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Hydrodimerization* of Benzene to Phenylcyclohexane over Supported Transition Metal Catalysts

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Phenylcyclohexane has been obtained in high yield from the hydrogenation of benzene over a variety of supported transition metal catalysts. Both acidity and hydrogenation activity are necessary catalyst properties. Cyclohexene is believed to be a key intermediate which migrates from metal hydrogenation sites to acid sites where subsequent alkylation of benzene occurs.

INTRODUCTION

In 1934 Truffault reported that some phenylcyclohexane is formed, in addition to cyclohexane, when benzene is hydrogenated in the presence of phosphoric anhydride and a nickel black catalyst (*1*). Recent patents have claimed that phenylcyclohexane is obtained from the hydrogenation of benzene over certain supported transition metal catalysts (*2–4*). Catalysts claimed are a Group VIII metal on silica-alumina (*4*), a hydrogenation metal on a cracking catalyst (*2*), and a combination of a hydrogenation metal and a heteropolyacid (silicatungstic acid, phosphomolybdic acid, etc.) on a variety of supports (*3*). We had independently studied this novel reaction in considerable detail and would like to report on the mechanism of the reaction and to discuss the important properties of the catalysts.

It is interesting that catalysts of a different type, namely, supported alkali metal catalysts, also promote the hydrogenation of benzene to phenylcyclohexane in good yield (*5*).

EXPERIMENTAL

Reagents. The catalyst supports were either purchased or prepared as described in the literature. Descriptions of most of these materials are given in Tables 1–3. Sodium Y faujasite was obtained from the Linde Division of the Union Carbide Company. Sodium mordenite was supplied by the Norton Company. Ammonium mordenite, kindly supplied by Dr. H. A. Benesi, was prepared from Na mordenite by washing the latter with aqueous ammonium nitrate at room temperature. The metal salts employed were all commercially available in high purity. The benzene was Baker's analytical grade material and was either used as is or was purified by passing the hydrocarbon through Linde 4A molecular sieve. The water and sulfur contents of the benzene are listed in the text.

Supported catalysts prepared from nickel fluoride. The support (crystalline zeolites not included) was added to a water solution of nickel fluoride and the mixture stirred until the supernatant liquid was nearly colorless. The catalyst was recovered by filtration and washed with distilled water to remove the nickel which was not strongly adsorbed. The material was heated to 500° in air for 2–4 hr.

Supported catalysts from nickel nitrate. The support (crystalline zeolites not included) and an aqueous solution of nickel nitrate were stirred together for 1 hr and

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[*] For convenience, this term is used, without mechanistic implications intended, to designate the formation of phenylcyclohexane from benzene and hydrogen.

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then the solvent was removed on a rotating evaporator. The resulting solid was not washed but was heated in air at 500° for 2–4 hr.

Supported nickel/tungsten catalysts. First, the nickel salt was placed on the support (crystalline zeolites not included) via the appropriate procedure above. Next, the tungsten salt, either tungstic acid dissolved in ammonium hydroxide or ammonium metatungstate dissolved in water, was placed on the support by the same procedure as was used for supporting nickel nitrate (see above). The resulting catalyst was heated in air at 500–550° for 2–4 hr.

Supported palladium and platinum/MS-A-3 catalysts. These catalysts were prepared by impregnating MS-A-3 powder with a minimum volume of a solution of either diamminopalladous chloride or diamminoplatinous chloride. Fluorine was added as aqueous hydrogen fluoride. The resultant solid was heated in air at 500° for 2–4 hr.

Nickel on Y faujasite or mordenite supports. The following procedure is typical of the procedure employed to support nickel on sodium Y faujasite, sodium mordenite or ammonium mordenite. Ten grams of nickel acetate (40 mmoles) in 80 ml of water was added to 20 g of sodium Y faujasite. The mixture was stirred and refluxed for 1 hr. The solid was filtered and washed with water until no nickel could be detected in the wash with diglyoxime. With some catalysts, the procedure was repeated to increase the nickel content. The resultant solid was heated in air at 500–600° for 1–2 hr.

Supported $NiF_2/ZnCl_2$ and $NiF_2/AlCl_3$ catalysts. Nickel fluoride (1.7 g) was dissolved in hot water and 20 g of alumina (Al_2O_3-C, see footnote *b*, Table 1) added to make a slurry. The mixture was stirred for 1 hr. The solid was filtered and washed with 500 ml of hot water and then dried on a hot plate. The dried solid was added to water containing 2 g of dissolved zinc chloride. The solvent was evaporated and the solid dried on a hot plate. Finally the solid was heated at 400° for 20 min and used immediately as a catalyst.

The same procedure was used for supporting nickel fluoride and aluminum chloride on alumina.

Hydrodimerization of benzene in stirred autoclaves. The benzene and freshly predried catalyst were placed in a stainless steel, 85-ml autoclave. The quantities of the reagents and the reaction conditions are listed in Tables 1–3. After the vessel was sealed and hydrogen introduced, the system was heated to the desired temperature. The autoclave was heated by placing it in a brass cup which was wrapped with a heating coil. Stirring was provided by a bar magnet (sheathed with stainless steel) placed inside the autoclave. The bar magnet was set in motion by an external magnetic stirrer. The progress of the reaction was followed by the decrease in the pressure, as measured by a suitable transducer and recorder. The reactions were not rate-limited by the rate at which hydrogen dissolved in the solvent since, under the same conditions, rates of hydrogenation of olefins have been observed to occur at rates 10 to 100 times greater than those observed for the above hydrogenations of benzene.

Occasionally, the catalyst was prereduced in the absence of benzene by heating it in the autoclave under hydrogen pressure for 20 min at 300°. The system was then cooled and the benzene introduced.

The compounds in the products were identified by the coincidence of their glpc emergence times and mass spectrometric fragmentation patterns with those of authentic materials. The phenylcyclohexane was further identified by its unique infrared spectrum. Quantitative analyses of the products also were made by glpc.

