as a hydrogen source in hydroconversion processes is attractive because of the increasing cost of molecular hydrogen and efficient heat balance which can be obtained by combining the conventional steam reforming process (endothermic) and the hydrotreating processes (exothermic).

A prototype of a selective steam reforming process is the steam-dealkylation reaction for which considerable literature data exist (*1–5*). This study was undertaken to evaluate various noble metal catalysts for this reaction and to examine the reactions of a variety of structurally different hydrocarbons with water over a selected catalyst system.

EXPERIMENTAL

Materials. A 0.6% Ru/Al_2O_3 and a 0.6% Ir/Al_2O_3 catalyst, both characterized to have fully dispersed metal components, were obtained from D. J. C. Yates, and a Ba promoted massive nickel catalyst (*6*) from A. Barnett of this laboratory. Other catalysts were prepared by the usual incipient wetness impregnation technique using aqueous solutions of $RhCl_3 \cdot xH_2O$, H_2PdCl_4, H_2PtCl_6, $Ni(NO_3)_2 \cdot 6H_2O$ and a freshly calcined γ-Al_2O_3 of 20–40 mesh size and 100-m^2/g surface area. After drying, the Pt, Rh, and Pd catalysts were further calcined in air at 450°C for 1 hr. Rhodium catalysts containing vanadium oxide promoter were prepared by two methods. In one case alumina is impregnated with an ethanol solution of $VOCl_3$, dried in air at 120°C, and impregnated with a $RhCl_3$ solution in the usual way. This method was used to obtain a 1.35% Rh–VO_x (2.4% as metal)/Al_2O_3 catalyst. In another case a VO_x/Al_2O_3 catalyst is prereduced at 500°C with hydrogen before the Rh deposition step. A 0.6% Rh–5.6% VO_x/Al_2O_3 catalyst

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TABLE 1

Dispersion and Specific Activities in Water–Toluene Reaction

Catalyst wt% as metal on Al_2O_3	H_2-Chemisorption		H_2O/Toluene reaction[b]	
	H/M[a]	Percentage dispersion	10^3 × turnover number at 400°C[c]	Apparent Ea (kcal/mol)
0.6 Rh	1.11	100	13.4	32
0.6 Pd	0.81	81	7.7	31
0.6 Pt	1.33	100	3.5	35
0.6 Ru	1.50	100	2.0	35
0.6 Ir		100	1.5	32
10 Ni	0.20	20	2.0	29
0.3 Rh/0.3 Pt		(100)	18.0	34
0.6 Rh/5.6 VO_x	0.69	69	61.0	32
1.35 Rh/2.4 VO_x	0.62	62	34.0	31

[a] Group VIII metal.

[b] H_2O/Toluene mole ratio: 3.9, toluene feed rate: 2.0 ml/hr.

[c] Molecules benzene formed/surface Group VIII metal atom × sec.

was made according to this method. Reagent grade chemicals purchased from Aldrich were checked by glpc analyses and used without further purifications. Deionized water was used in the catalyst preparation as well as in the reactions.

Procedures. The chemisorption measurements were performed according to the procedure described by Vannice (*7*). A 70°C isotherm at low H_2 pressure was determined for the palladium catalyst (*8*). A quartz tube (13-mm i.d.) with a Pyrex wool plug was used as a micro fixed bed reactor. The hydrocarbon and water feeds were introduced to the preheating zone of the reactor with syringe pumps and the effluents from the reactor were passed through a trap cooled at −78°C. The gaseous and liquid products thus separated were analyzed by glpc and mass spectroscopy. Temperature control was accomplished with a thermocouple directly inserted into the catalyst bed and a proportional controller, West Model JP. All measurements were done under 1 atm.

