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LETTER TO THE EDITOR

Comment on "On the Temperature Dependence of the Arrhenius Activation Energy for Hydroisomerization Catalyzed by Pt/Mordenite" by A. van de Runstraat, J. van Grondelle, and R. A. van Santen

Reference (1) presents results of microkinetics simulation studies of the temperature behavior of a chemical reaction in a typical single-file system which are supposed to contradict the results of our studies on this topic (2–5). In the present letter, we show that the results of Ref. (1) are by no means in conflict with our findings; they complement the experimental evidence supporting the validity of a general treatment of the temperature dependence of reaction rates in single-file systems, outlined in Ref. (6).

As a well-known feature of transport-reaction systems, molecular transport affects the temperature dependence of the total output. This is most illustratively expressed by a comparison of the apparent activation energy, E_{app}, with the intrinsic activation energy, E_{true}, of the reaction. If, e.g., the transport is by Fickian diffusion, one generally finds $E_{\text{app}} \leq E_{\text{true}}$. However, for neopentane conversion and H/D exchange in Pt/mordenite (2–4), the apparent activation energy was found to exceed the true one, $E_{\text{app}} > E_{\text{true}}$. This was even more striking since the transport in this zeolitic system may be assumed to proceed according to single-file diffusion, implying a transport inhibition much stronger than that of Fickian diffusion. We argued, however, that single-file diffusion might in fact be the cause of the observed phenomenon (4). Subsequently, Monte Carlo simulations (5) and numerical model calculations (6) confirmed that single-file systems can indeed exhibit a temperature behavior of the type observed experimentally, i.e., $E_{\text{app}} > E_{\text{true}}$.

The microkinetics simulation study presented in Ref. (1) also considered the temperature behavior of such a heterogeneously catalyzed reaction (hydroisomerisation in Pt/mordenite). The simulations presented there show that in the chemically controlled regime where transport effects are negligible, one has $E_{\text{app}} = E_{\text{true}}$ at low temperatures and $E_{\text{app}} < E_{\text{true}}$ at high temperatures, in agreement with experimental results. In contrast to the conclusion given in Ref. (1), this does not exclude the possibility that in the transport-controlled regime E_{app} can exceed E_{true}. Consequently, the treatment in Ref. (1), which disregards diffusion effects, does *not* invalidate the statement that the finding $E_{\text{app}} > E_{\text{true}}$ is caused by the transport pattern of single-file diffusion.

In order to further clarify the situation, we will briefly sketch the principal temperature behavior of a transport-reaction system as obtained in Ref. (6). Quite generally, a gradual increase in the temperature will lead to two effects:

1. The intrinsic conversion rate will increase. While at a low conversion rate, the system will be chemically controlled (effectiveness factor $\eta = 1$); it will eventually enter the transport controlled regime, where the effectiveness factor gradually drops.
2. The adsorption layer becomes depopulated. Whereas it is saturated (coverage $\theta \approx 1$) at low temperature, the sorbate concentration will decrease at higher temperature.

This leads to four possible situations with different temperature behavior of the overall rate:

	Coverage ≈ Saturation	→ Coverage < Saturation
Chemical control	$E_{\text{app}} = E_{\text{true}}$	$E_{\text{app}} < E_{\text{true}}$
↓		
Transport control	both $E_{\text{app}} \leq E_{\text{true}}$ and $E_{\text{app}} > E_{\text{true}}$ are possible	$E_{\text{app}} < E_{\text{true}}$

The arrows indicate the direction of the shifts to different regimes with increasing temperature.

It follows that:

- Within the chemically controlled regime, one has $E_{\text{app}} = E_{\text{true}}$ at temperatures low enough to maintain coverage near saturation, but $E_{\text{app}} < E_{\text{true}}$ when the temperature is sufficiently high so that the decrease in coverage prevails. This is in qualitative agreement with Ref. (1).
- In the transport-controlled regime at nearly saturated coverage, the case $E_{\text{app}} > E_{\text{true}}$ can occur. Whether it actually does depends on the particular transport pattern: Fickian diffusion will always lead to $E_{\text{app}} \leq E_{\text{true}}$, but single file diffusion may lead to $E_{\text{app}} > E_{\text{true}}$.

In summary, there is no contradiction between Ref. (1) and Refs. (2–6). Both groups refer to different situations

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(chemical vs transport control) and consider different phenomena. $E_{\mathrm{app}} = E_{\mathrm{true}}$ holds at low temperature, decreasing E_{app} with increasing temperature for chemically controlled reactions, but $E_{\mathrm{app}} > E_{\mathrm{true}}$ for some single-file diffusion-controlled situations.

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