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Continuous-Stirred Tank Reactor (CSTR) Transient Studies in Heterogeneous Catalysis

CO Oxidation over CuY Zeolite

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CuY zeolites develop a high activity to catalyze CO oxidation upon reduction in CO at 750°C. A continuous-stirred tank reactor (CSTR), Bennett-type unit, operated both in the transient and steady-state regimes was used to determine the rate constant, the adsorption equilibrium constant, and the effective diffusivity under reaction conditions. The reactor, loaded with powdered catalyst, was operated at reaction temperatures between 150 and 300°C, atmospheric pressure, and usually in an oxydizing atmosphere ($CO/O_2 \leq 2$). Under these conditions the rate function was found to be first order in CO pressure and zero order in oxygen pressure. The weighted, rather than ordinary moments method, was used for it was shown to give a better estimation of the reaction parameters. The use of step functions was useful to detect an activation process which occurs when the solid is contacted with the reacting mixture. The reaction was shown to be diffusion limited in the temperature range studied. The diffusivity obtained was $D = 2.5 \times 10^{-7} \exp(-4.0/RT)$, the adsorption constant $K = 8.2 \exp(3.9/RT)$ and the surface rate constant $k = 1.6 \times 10^5 \exp(-13.4/RT)$. Energy values are given in kilocalories per mol. These data are analyzed in terms of relevant literature information on related systems.

INTRODUCTION

The importance of obtaining experimental data about the physical and chemical phenomena simultaneously occurring when a chemical transformation is being catalyzed by a solid, is widely recognized. This is an area in which there has been a great deal of theoretical work but too few experimental studies. An interesting approach to obtain this kind of data is the analysis of the transient period of a reacting system, e.g., Bennett (*1*) and Kobayashi and Kobayashi (*2*) have made this sort of studies using different types of reactors to characterize the oxidation of CO and the decomposition of N_2O over metal oxides.

When zeolites are used as catalysts the intracrystalline diffusion process becomes very important. Diffusivity data of common gases and liquids in zeolites are available in the literature, but they have been usually obtained at low temperatures and their extrapolation at reaction conditions is at best uncertain. Besides, the data not obtained under reaction conditions may be essentially different from those determined when a chemical transformation is occurring together with the diffusion process. In this vein, Lombardo *et al.* (*3*) have obtained, applying the Wei (*4*) analysis, the diffusivities of *n*-butenes in Na, CaY zeolites, while Schobert and Ma (*5, 6*) have calculated rate constants, diffusivities, and adsorption equilibrium constants for cyclopropane isomerization catalyzed by Y zeolite, using a continuous-stirred tank reactor (CSTR) operating in the transient regime.

The goal of this work was to simultaneously determine the kinetic, adsorption,

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and diffusion parameters of the oxidation of CO over CuY zeolite using a CSTR system and analyzing its behavior both in transient and steady-state regimes. The experiments were also programmed to detect either activation or deactivation processes occurring when the solid was first contacted with the reacting mixture, taking in this way advantage of the diagnostic capability of the transient method.

EXPERIMENTAL

Catalyst and Pretreatment

Linde SK 40 NaY zeolite, Lot N° 1280-133 $Na_{59}(AlO_2)_{59}(SiO_2)_{134}$, was the starting material. This sieve was carefully washed before ion exchange using a buffer solution (pH 5) of sodium acetate–acetic acid. This exchange was done using a 0.01 *M* solution of $Cu(NO_3)_2$, a zeolite/solution ratio of 1 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, 67% of the original sodium was replaced by copper with no loss in crystallinity as shown elsewhere (*7*). This exchanged solid was reduced in CO for 1 h at 750°C and then oxidized at 500°C in O_2 for the same period. After this treatment part of the copper appeared as CuO in the X-ray diffraction pattern but the zeolite still retained its crystallinity and pore volume (*7*). The physical properties of the catalyst used in processing the data obtained were: porosity $\varepsilon = 0.48$ (calculated from the zeolite structure), $\rho = 1.9$ g/cm^3 and average particle diameter $d_p = 5 \times 10^{-5}$ cm.

Gases

All CP grade gases were dried with 5 A molecular sieves before use. Moreover, the CO tubing included a section surrounded by an oven maintained at 300°C to eliminate carbonyls, followed by a sintered metal filter.