For rate measurements, catalysts were ground to collect a 60–80 mesh fraction, an amount in the range of 0.2–1.0 g was charged to the reactor and reduced in H_2 at 500°C for 1 hr. At a preset temperature, water and toluene were pumped at rates of 1.31 and 1.73 g/hr, respectively. After 30 min from the start of feeds, products were collected for 30 min and analyzed. Runs were carried out at several temperatures under conditions where conversions did not exceed 10%.

In runs at high conversions, the original catalysts of 20–40 mesh size were used after reduction at 500°C. Products eluting at 30–150 min from the start were analyzed. In all runs involving the Rh–VO_x catalyst, no significant activity decline was observed during periods of at least 8 hr. The spent Rh–VO_x catalysts from such runs typically contained 0.5 wt% carbon. Naphthalene was pumped as a melt. Glpc analyses were done with a Porapack Q column for gases and a silicon oil DC 550 column for liquids. The carbon and hydrogen balances were usually 100 ± 5%.

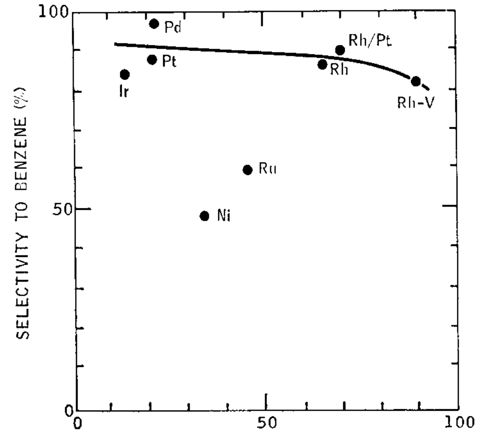


FIG. 1. Conversions and selectivities achieved by various catalysts in the H_2O/toluene reaction at 460°C. In each run 1.6 g of catalyst (0.6% noble metal/Al_2O_3, 0.6% Rh/5.6%VO_x/Al_2O_3, 5% Ba/25% Ni/Al_2O_3) was used with a toluene flow rate of 2.0 ml/hr and H_2O/toluene mole ratio of 3.9.

RESULTS AND DISCUSSIONS

Water-Toluene Reaction

Since the original concept of a steam dealkylation reaction was reported by Haensel (*9*) in 1948, the catalysis for this reaction has become the subject of extensive investigations especially in the last decade. This is primarily due to the projected incentive for a process that produces benzene and hydrogen from toluene compared to the conventional hydrodealkylation process that consumes hydrogen.

From the thermodynamic point of view, the dealkylation reaction is the least favored of the following paths:

		ΔG700°K kcal/mol
(1)	$C_6H_5CH_3 + 2H_2O \rightarrow C_6H_6 + CO_2 + 3H_2$	-1.6
(2)	$C_6H_5CH_3 + 14H_2O \rightarrow 7CO_2 + 18H_2$	-17.7
(3)	$C_6H_5CH_3 \rightarrow 5C + 2CH_4$	-61.2

The nickel catalysts that were used in earlier works (*10–12*) lack satisfactory selectivity features, e.g., Slovokhotova *et al.* (*11*) estimate that with a 5% Ni/SiO_2 catalyst the reaction proceeds 40% via path 1, 45% via path 2, and 15% via path 3. Noble metal catalysts, on the other hand, are claimed to be much more selective, 80–95% for path 1 at conversion levels up to 70% and minimal coking (*1–5*). A study was undertaken to confirm these claims and to establish a meaningful basis in selecting a standard catalyst for the model compound studies.

