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Parametric Sensitivity in the Simulation of γ-Alumina Dehydration Catalysis

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A study on the sensitivity of a simulation of alcohol dehydration on γ-alumina, previously reported, to several parameters of the simulation is described. It is found that the simulation is relatively insensitive to variation of these parameters—surface index plane, competitive reaction probability of ether or ethylene formation, and the sites involved in ethylene desorption—within physically reasonable bounds.

INTRODUCTION

We have previously reported (*1*) a simulation of the activity and selectivity of γ-alumina for ethanol dehydration using a Monte Carlo calculation employing an idealized model of the alumina surface and a surface reaction mechanism involving a chemisorbed ethoxide intermediate. The simulation was quite effective in predicting trends in selectivity (ether formation vs olefin formation) and activity as affected by competitive adsorption of water on the surface and by temperature level (in terms of the degree of dehydration of the surface). However, the simulation is based on a number of *a priori* assumptions, and it is legitimate to inquire as to what their cumulative effect on the computed results might be.

In the present communication we treat three major assumptions of the prior work: (i) that only a single crystallographic plane is used to model the surface, (ii) that the ethoxide intermediate has an equal probability of forming ether or ethylene product, and (iii) that only nearest neighbor oxide sites are involved in the desorption of ethylene. The details of the computa-

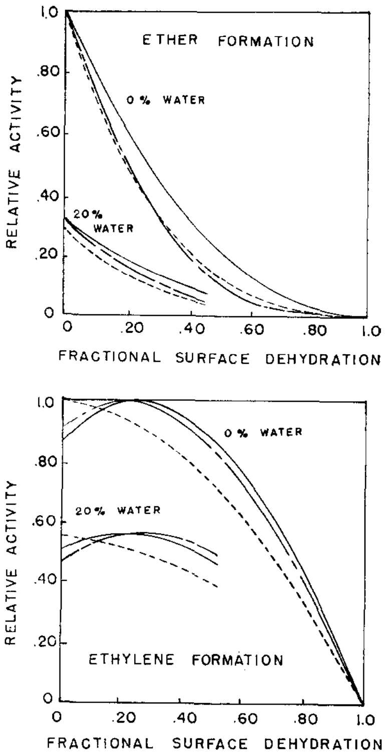

FIG. 1. A comparison of the relative number of reaction configurations, or relative activity, for ether and ethylene formation on the 110, 111 and 100 surfaces of γ-alumina with pure ethanol and 80% ethanol–20% water reaction mixtures. (—) 110; (- -) 111; (— -) 100.

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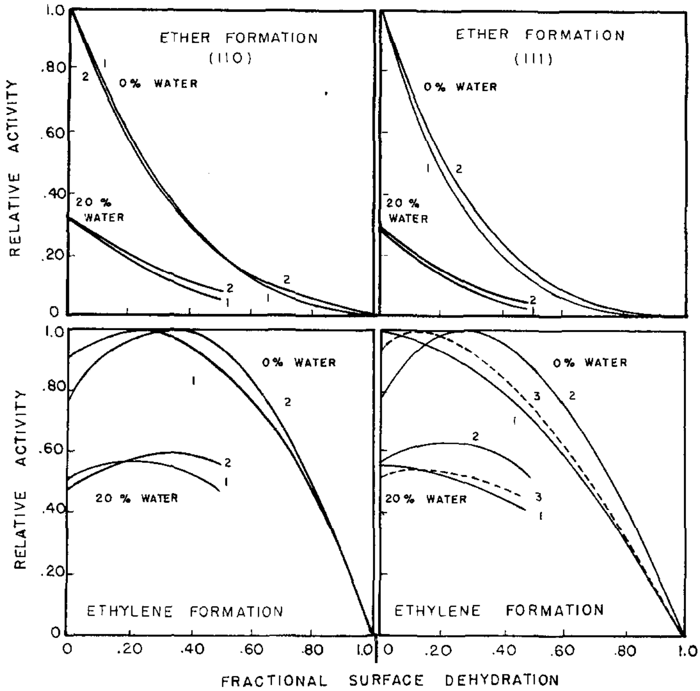


FIG. 2. Comparison of calculations for weighted and nonweighted ether-ethylene reaction probabilities on the 110 and 111 surfaces. (1) Nonweighted; (2) weighted; ether:ethylene, 1.5:1; (3) Nonweighted with next-nearest neighbor oxide sites.

tional procedure and the treatment of results are the same as those described before (*1*).

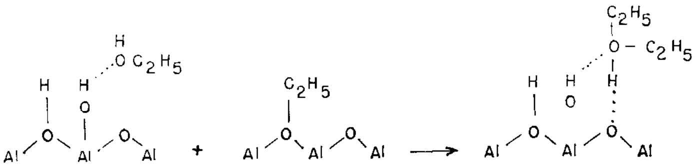
MODELS OF THE SURFACE

In Fig. 1 is given a comparison of results, in terms of relative numbers of reaction configurations as influenced by surface hydration and competitive chemisorption of water, for the 110, 111, and 100 planes of γ-alumina [cf. Figs. 8 and 9 of (*1*)]. Details of the differences in structures of these planes are given by Lippens (*2*).

Both surface hydration and competitive chemisorption effects are modeled in about the same way by the three surfaces. The only significant differences are found in the results for the 110 and 111 planes, particularly with regard to ethylene formation in the latter case. Here there is no maximum in ethylene production at intermediate surface hydration as found in all other cases. This can be attributed to a screening of a portion of the octahedral aluminum in the 111 plane by surface oxygen ions, reducing the effect of hydroxylation on the ethylene reaction which requires an oxide site for hydrogen abstraction from the ethoxide complex (*1*). The difference is not large, however, and as will be seen disappears if next-nearest neighbor oxide sites are included in the simulation. In all cases the surface is considered to terminate in anions and the outermost aluminum ions are below the surface oxide plane (*3*).