Flow experiments with tubular reactors. Two techniques were employed in these experiments. In one case, benzene (also hydrogen) was introduced at the top of the reactor tube and allowed to trickle through the catalyst bed (downflow experiments). In the second case, the benzene (also hydrogen) was introduced at the bottom of the reactor tube and forced through the catalyst bed (upflow experiments). The yields of products differed somewhat in the downflow and upflow experiments. In the downflow experiments, the yields of the by-products cyclohexane and trimeric (C_{18}) compounds were both significantly higher by 10–15% than in the corresponding upflow experiments. Whereas an entirely liquid-phase condition exists in the latter case, considerable vaporization of the benzene must occur in the downflow experiments since the tube is only partially filled with the substrate. We believe the higher yields of C_{18} components formed in the downflow experiments are a consequence of a resultant greater concentration of phenylcyclohexane in the liquid medium. The increased amount of cyclohexane formed in this case, probably, is a result of greater availability of hydrogen on the catalyst surface which diverts intermediate species (see below) to cyclohexane rather than to phenylcyclohexane.

Hydrodimerization of benzene with physically mixed catalyst pairs. A 2.6% Ni/Al_2O_3 catalyst was prepared from nickel nitrate and Alcoa F-20 alumina and pretreated in the usual manner. Likewise, a Ni/SiO_2 catalyst was prepared. The hydrogenation of benzene (0.45 mole) with these catalysts (5 g) at 200° and 800 psi produced only cyclohexane. Under similar conditions, MS-A-3 was totally inactive.

When a physical mixture of either Ni/Al_2O_3 and MS-A-3 or Ni/SiO_2 and MS-A-3 were used, phenylcyclohexane was formed. The supported nickel catalysts and the MS-A-3 employed were independently ball-milled, dried at 500° for 2 hr, and then prereduced with hydrogen at 300° for 0.3 hr. The catalyst pairs were mixed by shaking together in a bottle prior to introduction into the autoclave. The reaction conditions were the same as those given above. The reaction times were 11 and 2 hr, respectively, for the two mixtures Ni/Al_2O_3 and MS-A-3, and Ni/SiO_2 and MS-A-3. In the former case with 11% of the benzene converted, the yields were as follows: phenylcyclohexane, 83.9%; cyclohexylcyclohexane, 5.8%; trimer, 3.1%; cyclohexane, 6.2% and methylcyclopentane, 1.0%. With the Ni/SiO_2 and MS-A-3 mixture, the yields with 16% of the benzene converted were as follows: phenylcyclohexane, 66.9%; cyclohexylcyclohexane, 6.4%, trimer, 5.9%; cyclohexane, 18.2%; and methylcyclopentane, 2.5%.

Thermal reaction of benzene with a Ni/W/F/MS-A-3 catalyst. A test of the feasibility of the mechanism shown by Eqs. (9) and (10) of the text was made as follows. An 0.8% Ni/18.4% W/2.4% F/MS-A-3 catalyst (5 g) was prepared and benzene hydrodimerized in the usual manner to verify that the catalyst was active. Subsequently, the catalyst was recovered by filtration in a nitrogen-filled drybox, washed with benzene, and placed in an autoclave with fresh benzene and heated (nitrogen atmosphere). Glpc analysis indicated that no dimeric products were formed. To make sure that the catalyst had not been deactivated by the filtration, hydrogen (800 psi) was then introduced at 200°: phenylcyclohexane was formed in a 79% yield (18% conversion of benzene).

RESULTS AND DISCUSSION

Both stirred autoclaves and tubular, continuous-flow reaction vessels capable of withstanding elevated hydrogen pressures were employed for this study; the appropriate distinctions in the data are made below. The catalysts were prepared by impregnation techniques, as described in the Experimental Section, and then heated to ~500°. To avoid induction periods, the catalysts, after being heated, were frequently pretreated with hydrogen at 300° for ~20 min. Analytical grade benzene containing ~60–160 ppm of water and 0.3 ppm of sulfur compounds was used without further purification for part of the autoclave experiments, which were designed to determine the most suitable types of catalysts. It was learned subsequently that water and sulfur compounds in the benzene have deleterious effects on the catalysts. However, the above-mentioned experiments appear to be valid for the intended purpose since, in flow experiments (discussed below), there was little effect of these impurities on the yields of products unless significantly longer reaction times were employed.

The data for the autoclave, catalyst evaluation experiments are listed in Tables

TABLE 1
HYDROGENATION OF BENZENE[a]