TABLE 2

Water–Hydrocarbon Reactions over Rh–V/Al_2O_3 at 480°C[a]

Compound	H_2O/HC mole ratio	Conv. (%)	100 × moles product/mole feed converted								
			H_2	CO_2	CO	CH_4	C_2H_6	Benzene	Toluene	Others	
Benzene	4.9	40.5	875	381	80	102	tr	—	1.5		
Toluene	5.7	92.7	435	180	30	43	1.4	83.7	—	Xylenes	0.17
n-Propylbenzene	7.6	67.9	518	203	29	40	19	38.6	35.7	Et-Benzene	14.4
n-Heptane	8.1	76.1	990	319	60	106	30	8.7	5.4	C_4–C_6	2.5
Me-Cyclopentane	6.1	58.8	793	264	78	113	28	14.9	3.8	C_3–C_5	1.0
Me-Cyclohexane	7.2	99.5	630	102	39	16	tr	69.8	13.3		
Diphenylmethane	9.1	64.2	1070	378	72	24	tr	66.5	20.0	Flourene C_8–C_{12} Arom.	6.5 16.3
Diphenylethane	10.8	79.2	780	305	40	14	tr	87.6	35.9	C_{14} Arom. C_8–C_{12} Arom.	7.6 12.8
cis-Decalin	8.4	97.4	634	44	5.5	12	tr	7.5	4.0	Tetralin Naphthalenes	2.4 78.9
Tetralin	7.4	100	480	119	18	9.4	tr	22.6	6.6	Naphthalenes	70.4
Naphthalene	7.1	40.2	980	449	64	30	tr	54.6	12.2	$C_8 + C_{11}$	2.2
9,10-Dihydrophenanthrene[b]	9.0	100	790	268	103	2.3	tr	12.1	2.7	Naphthalene Phenanthrene	36.6 40.2

[a] 1.6 g of 1.35% Rh–VO_x (2.4% as metal)/Al_2O_3 was used with 4.0 ml/hr liquid feed rates for both the hydrocarbon and water

[b] 540°C

TABLE 3

Reactions of Naphthalene Derivatives with H_2O and H_2[a]

	H_2O/Naphthalene	H_2O/Tetralin	H_2O/Decalin	H_2/Naphthalene
Mole ratio	7.1	7.4	8.4	7.8
Conversion to products excluding naphthalene and tetralin, (%)	40.2	32.7	17.0	16.0
Selectivity[b] (%)				
Methylnaphthalenes	1.6	2.1	6.3	27.9
Xylenes	0.7	1.0	5.4	7.9
Toluene	12.5	19.6	21.2	25.2
Benzene	55.6	66.9	39.7	22.4
Total gasification	29.6	10.4	27.4	16.6

[a] For reaction conditions, see footnote *a* of Table 1.

[b] Calculated based on materials recovered.

The results of hydrogen chemisorption and kinetic measurements are summarized in Table 1. The rate data for the Rh, Pd, Pt, Ir, and Ni catalysts are in close agreement with the results published by Grenoble (*5*), the turnover numbers differing by a factor not greater than 1.5. The activity of the Ru catalyst used in this study was, however, about three times lower than that reported by Grenoble.

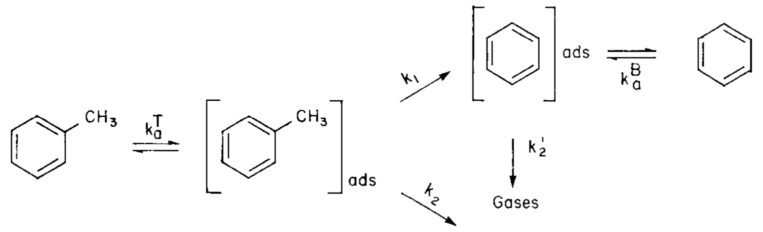
An important finding of this study is that vanadium is a strong promoter in the Rh/Al_2O_3 system causing a two- to fourfold activity enhancement, while it is inactive by itself. Mori and Uchiyama noted that a similar rate enhancement was observed when a UO_2 component was incorporated into a Rh/Al_2O_3 catalyst (*4*). This was attributed to the ability of UO_2 in removing CO from Rh sites via a facile redox cycle involving water. In the present study, no significant variation in the amount of CO in the product gas stream was observed by changing the catalyst from Rh/Al_2O_3 to $Rh–VO_x/Al_2O_3$. Although it is not possible to rule out the mechanism of Mori and Uchiyama for the present stystem, the following alternative explanation seems to be more attractive at this time. It was previously observed that a vanadium oxide/Al_2O_3 catalyst is active in an olefin–water reaction leading to saturates and CO_2 (*13*). For example, over a reduced VO_x/Al_2O_3 catalyst styrene readily reacts with water to give mostly ethylbenzene along with benzene, toluene, and CO_2, indicating that partial steam reforming coupled with *in situ* hydrogenation is occurring. It is conceivable that in the toluene reaction, some of the hydrogen-deficient intermediates produced on Rh sites move to vanadium sites to complete the reaction.

