

CONTACT CATALYTIC REACTIONS WITH CO-CATALYTIC PARTICIPATION OF HYDROGEN

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On the basis of our experiments, the co-catalytic role of the hydrogen was extended to different types of carbon compounds.

The purpose of this report is to generalize a correlation concerning the co-catalytic role of hydrogen. This generalization has been achieved through demonstrations of several new catalytic reactions taking place in the presence of hydrogen, some of which are described in the literature, and some were studied by us.

In several papers [1—9] there are some references to the fact that, in the case of hydrocarbons, chemisorbed hydrogen has an important role in the catalytic processes taking place on certain metal catalysts. This role exists even when the participation of hydrogen as a reactant cannot be directly observed in the stoichiometry of the reaction. The literature is not consistent in this respect; namely, sometimes it affords a view on detailed investigations but in some other cases, no remark concerning the role of hydrogen is made.

In cases of chemical transformations on catalysts sorbing hydrogen, according to our hypothesis, hydrogen has a determinant role even when its participation cannot be observed stoichiometrically in the chemical process. We had supposed earlier [10] and later also proved experimentally in several cases [11, 12], the co-catalytic role of the chemisorbed hydrogen.

Our hypothesis concerning an $A-H \rightarrow B-H$ reaction scheme (where $M_{A-H} = M_{B-H}$) is given below — without a claim of going into details here.

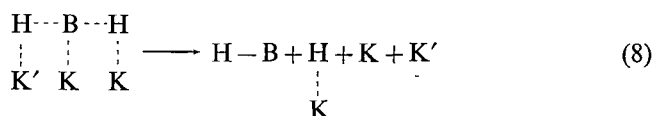
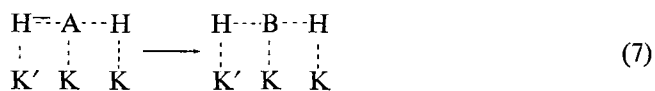
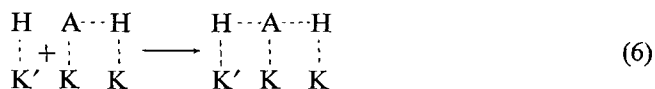
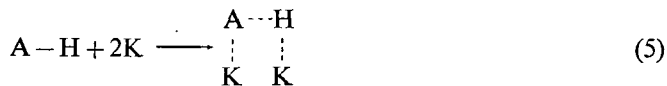
In case of a dissociative mechanism:





K, K' denote centres of the catalyst participating in the reaction.

In case of an associative mechanism:



Some experimental results described in the literature also served as basis of the above generalization relating to the role of hydrogen. According to these results, the participation of hydrogen in certain processes is experimentally proved on different metal catalysts capable of chemisorbing hydrogen, both with and without carriers. These are:

1. Isomerization of saturated and alicyclic hydrocarbons [5, 7—9, 13, 14];
2. Racemization of saturated hydrocarbons [15];
3. Dehydrocyclization and aromatization of saturated hydrocarbons [16—19];
4. Configurational isomerization of alicyclic hydrocarbons [6, 20, 21];
5. *Cis-trans* isomerization of olefins [22];
6. Migration of the double bond in olefins [23—25];
7. Configurational isomerization of the diaminocyclohexanes [26];
8. Cyclodehydration of aminoalcohols, and de-amination of polyamines [27, 28].

The mechanism of the isomerization of unsaturated hydrocarbons and that of some of their derivatives can also be interpreted in the same way, under homogeneous catalytic conditions, in the presence of transition metal complexes [29].

We have studied the transformations of heterocyclic compounds containing oxygen, taking place under the influence of platinum metals. In the course of this investigation, we have proved hydrogen participation in the chemical processes during the isomerization of the following types of compounds: isomerization of oxacycloalkanes to oxo compounds [12, 30], isomerization of 1,3-dioxolanes and 1,3-dioxanes to esters [31, 32], and configurational isomerization of 1,3-dioxanes [11].

In the absence of hydrogen, these transformations fail to take place on the metal catalysts investigated. The mechanism of the above processes can be explained according to the general scheme sketched previously.

We reviewed the co-catalytic role of hydrogen in the heterogeneous catalysis, in spite of EIDUS' more general view [33] regarding the role of stoichiometric components — and not only about that of hydrogen. We found this necessary for two reasons. On the one hand, we showed several reactions in which the co-catalytic participation of hydrogen was previously unknown; on the other hand, our purpose was to emphasize the general character of the phenomenon. This generalization concerns the isomerization reactions of all kinds of carbon compounds as well as a number of catalysts chemisorbing hydrogen which are, at the same time, capable of performing dissociative chemisorption of the substrates involving hydrogen splitting.

Our further aim is to study some general correlations concerning the co-catalytic role of hydrogen, on certain types of catalysts and compounds not investigated so far. It is also necessary to examine what types of hydrogen species play roles in the case of each catalyst and substrate.

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КОНТАКТНО-КАТАЛИТИЧЕСКИЕ РЕАКЦИИ
С СОКАТАЛИЗАТОРНЫМ УЧАСТИЕМ ВОДОРОДА

М. Барток

На основании полученных экспериментальных данных, сокаталитическое участие водорода распространено на реакции различных органических соединений.