Hydrocracking of *n*-Butylbenzene, *sec*-Butylbenzene and Benzene with Palladium on Silica–Alumina Catalysts

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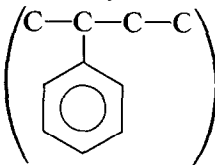*Chevron Research Company, Richmond, California 94802*

Observation of the changes in product distribution during catalyst aging permits deduction of reaction paths and the relationship among the main conversion processes taking place. For example, the principal hydrocracking route of *n*-butylbenzene with fresh 0.3% palladium on silica–alumina catalysts involves prehydrogenation to an isomeric mixture of C_{10} naphthenes followed by cracking (by the paring reaction) to mainly methylcyclopentane (MCP) and isobutane. At 4 LHSV, 330°C, 82 atm, and 10 moles H_2/hydrocarbon, some of these catalysts lose activity for complete hydrogenation in about 40 hr. After the catalysts are aged, dealkylation of the reactant to benzene and normal butane becomes a significant reaction. During the aging period, the ratio of isobutane to normal butane in the product decreases from about 3 to 0.5. When *n*-butylbenzene appears in the product, the rate of cracking may decrease appreciably. Then alkyl group transfer occurs.

With *sec*-butylbenzene, the presence of the tertiary carbon in the side chain causes dealkylation to occur so rapidly that no paring reaction (hydrogenation followed by cracking) is observed. Again, activity for complete hydrogenation of the product is lost in about 40 hr. In contrast to *n*-butylbenzene, however, the level of dealkylation remains high at 95% because the palladium is still effective in preventing poisoning of the acid sites.

Experiments with benzene involve little cracking (4%) but still show a loss of activity for complete hydrogenation in about 100 hr, similar to that observed with the butylbenzenes. The results suggest that intermediate species (including alkylation products) that are generated on the acid sites of the silica–alumina migrate to the palladium sites and cause deactivation. This is confirmed by the longer time of complete hydrogenation observed when palladium-on-alumina is physically mixed with inert Alundum instead of with silica-alumina.

INTRODUCTION

A recent review of the chemistry of hydrocracking (*1*) by Langlois and Sullivan indicates that most of the published noble metal catalyst studies on the hydrocracking of pure hydrocarbons involve platinum, not palladium, catalysts. Also, most of the reported work on the hydrocracking of *n*-butylbenzene has been with nickel sulfide on silica-alumina catalysts (*2,3*).

When *n*-butylbenzene or *sec*-butylbenzene

zene is hydrocracked

with a catalyst that has high hydrogenation activity, such as palladium on silica-alumina, one can observe readily whether the reactant hydrogenates first before cracking or cracks (dealkylates) first. If the reactant hydrogenates first, then the mixture of C_{10} naphthenes formed will undergo the paring reaction to form principally MCP and isobutane. [The term "paring" denotes a series of isomerizations followed by a cracking reaction wherein the cyclic structure is preserved and wherein the predominant paraffinic product from cracking is isobutane (*4*).] If the initial reaction is cracking of the alkylbenzene, then the first products are benzene and normal butene which is hy-

drogenated to normal butane. Thus, the ratio of isobutane to normal butane will be sensitive to the extent of the prehydrogenation. The extent of cracking is the weight percent of the product which has a carbon number less than 10.

This paper discusses the effect of catalyst age on the extent of the above reactions and presents results on catalysts having the hydrogenation sites and acid sites on different particles in a physical mixture. Although most of the experiments were performed at 4 LHSV, 330°C, 82 atm, and 10 moles hydrogen/mole of hydrocarbon, the conclusions should apply for similar conditions and with similar hydrocracking catalysts. The same type of curves would be expected, although the time scale may be different. Traces of sulfur in the reactant shorten the time of complete hydrogenation of the reactant. Loss of activity for complete hydrogenation, however, has been observed in 60 hr with n-butylbenzene containing less than 0.1 ppm sulfur.

METHODS

Equipment

The experiments were performed in a continuous flow, fixed bed microcatalytic unit. The 1 ml of catalyst was supported inside a 0.46-cm i.d. stainless steel tube 60 cm in length, which was surrounded by a heavy walled aluminum–bronze liner inside an electrically heated oven. Catalyst temperatures were measured by a chromel–alumel thermocouple located on the reactor wall. The hydrocarbon rate was measured with a Ruska pump.

