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Diffusion Limitations in CO Oxidation over Cu-Mordenite

Reactions occuring on the surface of a porous catalyst are accompanied by transport of heat and mass in the pores of the catalyst and across the boundary layer at the external surface. In such instances, the resulting rate of reaction is governed by both the kinetics of the reaction and the transport process (or processes). Hence the dependence or the overall rate on both the temperature and the partial pressure of the reacting species can no more be expressed by the intrinsic kinetics of the reaction, but is also influenced by the transport parameters of the system.

In other words, in the presence of finite transport limitations, inter- or intraparticle, the catalyst exhibits kinetics falsified by transport processes.

If these effects are not taken into account serious errors of interpretation could occur (*1, 2*). Besides, many papers have been published where the transport limitations have been carefully and rationally studied, but the results obtained have not found great application on routine work because of their mathematical complexity.

An interesting approach to simplify this treatment was proposed by Gonzo and Gottifredi (*3*) but even this method requires that the transfer coefficients and reaction rates be known.

The goal of this note is to present through the analysis of the transient period of a reacting system a simple but rigorous method to determine the parameters of adsorption and diffusion and its application to ascertain the role of mass transport limitations inside the micropores in the oxidation of CO on Cu-mordenite. A continuous-stirred tank reactor (CSTR) was used with this purpose.

The Bennett-type CSTR has a free volume of 270 cm^3. It was operated in the transient regime with pulse functions. More details about the reactor and its operation have been given elsewhere (*4*).

The starting material to prepare the catalyst was a high crystallinity Linde sodium mordenite (LZM5 Lot 8350-5). The exchange was done using a 0.01 *M* solution of $Cu(NO_3)_2$, a mordenite/solution ratio of 2 g/dm^3 at pH = 5, at room temperature, during 24 h. The exchanged sieve was washed with distilled water and dried at 80°C for 12 h. In this way, 55% of the original sodium was replaced by copper with no loss in crystallinity according to the XRD patterns. To determine adsorption behavior the solid was prereduced at the desired temperature with pure CO for 1 h. The CO was eliminated with flowing N_2 and then a pulse (4.5 cm^3 STP) of adsorbate was injected.

The exit stream was sampled using a 16-loop (2 cm^3) Valco valve and analyzed through a TCD detector.

Details of the assumption made to model the system have been given elsewhere (*4, 5*).

In the absence of reaction ($k = 0$) the continuity equation in the particle and the mass balance for the reactor are the following

$$D\left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right] = (1 + K)\frac{\partial C}{\partial t}$$

$$-FY - 4\pi R^2 N \varepsilon D \left.\frac{\partial C}{\partial r}\right|_R = V\frac{dY}{dt}$$

with the initial and boundary conditions

$$t = 0 \quad Y = Y_0$$

$$C = 0 \quad 0 \leq r < R$$

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$$t > 0 \quad \frac{\partial C}{\partial r} = 0 \qquad r = 0$$

$$C = Y \qquad r = R$$

The differential equations were solved applying the Laplace transform method. The moment was used to calculate K and D from the experimental response curve $Y(t)$.

For a given single value of the weight function s, the following equations are obtained.

$$I(s) = 1 + \tau s + \delta(\alpha \coth \alpha - 1)$$

$$I'(s) = \tau + \frac{\delta R^2}{2D}(1 + K)M(\alpha)$$

$$I''(s) = -\frac{3}{4}\delta\left[\frac{R^2}{D}(1 + K)\right]^2 N(\alpha)$$

where

$$\delta = \frac{4\pi R^2 \varepsilon ND/R}{F}$$

$$\tau = \frac{V}{F}$$

$$\alpha^2 = \frac{R^2}{D}(1 + K)s.$$

$M(\alpha)$ and $N(\alpha)$ are hyperbolic functions which were derived by Schobert and Ma (*5*) for a similar model.