Expt.	Catalyst[b]	Comp.[c] (%)			Pressure (psi)	Time (hr)	Conv. of C_6H_6 (%)	Yields[d]				
		Ni	W	F				MCP	CH	C_{18}	CYCH	PhCH
1	$Ni(NO_3)_2$, Al_2O_3-A	2.8	0	0	800	0.5	5	0	100	0	0	0
2	$Ni(NO_3)_2$, Al_2O_3-B	9.8	0	0	800	1.0	6	0	100	0	0	0
3	H_2WO_4, Al_2O_3-B	0	10	0	1025	1.0	0	—	—	—	—	—
4	NiF_2, Al_2O_3-C	7.4	0	4.2	800	0.3	28	0.8	96.5	—	0.1	2.7
5	$Ni(NO_3)_2$, Al_2O_3-C	8.9	0	0	800	3.0	14	0	100	0	0	0
6	$Ni(NO_3)_2$, H_2WO_4, Al_2O_3-B	4.7	13.9	0	800	1.0	20	1.8	34.6	11.4	2.2	50.0
7	$Ni(NO_3)_2$, H_2WO_4, Al_2O_3-B	1.0	17.3	0	520	3.8	22	5.0	13.7	13.9	7.5	59.9
8	$Ni(NO_3)_2$, MS-A-3	5	0	0	800	1.5	16	2.5	15.9	12.9	4.7	64.0
9	NiF_2, MS-A-3	5.2	0	2.4	800	2.3	14	0.5	7.8	8.3	4.3	79.2
10	$Ni(NO_3)_2$, H_2WO_4, MS-A-3	0.8	15.9	0	800	4	17	1.5	9.2	3.8	7.1	78.4
11	NiF_2, $(NH_4)_2W_4O_{17}$, MS-A-3	0.8	17.5	1.1	800	0.3	6	0.8	7.2	2.3	3.0	86.8
12	NiF_2, $(NH_4)_2W_4O_{17}$, MS-A-3	0.8	17.5	1.1	800	1.0	32	1.7	6.7	16.3	3.6	71.6
13	$Ni(NO_3)_2$, $(NH_4)_2W_4O_{17}$, MS-A-1	1.0	17.0	0	800	2.0	24	1.6	10.6	13.8	6.2	67.9
14	$Ni(NO_3)_2$, H_2WO_4, SiO_2	4	11.5	0	800	0.5	43	1.0	88.7	0.5	0.7	9.1
15	$Ni(NO_3)_2$, H_2WO_4, Al_2O_3-A	3.7	12.0	0	800	0.5	44	0.9	94	4.7	0.4	4.7
16	$Ni(NO_3)_2$, H_2WO_4, Al_2O_3-A	3.7	12.0	0	300	1.0	6	0	75.7	0	0	24.3
17	NiF_2, $(NH_4)_2W_4O_{17}$, 75% SiO_2–25% MgO	0.9	15.7	1.0	800	6	18	0	65.4	2.4	1.0	31.2
18	NiF_2, 75% SiO_2–25% MgO	1.0	0	1.1	800	0.3	21	0	88.9	1.3	0	9.8
19	NiF_2, Al_2O_3-C	2.8	0	1.8	800	0.5	13	0	100	0	0	0
20	NiF_2, $(NH_4)_2W_4O_{17}$, Al_2O_3-C	1.8	10.1	0.5	800	0.3	16	2.9	64.5	2.3	0.6	29.8
21	NiF_2, $ZnCl_2$,[e] Al_2O_3-C	2.3	0	0.8	800	1.0	9.8	0.9	67.1	2.0	0.9	29.0
22	NiF_2, $AlCl_3$,[f] Al_2O_3-C	2.2	0	1.9	800	1.8	11.9	2.5	87.8	0	0	9.7

[a] Autoclave reaction vessel was employed. Baker's reagent grade benzene (not further dried), 0.45 mole; catalyst amount, 7 g except for Expts. 17 and 18 where 5 g was employed; temperature was 200°C for all experiments except 1, 3, and 7, where it was 250°C.

[b] Catalysts in powder form were prepared by impregnation techniques with the indicated salts (see Experimental section) and dried at 500–550°C in all experiments except 21 and 22, where the temperature was 400°C. Al_2O_3-A, unwashed Alcoa F-20 alumina (212 m^2/g); Al_2O_3-B, pseudoboehmite alumina (335 m^2/g); Al_2O_3-C, Harshaw alumina (246 m^2/g); MS-A-3, 75% SiO_2–25% Al_2O_3, obtained from American Cyanamid (530 m^2/g); MS-A-1, 89% SiO_2–11% Al_2O_3, American Cyanamid; 75% SiO_2–25% MgO, American Cyanamid silica-magnesia; SiO_2, Davison silica gel (241 m^2/g). Catalysts in Expts. 7, 10–13, 17, and 18 were treated with H_2 at 300°C for 0.3 hr before they were used. $(NH_4)_2W_4O_{17}$ is ammonium metatungstate.

[c] The catalyst compositions listed for Expts. 3, 8, and 14 are estimated values based on other similar preparations.

[d] Yields are based on converted benzene; MCP, methylcyclopentane; CH, cyclohexane; C_{18}, trimeric products; CYCH, cyclohexylcyclohexane; PhCH, phenylcyclohexane.

[e] Zn, 4.9%.

[f] Cl, 4.2%.

1 and 2. Suitable experimental conditions include reaction temperatures and pressures in the region of 200° and 800 psi, respectively. In addition to phenylcyclohexane, cyclohexylcyclohexane, cyclohexane, methylcyclopentane, and trimeric (C_{18}) compounds are formed in varying amounts. Throughout this paper, reported yields are based on the converted benzene. Also, the relative extents to which various catalysts convert benzene in a given time are taken as a measure of the respective catalyst activities. To maximize the yield of phenylcyclohexane, the conversion of benzene was limited: yields of trimeric compounds increase with the extent of conversion.

It is readily apparent from the data that the support and the metal on the support

TABLE 2
HYDROGENATION OF BENZENE[a]

Expt.	Thiophene added[b]	Catalyst[c]	Comp. (%)			Time (hr)	Conv. of C_6H_6 (%)	Yields[d]				
			M	W	F			MCP	CH	C_{18}	CYCH	PhCH
23	0	$Pd(NH_3)_4Cl_2$, MS-A-3	Pd, 0.24	0	0	0.2	22.3	2.6	55.7	2.8	4.1	34.9
24	0.38 mg	$Pd(NH_3)_4Cl_2$, MS-A-3	Pd, 0.24	0	0	4.5	11.9	2.6	39.1	0	7.3	50.9
25	0	$Pd(NH_3)_4Cl_2$, HF, MS-A-3	Pd. 0.24	0	2.3	5.7	20.3	11.1	15.6	5.9	12.2	54.8
26	0	$Pd(NH_3)_4Cl_2$, $(NH_4)_2W_4O_{17}$, MS-A-3	Pd, 0.1	9.3	0	4.5	22.8	1.1	12.3	13.6	5.7	67.3
27	0	$Pd(NH_3)_4Cl_2$, HF, $(NH_4)_2W_4O_{17}$, MS-A-3	Pd, 0.1	9.2	1.9	0.5	19.9	4.3	8.8	5.9	6.0	74.9
28	0	$Pt(NH_3)_4Cl_2$, MS-A-3	Pt, 1.5	0	0	0.16	21.3	1.7	81.3	0.6	1.4	14.9
29	0.38 mg	$Pt(NH_3)_4Cl_2$, MS-A-3	Pt, 1.5	0	0	2.0	5.7	4.8	75.3	0	0	19.9
30	0	$Pt(NH_3)_4Cl_2$, HF $(NH_4)_2W_4O_{17}$, MS-A-3	Pt, 1.4	8.4	2.0	0.4	29.0	2.2	17.4	10.8	5.1	64.5
31	0.38 mg	$Pt(NH_3)_4Cl_2$, HF $(NH_4)_2W_4O_{17}$, MS-A-3	Pt, 1.4	8.4	2.0	4.0	30.5	3.3	17.0	13.0	5.6	61.2
32	0	$Ni(OAc)_2$, Na mordenite	Ni, 12.8 Na, 1.4	0	0	0.3	9.2	1.6	91.1	0	0	7.3
33	0	$Ni(OAc)_2$, Na Y faujasite	Ni, 13.2 Na, 2.6	0	0	2	19.6	0.8	12.6	5.5	2.2	78.9
34	0	$Ni(OAc)_2$, NH_4 mordenite	Ni, 2.6	0	0	1.0	13.3	1.4	19.1	3.1	7.6	68.8
35	0	Pd, Y faujasite	Pd, 0.3 Na, 2.7	0	0	0.2	23.4	1.0	42.0	2.3	2.5	52.3

