JOURNAL OF CATALYSIS 34, 203–208 (1974)

The Determining Characteristics of Mechanisms of Catalysis

GYULA GÁTI

*High Pressure Research Institute, P. O. Box 208, Budapest 5, Hungary**

Received October 2, 1973

It is a common drawback and the reason for many contradictions among the different theories of catalysis (acid–base-, electronic-, multiplet-, ligand field-, etc.) that each concept about the mechanism of the catalytic reaction is throughout onesided. Here we will try to formulate the determining characteristics of the mechanisms (DCM) of catalytic reactions, which could now be regarded as a good approximation of the essential features of the mechanisms. The concrete meaning of the six DCM's defined here is illustrated by possible mechanisms of catalytic double bond isomerization of olefins and of the oxidation of CO. We have shown that the subsequent systematic application of the DCM allows to systematization of the possible mechanisms of catalytic reactions, the evaluation of the real potential of each experimental method for the determination of the mechanisms (the CO oxidation on Cr_2O_3–MoO_3 as a concrete example) and the critical evaluation of the individual theories of catalysis.

1. INTRODUCTION

The main goal of theories of catalysis is to elucidate the laws which control the dependences of catalytic phenomena on the properties of catalytic systems (catalyst and reactants). This is generally done by developing special ideas about the mechanisms of catalytic reactions, and these ideas play a central role in works on the theories (and generally on the laws) of catalysis. It is an important drawback of the theories (*1–7*) and generally of works discussing the laws of catalysis (and the reason for many contradictions) that their ideas about the mechanisms are throughout onesided (*2*, *8*, *9*) because they are based only on some of the properties of the catalytic system, neglecting many others which may also be of primary importance. There is at present no generally acceptable definition of the essence of complete mechanisms. In this paper we shall try: (i) to formulate what are the characteristics of the mechanisms of catalytic reactions which can now be regarded presently as the determining (necessary and sufficient) characteristics of mechanisms (DCM), (ii) to show that the systematic consideration of DCM's gives a unified and fruitful basis:

For critical evaluation of the various theories of catalysis (to discuss their suppositions, omissions and advantages and the possibilities of their simultaneous application).

For the evaluation of the real possibilities and potential force of each experimental method (this gives a guiding principle for the research program on the determination of the complete essence of the mechanism of catalytic reactions).

It must be emphasized that our proposals are not new in themselves; indeed, there is much work of this kind already in the literature, including examples of consideration of some of our proposals (*12*, *13*). But here we will try to select the really determining (necessary and sufficient) characteristics of mechanisms and to show that taking them systematically into consideration in investigating the mechanisms and general laws of catalysis has a large

---

* This work was carried out at the Institute of Chemical Physics of the Academy of Sciences of the USSR, Moscow.

Copyright © 1974 by Academic Press, Inc.

heuristic power. This is demonstrated below by some specific examples.

2. THE DEFINITION OF THE DETERMINING CHARACTERISTICS OF THE MECHANISMS (DCM) OF CATALYTIC REACTIONS

On the basis of a critical analysis of the acceptable ideas about the mechanisms of catalysis we think that in defining the DCM it is most reasonable to start with the reaction-center model (RZ-model) of catalytic reactions, in which the ideas developed in catalysis can be reasonably and usefully combined in a single system. According to this model we can distinguish in a catalytic system a group of atoms of the catalyst and the reactants (RZ-atoms of the catalytic system) the common characteristic of which is their participation in local interactions during the catalytic act, i.e., their chemical bonds are temporarily or permanently changing (i.e., are destroyed, transformed, formed). All the other atoms of the catalyst and reactants (outer RZ-atoms) influence the catalytic reaction by their collective interaction with the reaction center.

On the basis of a systematic evaluation (*11*) of the ideas behind various theories and mechanisms existing in catalysis (*1–9*) we think that at the present level the following characteristics of states and interactions in catalytic systems can be used as the most reasonable and useful approximation to express the full essence of the catalytic reaction, which we term the determining characteristics of the mechanisms. (DCM):

1st DCM. The chemical nature and the geometry of the catalyst centers (Z_1, Z_2, ... Z_n) taking part intimately in the catalytic reaction, i.e., the ensemble of the active centers of the catalyst.

2nd DCM. The kind of motion in time and space of the atoms of the reaction center (for example associative, dissociative, synchronous, intramolecular mechanisms). This DCM reflects most directly the cyclic character of catalytic mechanisms.

3rd DCM. The orbital states of RZ-atoms or in the more simple approximation the types of bonding (π, σ, ionic bonds, etc.) between the active sites of the catalyst and the intermediates of the reaction.

