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ON THE MECHANISM OF CYCLOHEXENE DISPROPORTIONATION CATALYZED BY SUPPORTED PALLADIUM

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The disproportionation of cyclohexene to benzene and cyclohexane:

$$3\ C_6H_{10} \longrightarrow C_6H_6 + 2\ C_6H_{12}$$

is catalysed by palladium black, and a previous work it was shown to proceed through 1,3-cyclohexadiene(1). The reaction has now been kinetically studied with alumina supported palladium, by means of 19 different samples of catalyst with different amounts of metal. The quantity of palladium never exceeded 6% of the amount required for a complete coverage of the support surface.

The catalyst samples were prepared by impregnation of Alcoa Chemicals alumina F-110 (surface 200 m^2/g) pellets (40-60 mesh) with an acid aqueous solution of palladium chloride. The samples were reduced at 330° with a stream of hydrogen. A standard procedure was rigorously followed in the preparation of catalysts. The analyses of the amount of palladium in each sample were made with a Philips X ray fluorescence spectrograph after calibration with samples of known palladium content.

The reactions were performed at 40° in a continuous flow reactor employing vapour phase chromatography for the analysis.

Two kinetic models were employed for the interpretation of the experiments; in both cases it was assumed that the rate determining step is the surface reaction considered to be either monomolecular or bimolecular.

Only the second model gave completely satisfactory agreement with experiment data. The results, which will be reported in detail elsewhere, fit the following simplified rate equation very well:

$$r = k \frac{(1 - x)^2}{(1 + ((Z_B/3) - 1)\ x)^2}$$

where x is the degree of conversion of cyclohexene and Z_B the ratio of the adsorption equilibrium constants of benzene and cyclohexene.

Both the constants k and Z_B were determined by a nonlinear least-square procedure. An almost constant value of Z_B (0.72) was found for all the catalyst samples.

Each sample's specific activity, referred to one gram of palladium and evaluated as the inverse of the half-life of cyclohexene, is graphically reported in fig.1.

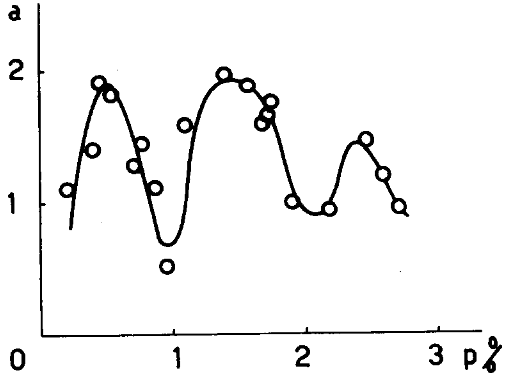

Fig.1- Specific activity of catalyst samples vs. the palladium percentage.

A peculiarity of such a diagram is the presence of three well-defined maxima. Because the percentage of palladium on the support surface is small, the interpretation of the behaviour of the curve of fig.1 can be made on the basis of the "active ensembles" theory(2).The catalyst phase is assumed to be in a precrystalline state and to consist of a number of ensembles of metallic atoms (active centres). A statistical analysis(3) of the experimental data plotted in fig.1 has shown that the ensembles corresponding to the highest values of the specific activity contain 4, 10-11, and ca.20 atoms, respectively Therefore the lowest number of palladium atoms necessary for accomplishing the reaction is 4, and on this basis it can be suggested that the rate determining step of cyclohexene disproportionation is the direct hydrogen transfer between two adsorbed molecules as shown in the following scheme:

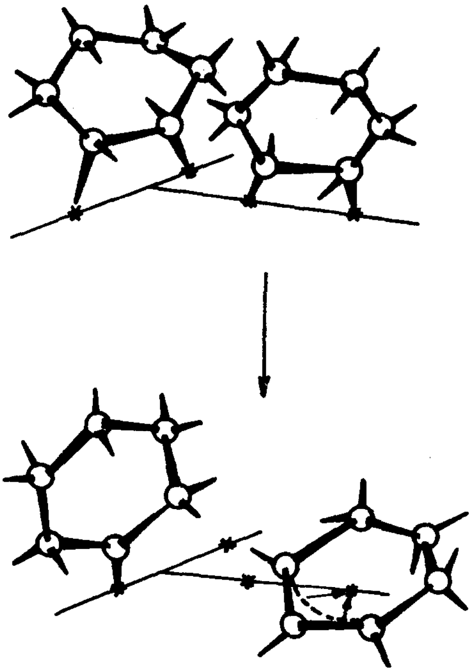

Fig.2-Scheme of hydrogen tranfer reaction.The stars indicate the palladium atoms.

In fig.2 two molecules of cyclohexene are associatively adsorbed on a four atom centre;one hydrogen atom exchange can produce a π-allyl palladium complex which is an intermediate for the formation of cyclohexadiene and benzene.The minimum of activity corresponding to ensembles of 5-8 palladium atoms might be due to an irreversible adsorption of benzene that removes the four atom systems necessary for the accomplishment of the reaction as it is shown in fig.2.

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