[a] Autoclave reaction vessel was employed. Baker's analytical grade benzene (0.45 mole in all cases) was used without further purification in Expts. 32–35 and was purified over 4A Linde molecular sieve for Expts. 23–31. Temperature, 200°C; pressure, 800 psi; catalyst, 2 g in all experiments except 32 and 34, where 7 g was present.

[b] In those experiments where thiophene was added, the catalyst used was the catalyst recovered by filtration, in a drybox, of the reaction mixture from the previous experiment.

[c] All catalysts in powder form were prepared by impregnation techniques with the indicated metal compounds and were dried at 500°C for 2 hr. Catalysts in Expts. 23–31 were treated with H_2 (800 psi) at 300°C for 0.3 hr before they were used. MS-A-3, 75% SiO_2–25% Al_2O_3 (American Cyanamid); see Experimental section for description of mordenites and faujasite. $(NH_4)_2W_4O_{17}$ is ammonium metatungstate. The catalyst in Expt. 35 was obtained from the Linde Division of the Union Carbide Co.

[d] Yields are based on converted benzene. Material balances for glpc analyses were generally 97–102%; MCP, methylcyclopentane; CH, cyclohexane; C_{18}, trimeric products; CYCH, cyclohexylcyclohexane; PhCH, phenylcyclohexane.

are both important features of the catalysts. Whereas aluminas impregnated with nickel produced predominantly cyclohexane (Expts. 1, 2, 5, and 19) and tungsten on alumina [pseudoboehmite (*6*)] exhibited no activity (Expt. 3), the two metals combined on alumina gave an effective catalyst and phenylcyclohexane was formed in 50–60% yields with ~20% of the benzene converted (Expts. 6 and 7).

A similar synergistic effect is to be noted in Expts. 19 and 20. The type of alumina seems to be important since nickel-tungsten on Alcoa F-20 alumina was less effective for the hydrodimerization reaction (Expt. 15) than similar catalysts of pseudoboehmite (*6*).

If a silica-alumina support of composition 75% SiO_2 and 25% Al_2O_3 (MS-A-3; obtained from American Cyanamid Co.) is used, the presence of tungsten is not essential for the hydrodimerization reaction to occur. MS-A-3 impregnated with $Ni(NO_3)_2$ gave a 64% yield of phenylcyclohexane with a 16% conversion of benzene (Expt. 8). MS-A-3 impregnated with NiF_2 is an even better catalyst than the one prepared from $Ni(NO_3)_2$. With comparable conversions of benzene (14–16%), the yield of phenylcyclohexane increased from 64% to 79% for the two respective catalysts (Expts. 8 and 9). MS-A-3-based catalysts containing nickel, fluorine, and tungsten are particularly effective (Expts. 11 and 12). Tungsten appears to have a promotional effect when combined with nickel [from $Ni(NO_3)_2$] on silica-alumina (Expts. 8 and 10) just as it did with alumina supports (see above).

Several other experiments further indicate that the support has an important function. Tungsten-nickel on a silica-alumina of composition 89% SiO_2 and 11% Al_2O_3 (MS-A-1; obtained from American Cyanamid Co.) gives somewhat lower yields of phenylcyclohexane than are obtained with a similar catalyst where the support is MS-A-3 (Expts. 13 and 10).* Silica-magnesia is not as good a support as the silica-aluminas: Ni/W/MS-A-3 gave a 71.6% yield of phenylcyclohexane with 32% of the benzene converted (Expt. 12), whereas Ni/W/silica-magnesia produced only a 31.2% yield at an even lower conversion (17%) of benzene (Expt. 17).

Although good yields of phenylcyclohexane can be obtained with certain supported palladium catalysts, generally these tend to produce more cyclohexane than the corresponding nickel-containing catalysts. Whereas $Ni/W/Al_2O_3$ catalysts produced phenylcyclohexane in good yields (see above), $Pd/W/Al_2O_3$ catalysts† produced exclusively cyclohexane at 25–200° (experiment not tabulated). Further indicative of the greater hydrogenation activity of palladium catalysts, Pd/MS-A-3 and Ni/MS-A-3 catalysts gave, respectively, 34.7% (Expt. 23) and 64% (Expt. 8) yields of phenylcyclohexane. As was demonstrated for nickel-containing catalysts, the incorporation of fluorine into the Pd/MS-A-3 catalyst strongly promoted the formation of phenylcyclohexane (compare yields of Expts. 23 and 25). However, the fluorine diminished somewhat the overall catalyst activity. Tungsten also has a similar promotional effect on Pd/MS-A-3 catalysts (Expts. 23 and 26). The promotional effects of tungsten and fluorine are additive so that the best MS-A-3-based palladium catalyst contains both tungsten and fluorine (Expt. 27). Similar promotional effects of tungsten and fluorine occur with Pt/MS-A-3 catalysts as well: in Expts. 28 and 30 the yield of phenylcyclohexane increased from ~15% to ~65%. Assuming that the difference in metal content is not a large contributing factor, the palladium catalysts appear to be better hydrodimerization catalysts and give lower yields of cyclohexane than the corresponding platinum catalysts (Expts. 23 vs. 28 and 27 vs. 30).