Catalysts

The catalysts (20–60 mesh) consisted of palladium (usually 0.3% Pd) on a silica-alumina cracking support. They were prepared by impregnation with a solution of palladium nitrate followed by drying and calcination. Surface areas are 300–350 m^2/g. The catalysts were reduced 3 hr in hydrogen at 316°C before use.

Chemicals

The n-butylbenzene and sec-butylbenzene were Phillips 99% pure grade and contained 0.4 and 1.7 ppm S, respectively, and less than 1 ppm N. The benzene was Baker Analyzed Reagent and contained 0.2 ppm S and less than 1 ppm N.

Analysis

The gaseous product was sampled by a Beckman valve and analyzed by a Perkin-Elmer Model 900 chromatograph with a silicone column.
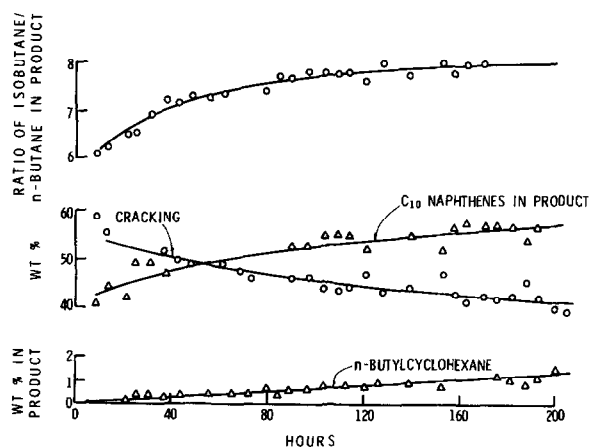

FIG. 1. Hydrocracking n-butylcyclohexane at 4 LHSV, 330°C, and 82 atm.

n-BUTYLBENZENE

Results

To ascertain the product distribution expected if n-butylbenzene hydrogenates first before cracking, we hydrocracked n-butylcyclohexane.

Figure 1 shows that the ratio of isobutane to normal butane in the product is high, between 7 and 8. [The equilibrium ratio at 330°C is 0.84 (5).] The ratio of MCP to cyclohexane of 7 is also high. [The equilibrium ratio at 330°C is 5.8 (5).] The cracking, which is in the range 40–50 wt%, decreases slightly in the period 100 to 200 hr. The C_{10} product is principally a mixture of naphthenic isomers instead of n-butylcyclohexane, which is present at about 1%.

Figures 2 and 3 show typical results for the hydrocracking of n-butylbenzene. Figure 2 shows that the cracking decreases more rapidly than the cracking of n-butylcyclohexane because the aromatics cause poisoning of the acid and hydrogenation sites. At 40 hr onstream, n-butylbenzene appears in the product; and subsequently,
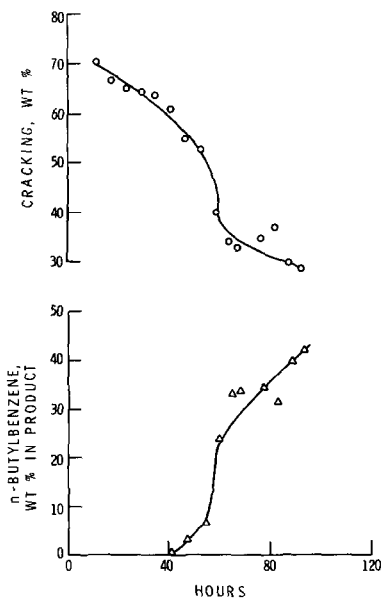

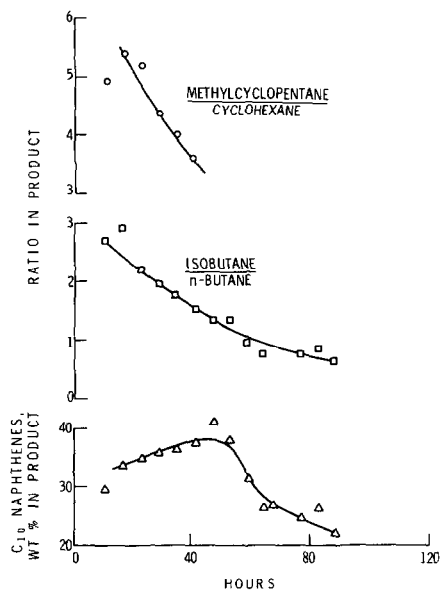FIG. 3. Hydrocracking n-butylbenzene at 4 LHSV, 330°C, and 82 atm.

