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Abstract

Full Text

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ON STRUCTURAL CORRESPONDENCE IN CATALYSIS

The development of a theory for the selection of catalysts is an urgent problem of modern chemistry. From the multiplet theory of catalysis ([1]) there follow principles, important in this respect, of structural and energetic correspondence between the catalyst and the reacting molecules. The first of these principles was established by the author ([2]) in 1929, and already then, as one of the proofs, a table was given of metals arranged according to the type of their crystal lattice and according to atomic radii. In this case, the catalysts of the low-temperature (~300°) dehydrogenation of hydrocarbons of the cyclohexane series (or of the reverse reaction, the hydrogenation of hydrocarbons of the benzene series), in agreement with the sextet model of the multiplet theory, proved to be metals belonging to the A1 and A3 systems and having atomic radii within the limits from 1.397 to 1.236 Å. This table has remained unchanged up to the present time, apart from the fact that Treppel ([3]) simplified it in 1951 and supplemented it somewhat. Long, Fraser, and Ott ([4]), Emmett and Skau ([5]), and Rineker and Unger ([6]) extended the same regularity to alloys.

With time, further evidence accumulated for the importance of structural factors in catalysis and, in particular, experimental results supporting the sextet model. A review of them was given by the author in ([7-10]), and most fully in ([11]). However, since 2 years have already passed since the writing of work ([11]), it is useful to present still further data.

In 1958 a new, detailed compilation of interatomic distances appeared ([12]). On its basis one may compile Table 1, which is given below. Table 1 includes only metals, and moreover those crystallizing in the simplest systems A1, A2, A3, and A4. Metals crystallizing in more complex systems, and still more nonmetals, as well as forms stable only at high temperatures (at which catalysts sinter), are not included in Table 1. Therefore, for example, it does not include γ-U, A2, d = 3.058 Å (805°C), β-Ti, A2, d = 2.8636 Å (900°), γ-Fe, A1, d = 2.578 Å (916°).

From Table 1 it is evident that the regularity previously found is fully preserved also for the new values of interatomic distances. Namely, the elements known as catalysts for the dehydrogenation of cyclohexane in fact belong only to metals with lattices of types A1 and A3, and moreover with the shortest interatomic distances d, lying within the limits from 2.7746 Å (Pt) to 2.4916 Å (Ni) (or, cor-

respondingly, with atomic radii $R = d/2$ from 1.3873 Å to 1.2458 Å; cf. above). These elements are enclosed in frames in Table 1.

Within the frame of Table 1 falls rhenium, for which the X-ray structural study and determination of catalytic activity had not yet been carried out when the initial table ([2]) was compiled. The fact predicted by the multiplet theory, that Re dehydrogenates cyclohexane, was proved by the author, Karpeiskaya, and Tolstopyatova ([13]).

In further study of catalysis over Re, it proved possible to find a case in which the so-called irreversible catalysis of cyclohexene (according to the terminology

N. D. Zelinsky) over Re proceeds more slowly than the dehydrogenation of cyclohexane to benzene. Since these cases do not differ in any fundamental way from the dehydrogenation of cyclohexane on Pt and other analogous

Table 1

Types of crystal lattices and the smallest interatomic distances d (in Å)

Face-centered cubic lattice A1	Body-centered cubic lattice A2	Hexagonal lattice A3	Diamond lattice A4
α-Ca 3.947Yb 3.880γ-Ca 3.877Ac 3.756β-La 3.745Ce 3.650α-Pr 3.649α-Th 3.595δ-Pu 3.279Sc 3.212Ag 2.8894Au 2.8841Al 2.8635Pt 2.7746Pd 2.7511Ir 2.714Rh 2.6901Cu 2.5560Co 2.5061Ni 2.4916	Cs 5.309Rb 4.95K 4.544Ba 4.347γ-Sr 4.20Eu 3.989Na 3.7157β-Tl 3.362ε-Pu 3.150Li 3.0390Ta 2.86Nb 2.8584W 2.7409Mo 2.7251V 2.6224Cr 2.4980α-Fe 2.4823	β-Sr 4.32; 4.324α-La 3.739; 3.770Nd 3.628; 3.658Gd 3.573; 3.636Y 3.551; 3.647Tb 3.525; 3.601Dy 3.503; 3.590Ho 3.486; 3.577Er 3.468; 3.559Tu 3.447; 3.538α-Te 3.4076; 3.4566Lu 3.435; 3.503α-Po 3.345Sc 3.256; 3.309Mg 3.1971; 3.2094α-Zr 3.1790; 3.2313α-Hf 3.1275; 3.1947Cd 2.9788; 3.2933α-Ti 2.8956; 2.9505Re 2.741; 2.760Tc 2.703; 2.735Os 2.6754; 2.7354Zn 2.6649; 2.9129Ru 2.6502; 2.7058α-Be 2.2260; 2.2856	α-Sn 2.8099Ge 2.4498Si 2.3517C 1.5445

metals, this refutes the assumption, contradictory to the sextet scheme, made by some authors ([14]), that the dehydrogenation of cyclohexane proceeds through irreversible catalysis (i.e., cyclohexene is first formed, which then disproportionates into cyclohexane and cyclohexadiene, the latter yielding benzene).