Reaction System and Procedure

The heart of the system was a Bennett-type CSTR unit with a 270-cm^3 free volume, able to operate between 1500 and 4000 rpm. The reactor was usually loaded with 300 mg of powdered catalyst. Satisfactory mixing tests were run at various temperatures and flow rates. Under reaction conditions it was further checked that the external mass transfer resistance was negligible above 1500 rpm. The reactor was operated in the transient regime with either step or pulse functions. In another set of experiments it was run under steady-state conditions. The reactants were fed through the agitator shaft, the flow rates were controlled using upstream Moore regulators and measured with a bubble flowmeter.

When pulses were fed to the system it was operated as follows: the catalyst was pretreated at 300°C for 30 min with a gas mixture made of N_2, O_2 (15–20%), and CO (12–14%), flow rate 10–15 cm^3/s. The CO flow was then stopped, the temperature adjusted to the desired reaction value, and the N_2–O_2 flow kept during one additional hour. At this point a pulse of CO was injected into the reactor and the response signal measured at time intervals of 5 to 10 s. The reacting mixture always contained oxygen more than three times in excess of the stoichiometric ratio.

When a step function was used the catalyst was not pretreated. To start each experiment N_2 was flowed through the reactor while the temperature was adjusted to desired values. At the same time, a N_2, O_2 (15–20%), and CO (12–14%) gas stream was flowing through a bypass. At time zero the reactant mixture was switched into the reactor and the CO concentration was measured until the steady-state regime was reached.

The pulse function was generated using a sampling valve containing two exchangeable loops of either 2 or 16 cm^3. The exit stream was sampled using a 16-loop (2 cm^3) Valco valve and analyzed using a TCD detector.

DATA PROCESSING

Pulse Experiments

The following assumptions were made to model the system:

The surface reaction was first order in CO and zero order in O_2. This was based on previous studies (*7*) which have shown that on this catalyst a redox mechanism is in operation, the reduction step being rate controlling when $CO/O_2 \leq 2$. This was further checked in this case (vide infra).

Both concentration and temperature gradients in the gas phase were negligible.

The temperature gradient within the catalyst particle was also negligible. This was tested using the criteria given by Carberry (*8*).

The particles were spherical and uniform in size.

The flow rate changes due to the reaction were negligible (diluted reaction mixture).

With this model both the continuity equation in the particle and the mass balance for the reactor are quite similar to those given by (*5*)

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

$$-FY - D4\pi R^2 N\varepsilon \left.\frac{\partial C}{\partial r}\right|_{r=R} = V\frac{dY}{dt}$$

with the boundary conditions

$$C(R,t) = Y(t) \qquad \left.\frac{\partial C}{\partial r}\right|_{r=0} = 0$$

and initial conditions

$$0 \leq r \leq R \quad C(r,0) = 0$$

$$r > R \quad Y(0) = Y_0.$$

Applying the Laplace transform method the set of equations can be elegantly solved

$$\bar{Y}(s) = \mathscr{L}[Y(t)]$$

$$\bar{Y}(s) = \tau Y_0[1 + \tau s + \delta(\alpha \coth \alpha - 1)]^{-1},$$

where

$$\tau = V/F$$

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

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

TABLE 1

Errors in Weighted and Ordinary Moments

$s\tau$	E_0	E_1	E_2
0	−0.30	−3.40	−10.84
0.5	0.25	−1.30	−4.74
1.0	0.43	0.25	−0.18
1.25	0.51	0.30	0.09
1.50	0.60	0.41	0.26

Note. E_j: percentage relative error in j-order moment. Parameter values: $K = 875$, $D = 2.05 \times 10^{-9}$ cm²/s, $k = 0.02$ s⁻¹.

To obtain the parameters k, K, and D the moments method may be applied, from which the following relationships are derived

$$M_p = \int_0^\infty e^{-st} t^p Y(t)\, dt = \mathscr{L}[t^p Y(t)]$$

$$\frac{d^p \bar{Y}(s)}{ds^p} = (-1)^p M_p.$$

When M_p is evaluated at $s = 0$, ordinary moments are obtained with which estimation of parameters is rather simpler than with weighted moments. However, the analytical system is not accurate enough to measure CO concentration below 0.05% and the response curve must be truncated there. This generates, in turn, a considerable error in ordinary moments M_1 and M_2, which decreases noticeably when weighted moments are used. Table 1 shows a confrontation of errors in both techniques, the exact moments having been obtained from K, D, and k. Curve $Y(t)$ was obtained by antitransformation of $\bar{Y}(s)$ and was truncated at $Y = 0.05\%$. A marked, drastic increase in accuracy for M_2, can be clearly appreciated with adequate s values.

