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# Evidence for a Diels–Alder Reaction between Dienes and Olefins in the Dehydrocyclodimerization of Butene-1 on Tellurium-Loaded Zeolites

In several investigations Csicsery (*1–3*) and Janowski (*4, 5*) have dealt with the dehydrocyclodimerization of lower olefins and paraffins to aromatics on catalysts, which possess both acidic and dehydrogenation sites.

In a recent review Csicsery (*6*) developed a reaction mechanism in which the formation of aromatics is postulated to proceed via three steps: (1) dimerization of the olefins on acidic sites of the catalysts, (2) intramolecular cyclization on acidic or metallic sites, (3) dehydrogenation on metallic sites.

We now have strong evidence that dimerization and cyclization may also take place simultaneously on certain catalysts by a Diels–Alder addition between a diene, formed on a dehydrogenation site, and an olefin.

The catalysts that we used for the dehydrocyclodimerization of butene-1 were modified tellurium-loaded Y-zeolites. Similar catalysts were first described by Lang *et al.* (*7*), Mikovski *et al.* (*8*) and Olson *et al.* (*9*) as very effective and selective catalysts in the aromatization of *n*-hexane. But it turned out that butene-1 was mainly converted to cracking products, when contacted with the tellurium-loaded Y-zeolite prepared by the procedure given by Lang *et al.* (*7*). This may be attributed to the higher reactivity of butene for oligomerization–cracking reactions (for the mechanism of these reactions see (*10*)) compared with that of *n*-hexane. Therefore, most of the acidic sites which are present even in a nonexchanged, commercial NaY (Linde type 30-200) have been destroyed by the addition of 9% solid sodium chloride to the NaY base and a treatment at 700°C overnight after the addition, during which an exchange of most of the acidic hydroxyl groups against sodium takes place by the evolution of hydrogen chloride. (The effect of sodium chloride on the acidity of NaY has been discussed by Rabo (*11*).)

This catalyst shows only minor activity for cracking reactions but is still an effective catalyst for the isomerization of butene-1 to butene-2. This "deactivated" NaY was mixed with 13% tellurium and treated in a hydrogen flow at 540°C for 3 h.

At low conversions (about 3.5% referred to the sum of all $C_4$ hydrocarbons), this brownish, tellurium-loaded zeolite catalyst shows a selectivity of more than 60% for the formation of monoaromatic compounds—mainly $C_8$ aromatics—in the dehydrocylodimerization of butene-1 at a reaction temperature of 475°C ($v_{\text{Butene}} = 0.7$ liter/h, amount of catalyst = 0.9 g) in a flow reactor.

The distribution of the $C_8$ aromatics formed shows distinct deviations from the thermodynamic equilibrium. There is much more *o*-xylene and ethylbenzene in the reaction mixture than expected from a calculation of the thermodynamic equilibrium, which becomes even more pronounced if the deactivation of the catalyst proceeds (Fig. 1). But, if the aromatization proceeds by an intramolecular cyclization reaction to a five-membered ring followed by ring expansion, a roughly thermodynamic distribution with a higher relative amount of *m*- and *p*-xylenes should result. Therefore, we must assume that the cyclization occurs by the reaction of butadiene, formed by the

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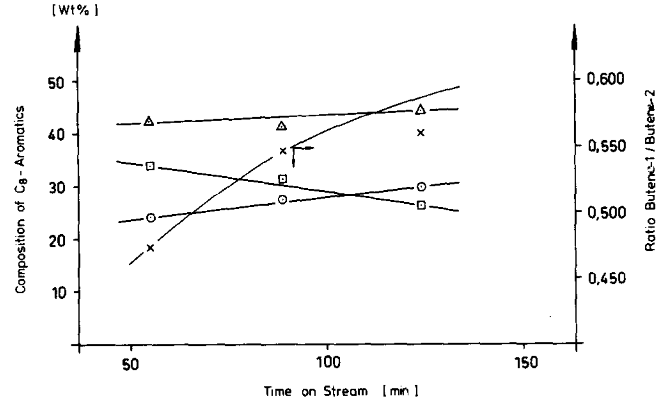
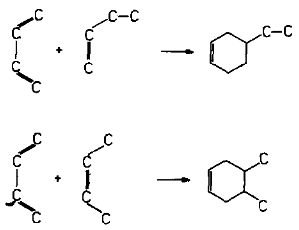


FIG. 1. Relative composition of the $C_8$ aromatics (⊙ = ethylbenzene, ⊡ = ($m$ + $p$)-xylene, △ = $o$-xylene) and ratio of butene-1/butene-2 (×) in the reaction of butene-1 on tellurium-loaded NaY (thermodynamic equilibrium of the $C_8$ aromatics: ethylbenzene = 9.5%, ($m$ + $p$)-xylene = 67.9%, $o$-xylene = 22.6%).

dehydrogenation on the tellurium sites, and the butene isomers:



This mechanism is able to account for the relatively high amounts of $o$-xylene and ethylbenzene in the reaction mixture. The $m$- and $p$-xylenes are formed on weakly acidic sites by isomerization of the Diels–Alder adducts (some experiments with $o$-xylene as feed have demonstrated that the isomerization reactions probably proceed via the cycloolefins and do not proceed via the aromatics). During the reaction the relative proportion of ($m$ + $p$)-xylene even decreases, because the isomerization sites of the catalysts are poisoned—probably by coking. Furthermore, the ratio ethylbenzene/$o$-xylene increases in the same manner as the extent of the isomerization of the butene-1 decreases, according to the proposed Diels–Alder mechanism, because the lower amount of butene-2 in the reaction mixture implicates a lower amount of $o$-xylene.

The catalytic sites which are responsible for the reaction steps can be recognized partly by the dependence of the yield of two key compounds during time on stream. The decrease of the aromatics and the increase of the butadiene yield during time on stream (Fig. 2) indicate that different catalytic sites are responsible for the dehydrogenation and cyclization reactions. Therefore, we assume that the cyclization occurs on acidic sites, perhaps on Lewis sites, which are known to possess catalytic activity for Diels–Alder additions (*12*). That acidic sites are responsible for the cyclization is supported by the results obtained by the addition of more than 10% sodium chloride to the zeolite: there is no catalytic activity for both isomerization and aromatization reactions anymore, but considerable activity for butadiene formation.

Although the low yields (which can be increased by an increase of the reaction temperature and by an increase of the residence time at the expense of the selectivity for the aromatics) make the tellurium-loaded zeolite unattractive for a commercial application in the dehydrocyclodimerization of butenes, the proposed new mechanism for this reaction—valid under

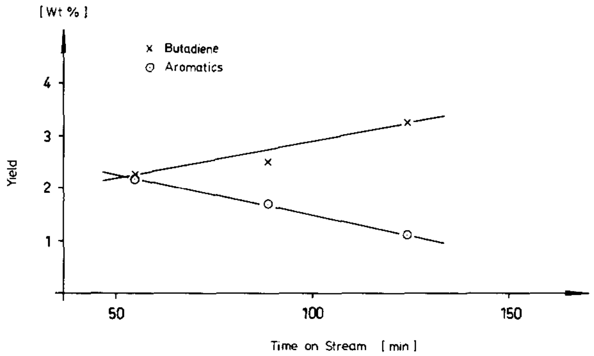


FIG. 2. Change of the yield of butadiene (×) and of the aromatic compounds (⊙) during time on stream.

certain conditions—may stimulate the search for new catalytic systems, which are able to catalyze Diels–Alder additions or similar cycloadditions between dienes and olefins.

## ACKNOWLEDGMENT

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