FIG. 2. Hydrocracking n-butylbenzene at 4 LHSV, 330°C, and 82 atm.

the conversion drops rapidly. Part of this decrease could be due to the lower catalyst temperature due to the smaller amount of hydrogenation. Figure 3 shows that prior to the appearance of n-butylbenzene (at 40 hr) the ratio of isobutane to normal butane decreases from 2.7 to 1.5, and the ratio of MCP to cyclohexane decreases from 5 to 3.5. This shows the decrease in the extent of the paring reaction and the increase in the extent of dealkylation. At 90 hr, the ratio of isobutane to normal butane is 0.6, which is lower than the equilibrium ratio.

Early in these experiments, the C_{10} naphthene content of the product increases because the rate of cracking of the C_{10} naphthenes decreases faster than the rate of formation decreases. The C_{10} naphthene content peaks at the time the n-butylbenzene appears in the product and then decreases.

Discussion

In addition to the two cracking routes mentioned in the introduction, another reaction, alkyl group transfer, becomes significant after the hydrogenation activity
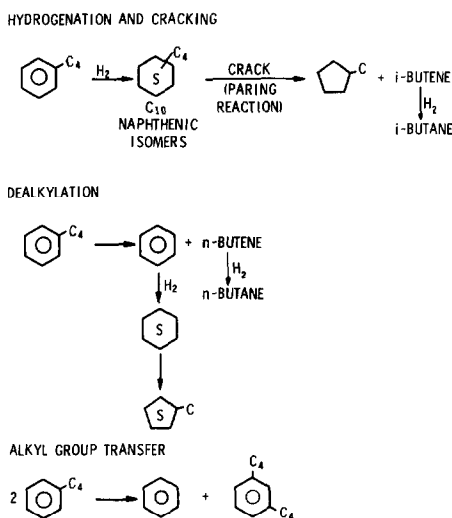
HYDROGENATION AND CRACKING

DEALKYLATION

ALKYL GROUP TRANSFER

FIG. 4. Principal cracking reactions of n-butylbenzene with palladium on silica–alumina catalysts.

of the catalyst is poisoned. Fig. 4 shows equations for the three principal reactions. Five additional cracking reactions (including ring opening) occur to lesser extent and are not shown. They produce small amounts of C_8's, C_7's, C_6 paraffins, C_5's, and C_3.

The approximate extent of the paring, dealkylation, and alkyl group transfer reactions are estimated as follows:

From the n-butycyclohexane experiment, the total amount of MCP plus cyclohexane is 1.14 times the MCP. Thus, if one assumes essentially all of the MCP is from the paring reaction:

moles undergoing paring $= 1.14$ (moles MCP); moles undergoing alkyl group transfer $= 2$ (moles of single-ring aromatics heavier than n-butylbenzene); moles

undergoing dealkylation = moles of benzene + cyclohexane − moles of cyclohexane from the paring reaction − moles of benzene from alkyl group transfer.

Figure 5 shows the relative extent of these reactions as the catalyst ages. The total number of moles reacting decreases with catalyst age as follows: 100 moles at 20 hr; 90 moles at 50 hr; 62 moles at 70 hr; 56 moles at 90 hr.

sec-BUTYLBENZENE

Results and Discussion

Figure 6 shows that the cracking of sec-butylbenzene remains constant at about 95% during the first 100 hr, even though benzene appears in the product at about 40 hr. The ratio of isobutane to normal butane in the product is low, 0.1 This shows that sec-butylbenzene dealkylates so fast that the hydrogenation and paring reaction do not occur appreciably, even with a fresh catalyst. MCP and cyclohexane are the principal cyclic products for the first 40 hr. The MCP to cyclohexane ratio is 1.8 compared to about 4.5 from n-butylbenzene. The MCP is formed from isomerization of cyclohexane produced by hydrogenation of benzene formed in dealkylation. Figure 7 shows the principal reactions occurring with sec-butylbenzene.