The system of equations obtained may be simplified when ordinary moments are used ($s = 0$).

$$I = 1$$

$$I' = \tau + \frac{\delta R^2}{3D}(1 + K)$$

$$I'' = -\frac{2}{15}\delta\left[\frac{R^2}{D}(1 + K)\right]^2.$$

If the values of I' and I'' are calculated, K and D can be obtained. Due to instrumental error in measuring low values of CO concentration (<0.05%) it is necessary to extrapolate the tail of the $Y(t)$ response to apply the ordinary moments method. The length of the tail of the response can be reduced through an increase in flow rate or using small amounts of sample, but in these cases an undesirable effect could arise that is an increase in parameter sensitivity to the experimental error.

If instead of ordinary moments weighted moments are used with a suitable value, the low concentration data are not so important and an extrapolation of the tail of the response curve is not needed. K and D values are then calculated from $I(s)$ and $I'(s)$. The following simplification is admitted in such a case:

$$\text{for } \alpha > 3, \quad \coth \alpha_s \cong 1$$

K and D are calculated from the following equations:

$$D = \frac{[(2I'(s) - \tau)s + (1 - I(s))]F}{4\pi RN\varepsilon}$$

$$K = (I'(s) - \tau)\frac{2D\alpha}{\delta R^2}$$

Taking into account that the error in moment estimation increases with the moment order it is preferable to use the weighted moments method. In our case $s\tau$ values between 0.5 and 1 were appropriate. In a few experimental conditions (e.g., high loading of sample), however, it was not possible to optimize the value of the s function to obtain a good estimate of the parameters. In these cases the ordinary moments calculated through an exponential extrapolation of the tail gave good results.

In all cases to check the validity of each set of R and D values the antitransform of $\overline{Y}(s)$ was obtained by the method of the residuals (*4*).

Figure 1 illustrates the ability of the method of the weighted moments to obtain adsorption and diffusion parameters from pulse experiments.

An excellent agreement is observed between the experimental points and the curve (175–300°C) which was calculated through the antitransform, using the value of K and D obtained in the pulse experiments. The same good fitting shown in Fig. 1 was also observed at all other tempera-

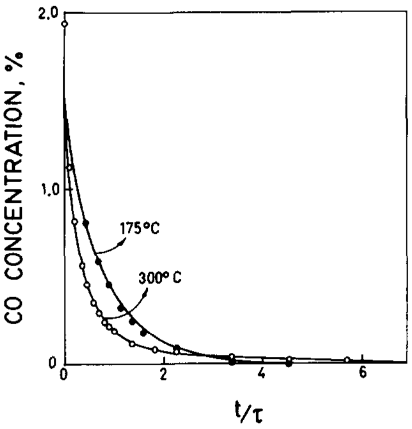

FIG. 1. CO adsorption. CSTR response curves to CO pulses over reduced Cu-mordenite. Gas composition: 100% N_2. CO pulse: 4.6 cm^3 STP. Flow rate: 6.2 cm^3/s. Catalyst weight: 1 g (powder).

tures. In Fig. 1 the rise section of the pulse signal is not shown because the time scale used does not permit its detection. This situation does not produce error in parameter estimation.

In Fig. 2 the Arrhenius plots are shown for K and D in the 125–300°C temperature range. It has previously been reported (*6*) that CO oxidation over Cu-mordenite in the 240–330°C temperature range proceeds through a redox mechanism, where the Cu^{2+} reduction is the rate-limiting step.

In Fig. 3 the kinetic results at 300°C are shown. The reaction was zero order in O_2 and first order for CO.

To estimate the extent of diffusion limitation the modified Thiele moduli and the corresponding effectiveness factor were calculated using

$$\eta = \frac{3}{\phi^2}(\phi \coth \phi - 1)$$

where

$$\phi = \left(\frac{kR^2}{D}\right)^{1/2}.$$

In Table 1 the η and ϕ values obtained are listed in the 250–330°C temperature range; this demonstrates the limiting effect of the CO transport into the micropores of the CuM on the carbon monoxide oxidation.