4th DCM. The influence of the outer reaction-center atoms of the catalytic system, especially the roles of the collective electronic properties of the catalyst and of the substituent effects on the part of the adsorbed reactants.

5th DCM. The influence of the distribution of fractional charges in the reaction center in the course of the reaction, or in a more simple approximation the charge on the intermediate products of the reaction (for example, carbonium-ionic and oxonium-ionic mechanisms).

6th DCM. The energy profile of the catalytic reaction, or the values of the decisive minima and maxima of the energy profile (heats of adsorption, energy of activation) or in an even simpler sense the nature of the rate determining step of the reaction.

To give an impression of the concrete meaning of these characteristics we have schematically illustrated in Fig. 1. one of the many possible mechanisms (a dissociative mechanism) of the double bond isomerization of olefins on a transition metal oxide catalyst and in Fig. 2. one of the possible mechanisms of CO oxidation on a chromia–molybdena oxide catalyst. It can be seen that for completely defining the mechanism all the DCM's must be known in both cases, i.e., the type of active centers (1st DCM), the kind of motion (2nd DCM) of reactants (dissociative mechanism, reaction of atomically adsorbed oxygen and adsorbed CO), the type of bonding (3rd DCM), the role of collective electronic interactions (4th DCM), the partial charges of adsorbed species (5th DCM) and the rate determining step (6th DCM) of the reaction. It is clear that there are some interdependences. Thus, for example, the partial charge of the adsorbed species is determined by the nature of the centers, the type of bonding and the role of collective electronic interactions, while the energy profile of the reaction is determined in principle by the combined effect of all other characteristics, but in general these interdependences are at present not

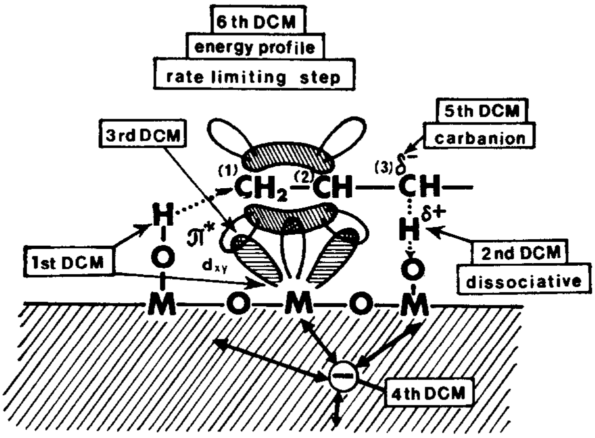

Fig. 1. A possible mechanism (a dissociative mechanism) of the double bond isomerization of olefins on a transition metal oxide catalyst.

known exactly. Therefore we must now regard the DCM's as individual but not independent characteristics of mechanisms. It is also important to emphasize that although at present it is generally not possible to determine all these characteristics in each case (especially in their full sense), their possible role must always be taken into account in making conclusions or generalizations in order to avoid the many seemingly correct, but in reality erroneous, conclusions.

3. The Possible Uses of the DCM

The most plausible application of the DCM is the systematization of the theoretically possible mechanisms of particular catalytic reactions. In the case of the double bond isomerization of olefins, for example, there may occur associative (A), dissociative (D), intramolecular (I) and synchronous (Sy) mechanisms with respect to the kind of motion (2nd DCM) of hydrogen atoms (Fig. 3). In general, the form of the motion of the hydrogen can in each case be H^+, H^-, H^0, i.e., the possible intermediates of the reaction may have a cationic, anionic or radical character (5th DCM). Furthermore, the intermediate products may be bonded to the catalyst by different types of bonds (3rd DCM), for example by π-bonds, σ-bonds, intermolecular forces and so on. The rate determining step of the reaction (6th DCM) may be, in general, any of the above elementary steps and interactions or their combination. For actual catalysts, the systematization of the existing centers and their combina-

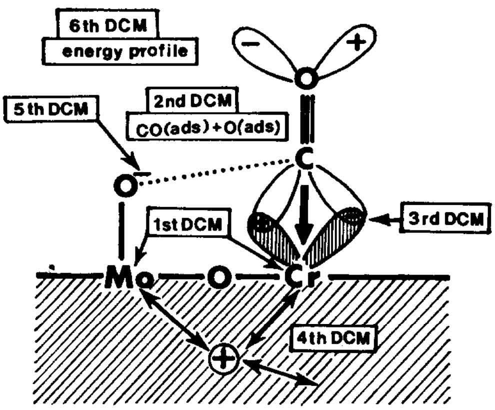

Fig. 2. A possible mechanism of CO oxidation on a chromium oxide–molybdenum oxide catalyst for illustrating the meaning of the determining characteristics of mechanisms (DCM).