An experiment was performed with a higher palladium content catalyst, 2.7% Pd, in an effort to have the sec- butylbenzene undergo the paring reaction. Even with this larger amount of hydrogenation component, the ratio of isobutane to n-butane
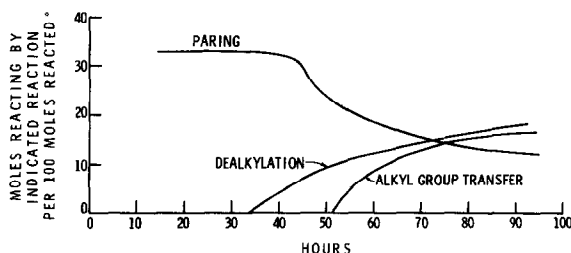

FIG. 5. Extent of principal cracking reactions in hydrocracking of n-butylbenzene at 4 LHSV, 330°C, and 82 atm. Other reactions not shown include hydrogenation to C_{10} naphthenes and other minor cracking reactions.
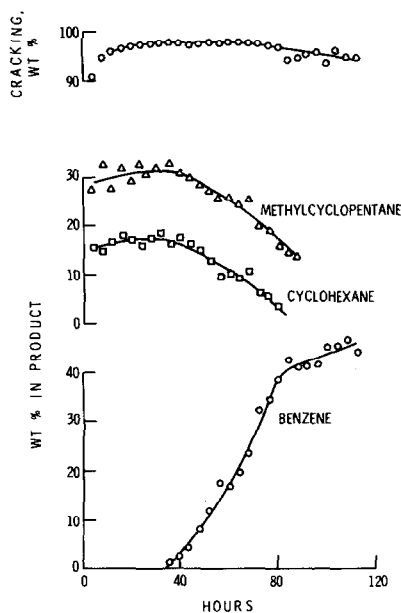
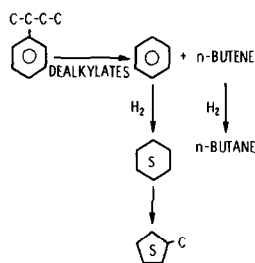FIG. 6. Hydrocracking sec-butylbenzene at 4 LHSV, and 82 atm.

FIG. 7. Principal reactions in hydrocracking sec-butylbenzene.

in the product is still 0.1. This shows the rapid rate of cracking due to the tertiary carbon in the side chain; however, the hydrogenation capacity improved as no benzene appeared in the product during the 100-hr experiment.

Results with a Physically Mixed Catalyst

This catalyst consists of 0.2% palladium on alumina (20–60 mesh) physically mixed with an equal volume of silica–alumina (20–60 mesh). This arrangement should increase the opportunity for part of the sec-butylbenzene to be hydrogenated prior to cracking.

Figure 8 shows that complete hydrogenation occurs for 40 hr at 2 LHSV on total catalyst, after which both benzene and sec-butylbenzene appear in the product. The ratio of isobutane to n-butane decreases from 0.16 at 10 hr and remains constant at 0.05 at 40 hr, indicating again that dealkylation is the principal cracking route.

The extent of cracking increases from 70 to 80% in the first 40 hr and then decreases to 60% at 70 hr. The lower cracking at the start of the run can be accounted for by hydrogenation of sec-butylbenzene to sec-butylcyclohexane and C_{10} naphthenic isomers which crack more slowly than the aromatic. As the hydrogenation sites age, more sec-butylben-

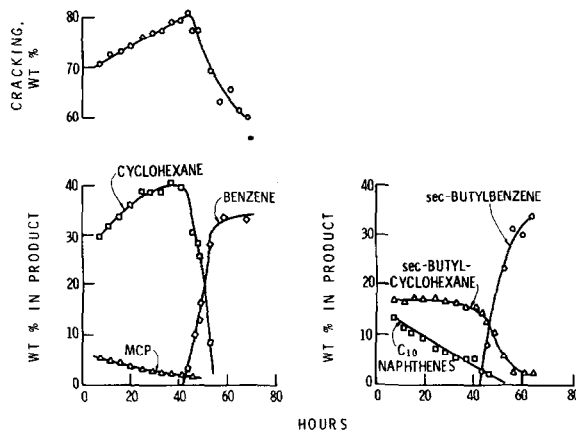FIG. 8. Hydrocracking sec-butylbenzene with a mixture of 1 vol of 0.23% palladium on alumina (20–60 mesh) with 1 vol of silica–alumina (20–60 mesh) at 2 LHSV, 330°C, and 82 atm.

zene is available to crack. Figure 8 shows also how the *sec*-butylcyclohexane and C_{10} naphthenes in the product decrease in the first 60 hr.