The performance of catalysts at high conversions was also examined and the results are represented by the selectivity–conversion plot shown in Fig. 1. Clearly Ru and Ni catalysts are not nearly as selective as the other noble metal catalysts which give 83–96% selectivity at various conversion levels up to 89%. The selectivity is thus determined mainly by the metal (*1*, *5*) but is also a function of the degree of conversion (*14*). The $Rh–VO_x$ catalyst, for example, gives an increased selectivity of 93% at 55% conversion at 400°C.

Water–Hydrocarbon Reaction Paths

The reactions of a number of structurally different hydrocarbons with water were examined over a $Rh/VO_x/Al_2O_3$ catalyst. The following standard reaction conditions were used: 480°C, 1 atm pressure, 4.0 ml/hr liquid feed rate for both the hydrocarbon and water, and 1.6 g (2.0 cm^3 bulk volume) of 1.35% Rh/2.4% VO_x/Al_2O_3. This allowed high conversions of feed, usually above 50%, which allowed easy and unambiguous identification of the products, especially those from minor reaction paths. The results, summarized in Table 2, are discussed separately for each class of compounds.

Alkylbenzenes. Benzene readily undergoes gasification to C_1 gases with a conversion of 41% under the standard conditions. Yet, the reaction of toluene leads to benzene with 84% selectivity at a 93% conversion level. This result cannot be explained by a scheme involving simple successive reaction steps, for the adsorbed benzene precursor generated in the toluene reaction has a minimum 40% chance of undergoing further fragmentation reactions. One reasonable explanation involves competitive adsorption phenomena such as the following:



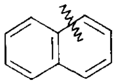
It is suggested that readsorption of benzene is effectively suppressed because of $k_a^T \gg k_a^B$. This is in line with the observation that the selectivity of a particular catalyst changes very little over a wide conversion range from less than 10 up to 70% (cf. data in *1*, *5*, and Fig. 1). Other observations also consistent with such a view have been frequently made throughout this study, e.g., toluene, when mixed with strongly adsorbing species such as condensed aromatic compounds, did not undergo significant conversion under the standard condition.

Another aspect of interest is the cracking modes of long side chains. *n*-Propylbenzene converts with a combined selectivity of 89% to a mixture of benzene, toluene, and ethylbenzene, showing no particular preferences. Maslyanskii *et al.* proposed (*15*) that over a nickel catalyst alkylbenzenes are adsorbed via the alkyl groups, the benzene ring oriented away from the surface. They suggested the initiation of cracking proceeds from the end of the alkyl chain opposite to the ring. With diphenylmethane and 1,2-diphenylethane, an adsorptive configuration of both rings oriented away from the surface would be difficult to attain because of the expected steric crowding. Yet the reactions proceed smoothly to give high yields of benzene and toluene together with some by-products from dehydrogenation and dehydrocyclization paths, fluorene, stilbene, phenanthrene, etc. Thus, the exact sequence of cracking steps is not clear at this time. Random side-chain scissions, like that observed in the hydrogenolysis of *n*-butylbenzene over a Pt/Al_2O_3 catalyst (*16*), may take place, the resulting alkyl fragments undergoing further reactions to C_1 gases.