It is known that an optimum value of s exists for different moments. Anderssen and White (*9*) favor averaging these values to obtain satisfactory results. We followed suit for an initial estimation of s, with later adjustments in order to minimize error between experimental data and predicted curve.

The equations used to calculate the desired parameters were

$$I(s) = \frac{\tau Y_0}{M_0}$$

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

$$F(\alpha) = \frac{I''(s)(I(s) - \tau s - 1)}{(I'(s) - \tau)^2},$$

where $M(\alpha)$ and $F(\alpha)$ are the hyperbolic functions given by (5), and

$$I'(s) = \frac{dI(s)}{ds},$$

$$I''(s) = \frac{d^2I(s)}{ds^2}.$$

In order to check the validity of the set of parameters calculated the antitransform was obtained by the method of the residuals

$$Y(t) = \sum_{n=1}^{\infty} a_n e^{s_n t},$$

where

$$a_n = \tau Y_0 \left[\tau + \frac{\delta R^2}{2D}(1 + K)\left(\frac{1}{\text{sen}^2\alpha_n} - \frac{1}{\alpha_n \tan \alpha_n}\right)\right]^{-1}$$

$$\alpha_n^2 = -\frac{R^2}{D}[(1 + K)s_n + kK]$$

and s_n are periodic roots of the equation

$$\tan \alpha_n = \frac{\delta \alpha_n}{\delta - 1 - \tau s_n}.$$

Steady-State Experiments

In this case the variation of the flow rate due to chemical reaction was taken into account. Through this method a global rate constant was obtained.

For $dY(t)/dt = 0$, results

$$kK\eta = \frac{X - bY}{Y}\frac{3F}{4\pi R^3 N\varepsilon},$$

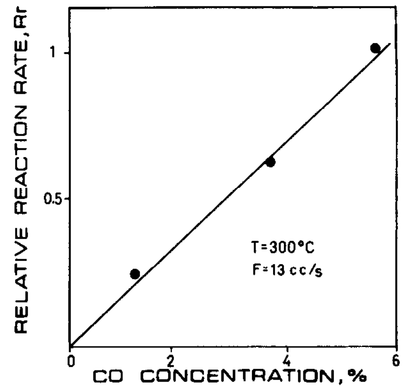

FIG. 1. First-order CO pressure dependency of the kinetic law. Reaction conditions, CSTR reactor; gas composition range, 1–6% for CO and 15% O_2, in nitrogen (1 atm). Catalyst weight, 300 mg (powder).

where

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

$$\phi = \alpha(s = 0)$$

$$b = \frac{P/RT - X/2}{P/RT - Y/2}.$$

RESULTS

The experiments whose results are shown in Fig. 1 were run to further check the first-order dependency of the reaction rate upon the CO concentration. It was also verified that the oxygen partial pressure did not affect the reaction rate within the reactant ratio range explored in full agreement with previous results reported by Petunchi and Hall (7) for the same system.

Figure 2 is included to illustrate the ability of the method of the weighted moments to obtain kinetic, adsorption, and diffusion parameters from pulse experiments. In Fig. 2 a pulse of CO was injected into the reactor operated at 215°C. An excellent agreement is observed between the experimental points of the three repetitive runs and the theoretical curve which was calculated, through the antitransform, using the values of k, K, and D obtained in the pulse experiments. The same good fitting shown in Fig.

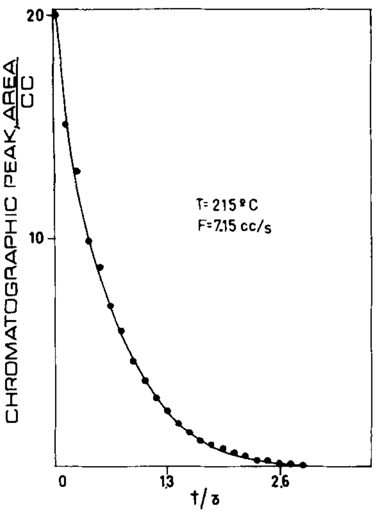

FIG. 2. CSTR response curve to pulse function. Gas composition, 15% O_2 in N_2 (1 atm); CO pulse, 16 cm^3. (●) Experimental data; (—) theoretical curve.