It is interesting that technetium also falls among the dehydrogenation catalysts according to Table 1. Therefore, catalytic dehydrogenation of cyclohexane rings over Tc should theoretically be expected. It would be desirable to test this prediction experimentally; probably, owing to the radioactivity of technetium, its catalytic properties will be difficult to investigate.

There has been discussion as to whether Cu, which falls within the scope of Table 1, is a catalyst for the hydrogenation of benzene. A recent study by Erofeev

and Nikiforova ([15]), using IR spectroscopy, showed that Cu is indeed a catalyst for this reaction, as well as for the direct dehydrogenation of cyclohexane to benzene. This confirms the sextet model. The weak activity of Cu in these reactions is explained by other, nonstructural factors (cf. ([1])).

Manganese is not reduced to the metal from its oxides at temperatures below the onset of sintering. Therefore nothing was known about its ability to dehydrogenate cyclohexane. Recently Agronomov and Luzikov ([16]) prepared catalytically active, chemically pure metallic Mn by electrolysis. The low-temperature modification of Mn has a complex lattice (A12), and therefore it is not included in Table 1. In agreement with the theory, cyclohexane could not be dehydrogenated over manganese ([16]).

The fact that reduced iron catalyst is incapable of carrying out the hydrogenation of benzene and the dehydrogenation of cyclohexane has been shown by many investigators; see, for example, ([4–6]). Indeed, Fe falls outside the framework of Table 1. Meanwhile, as Anderson and Kemball ([18]) showed, in films condensed from vapors, Fe and W prove to be active for the hydrogenation of benzene. It should be noted, however, that the mechanism of reactions for reduced catalysts and for films can be different; for example, for the chemisorption of N_2 on Fe. The rate of this process on reduced Fe is proportional to the pressure of N_2 ([18]), while on Fe films it is proportional to the square root of the pressure of N_2 ([19]). Therefore, in the hydrogenation of benzene on Fe and W films, apparently, it is not the sextet mechanism (with planar orientation of benzene) that operates, but another, slower one—namely, the doublet mechanism (with edgewise orientation of the molecule). The latter has long been known for the dehydrogenation, for example, of ethane on Pd at high temperatures (cf. the work by the author and Brusov ([20])). Therefore the data of Anderson and Kemball ([17]) do not contradict Table 1.

The dehydrogenation mechanism considered here can be tested from a new standpoint, namely, from the standpoint of the dehydrogenation of seven- and five-membered rings with the formation of nonbenzenoid aromatic compounds.

It was recently found ([21]) that over Pd, 2,7-dibenzylidenecycloheptanone (I), by isomerization and dehydrogenation at 290° in solution, is converted in 16% yield into 2,7-dibenzyltropone (II), in which the seven-membered ring has aromatic character.

$$\mathrm{I} \xrightarrow[\mathrm{Pd{-}C}]{} \mathrm{II} + \mathrm{H_2}$$

Similarly to I, its analogs with a substituent in the phenyl groups behave. In this process, one molecule of H_2 is split off from I, and consequently dehydrogenation here proceeds by the doublet mechanism (cf. above concerning dehydrogenation of ethane over Pd). Incidentally, migration of a double bond is also a doublet reaction known for Pd.

structural formulas III and IV

Figure 1: structural formulas III and IV

A remarkable confirmation of the sextet model is the fact that bicyclo-(0,3,5)-decane is dehydrogenated over Pd ([22]) only in low yield to azulene (III), which possesses aromatic properties. As in the case of I, the greater part of the substance decomposes, and azulene is evidently formed by dehydrogenation according to the doublet mechanism. Thus, aromatic character, although it does influence catalysis to a certain extent ([23]), nevertheless by itself is incapable of leading to the smooth dehydrogenation that occurs in the case of cyclohexane. For catalysis to occur, structural correspondence is also necessary. Bicyclo-(0,3,5)-decane has no common symmetry elements with the $A1$ lattice of palladium and cannot be placed on it according to the sextet model, whereas cyclohexane is fully capable of this (IV).

Table 1 of the present communication should replace the earlier, less accurate tables—the table in the author' s article ([2]) of 1929 and the one compiled on the basis of

on its basis, Trappnell' s table [3] of 1951. It goes without saying that Table 1 can be applied not only to sextet reactions, but also to other catalytic reactions on metals, for example to the hydrogenation of olefins or aldehydes. In this case the optimum catalysts will be determined by other structural principles, also following from multiplet theory, in particular by the principle of conservation of the valence angle [24]. The optimum catalyst for the doublet hydrogenation reaction of the bond $>C=C<$ proves to be Rh [25] ($d = 2.6901$ Å), whereas for the hydrogenation of the shorter bond $>C=O$, Ru, for which d is correspondingly smaller ($d = 2.6502$ Å), should be best suited. Ruthenium is indeed an excellent catalyst [26] for the reaction we proposed of the hydrolytic hydrogenation of cellulose to sorbitol.

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Note: Figure translations are in progress. See original paper for figures.