Metals supported on certain crystalline zeolites also are effective for the hydrodimerization of benzene (Table 2). A catalyst prepared from nickel acetate and NH_4^+ mordenite gave a high yield of phenylcyclohexane (Expt. 34); however, a similar catalyst prepared from Na^+ mordenite produced only a low yield of the product (Expt. 32). Nickel supported on Y faujasite was a particularly good catalyst (~79% yield), whereas palladium sup-

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* Although we feel this effect is due to the difference in the supports, it should be noted that different tungsten salts, i.e., tungstic acid and ammonium metatungstate, were used to impregnate the respective supports. The two forms of tungsten are believed to be equivalent.

† A Harshaw alumina (Al_2O_3-C, Table 1) impregnated with palladium chloride and ammonium metatungstate.

ported on Y faujasite gave only modest yields of phenylcyclohexane (Expts. 33 and 35).

A few general observations regarding hydrodimerization catalysts are important to note. The temperature at which the impregnated catalysts are heat-treated before being used should not be too high, preferably ~500° for ~ 2 hr. If the temperature is not carefully controlled, catalyst activity may be greatly impaired, as was noted when a Ni/F/MS-A-3 catalyst was heated at 650°. After the heat treatment, it is usually, but not always, beneficial to treat the catalyst with hydrogen at ~300° and 800 psi for ~20–30 min. If this is not done, an induction period may be observed and the rate of hydrogen consumption will tend to increase with time. Prereduction with hydrogen at higher temperatures, 350–400°, may greatly deactivate the catalyst, as was observed in the case of Ni/MS-A-3 and Ni/W/MS-A-3. Longer periods of hydrogen pretreatment do not significantly alter the product composition obtained with Ni/MS-A-3 catalysts (the only catalyst type examined in this regard) except in cases where the nickel content is >2%. With a catalyst of the latter type (Ni, 2.4%; F, 2.9%), the yield of cyclohexane increased from ~10% to ~20%, with a concomitant decrease in the yield (~77% to ~68%) of phenylcyclohexane as the prereduction period was extended from 0.5 to 1.0 or 2.0 hr (~20% conversion of benzene in all cases).

As mentioned above, the yield of phenylcyclohexane decreases as the extent of conversion of benzene increases. The data of Expts. 11 and 12 show that this decrease is due to the formation of trimeric, C_{18}, compounds, undoubtedly via a subsequent reaction of the phenylcyclohexane. Limited data indicate that the conversion of benzene in a given time is diminished by decreasing the hydrogen pressure (Expts. 15 and 16).

The performance of MS-A-3-supported catalysts was studied over an extended period of time in a tubular flow reactor. When analytical grade benzene was used without further purification (60–160 ppm of water and 0.3 ppm of sulfur compounds

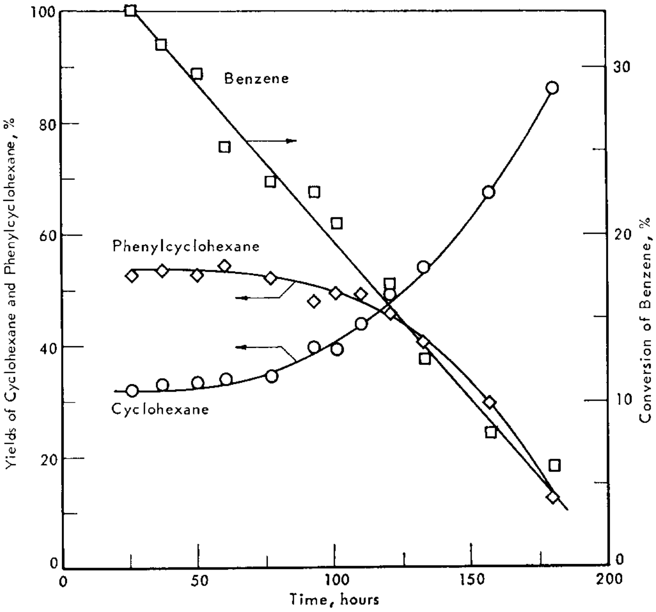


FIG. 1. Effects of substrate impurities on the hydrodimerization of benzene in a continuous-flow reactor. Catalyst, 0.4% Ni, 0.4% F, and 11.8% W on MS-A-3. Analytical grade benzene was used without further purification (contained 60–160 ppm water and 0.3 ppm sulfur in the form of organosulfur compounds). Reaction conditions: 120° (same results obtained at 140°), 800 psi, LHSV = 0.42. The arrows on the curves point to the appropriate reference ordinate.

present), the conversion of benzene with a 1.5% Ni/2.4%F/MS-A-3 catalyst declined over a 175-hr period (LHSV = 0.4, 140°, 800 psi) while the product composition changed to one containing mainly cyclohexane. The inclusion of tungsten in the catalyst composition (Ni, 0.4%; F, 0.4%; W, 11.8%) gave similar results, indicating that after 200 hr cyclohexane would be the sole product (Fig. 1).

It seemed likely that the source of catalyst instability was water, and sulfur- and/or nitrogen-containing compounds in the benzene. Analysis of the benzene used to obtain the data in Fig. 1 gave the following results in ppm: nitrogen, 0.05; sulfur, 0.3; water, 60 (160 ppm water was indicated after the benzene had been allowed to stand exposed to the atmosphere). After the benzene was purified via circulation through Linde 4A molecular sieve, analysis indicated, in ppm: sulfur, 0.03; water, <8. In contrast to the results obtained without purification of the benzene, catalyst (1.6% Ni/2.1% F/MS-A-3) activity declined only slightly during the course of 200 hr when the purified benzene was employed. Furthermore, the product composition, containing ~58–65% phenylcyclohexane, remained relatively constant throughout the entire period. Thus, it is clearly evident that either the water or the sulfur compounds are ultimately detrimental to catalyst performance. The specific effects of each of these substrate impurities are discussed below.