2 was also observed at all other reaction temperatures. The pulse technique was used to establish catalyst reaction with CO in absence of O_2. Figure 3 shows a comparison of response for reaction and reduction.

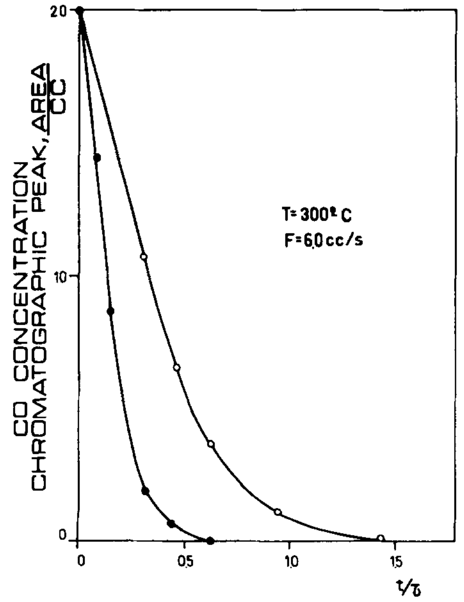

FIG. 3. CSTR response curve to pulse function with and without oxygen. Gas composition, (●) 15% O_2 in N_2, (○) 100% N_2; CO pulse, 16 cm^3.

Rate of the latter is clearly seen to be lower. CuY zeolite with no CO pretreatment at 750°C showed the same behavior.

The step function experiments were useful to detect an activation process which occurred when the solid was contacted with the reacting mixture. Figure 4 shows the behavior of pretreated CuY. A maximum in CO concentration appears in the pre-steady-state portion of the curve at all reaction temperatures above 180°C. Both the size and temporal location of the maximum are strongly dependent upon the reaction temperature and to a certain extent on the previous history of the solid. In this case the experiments were run in the direction of decreasing temperatures; if they were done in the opposite sense the steady-state regime would take longer to occur. Figure 5 shows the behavior of unpretreated CuY. None of the above occurs. Additional evidence of the above-mentioned process being an activation one under reaction conditions is provided by the results in Fig. 6 where the sample pretreated (open points) at 300°C shows a higher activity than both the fresh one (open triangles) and the catalyst previously deactivated in $N_2 + O_2$ flow (solid points).

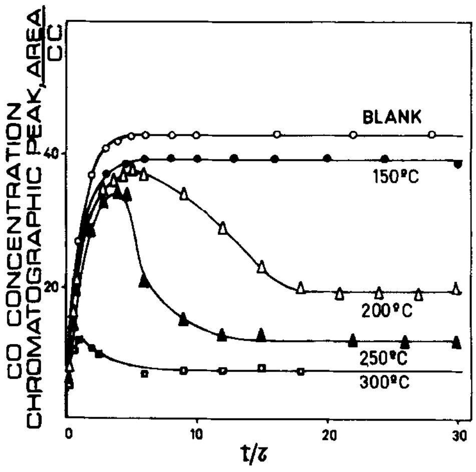

FIG. 4. CSTR response curve to step function. Gas composition, 12% CO, 15% O_2, in N_2 (1 atm); flow rate, 14.4 cm^3/s. Catalyst weight, 300 mg (powder).

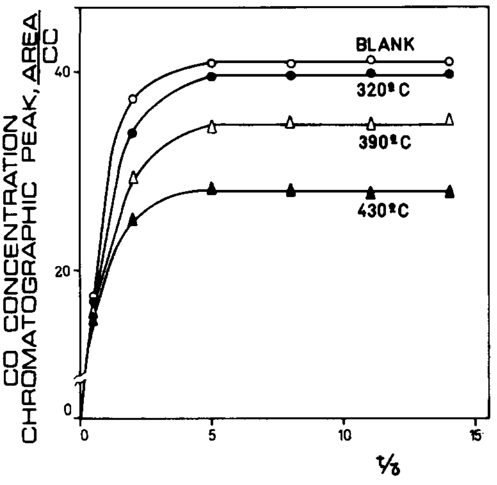

FIG. 5. CSTR response curve to step function. Unreduced CuY; reaction conditions identical to Fig. 4.