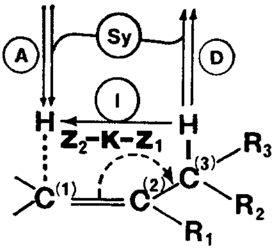

Fig. 3. The possible mechanisms of the double bond isomerization of olefins with respect to the kind of motion (2nd DCM) of hydrogen atoms.

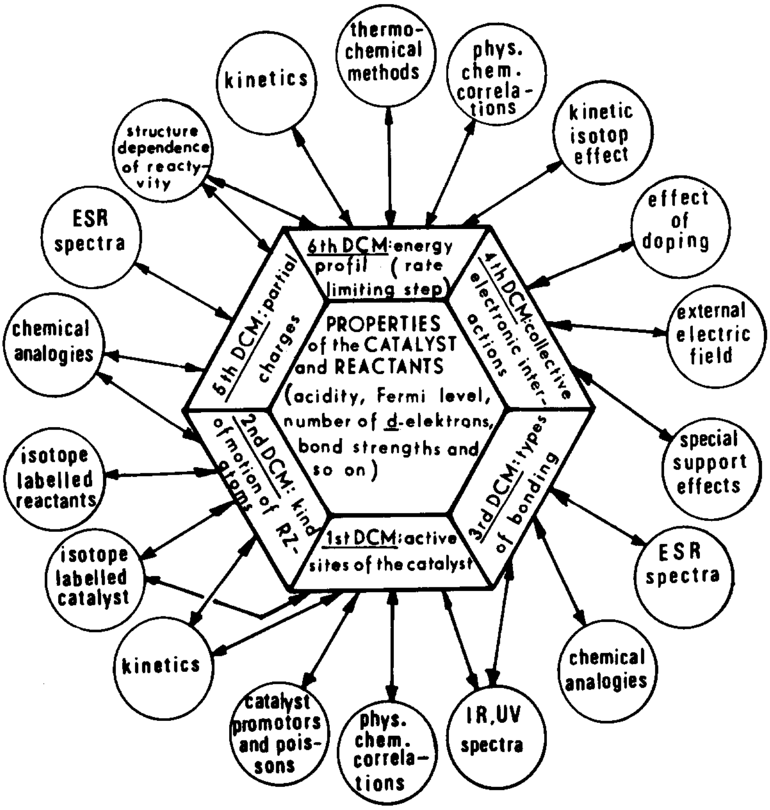

FIG. 4. Schematic illustration of the connection between the DCM and catalytic phenomena, the methods of investigation and the properties of the catalyst and reactants.

tions in active ensembles (1st DCM) shows which of the above described mechanisms are formally possible in any given case. If we wish to determine which of these formally possible mechanisms is the actual operating one, we must analyze the potentialities of the various methods of investigation of the mechanisms for determining the individual DCM. The connections between the various methods of investigation (the majority of which bear upon catalytic phenomena) and the individual DCM is schematically illustrated in Fig. 4. As a practical illustration, let us quote briefly some results of the complex investigation of the mechanism of CO oxidation on chromia-molybdena (*10*):

The kinetic investigations show that the reaction proceeds between adsorbed oxygen and adsorbed carbon monoxide (2nd DCM) and the rate determining step is the surface reaction (6th DCM).

For the mixed oxides of different composition there is a correlation between the catalytic activity and the bond strength of surface oxygen to catalyst (characterized by the reducibility of the samples), as well as between the catalytic activity and the electrical conductivity of the samples. These correlations make it probable that the splitting of the oxygen–catalyst bond (2nd DCM) as well as the collective electronic interactions (4th DCM) are deciding factors for the rate determining step' (6th DCM) of the reaction.

It was found by pulse technique experiments that the partial reduction of the surface increases the catalytic activity. This effect makes it probable that incompletely coordinated surface atoms are parts of the active sites of the catalyst (1st

DCM). The present results do not allow us to distinguish clearly which of the metal ions are the active centers for adsorption of CO, i.e., Cr (as illustrated in Fig. 2) or Mo.

On the basis of chemical analogies, it is probable that the type of bonding (3rd DCM) between the incompletely coordinated transition metal ion and CO may be similar to metal carbonyls. The mechanism of CO oxidation illustrated in Fig. 2 is in accordance with the cited results, but it cannot be regarded as being proved. By including in such a discussion other suitable methods of investigation, it can be generally shown which aspects of the complete mechanisms are indicated by the different methods and what is their conclusive force. It can be seen, too, what kind of new investigations are needed to gain complete information about the essence of the mechanisms. Such a systematic general discussion of the real possibilities of the methods of investigation in determining the mechanisms of catalytic reactions is the second important application of the DCM's.

