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KINETIC DETERMINATION OF EFFECTIVE DIFFUSION COEFFICIENT AND TORTUOSITY FACTOR OF A $LaMn_{0.8}Cu_{0.2}O_3$ - CATALYST IN HYDROGEN OXIDATION

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ABSTRACT. The effective diffusion coefficient of hydrogen in porous pellets of $LaMn_{0.8}Cu_{0.2}O_3$ was indirectly determined using kinetic data on hydrogen oxidation taken in a gradientless recirculation reactor. Using the pore diffusion coefficient, evaluated by means of the usual procedures on the basis of textural characteristics of the catalyst, the tortuosity factor of the porous structure was also calculated.

INTRODUCTION

The mathematical modelling of catalytic processes, under conditions where the intrinsec chemical kinetics are coupled with internal mass and heat transfer phenomena, is often rendered difficult by the existing procedures for estimation of the effective diffusion coefficient for the porous catalyst pellet.

The common method used to get at least an approximate value of the effective diffusion coefficient involves the following steps [1-3]:

- calculation of the binary (molecular) diffusion coefficient (if no experimental values are available) [4];

$$D_{m,H} = \frac{\left(\frac{M_H + M_A}{M_H \cdot M_A}\right)^{1/2} \cdot T^{1.75}(K) \cdot 1.013 \cdot 10^{-3}}{P(bar) \cdot \left(v_H^{1/3} + v_A^{1/3}\right)^{1/2}} \tag{1}$$

♦ calculation of the Knudsen diffusion coefficient. Taking into account that the real porous system consists of pores of different radii, an approximation regarding the average pore size is to be made:

$$D_{K,H} = 9.7 \cdot 10^3 \cdot \bar{r}_p \cdot \sqrt{\frac{T}{M_H}} \tag{2}$$

♦ calculation of the combined molecular and Knudsen diffusion coefficient:

$$\frac{1}{D_p} = \frac{1}{D_{m,H}} + \frac{1}{D_{K,H}} \tag{3}$$

♦ calculation of the effective diffusion coefficient of the catalyst pellet:

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$$D_{eff} = \frac{D_P \cdot \Psi}{\tau} \tag{4}$$

The tortuosity factor τ is meant to account for *(a)* the prolongation of the diffusion path because of the irregular form of the pores and their randomly orientation and *(b)* the resistance opposed to the transport by the strangled and closed pores. For some simplified models of pore systems it is possible to calculate the tortuosity factor using measurable structural parameters though for real systems they generally do not allow one to get satisfying values [2,5]. This is the reason why a number of methods for the experimental determination of the effective diffusion coefficient have been developed and are widely used. Most of them are based on the kinetics of some physical processes, as for example the permeation of gases through a catalyst pellet, the binary counter-current gas diffusion (the method of Wicke and Kallenbach [6]), the liquid phase diffusion, or the diffusion-controlled adsorption-desorption processes [5,7].

There is still considerable uncertainty whether the data obtained under conditions of the aforementioned experiments can be used for solving the problem of coupling diffusion and reaction within the porous structure. For this purpose, the most meaningful values of D_{eff} would be those obtained indirectly from data on chemical reaction rates [1].

The aim of the present contribution is to characterise the textural properties of an oxidation catalyst belonging to the family of perovskite oxides (formula: $LaMn_{0.8}Cu_{0.2}O_3$) and to evaluate its effective diffusion coefficient and tortuosity factor using kinetic data on hydrogen oxidation.

EXPERIMENTAL

Catalysts. Cylindrical pellets of $LaMn_{0.8}Cu_{0.2}O_3$ (diameter x height = 4 x 1 mm) were prepared by pressing the powder at 10 bar. For the kinetic runs, the pellets were crushed and a fraction of 0.3-0.5 mm was used.

BET - surface area. The surface area of the catalyst was measured by N_2 adsorption by means of the BET method using automatically operated equipment.

Hg - porosimetry. The porosity and the pore-size distribution of the catalyst were obtained by Hg-penetration in a Carlo-Erba porosimeter model 1540 with computer-assisted data acquisition and processing.

Kinetic tests for hydrogen oxidation. The catalytic experiments were carried out in a recirculation reactor equipped with a cold trap. The recycle ratio was close to 40, ensuring the gradientless behaviour of the system. The reactor was operated in a differential manner by keeping the grade of conversion under 10 %. Kinetics tests were performed using a mixture of 0.2-1.0 % (vol.) hydrogen in air at atmospheric pressure in the temperature range of 210 - 430 °C.

RESULTS AND DISCUSSION

Textural properties of porous pellets. The penetration curve and the pore-size-distribution are illustrated in Fig. 1.