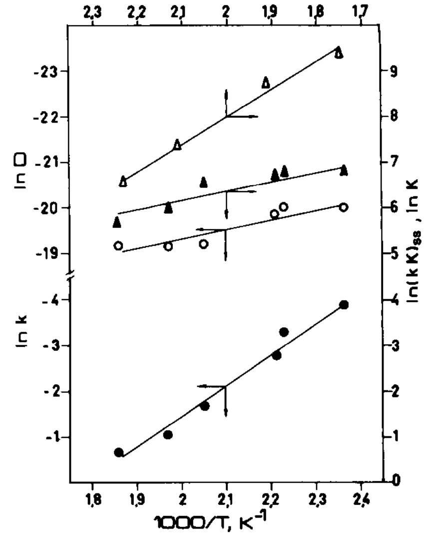

FIG. 7. Arrhenius plots. (●) ln *k*; (▲) ln *K*; (○) ln *D*; (△) ln *kK* (steady state). Reaction conditions: see footnotes in Tables 2 and 3.

In Fig. 7 the Arrhenius plots are shown for *k*, *K*, and *D* calculated through the pulse method plus the *kK* product obtained from the steady-state experiments after taking into account the effectiveness factor. The Arrhenius parameters calculated in this way are collected in Table 2.

As should be expected after the results shown in Fig. 4, the steady-state reaction rates were much higher than those calculated from the pulse experiments (Table 2). Note that this resulted from the large increase in preexponential factor, for the apparent activation energy was even somewhat higher under steady-state conditions than in the pulse experiments.

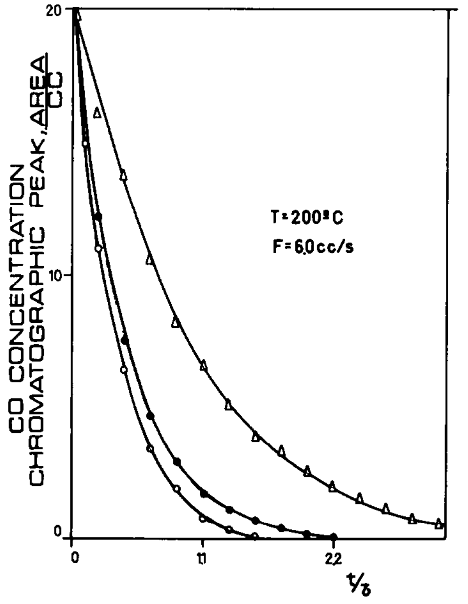

FIG. 6. CSTR response curve to pulse function. (○) Activated catalyst, (●) partially deactivated catalyst (after 30 min in air), (△) fresh sample. Reactions conditions identical to Fig. 4.

TABLE 2

Arrhenius Parameters in CO Oxidation over CuY Zeolite by Pulse Method[a]

E	Δh	E_d	$E + \Delta h$ (kcal/mol)
13.4 ± 0.5	−3.9 ± 0.5	4.0 ± 0.5	9.5 ± 1.0 (12.1 ± 0.4)[b]
ln *A*	ln *K**	ln *D**	ln *AK**
12.0	2.1	−15.2	14.1(20.1)[b]

[a] Reaction conditions: CSTR reactor, gas composition: 15% O_2 in N_2 (1 atm). CO pulse 16 cm^3. Flow rate range: 5–9 cm^3/s. Temperature: 150–260°C. Catalyst weight: 300 mg (powder). The error span corresponds to the standard deviation of the linear regression. $k = A \exp(-E/RT)$, $D = D^* \exp(-E_d/RT)$, $K = K^* \exp(-\Delta h/RT)$.

[b] Numbers in brackets represent steady-state values. Temperature range: 175–300°C.

TABLE 3

Values of Modified Thiele Moduli and Effectiveness Factors for CuY Zeolite at Different Temperatures[a]

T (°C)	Pulse method		Steady state	
	ϕ	η	ϕ	η
150	2.35	0.76		
175	3.10	0.66	13.32	0.21
180	3.49	0.61		
200			17.23	0.61
215	4.08	0.56		
235	4.30	0.54		
250			27.53	0.10
265	4.44	0.52		
300			34.50	0.08

[a] Reaction conditions: pulse method; see footnote of Table 2. Steady state: CSTR reactor. Gas composition: 17% O_2, 12% CO, in N_2 (1 atm). Flow rate: 14 cm^3/s. Catalyst weight: 300 mg (powder).

