Validity of the Madon-Boudart test for analysis of inter-particle dilution effects in a catalytic packed bed reactor

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Highlights

- Madon-Boudart test for intra-particle dilution may fail for inter-particle dilution
- Constant turnover rate with inter-particle dilution does not ensure kinetic regime
- Low conversion may not always ensure absence of diffusional limitations
- Inferences valid for both positive and negative order reactions

1. Introduction

Various criteria are utilized to ensure that the observed reaction rates are free from transport artifacts. Koros and Nowak [1] proposed the use of catalyst pellets with varying degree of dilution to check for transport limitations in reactors. It was shown that a relatively constant turnover rate (TOR) with respect to a change in the dilution ratio indicates the absence of diffusional limitations. Madon and Boudart [2] explained the use of the Koros-Nowak test for supported metal catalysts. However, the Madon-Boudart test, which was originally developed for intra-particle dilution effects, has been erroneously extended by various researchers to study inter-particle dilution effects. In this work, we show that the Madon-Boudart test based on the intra-particle dilution cannot be used in its original form to interpret the inter-particle dilution data.

2. Methods

A packed bed consisting of spherical inert and catalyst particles was considered and a plug flow reactor model was developed for isothermal bed conditions. The system of equations representing the convection, diffusion and reaction behavior were solved analytically for a positive first order reaction and the dependence of the turnover rate on the inter-particle and intra-particle dilution was obtained. A similar analysis was performed for a negative order reaction using numerical techniques.

3. Results and discussion

For a positive first order reaction, the dependence of turnover rate (TOR) on the operating parameters was found for low conversions and is given by Eq. (1) as follows:

$$TOR = \frac{c_m^{in} k_c A_p}{c_c V_p} \frac{\frac{\eta\varphi^2}{3Bi}}{1+\frac{\eta\varphi^2}{3Bi}} \qquad (1)$$

c_m^{in} in Eq. (1) is the inlet reactant concentration in the fluid phase, k_c is the mass transfer coefficient, A_p is the particle surface area, c_c is the active catalyst concentration, V_p is the particle volume, Bi is the Biot number, η is the effectiveness factor and φ is the Thiele modulus. It can be shown that in the absence of diffusional limitations ($\eta \approx 1$), the TOR is independent of c_c, which is the basis of the Madon-Boudart test for intra-particle dilution. However, it is also observed from Eq. (1) that the TOR for low conversions does not depend on the catalyst particle number density and this result is independent of the value of the effectiveness factor. For a fixed bed volume and porosity, a decrease in the catalyst particle number density indicates an increase in the inter-particle dilution. Hence, if the turnover rate is found to be independent of the inter-particle dilution ratio, it does not always imply that diffusional limitations are absent.

The effect of catalyst particle number density on the reaction rates was analyzed for a packed bed reactor in which NO was reduced to N_2 with the reaction rate exhibiting a positive first order dependence with respect to NO. The effectiveness factor was calculated to be 0.16, thereby indicating the presence of diffusional limitations. This was further confirmed by increasing the diffusivity in the catalyst particles, which resulted in an increase in the conversion. However, it was found that the turnover rate is nearly independent of the catalyst particle number density and is shown in Figure 1. This shows that a constant TOR with respect to the catalyst particle number density does not indicate the absence of diffusional limitations. It was also observed that the conversions are below 4.1% for various catalyst particle number densities. Hence, maintaining low conversions does not always ensure that experiments are being performed in the kinetic regime.

To verify the applicability of our result to a negative order reaction, a similar analysis was performed for CO oxidation over supported Pt catalysts in a packed bed reactor [3]. The effectiveness factor was calculated at various axial positions for the lowest and highest catalyst particle number density and is plotted in Figure 2. It is observed that for both the cases, the effectiveness factor is greater than one throughout the bed, hence confirming the presence of diffusional limitations. Despite an increase in the number density of catalyst particles by 50 times, the increase in turnover rate is less than 8% of the minimum value. This confirms that even for a reaction exhibiting negative order kinetics, the near independence of the TOR with respect to the catalyst particle number density should not be used to determine the absence of diffusional limitations.

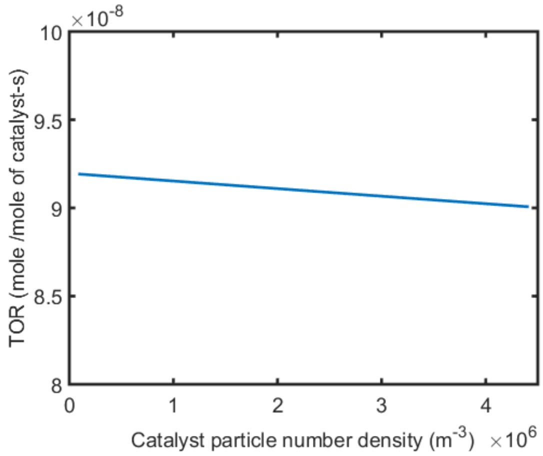

Figure 1. Variation of turnover rate with catalyst particle number density for NO reduction.

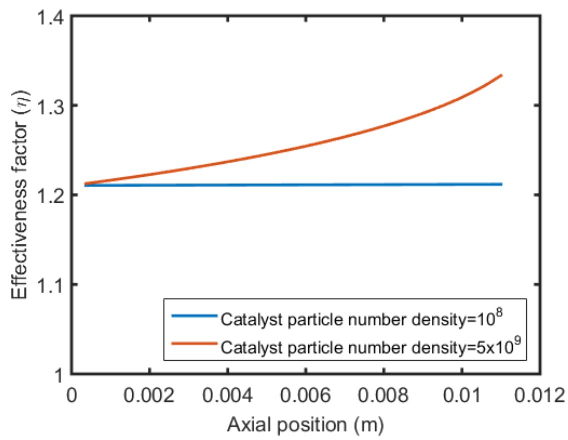

Figure 2. Variation of effectiveness factor with axial position in bed for CO oxidation.

4. Conclusions

The dependence of turnover rate on the catalyst particle number density is analytically obtained for a positive first order reaction. The packed bed reactor equations are solved independently for the NO reduction reaction exhibiting positive first order kinetics and CO oxidation exhibiting negative first order kinetics. Despite the existence of diffusional limitations in these cases, the turnover rate was nearly independent with respect to the inter-particle dilution. Hence, the use of Madon-Boudart test for inter-particle dilution does not establish the absence of diffusional limitations, in contrast to the intra-particle dilution for which it can be used. It is also emphasized that maintaining low conversions does not always give the true kinetics of a reaction.

In addition to the isothermal case, the effect of inter-particle and intra-particle dilution on the correctness of the estimated kinetics under non-isothermal conditions will be reported in the complete manuscript. Guidelines for the use of these dilution tests under various operating conditions will also be discussed.

References

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Keywords
Madon-Boudart test; intra-particle dilution; inter-particle dilution; diffusional limitations.