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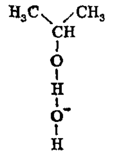
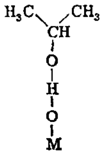
Models of Active Centers in Quantum-Chemical Study of Catalytic Dehydrogenation on Metal Oxides

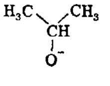
In quantum-chemical studies of adsorption states and reactive intermediates on solid catalysts, the crucial problem is the choice of a suitable model of the active center. It is clear that models consisting of many atoms of the solid would be much more realistic and, in consequence, the results of the calculations more reliable. However, the technical limitations given by requirements on the memory of the computer and on computing time are severe. The problem is quite difficult when the adsorbing molecule is polyatomic and/or the solid contains heavy atoms (cf., for example, ref. *1*).

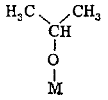
In a recent paper from this Laboratory (*2*), the quantum-chemical study of dehydrogenation of 2-propanol on oxide surfaces was based on very primitive models of the active center (models A1 and B1 in the present paper). In order to find out whether the qualitative conclusions and agreement with the experiment would be changed by extending the models, calculations were made for models A2–A4 and B2–B6 which involve a metal atom from the surface of the oxide. In respect to the weak band structure and to the localization of states in oxides, we can accept a metal alcoholate as a good approximation of a surface alcoholate.

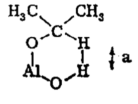
The pertinent values of calculations obtained by means of the CNDO/2 method are summarized in Tables 1 and 2. The same program as in a preceding paper (*3*) was used. The models of the A series correspond to molecular adsorption by means of a hydrogen bridge. The B models are surface alcoholates; in B2 to B4 the active center is formed by a single metal atom; in B5 and B6 it consists of the grouping M–O–H. The models B5 and B6 differ in the distance between the two hydrogen atoms which would eventually form the hydrogen molecule. Otherwise standard geometry and bond lengths, which were specified in the preceding paper (*3*) were used in all models.


A1


A2; M=Al
A3; M=Sc
A4; M=Cr


B1


B2; M=Al
B3; M=Sc
B4; M=Cr



B5; a = 0.187 nm
B6; a = 0.080 nm

The data in Tables 1 and 2 show no qualitative change of the observed effects due to improvement of the model. In the A series the positive charge on hydrogen in the hydroxyl group is increased and H_α is more activated than H_β for leaving the molecule with two electrons (as H^-) under the influence of OH^- or a metal atom. Similar agreement is found in

TABLE 1

Calculated Charges on Selected Atoms of 2-Propanol and Models A1–A4, B1–B6 (in $10^{-2} \cdot e$)

Species	H in OH	H_α	H_β[a]
$CH_3CHOHCH_3$	13.40	− 3.15	0.88
A1	25.58	− 5.15	−3.12
A2	18.57	− 3.61	0.23
A3	18.46	− 3.63	0.15
A4	21.09	− 3.89	−0.33
B1	—	−12.92	−7.19
B2	—	− 4.64	0.62
B3	—	− 6.93	−0.57
B4	—	− 4.84	−0.56
B5	—	− 3.78	0.36
B6	—	− 0.32	0.07

[a] In antiperiplanar position relative to OH group.

TABLE 2

Calculated Changes of Wiberg Bond Index (*4*) (in Percentage) Caused in Selected Bonds by Transition from Parent Alcohol $CH_3CHOHCH_3$ to Models A1–A4 and B1–B6

Model	O–H	C_α–H	C_β–H[a]
A1	−20.28	−0.69	−0.13
A2	−6.27	−0.12	0.01
A3	−6.49	−0.13	0.01
A4	−10.05	−0.22	0.00
B1	—	−4.04	−0.97
B2	—	−2.91	−0.31
B3	—	−1.95	−0.16
B4	—	−3.83	−0.43
B5	—	−5.39	−0.05
B6	—	−6.28	−0.09

[a] In antiperiplanar position relative to OH group.

changes of bond strength. The same behavior was observed in the B series where three levels of model complexity were adopted (B1; B2 to B4; B5 and B6). In all cases the change in the molecule suggests dehydrogenation as the next step in the development of the reaction system along the reaction coordinate (if H_β would be activated the reaction course should be dehydration; see ref. *5*).

It can be concluded that for analysis of trends in change of electron distribution due to adsorption or for qualitative comparison of effects caused by two different catalysts (or types of active centers) quite simple models of active centers may be useful. The alternative approach to the estimation of the reaction course, i.e., use of a model consisting of a larger fragment of the solid lattice and use of simplified calculation procedure (EHT method), ended in our case with a complete failure.

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