To estimate the extent of diffusion limitations in both the pulse and steady-state experiments the modified Thiele moduli and the corresponding effectiveness factors were calculated and listed in Table 3. It was assumed that the effective diffusivities obtained in the pulse experiments could be used to calculate the Thiele moduli under steady-state conditions.

DISCUSSION

The excellent correlationship between the experimental points and the calculated curve obtained using the weighted moments method (Fig. 2) demonstrates its suitability to derive meaningful reaction parameters. When the ordinary moments technique was applied to this system, limitations in the GC system made it necessary to truncate the response curve, and this produced unsatisfactory large variations in the magnitude of the parameters obtained. The use of the weighted moments, although slightly more complicated, has the great advantage of minimizing the error introduced in the estimation procedure when the data pertaining to the tail of the response curve to a pulse signal is processed (Table 1). Note that these tail points are on the one hand extremely important to obtain the moments of order higher than 1, while on the other they reach concentration values which dangerously approach the noise level of the measurement system. Therefore, data obtained using unweighted moments should be carefully checked to detect possible magnification of errors in higher order moments.

It should be noted that in linear models, as the one reported here, it is possible to obtain the analytical solution in the time domain which allows testing the validity of the parameters obtained without applying numerical methods to solve the differential equations. Besides, an additional check of the overall consistency of the calculated parameters is the relatively low scattering observed in the Arrhenius plots shown in Fig. 7.

A likely explanation for the difference in rate between reaction and reduction (Fig. 3) might be that the CO + O_2 reaction repeatedly utilize only a fraction of reducible sites, whereas in the reduction reaction the fraction is rapidly reduced and the majority of sites react at a slower rate.

Figure 4 reconfirms the ability of the transient method to detect changes occurring in the solid when this is contacted with the reacting mixture. It could be argued that this effect may be due to the existence of multiple steady states of the system. However, the fact that a pulse experiment run at 200°C gives a much higher activity after the catalyst has been preconditioned with the reacting mixture at 300°C (Fig. 6), as compared with the untreated solid, is strong evidence that some sort of modification of this solid occurs in the early stages of the reaction. Besides, this kind of effect has been reported in many catalytic systems and particularly concerning CO oxidation over Rh/γ-Al_2O_3 (*10*) and CuO/γ-Al_2O_3 (*11*).

The cation mobility in CuY zeolite could explain the activation phenomenon, for it is well known that upon adsorption of CO the copper ions move to a more accessible position within the sieve framework (*12*). Another alternative explanation is that CO could redisperse the CuO which was produced in the zeolite matrix during the pretreatment with CO at high temperature. It should be noted though, that CuY zeolite which has not been reduced with CO at 750°C shows a much lower activity, the reaction rate controlling step is different (*7*) and the response to a step signal of CO + O_2 in a CSTR unit does not show the maximum that reveals the occurrence of an activation process (Fig. 5). Further research is needed to ascertain the origin of this behavior.

It is interesting at this point to compare the data reported here with those available in the literature. The heat of adsorption of CO, $\Delta h = -3.9 \pm 0.5$ kcal/mol (Table 2) is lower than those reported by Miwa *et al.* (*12*) on Cu(II)Y zeolite. Using a calorimetric method they have obtained a limiting value of -5 kcal/mol for high coverages, while the extrapolated values at zero coverages were -12 and -20 kcal/mol for samples in which 14.3 and 50.3% of Cu was exchanged into the sieve, respectively. Several reasons could be named for the lower value obtained in this work, among which the most straightforward are the prereduction of our sample with CO at high temperature and the completely different experimental conditions used in both cases.

Regarding the diffusivity values, it has been impossible to find data concerning CO on Y zeolite. Sargent and Whitford (*13*) have reported carbon dioxide diffusivity in 5 A sieves of 10^{-11} cm^2 s^{-1} between 0 and 25°C, a value which extrapolates to 10^{-10} cm^2 s^{-1} at 200°C. Ruthven (*14*) has reported data for both O_2 and N_2 in 4 A zeolite. The activation energies were 4.5 kcal/mol for O_2 and 6.1 kcal/mol for N_2. The extrapolated diffusivity values at 200°C are of the order of 10^{-9} cm^2 s^{-1} for both gases. It should be expected that CO diffusivity in Y zeolites with larger window openings were higher than those given above. However, from the data reported in Table 2 the diffusivity at 200°C results 3.3×10^{-9} cm^2 s^{-1}. This low value may be due to a combination of factors, such as the higher polarity of the CO molecule, the presence of exchanged copper and the formation of CuO during the pretreatment. Besides, it should be recalled that in this work the effective diffusivity under reaction conditions was obtained. It is well known that in other cases a large difference between extrapolated values and those obtained during the reaction has been noticed (*3, 6, 15*).