Mechanism

For catalysts to be effective for the conversion of benzene to phenylcyclohexane, both acidity and hydrogenation activity are necessary. Furthermore, if a proper balance between hydrogenation activity and acidity does not exist and the hydrogenation activity is too great, mainly cyclohexane results. The importance of hydrogenation activity is obvious since no reaction occurs unless a metal with hydrogenation activity is present. The importance of acidity is indicated by several lines of evidence. For example, silica-alumina is a stronger acid than alumina or silica (*7*) and is a more effective support. MS-A-3 is more acidic (*8*) than MS-A-1 and, as would be expected, is a preferred support. A further correlation of acidity and hydrodimerization activity is found for silica-alumina and silica-magnesia. The latter has more but weaker acid sites (*8*) than the former and was found to be a less effective support.

The increase in the yield of phenylcyclohexane which results from the incorporation of fluorine in MS-A-3-based catalysts also is consistent with the acidity postulate since fluorine is known to enhance the activity of silica-alumina catalysts for acid-catalyzed reactions (*9*). It is a little surprising that fluorine did not activate the alumina-based catalysts sufficiently to cause significant hydrodimerization to occur. However, there is some controversy as to whether or not the presence of fluorine strengthens or weakens acid sites on γ-alumina [for a discussion and references regarding this question see ref. (*10*)].

In further support of acidity as an essential catalyst property, Lewis acids in combination with a hydrogenation metal on a neutral support have been found to promote the hydrodimerization reaction. For example, Ni/F/Al_2O_3 promoted the hydrogenation of benzene to cyclohexane exclusively (Expt. 19), whereas a similar catalyst containing added zinc chloride produced phenylcyclohexane in 29% yield (Expt. 21). The incorporation of aluminum chloride also promoted the reaction (Expt. 22). The beneficial effect of the Lewis acids likely is due to the extraneous metal rather than to the chloride ion since the presence of another halogen—fluorine—had little effect on alumina-based catalysts (see above). It is noteworthy that another type of acidic material (*11*)—crystalline zeolite—is an excellent catalyst support for the conversion of benzene to phenylcyclohexane.

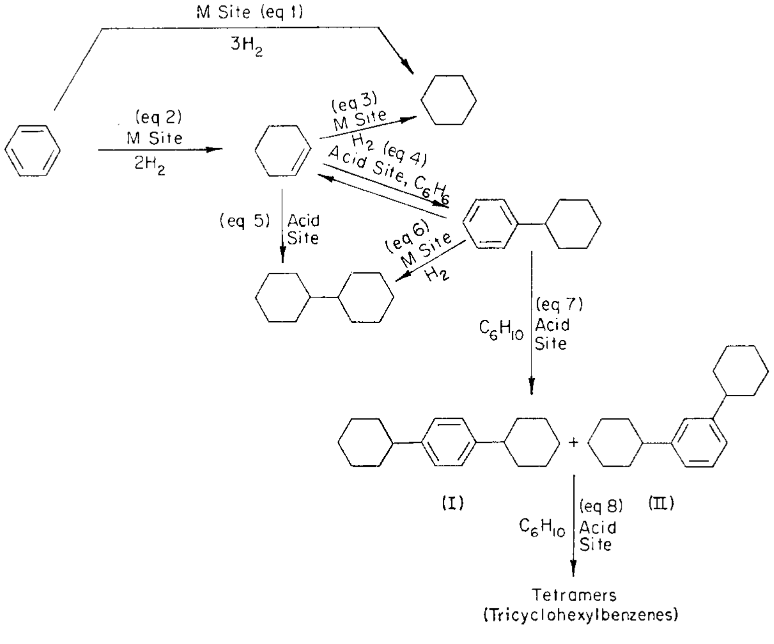
The observed deleterious effect of extraneous water in the benzene (see above) also is consistent with the above acidity postulate, since excess water is known to poison acid sites (*12*).

Via the technique described by Weisz and Swegler (*13*), the bifunctional nature of the hydrodimerization catalysts was convincingly established by using a mixture of particles of Ni/Al_2O_3, a hydrogenation catalyst, and particles of MS-A-3, an acidic support. In independent experiments with identical conditions, a Ni/Al_2O_3 catalyst converted benzene in the presence of hydrogen to only cyclohexane, while MS-A-3 was totally inactive. However, when a physical mixture of the two catalysts was employed, phenylcyclohexane was produced in a yield comparable to those obtained with Ni/MS-A-3 catalysts (vide supra), but at a slower rate (reaction times 4–5 times longer were required for comparable conversions of benzene). Similar results were obtained with a catalyst pair consisting of Ni/SiO_2 and MS-A-3. These results are taken as strong evidence that an intermediate is formed on one type of catalyst site and that it desorbs and migrates to another type of site where further reaction occurs to give the final product. The intermediate must be sufficiently stable to undergo interparticle migration as well as intraparticle migration between sites.

Based on the properties of catalysts described above and on additional evidence presented below, the mechanistic scheme of Eqs. (1)–(8) is proposed, in which cyclohexene is featured as the key intermediate. We believe that cyclohexene is formed on a metal, hydrogenation site (M) and that it either is further hydrogenated to cyclohexane [Eq. (3)] or that it desorbs and migrates to an acid site where alkylation of benzene occurs to give phenylcyclohexane [Eq. (4)].

Alternatively, one might envision the direct formation of cyclohexyl carbonium ions, or other unstable, reactive intermediates, on the hydrogenation sites as benzene combines with hydrogen and that these intermediates alkylate benzene either while on the hydrogenation sites or in bulk solution. However, the requirement of bifunctional catalysts would be difficult to rationalize on this basis. Besides, unlike cyclohexene, carbonium ions would be expected to have undergone extensive skeletal rearrangement in the experiments with the mixed catalyst pairs where interparticle migration was required. Methylcyclopentane was formed, but in low yield.