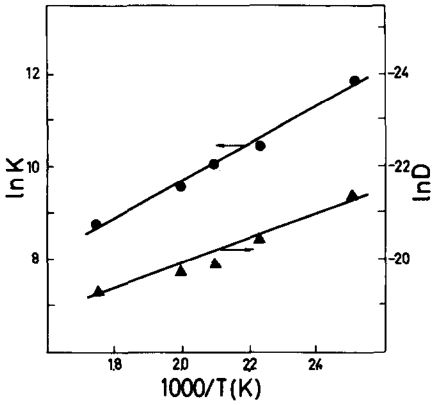

FIG. 2. Arrhenius plot. (●) ln K, (▲) ln D. Experimental conditions identical to Fig. 1.

The diffusion disguised activation energy in the 250–330°C temperature range was E_a = 17.6 kcal/mol. This value was corrected using the diffusion coefficients previously obtained. This gave us an intrinsic activation energy of E = 30.0 kcal/mol in agreement with the data reported by Paetow and Riekert (*7*) who worked under well defined conditions to avoid diffusion limitations. They have also reported a break in the Arrhenius plot at 220°C. Support for this result can be found in the value of the effectiveness factor η = 0.7 calculated with our data.

The diffusion coefficients fall in line with data pertaining to similar systems given in

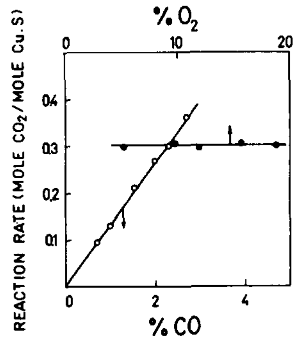

FIG. 3. Reaction order plots for Cu-mordenite (t = 300°C). Gas composition range: 1–20% for O_2 and 0.5–7.5% for CO (in N_2). Flow rate: 5–15 cm^3/s. Catalyst weight: 1 g (powder).

the literature. Unfortunately, it was impossible to find data for CO diffusion in mordenite.

TABLE 1

Values of Thiele Moduli and Effectiveness Factors for Cu-Mordenite at Different Temperatures[a]

T (°C)	ϕ^b	η^c
250	11.1	0.25
260	12.6	0.22
275	20.5	0.14
300	34.2	0.09
325	49.3	0.06
340	55.9	0.05

[a] Reaction conditions. Gas composition: CO (1–5%), O_2 (20%), in N_2. Flow rate: 5–15 cm^3/s. Catalyst weight: 1 g (powder).

[b] $\phi = (kR^2/D)^{1/2}$.

[c] $\eta = (3/\phi^2)(\phi \coth \phi - 1)$.

Satterfield and Margetts (*8*), using a constant volume system, have reported values of D between 10^{-8} and 10^{-9} cm^2/s for CH_4, n-C_4H_{10}, iso-C_4H_{10}, and C_4F_{10} in mordenite at 25–100°C. The CO diffusivities calculated here were around 10^{-9} cm^2/s in the 125–300°C range with an activation energy of 5.4 kcal/mol (Fig. 2).

In short, the virtues have been shown of a simple, but rigorous method with a straightforward mathematical treatment, to obtain diffusion and adsorption parameters to detect transport limitations. The CSTR used, which was operated in the transient regime with pulse function, has the advantage of minimizing the external mass and heat transfer, which is hard to achieve either in a volumetric, gravimetric, or single pass flow system.

APPENDIX: NOMENCLATURE

D	D_{eff}/ε, diffusion coefficient, cm^2/s
F	flow rate, cm^3/s
$I(s)$	characteristic function, dimensionless
$I'(s)$	first derivative of characteristic function, s
$I''(s)$	second derivative of characteristic function, s^2
k	first-order reaction rate constant, s^{-1}
K	equilibrium constant for adsorption, dimensionless
N	number of crystals loaded in CSTR
R	radius of crystal, cm
s	Laplace transform parameter
t	time, s
V	volume of reactor, cm^3

Greek letters

ε	porosity, cm^3 volume/cm^3 pellet volume
ϕ	Thiele modulus, dimensionless
η	effectiveness factor
ρ	density, g/cm^3
τ	residence time, s

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