An activation energy for the surface reaction of 13.4 ± 0.5 kcal/mol is reported in this work (Table 2). Vandamme (*16*) has studied the same reaction on a CuY zeolite which he has shown to contain either the Cu^{2+}/Cu^{+} or Cu^{+}/Cu^{0} couple. In this case, he found the reaction to obey the same kinetic law as in our system and reported an activation energy of 16 kcal/mol.

Table 3 shows that the oxidation of CO on activated CuY zeolite is diffusion limited in the temperature range studied, a fact which is often overlooked in catalytic studies.

In summary, the virtues have been shown of the weighted moments method to obtain meaningful reaction parameters, as well as the ability of the response transient technique to detect activation processes occurring before the steady-state regime is reached. The data obtained in this way show an excellent overall consistency and fit well into the set of related parameters found in the literature.

APPENDIX: NOMENCLATURE

a_n	constant of Laplace antitransform
b	flow correction by reaction
C	concentration of CO in gaseous phase, mole/cm^3
D	D_{eff}/ε, diffusion coefficient, cm^2/s
E_j	percentual relative error in j-order moment

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 surface reaction rate constant, s^{-1}
K	equilibrium constant for adsorption, dimensionless
M_p	pth weighted moment
N	number of crystals loaded in CSTR
r	radial distance, cm
R	radius of crystal, cm
s	Laplace transform parameter
s_n	periodic roots of the residuals method
t	time, s
V	volume of reactor, cm^3
X	concentration of CO at inlet, mole/cm^3
Y	concentration of CO at outlet, mole/cm^3

Greek Letters

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

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REFERENCES

1. Bennett, C. O., *AIChE J.* **13,** 890 (1967).

2. Kobayashi, H., and Kobayashi, M., *Catal. Rev. Sci. Eng.* **10,** 141 (1975).

3. Vélez, J., Cornejo, E. A., and Lombardo, E. A., "Molecular Sieves," Vol. II, p. 616, ACS Symposium Series No 40. Amer. Chem. Soc., Washington, D.C., 1977.

4. Wei, J., *J. Catal.* **1,** 526 (1962).

5. Schobert, M. A., and Ma, Y., *J. Catal.* **70,** 102 (1981).

6. Schobert, M. A., and Ma, Y., *J. Catal.* **70,** 111 (1981).

7. Petunchi, J. O., and Hall, W. K., *J. Catal.* **80,** 403 (1983).

8. Carberry, J. J., "Chemical and Catalytic Reactions Engineering." McGraw–Hill, New York, 1976.

9. Anderssen, A. S., and White, E. T., *Chem. Eng. Sci.* **26,** 1203 (1971).

10. Kiss, J. T., and González, R. D., *J. Phys. Chem.* **88,** 892 (1984).

11. Pierron, E. D., Rashkin, J. A., and Roth, J. F., *J. Catal.* **9,** 38 (1967).

12. Miwa, Y., Tsutsumi, K., and Takahashi, H., *Bull. Chem. Soc. Jpn.* **53,** 2800 (1980).

13. Sargent, R., and Whitford, J., *in* "Molecular Sieve Zeolites," Vol. II, p. 155, Advances in Chemistry Series No 102. Amer. Chem. Soc., Washington, D.C., 1971.

14. Ruthven, D., "Molecular Sieves," Vol. II, p. 320, ACS Symposium Series No 40. Amer. Chem. Soc., Washington, D.C., 1977.

15. Satterfield, Ch., "Heterogeneous Catalysis in Practice," Chemical Engineering Series. McGraw–Hill, New York, 1980.

16. Vandamme, L. J., "The Catalytic Oxidation of Carbon Monoxide over Copper Exchanged Zeolites," PhD thesis. Catholic University of Leuven, Leuven, Belgium, 1976.