The third possible application of the DCM concept consists in the systematic examination of the various theories of catalysis by investigating which of the determining aspects of the full essence of mechanisms of catalytic reactions are taken into account or neglected by the individual theories. It can be easily realized that the individual DCM's are in connection not only with the catalytic phenomena, but that there also exist causal connections between them and the different properties of the catalyst and of the reactants, as schematically illustrated in Fig. 4. The ascertaining of these twofold causal connections of the mechanisms is the basic aim of the theories of catalysis. It is characteristic of the different existing theories of catalysis that they do not take into consideration the role of all of the determining characteristics of the mechanisms and of the determining properties of the catalytic system.

We can see, for example, in the case of the mechanism illustrated in Fig. 2 that in order to gain a complete knowledge of the reaction mechanism and of the laws of the catalytic oxidation of CO it is necessary to consider all the different types of interactions and elementary steps discussed by the electronic (*1*, *4*), ligand field (*2*, *3*) and kinetic theories (*1*, *7*) or by the theoretically interpreted correlations between the catalytic activity and the oxygen–catalyst bond strength (*2*, *5*). The mechanism of the double bond isomerization of olefins illustrated by Fig. 1 demonstrates the necessity, the possibility and the difficulties, as well, of the simultaneous application of the various theories of catalysis. It can easily be recognized that the following interactions are decisive aspects of the complete mechanism:

Abstraction of a hydrogen atom from the allyl-position (^{3}C) by a Lewis base (surface oxygen of the catalyst), (2nd DCM) and the addition of a hydrogen atom to the ^{1}C vinylic carbon atom (acid–base interaction, i.e., acid–base theory).

Formation of a coordinative bond (3rd DCM) between the double bond of the olefin and the coordinatively unsaturated surface metal atoms (1st DCM), (ligand field theory).

It is well known that the rates of catalytic reactions and their dependence on partial pressures and temperature will be fundamentally determined by the energy profile (6th DCM) of the reaction, and can be discussed by the kinetic theories. One can easily realize, on the other hand, that it is the first five DCM's that by the above-mentioned interactions determine the energy profile. The actual nature of this control can be discussed on the basis of the individual theories, taking always into consideration that the regarded interactions are only a part of the complete mechanism.

We believe that for such complex investigations the DCM concept gives at present the most reasonable basis. Thus it is possible to carry out systematic and critical investigation concerning which of the individual DCM's are taken into account correctly in the different theories of catalysis, which of them are assumed and which of them are neglected. In this way we can find out the limitations of the theories, the contradictions between them as well as their connections and the possibilities of their joint application. It can also be seen in what respect is needed a new theoretical approximation of the laws of catalysis. All these possibilities of the application of the above formulated DCM will be described in detail in separate publications.

ACKNOWLEDGMENTS

The author expresses his gratitude to Professor O. V. Krylov, Professor L. Ya. Margolis, Dr. I. I. Tretjakov and many other colleagues from the Institute of Chemical Physics of the Academy of Sciences of the USSR, to Professor Z. G. Szabó (Budapest), Professor W. M. H. Sachtler (Leiden) and to Dr. B. Jóvér (Budapest) for useful discussions.

REFERENCES

1. SZABÓ, Z., AND KALLÓ, D., Eds., "Contact Catalysis," Elsevier, Amsterdam, in press.
2. KRYLOV, O. V., "Catalysis by Nonmetals." Academic Press, New York, 1970.
3. DOWDEN, D. A., AND WELLS, D., *Actes Congr. Int. Catal., 2nd, 1960* **2** (1961).
4. WOLKENSTEIN, F. F., "Electronic Phenomena in Adsorption and Catalysis on Semiconductors" (in Russian). Izd. Mir., Moscow, 1969.
5. BORESKOV, G. K., *Kinet. Katal.* **14,** 7 (1973).
6. UGO, R., *Proc. Int. Congr. Catal., 5th,* plenary lecture, Palm Beach, *1972.*
7. KIPERMAN, S. L., Introduction to the kinetics of heterogenous catalytic reactions (in Russian). Izd. Nauka, Moscow, 1964.
8. GÁTI, G., AND KNÖZINGER, H., *Proc. Int. Congr. Catal., 5th,* Prepr. No. 57, Palm Beach, *1972.*
9. GÁTI, G., AND MÁNDY, T., *Proc. Int. Congr. Catal., 4th,* Akadémiai Kiadó, Budapest, *1971* **1,** p. 567.
10. GÁTI, G., FÁY, L., AND JÓVÉR, B., *Chem. Z.* **95,** 907 (1971).
11. GÁTI, G., unpublished data.
12. COSSÉE, P., *J. Catal.* **3,** 80 (1964).
13. ARLMAN, E. J., *J. Catal.* **5,** 178 (1966).