Consistent with the proposed mechanism are the results from a series of autoclave experiments in which small amounts of water or sulfur, as thiophene, were added to the benzene substrate. The results obtained for a Ni/F/MS-A-3 catalyst are



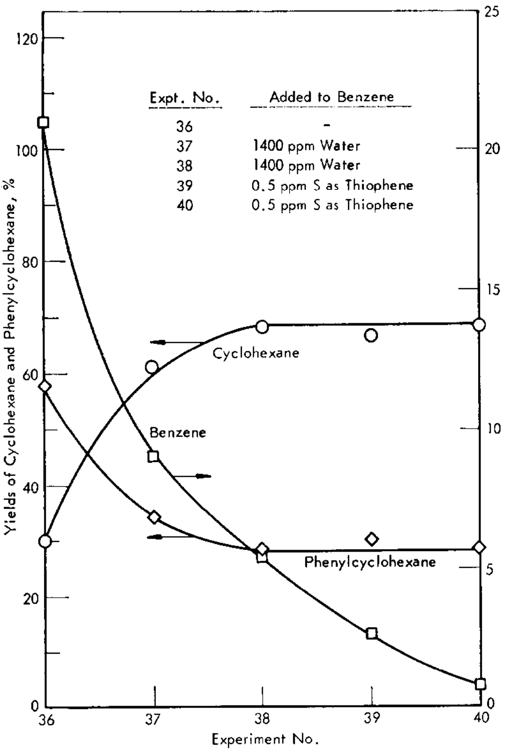


FIG. 2. Effects of added water and thiophene on the hydrodimerization of benzene to phenylcyclohexane. Catalyst, 2.4% Ni/2.9% F/MS-A-3 (5 g). Benzene, 0.45 mole; 200°; 800 psi. Reaction times were for Expts. 36 through 40, 0.33, 0.5, 0.66, 1.25, and 4 hr, respectively. After each experiment, the catalyst was isolated in a nitrogen-filled drybox by filtration, washed with dry benzene, and reintroduced into a clean autoclave along with purified benzene to which was added the indicated amounts of water or thiophene. In Expt. 36 the benzene was neat. The arrows on the curves point to the appropriate reference ordinate.

shown graphically in Fig. 2. With each addition of water, catalyst activity declined, but, more significantly, as the water deactivated the acid sites, alkylation of benzene diminished [Eq. (4)] and the relative yields of cyclohexane [Eqs. (1) and (3)] increased (Expts. 36–38, Fig. 2). The addition of thiophene apparently poisoned the hydrogenation sites so that the catalyst was less active (0.17 mg S/g Ni reduced activity ~50%); but, the relative amounts of cyclohexane and phenylcyclohexane were not changed. We anticipated that sulfur poisoning of the hydrogenation sites would actually increase the yield of phenylcyclohexane [Eq. (4)] since the competing hydrogenation of the intermediate cyclohexene to cyclohexane [Eq. (3)] should be diminished. Perhaps thiophene is sufficiently basic to also poison the acid site so that the anticipated effect was counterbalanced. In the case of a more active hydrogenation catalyst, Pd/MS-A-3, the addition of thiophene did increase the yields of phenylcyclohexane (Table 2, Expts. 23 and 24).

Further supporting evidence and additional information concerning the proposed mechanism was obtained by hydrogenating approximately equal molar amounts of benzene and cyclohexane-^{14}C over a Ni/F/W/MS-A-3 catalyst (Table 3). A comparison of the ^{14}C activity of the reactant cyclohexene with that of the products indicates that (1) only ~0.1% of the cyclohexene-^{14}C was converted to benzene; (2) ≥74% of the phenylcyclohexane resulted from a reaction of cyclohexene-^{14}C with benzene;* (3) 90% of the cyclohexylcyclohexane resulted from two molecules of

TABLE 3
HYDROGENATION OF A CYCLOHEXENE-^{14}C–BENZENE MIXTURE[a]

Reactant composition (mmoles)		^{14}C activity (dpm/mmole)
Benzene	206	0
Cyclohexene-^{14}C	196	1.48×10^6
Product composition (mmoles)		
Methylcyclopentane	4.8	Not counted
Cyclohexane	18.5	Not counted
Cyclohexene	0.9	Not counted
Benzene	97.1	1.93×10^2
Cyclohexylcyclohexane	5.8	2.66×10^6
Phenylcyclohexane	49.9	1.09×10^6
Trimers, C_{18}	25.8	Not counted

[a] Catalyst, 5 g: 0.6% Ni/0.6% F/14.5% W/MS-A-3. Pressure, 800 psi; temperature, 200°; reaction time, 3.8 hr.

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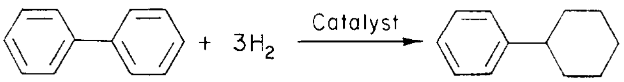
* With a shorter reaction time, the amount of phenylcyclohexane resulting from cyclohexene-^{14}C would have been higher. The reaction, inadvertently, was allowed to continue after most of the cyclohexene-^{14}C had been consumed, so that the product was diluted with phenylcyclohexane resulting from the conversion of unlabeled benzene.

(9)



(10)

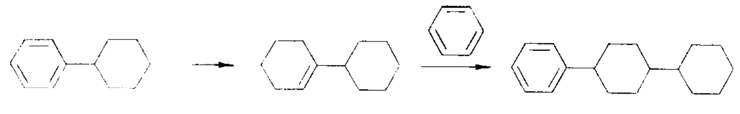
cyclohexene-^{14}C. These results clearly demonstrate the feasibility of cyclohexene as an intermediate in the formation of phenylcyclohexane. The ^{14}C-tracer study also shows, quite surprisingly, that most of the cyclohexylcyclohexane by-product does not derive from the hydrogenation of phenylcyclohexane but rather results from the alkylation of cyclohexene by cyclohexene.

A requirement of the proposed mechanism is that alkylation of benzene by cyclohexene compete favorably with the hydrogenation of the latter to cyclohexane. The high combined yields of phenylcyclohexane and trimeric products, relative to the low yield of cyclohexane, formed in the ^{14}C experiment (Table 3) demonstrates this to be the case.

