Kinetics and Catalysis, Vol. 41, No. 3, 2000, pp. 298–299. Translated from Kinetika i Kataliz, Vol. 41, No. 3, 2000, pp. 331–332.

Critical Phenomena as a Discriminating Factor in the Studies of Reaction Mechanisms

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Received December 23, 1998

Abstract—Eleven mechanisms for heterogeneous catalytic ethylene hydrogenation obtained with a computer program MECHEM were examined for possible multiplicity of steady states in an isothermal flow-type well-stirred reactor. Of these eleven mechanisms, four allow the multiplicity of steady states, but the others do not. The multiplicity of steady states is shown to be a strong discriminating factor when considering the hypothetical mechanisms of catalytic reactions.

In recent years we developed a rational strategy for mechanistic studies of complex reactions [1, 2]. A methodologically sound method is based on proposing a set of mechanistic hypotheses and designing experiments capable of rejecting any hypothesis from this set. Attempts to prove any known or proposed mechanism by experiments are misguided because it is only possible to determine whether or not the mechanism contradicts experimental observations. Thus, we have carried out research along two lines: (1) the development of computer programs to help propose mechanistic hypotheses of catalytic reactions [3–6] and (2) the

⟨1⟩

$2M + CH_2{=}CH_2 \rightleftharpoons MCH_2CH_2M$

$H_2 + MCH_2CH_2M \rightleftharpoons 2MCH_3$

$2MCH_3 \rightleftharpoons 2M + CH_3CH_3$

⟨2⟩

$2M + H_2 \rightleftharpoons 2MH$

$CH_2{=}CH_2 + MH \rightleftharpoons MCH_2CH_3$

$MH + MCH_2CH_3 \rightleftharpoons 2M + CH_3CH_3$

⟨3⟩

$2M + H_2 \rightleftharpoons 2MH$

$CH_2{=}CH_2 + MH \rightleftharpoons MCH_2CH_3$

$H_2 + MCH_2CH_3 \rightleftharpoons CH_3CH_3 + MH$

⟨4⟩

$2M + CH_2{=}CH_2 \rightleftharpoons MCH_2CH_2M$

$H_2 + MCH_2CH_2M \rightleftharpoons MH + MCH_2CH_3$

$MH + MCH_2CH_3 \rightleftharpoons 2M + CH_3CH_3$

⟨5⟩

$2M + CH_2{=}CH_2 \rightleftharpoons MCH_2CH_2M$

$H_2 + MCH_2CH_2M \rightleftharpoons MH + MCH_2CH_3$

$H_2 + MCH_2CH_3 \rightleftharpoons CH_3CH_3 + MH$

⟨6⟩

$2M + CH_2{=}CH_2 \rightleftharpoons MH + MCH{=}CH_2$

$H_2 + MCH{=}CH_2 \rightleftharpoons MCH_2CH_3$

$MH + MCH_2CH_3 \rightleftharpoons 2M + CH_3CH_3$

⟨7⟩

$2M + CH_2{=}CH_2 \rightleftharpoons MH + MCH{=}CH_2$

$H_2 + MCH{=}CH_2 \rightleftharpoons MCH_2CH_3$

$H_2 + MCH_2CH_3 \rightleftharpoons CH_3CH_3 + MH$

⟨8⟩

$2M + H_2 \rightleftharpoons 2MH$

$CH_2{=}CH_2 + MH \rightleftharpoons H_2 + MCH{=}CH_2$

$H_2 + MCH{=}CH_2 \rightleftharpoons MCH_2CH_3$

$MH + MCH_2CH_3 \rightleftharpoons 2M + CH_3CH_3$

⟨9⟩

$2M + H_2 \rightleftharpoons 2MH$

$CH_2{=}CH_2 + MH \rightleftharpoons H_2 + MCH{=}CH_2$

$H_2 + MCH{=}CH_2 \rightleftharpoons MCH_2CH_3$

$H_2 + MCH_2CH_3 \rightleftharpoons CH_3CH_3 + MH$

⟨10⟩

$2M + CH_2{=}CH_2 \rightleftharpoons MCH_2CH_2M$

$2M + H_2 \rightleftharpoons 2MH$

$MCH_2CH_2M + MH \rightleftharpoons 2M + MCH_2CH_3$

$MH + MCH_2{-}CH_3 \rightleftharpoons 2M + CH_3CH_3$

⟨11⟩

$2M + CH_2{=}CH_2 \rightleftharpoons MCH_2CH_2M$

$2M + H_2 \rightleftharpoons 2MH$

$MCH_2CH_2M + MH \rightleftharpoons 2M + MCH_2CH_3$

$H_2 + MCH_2CH_3 \rightleftharpoons CH_3CH_3 + MH$

Scheme 1.

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search for discriminating factors. One type of experimental information that can be used as a discriminating factor is the presence of critical phenomena, such as the multiplicity of steady states (MSS), oscillations, etc. In our recent papers [7, 8], we reported on critical phenomena in typical metal-complex homogeneous catalytic systems under the conditions of alkyne oxidative carbonylation. These phenomena have also been observed before in homogenous catalysis in similar systems, but they have been given no credence and remained unstudied.

In this short communication, we show that information on the presence of MSS is a strong discriminating factor. For this purpose, we used information [9] that MSS is observed in ethylene hydrogenation over a rhodium catalyst, taking into account that the hypothetical mechanisms proposed in [9] were not chemically plausible.

We used the computer program MECHEM [2, 4, 5] to generate hypothetical mechanisms of the heterogeneous catalytic hydrogenation of ethylene and obtained eleven plausible hypothetical mechanisms shown in the scheme. The technical details of mechanism generation were described in [2].

For mechanism generation, we used the computer program CNRT [10], which analyzes mechanisms for MSS in an isothermal well-stirred flow-type reactor. Note that the CRNT manual directly points to the fact that the program can be used for mechanism discrimination based on data on the existence and positions of multiple steady states.

Our formulation assumed that MSS are due to the mechanism structure and the nature of nonlinear steps. Thus, rate constants were considered independent of the surface coverage (uniform surface approximation). Effects due to possible surface reconstruction, interactions between coadsorbed species, species diffusion, and other factors were neglected. Of course, such an approach is not fully correct when studying heterogeneous catalytic reactions, but it is adequate for homogeneous catalysis studies. For reactions in solutions of metal complexes, conditions can be created under which the only factor responsible for critical phenomena is the structure of a mechanism.

All steps in the mechanisms shown in the scheme were considered reversible. We also assumed that H_2 and C_2H_4 are present at both an inlet and an outlet of a reactor, whereas C_2H_6 is present only at an outlet.

Our examination of the mechanisms generated with MECHEM showed that MSS can theoretically be observed for four mechanisms (2, 8, 10, and 11), but seven mechanisms (1, 3–7, and 9) do not allow MSS. Thus, seven of the eleven mechanisms were rejected. This confirms the idea that MSS is a strong discriminating factor. Interestingly, the Horiuti–Polanyi mechanism (mechanism 11) [11], which is proposed most frequently, does allow MSS, but the Twigg–Rideal mechanism [12] does not. Thus, based on MSS data, we managed to reject about 64% of the hypothetical mechanisms.

Many homogeneous oscillators display MSS as one varies the kinetic parameters [13]. If one could show that the presence of MSS over a wide range of parameters tends to increase the probability of oscillations, then the above methods could help to elucidate the mechanisms of oscillating reactions.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 97-03-32324).

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