Expansion of pulse responses from temporal analysis of products (TAP) for more accurate data analysis

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Introduction

Temporal analysis of products (TAP) [1] pulse responses are the exit flows of specific molecules from the micro-reactor as a function of time [2]. In TAP methodology, kinetics of elementary steps are derived using moments, which are integrals of the full TAP pulse response. However, in some cases the pulse response may be truncated due to technical reasons or human error, thereby compromising any data analysis due to moments generated from truncated pulse responses. Hence, the remainder of the TAP pulse response must be simulated in order that the true TAP pulse response can be properly analyzed. The current work discloses the development a function which mathematically expands TAP pulse responses, so that kinetic analysis can be accurately determined from truncated TAP responses.

Experimental

Since moments are integrals, the baseline of the entire pulse response needs to be accurately determined prior to moment based analysis. TAP thin zone theory suggests that slow pulse responses follow an exponential function when non diffusional processes cease [3]. Hence, if plotted in the logarithmic scale, this section of the pulse provides a straight line. Then, an equation for the straight line section that is generated is obtained. Using the exponential of this equation the TAP pulse response can be simulated beyond t, to the correct baseline. For validation, a number of entirely recorded pulse responses were truncated, with the expansion method then applied so that a comparison could be made between corresponding complete and expanded pulse responses. The method was then applied to pulse responses from oxidative dehydrogenation of ethane (ODHE) over a Cr-Mo-AuOx/α-Al2O3 catalyst and a Co-Cr-Sn-WOx/α-Al2O3 catalyst [4].

Results and Discussion

Previously, there were number of ways in which the baseline would be estimated in the case of truncated pulse responses, without expanding the pulse (see Figure 1). For instance, the baseline could be set as the initial point of the response, which actually results in the end of the pulse “levitating” above the baseline. An alternate to this is the use of the terminal point as the baseline. However, this inevitably leads to the initial part of the response being below the baseline. By way of compromise, the forced baseline approach can be used, which sets the baseline as the gradient between the initial and terminal points of the truncated pulse. However, this approach still results in a change of shape, and is also missing an unknown amount of the true pulse response. Using the expansion method listed above, it has been possible to accurately expand pulse responses, which has resulted in accurate determination of moments (see Figure 2), thereby allowing previously unavailable kinetic analysis for the ODHE reaction over Cr-Mo-AuOx/α-Al2O3 and Co-Cr-Sn-WOx/α-Al2O3 catalysts.

Significance

A function which can mathematically expand a TAP pulse response to its correct termination point has been developed and successfully applied. It may well be that this method could also be employed to reduce error in moment based analysis, but this requires further evaluation. The method has been successfully applied to an inert gas, a reactant and a desorbing product, thereby representing all possible pulse response types. Comparisons of the experimental data obtained for the ODH of ethane over Cr-Mo-AuOx/α-Al2O3 and Co-Cr-Sn-WOx/α-Al2O3 catalysts, analyzed with and without the “corrective” processing highlight the need for such correction to extract accurate kinetic information from TAP data.

References