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LETTER TO THE EDITORS

On the Adequacy of a Multi-Site Model Suggested for the Catalytic Hydrogenation of Olefins

INTRODUCTION

For the hydrogenation of propylene and isobutylene over platinum–alumina catalyst, Kolboe (*1*) recently proposed multisite rate models which are based on the associative and dissociative adsorption of olefins. Kolboe concluded that his dissociative model provided a statistically adequate representation of rate data gathered by Rogers (*2*) and Lih (*3*). He also concluded that his dissociative model was superior to models postulated by other investigators (*4, 5*) for the same reaction systems, because his model can explain the isotopic exchange reaction of hydrogen atoms, and because his model took up more of the variation in the rate data employed than did the previous models.

We agree that the dissociative adsorption model, in conjunction with multiadsorption sites, has potential. There are, however, some questionable points which need to be examined more carefully. The purpose of this letter is to discuss these briefly.

DISCUSSION

To examine the relative fits of his associative and dissociative models, Kolboe compares the two "variance estimates for the rate data" by an *F* test. As a result of this test he concludes that "the dissociative model [is] significantly better" and that the associative model "is therefore not consistent with the experimentally measured rates." Such sweeping conclusions may or may not be in fact true, but they are certainly not justified on the basis of the particular computation carried out by Kolboe. In the first place, because the models are both nonlinear [see Draper and Smith (*6*), Chap. 10] neither of the variance estimates necessarily follows a distribution proportional to the χ^2 distribution, and neither necessarily provides an unbiased estimator of the variance of an individual observation. In addition, the two estimates are not necessarily independent and, in fact, are almost certainly *not* independent. Thus the statistic used by Kolboe almost certainly does not have an *F*-distribution and the test applied is invalid, as are the "conclusions" that follow directly from it. The most that can be said from the fitting procedure is that the dissociative model with fewer parameters picks up more of the variation in the data than the associative model with more parameters.

However, even if we accept the dissociative model as comparatively the better bet, there still remains the question of whether or not it appears to be adequate to the task of representing the data. Two main ways of looking at this question are:

1. To use repeat observations to obtain some idea of what the true error variation might be and then to compare the residual variation with it [see Draper and Smith (*6*), Chaps. 1 and 10].
2. To obtain the appropriate residuals from the fitted model and to examine these residuals in all sensible ways [see Draper and Smith (*6*) Chap. 3]. Certain patterns indicate defects in the assumptions made to fit the model.

The first of these options is not available to use because there are no repeat runs in the data of Rogers (*2*) and Lih (*3*). We can however, examine the residuals from the dissociate model suggested by Kolboe and see if there are any discernible patterns that imply inadequacy.

Residuals Plots

In Kolboe's analysis, the parameters are evidently estimated by minimizing $\sum_{u=1}^{n} \{(Y_u - \eta_u)/Y_u\}^2$, the sum of squares of proportional deviations where Y_u represents an observed value, and η_u is the corresponding value given by the theoretical model which contains the parameters to be estimated. The divisor Y_u arises under an assumption that the errors in Y are proportional to Y. Thus, the appropriate n residuals here are the $e_u = (Y_u - \hat{Y}_u)/Y_u$, $u = 1,2, \ldots, n$, where $\hat{Y}_u$ denotes the fitted value predicted by the fitted model at the conditions specified in the uth run.

The standard residuals plots include those of residuals against the corresponding predicted values (in our case, the corresponding reaction rates predicted by the model), and residuals against the corresponding values of the independent (or predictor) variables temperature and the partial pressures of hydrogen and olefins. We display one of these plots which points up defects in Kolboe's model.

The data for our plot are obtained by using Kolboe's (*1*) dissociative model of propylene hydrogenation, and the estimates of parameters reported in his Table 1 (*1*). Figure 1 shows the plot of residuals versus their corresponding fitted values, that is, of the points $(\hat{Y}_u, e_u)$, $u = 1,2, \ldots, n$.

The plot exhibits a characteristic defect, see (*6*) for details, a "funnel" shape in this case narrowing from left to right. The implication is that, *contrary to what has been assumed in fitting the model by least squares*, the errors in the weighted response do *not* have constant variance at all hydrogenation rates. Thus the dissociative model must be deemed inadequate. The use of (differently) weighted least squares is one possible next step; revision of the model is another, perhaps by use of a suitable transformation on the response variable, or on the lines indicated below.

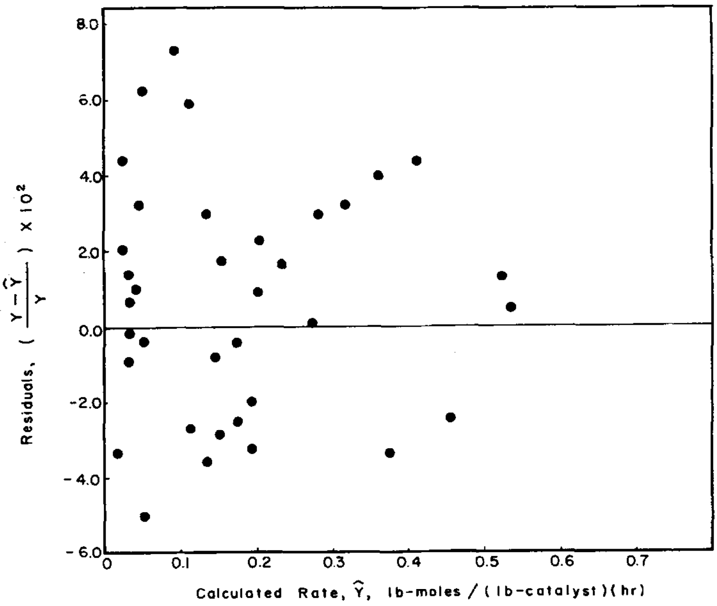

FIG. 1. Plot of residuals against corresponding fitted rate values, both calculated from Kolboe's dissociative model (*1*).

Further Comments

Kolboe's objective is to develop rate models which can reflect the general mechanistic features observed for the catalytic hydrogenation of low molecular weight olefins. One of the important features not included in previously considered models (*4*, *5*) is, as Kolboe correctly pointed out, an isotopic exchange reaction of hydrogen. Indeed, the associative and the dissociative mechanism together explain the isotopic exchange of hydrogen.

Hirota and Hironaka (*7*) studied the catalytic hydrogenation of propylene with a platinum catalyst at room temperature by applying microwave spectroscopic analysis, and postulated the hydrogenation mechanism of propylene. According to their results, the *associative adsorption* of propylene is predominant, but the dissociative adsorption of propylene also occurs to a certain extent under their experimental conditions. From the work of Hirota and Hironaka it seems improbable that the sole use of either the associative adsorption or the dissociative adsorption of propylene can properly describe the hydrogenation data taken with platinum–alumina catalyst at temperatures from 1.4 to 34°C. Perhaps a model combining both the associative and dissociative aspects is needed. In the light of these considerations and our comments above, acceptance of Kolboe's model, in which only a dissociative model is considered, is probably unwise.

CONCLUSION

Because of the considerations discussed above, we conclude that the dissociative model of Kolboe is not adequate for representation of the rate data gathered by Rogers and Lih and that more work is still needed to explain the discrepancies observed.

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