Although the palladium on alumina component does not hydrogenate an appreciable amount of aromatics at 60 hr, it is still effective in maintaining a high cracking activity of 63%. For comparison, in an experiment with the silica–alumina component alone, the cracking is only 2% after 16 hr. Thus the palladium is effective in lowering the aging rate of the silica–alumina component.

In contrast to the product from a single catalyst, the product from the physical mixture contains more cyclohexane than MCP. The cyclohexane formed from benzene at the palladium site is isomerized more slowly because of the longer path for it (and any cyclohexene) to reach acid sites (which are probably more deactivated in this mixed catalyst).

BENZENE

Benzene was hydrocracked with a palladium on silica–alumina catalyst to determine the effect of eliminating the alkyl side chain of the reactant.

Results

Figure 9 shows that the extent of cracking is less than 4%. The principal products during the first 100 hr are MCP and cyclohexane. A decrease in isomerization activity with time occurs. At 100 hr, the benzene concentration in the product rises. About 4% of C_7, C_8, and C_{12} hydrocarbons is observed.

Discussion

The fact that benzene causes fouling of the hydrogenation sites at a low extent of cracking suggests that the loss of hydrogenation activity with the butylbenzenes is not due entirely to cracking of the side chains nor due to the presence of the normal butene formed.
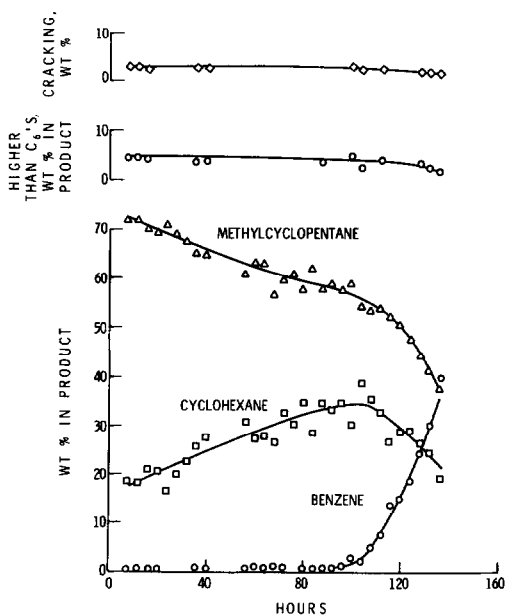

FIG. 9. Hydrocracking benzene at 4 LHSV, 330°C, and 82 atm.

A gas chromatographic–mass spectrometric analysis of the liquid product shows the presence of C_7, C_8, and C_{12} cyclic hydrocarbons (such as bicyclohexyl). In a similar experiment with a physically mixed catalyst, C_{12} aromatics, such as methylcyclopentylbenzene, are identified. The hydrodimerization of benzene to phenylcyclohexane and to cyclohexylcyclohexane at a lower temperature of 200°C and 54 atm over supported transition metal catalysts has been reported by Slaugh and Leonard. (6). They detected trace amounts of C_{18}, C_{24}, and C_{30} products also. Thus, with the present catalyst, part of the fouling of the hydrogenation activity could be due to intermediate species including these alkylation products.

Additional evidence for this conclusion is presented in Fig. 10, which shows that the hydrogenation capacity of a physically mixed catalyst is increased markedly when the silica–alumina component is replaced by inert Alundum which has no activity for cracking nor alkylation.
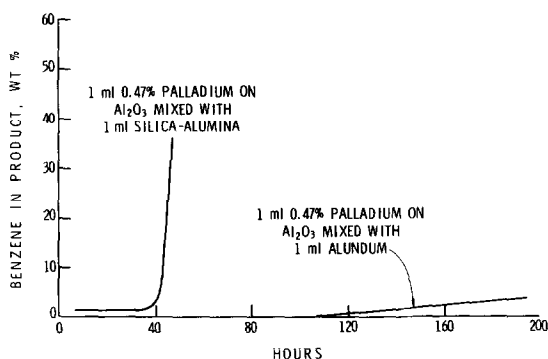
FIG. 10. Breakthrough times for benzene when processed at 2 LHSV, 330°C, and 82 atm.

ACKNOWLEDGMENTS

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