Although the above results strongly support cyclohexene as the intermediate which migrates from hydrogenation sites to acid sites, the intermediacy of cyclohexane must also be considered. Conceivably, the latter might react with benzene on a catalyst surface to form phenylcyclohexane and hydrogen. However, this possibility can be discounted because the yield of phenylcyclohexane was not increased by using cyclohexane as a solvent for the hydrogenation of benzene (Ni/F/W/MS-A-3; 200°; 800 psi; autoclave employed). The cyclohexane appeared to be serving only as an inert diluent.

Another possible path for the conversion of benzene to phenylcyclohexane is shown by Eqs. (9) and (10). If this path were operative, biphenyl and/ or phenylcyclohexane should be formed by heating the catalyst and benzene together without added hydrogen. However, when an active Ni/F/W/MS-A-3 catalyst, recovered from the product of a previous hydrodimerization reaction, was heated (200°, 6.3 hr) with benzene no dimeric products were formed. It appears that this mechanism does not contribute significantly to the formation of phenylcyclohexane.

The predominant mode of formation of trimers is indicated by the structure of the products to involve multiple alkylation of a benzene nucleus by cyclohexene rather than the reduction of phenylcyclohexane to cyclohexylcyclohexene which, in turn, alkylates benzene. Alkylation of benzene by the latter would give phenylcyclohexylcyclohexane [Eq. (11)], which was not observed in the product. The trimeric material, $C_{18}H_{26}$, obtained from autoclave and flow experiments consisted of approximately equal quantities of two isomers, one of which was positively identified by its NMR and infrared spectra as *p*-dicyclohexylbenzene. The infrared spectrum of the other isomer (characteristic absorption at 12.68 μ) indicated it to be *m*-dicyclohexylbenzene. The ortho-isomer was not present in significant amounts. Mass spectrometric analyses indicated the presence of trace amounts of dicyclohexylcyclohexane, $C_{18}H_{32}$, tetramer, $C_{24}H_{36}$ (presumably tricyclohexylbenzene), and pentamer, $C_{30}H_{46}$. The feasibility of the alkylation route to trimeric, etc., material was demonstrated by hydrogenating a mixture of phenylcyclohexane and cyclohexene



(11)

over a Ni/F/W/MS-A-3 catalyst. Considerable quantities of the higher molecular weight material were formed.

The reversibility of the cyclohexene alkylation of benzene [Eq. (4)] was demonstrated by the hydrogenation of neat phenylcyclohexane over a Ni/F/W/MS-A-3 catalyst (200°, 800 psi, 1.5 hr). Benzene, cyclohexane, trimer and some tetramer, but no cyclohexane, were isolated.

The present study contributes to the understanding of two topics which deserve further comment. As reported above, tungsten in catalysts has a promotional effect on the formation of phenylcyclohexane. For example, whereas Ni/Al_2O_3 produced predominantly cyclohexane and W/Al_2O_3 exhibited no activity, $Ni/W/Al_2O_3$ catalysts produced phenylcyclohexane in high yields. Since acidity of the catalysts has been shown to be responsible for phenylcyclohexane, rather than cyclohexane being formed, it appears that the incorporation of tungsten via impregnation with either tungstic acid or ammonium metatungstate greatly enhances the acidity of the catalysts. As far as we are aware, previous reports concerning the effect of tungsten on acidity have not been made. It may be that the hydrogenation of benzene to phenylcyclohexane could serve as a useful test reaction to determine whether other catalysts have acidic properties.

Small amounts of cyclohexenes have been detected in products from the hydrogenation of aromatic hydrocarbons over platinum, rhodium, and ruthenium catalysts (*14–17*). Some researchers are of the opinion that cyclohexenes are trivial intermediates in the hydrogenation of aromatic hydrocarbons (*15*, *17*), whereas others propose cyclohexenes to be key intermediates (*14*, *16*, *18*). The present study strongly supports the latter view. With the catalyst systems studied, cyclohexene is formed as an intermediate in high yields (indicated by yields of phenylcyclohexane) and benzene is serving the function of trapping the monoolefin before it is further reduced. Furthermore, it appears that cyclohexene can become desorbed from the metal sites and undergo not only intraparticle migration but interparticle migration as well.

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REFERENCES

1. TRUFFAULT, R., *Bull. Soc. Chim.* **1**, (5), 391 (1934).

2. French Patent 1,326,722 (to Stamicarbon N.V.) (1963).

3. LOGEMANN, J. D., U. S. Patent 3,153,678 (1964).

4. LOUVAR, J. J., AND FRANCOYATARES, A. G., U. S. Patent 3,317,611 (1967).

5. SLAUGH, L. H., *Tetrahedron* **24**, 4523 (1968).

6. PAPEE, D., TERTAIN, R., AND BIAIS, R., *Bull. Soc. Chim. France*, p. 1301 (1958).

7. OBLAD, A. G., MILLIKEN, T. H., JR., AND MILLS, G. A., *Advan. Catalysis* **3**, 199–247 (1951).

8. BENESI, H. A., *J. Phys. Chem.* **61**, 970 (1957).

9. PLANK, C. J., SIBBETT, D. J., AND SMITH, R. B., *Ind. Eng. Chem.* **49**, 742 (1957).

10. PERI, J. B., *Am. Chem. Soc., Div. Petrol. Chem., Preprints* **13**, (No. 1), 131 (1968).

11. BENESI, H. A., *J. Catalysis* **8**, 368 (1967).

12. HIRSCHLER, A. E., *Am. Chem. Soc., Div. of Petrol. Chem., Preprints* **13**, (No. 1), 142 (1968) and references cited therein.

13. WEISZ, P. B., AND SWEGLER, E. W., *Science* **126**, 31 (1957).

14. SIEGEL, S., KU, V., AND HALPERN, W., *J. Catalysis* **2**, 348 (1963).

15. HARTOG, F., AND ZWIETERING, P., *J. Catalysis* **2**, 79 (1963).

16. SIEGEL, S., AND KU, V., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, **1**, 1199.

17. HARTOG, F., TEBBEN, J. H., AND WATERING, C. A. M., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 1210.

18. SIEGEL, S., SMITH, G. V., DMUCHOVSKY, B., DUBBELL, D., AND HALPERN, W., *J. Am. Chem. Soc.* **84**, 3136 (1962).