REACTION PROBABILITIES

A reaction is considered to occur when the configuration of reactants around a given surface site conforms to the requirements of the surface reaction mechanism. These are taken to be a weakly adsorbed ethanol (bonded to a surface OH) adjacent to an ethoxide complex for ether formation, and an ethoxide complex adjacent to an unoccupied oxide for ethylene formation:


(I)

and:


(II)

As might be expected, it is possible for an ethoxide complex to be located such that the configuration requirements for both reactions are satisfied. Previously such "ties" were resolved by assigning equal probability to the two reactions. However, the apparent activation energies in the temperature range of 275 to 325°C have been determined experimentally (*1*) for conditions corresponding to the simulation and they are not the same, as shown in Table 1. The ratio of activation energies is used here as a rough weighting factor (1.5:1) in favor of the ether reaction when both configurational requirements are satisfied by a given complex.

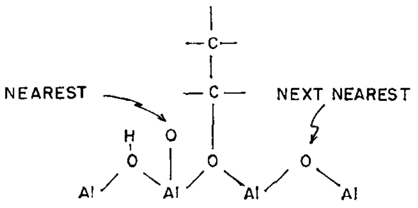
The trends for ether formation are essentially totally insensitive to weighting, as shown by the comparison between curves 1 and 2 on the top of Fig. 2, however ethylene is affected somewhat with the maximum configurations occurring at higher levels of surface dehydration (curve 2). This change in the locus of maximum formation of ethylene is reasonable, since with the enhanced ether reaction ethylene production will decrease unless additional oxide sites are made available (i.e., higher level of surface dehydration).

SITES FOR ETHYLENE FORMATION

As shown in Figs. 1 and 2, in general the maximum number of configurations for ethylene is found near 0.3 fraction surface dehydration, the result of a balance between hydroxides required for complex formation and oxides required for ethylene formation. Previously only the oxides formed on aluminum sites as a result of chemisorption and complex formation were taken to be active in hydrogen abstraction, since these comprise the nearest neighbors to the locus of the ethoxide complex. If we relax this requirement to permit any adjacent lattice oxide sites also to be active, the results are practically identical to the nearest neighbor calculation. This is shown by comparison of curves 1 and 3, for the 111 surface, on the lower right of Fig. 2. The particular sites involved are:

TABLE 1
APPARENT ACTIVATION ENERGIES FOR ETHER AND ETHYLENE FORMATION 275–325°C

Mole fraction water in reaction mixture:	0.0	0.0917	0.204	0.413
E (ether) (kcal/mole)	24.3	26.3	27.2	28.7
E (ethylene) (kcal/mole)	37.1	38.5	40.5	45.6



(III)

Similar results were also obtained for the other planes investigated, indicating only a small increase in the number of ethylene configurations on inclusion of next-nearest oxide sites.

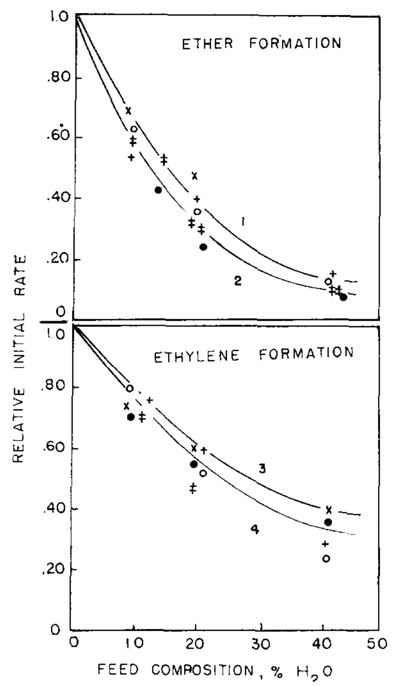


FIG. 3. Comparison of extremes of results for all parametric combinations with experimental data for activity and selectivity in ether and ethylene formation. (1) 110, nonweighted; (2) 111, nonweighted; (3) 111, weighted; (4) 111, nonweighted; Top: (×) 350°C; (+) 325°C; (○) 300°C; (‡) 275°C; (●) 250°C; bottom: (●) 385°C; (×) 350°C; (+) 325°C; (○) 300°C; (‡) 275°C.

CONCLUSIONS

Dabrowski, Butt and Bliss (*1*) have given experimental data on activity and selectivity for ether and ethylene formation. A summary of the parametric effects investigated here, in comparison with the previous experimental results, is given in Fig. 3. The solid lines represent the extremes of the simulation results determined from the three index planes, the two reaction probabilities, and the two site configurations for ethylene considered. These limits are the 110 surface, nonweighted, and the 111 surface, nonweighted, for ether formation, and the 111 surface, weighted, and the 111 surface, nonweighted, for ethylene formation, shown as curves 1–4, respectively, on Fig. 3. All other simulation results for the various surfaces with weighted and nonweighted reaction probabilities lie between the two curves shown for each product. We thus conclude that the simulation is not very sensitive to any of these parameters, a fact which is particularly convenient for purposes of surface modeling since a single plane can be used as representative, at least for low index surfaces. On the other hand, simulation results are strongly dependent on the sequence of steps involved in the reaction mechanism postulated, as we have discussed elsewhere (*4*).

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