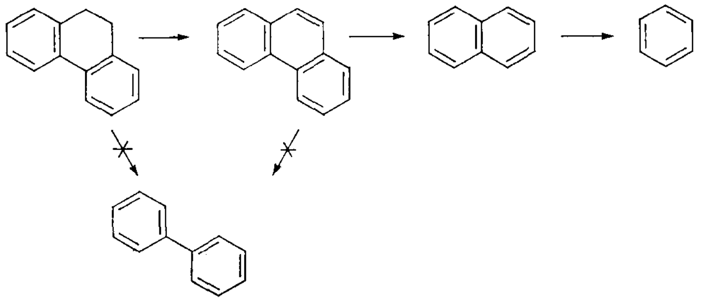
Alkanes. The reaction of *n*-heptane occurs via two major paths, gasification and dehydrocyclization, with selectivities of 86 and 14%, respectively. This is in accordance with the results obtained by Rabinovich *et al.* (*17*) with a Rh/Al_2O_3 catalyst. Characteristic of the gasification pathway is the virtual absence of C_4–C_6 products which are possible intermediates on the catalyst surface. Methylcyclopentane gives a similar reaction pattern, 81% total gasification and 19% reforming to aromatics. No trace of cyclopentane was detected. Methylcyclohexane, on the other hand, undergoes fast dehydroaromatization to toluene, followed by the usual steam dealkylation step. Assuming the benzene fraction was formed from toluene with a selectivity of 84%, it can be estimated that the first aromatization step occurs with a 97% selectivity. This shows that the total gasification path, which usually dominated the reactions of other alkanes, does not effectively compete with the aromatization reaction.

Condensed ring compounds. Naphthalene readily reacts with water to give 40% conversion under the standard condition with a relatively high 70% selectivity to liquid products, mainly benzene and toluene. 1,2,3,4-Tetrahydronaphthalene (tetralin) and perhydronaphthalene (decalin) undergo reactions that can be characterized by a general sequence of dehydroaromatization to naphthalene, followed by the reaction with water. For example, tetralin is converted almost quantitatively to naphthalene at 400°C and the reaction pattern at 480°C excluding the naphthalene fraction is very similar to that of the naphthalene run (Table 3). Along the series, naphthalene, tetralin, and decalin, however, trends can be detected in both the conversion and selectivity data shown in Table 3. An obvious factor is the hydrogen produced by the initial aromatization step, and accordingly a H_2-naphthalene reaction under a comparable condition was examined. As noted in the last column of Table 3, a reduced level of 16% conversion was obtained with a distinctly different selectivity pattern. The most interesting observation is the formation of a significant amount of a mixture of isomeric methyl-naphthalenes. This is exactly the reverse of the hydrodemethylation reaction and in this case the surface CH_x species is trapped by the feed. The ability of water to efficiently scavenge CH_x species from the catalyst surface (*5*) provides a simple explanation for the increased conversion and decreased methylnaphthalene selectivity in the H_2O/naphthalene run as compared with the H_2/naphthalene reaction.

An indication of the pathway leading from naphthalene to benzene derivatives is derived from the observation that xylenes are formed only in very small amounts that can be readily accounted for by a reverse demethylation path similar to that leading to methylnaphthalenes. As *n*-propylbenzene reacts to given major amounts of toluene and ethylbenzene, dialkylbenzenes would be expected to yield significant amounts of xylenes. Thus, the virtual lack of this product from the water–naphthalene reaction suggests that hydrogenated species, e.g., tetralin, are not intermediates in the cracking pathway. Direct scissions of aromatic carbon–carbon bonds represent the remaining possibility. The first step may well be the scission of the C_1–C_9 bond, as shown below.



9,10-Dihydrophenanthrene reacts in a manner predictable from the above results, a facile dehydrogenation to phenanthrene precedes successive end-ring gasification steps. No trace of biphenyl was detected in the product mixtures.



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