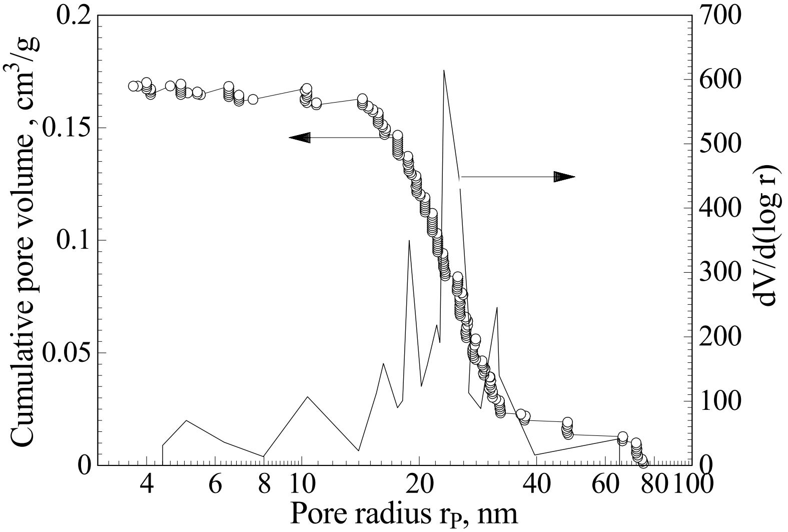

Fig. 1. Total pore volume and pore volume distribution curves of $LaMn_{0.8}Cu_{0.2}O_3$-pellets

It can be seen that the perovskite sample have a basically monodisperse pore structure with pore radii between 4 and 80 nm, the main fraction being that of ca. 15-40 nm. Other textural features of the catalyst are given in Table 1. The average pore radius can be estimated from the pore size distribution curve as about 24 nm. Using the Wheeler equation the average pore radius can also be evaluated on the basis of porosity, grain density and surface area [1]:

$$\bar{r}_P = \frac{2\Psi}{S_{BET} \cdot \rho_p} \tag{5}$$

Table 1.

Textural characterisation of $LaMn_{0.8}Cu_{0.2}O_3$ porous pellets

[a]Apparent (grain) density ρ_p, g/cm^3	[b] True (skeletal) density ρ_r, g/cm^3	[c]Porosity ψ, cm^3/cm^3	[d]S_{BET} (± 2 %) m^2/g	Average pore radius $\bar{r}_p$, nm	
2.90	5.56	0.4785	10.8	[e]24	[f]30.6

[a,b] measured picnometrically with mercury, before and after penetration, respectively; [c] $\psi=1-\rho_p/\rho_r$; [d] determined after BET-method; [e] from the pore size distribution curve; [f] after Wheeler formula.

Kinetic features of H_2 - oxidation. The experimental data obtained in the gradientless recirculation reactor were processed according to the differential method, yielding concentration-rate plots. Due to the large excess of oxygen, its partial reaction order was considered as zero. As concerns hydrogen, kinetic data obeyed a first order rate equation:

$$r_m = k_m \cdot C_H \tag{6}$$

The temperature dependence of the rate constants is represented in Fig. 2 according to the Arrhenius equation:

$$k_m = k_{m,0} \cdot \exp\left(-\frac{E_{a,ap}}{RT}\right) \qquad (7)$$

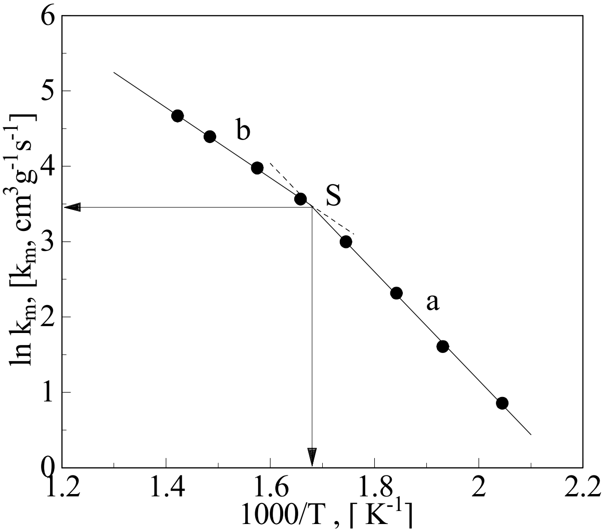

Fig. 2. The temperature dependence of the specific reaction rates for H_2-oxidation over $LaMn_{0.8}Cu_{0.2}O_3$.

The influence of internal diffusional limitations on the kinetical parameters. By examining Fig. 2 one can observe the existence of a turning point on the Arrhenius plot *ln k = f(1/T)* at 596.7 K, which marks the passing from the reaction-controlled to the reaction/internal diffusion-controlled regime.

By taking into account the definition of the effectiveness factor of a catalyst for a first order reaction in spherical pellets [1, 5]:

$$\eta = \frac{3}{\Phi_S} \cdot \left(\frac{1}{\tanh \Phi_S} - \frac{1}{\Phi_S}\right) \qquad (8)$$

with

$$\Phi_S = R_p \cdot \sqrt{\frac{k_m \cdot \rho_p}{D_{eff}}} \qquad (9)$$

depending on the relative values of k_m and D_{eff} there are two limit situations:

(a) $k_m << D_{eff}$; $\Phi_S << 1$ and $\eta \cong 1$

The intraparticle mass transport has no influence on the rate, which is controlled by the chemical reaction step. The corresponding kinetic equation has the form:

$$r_m = k_m \cdot C_H \tag{10}$$

(b) $k_m >> D_{eff}$; $\Phi_S >> 1$ and $\eta = 3/\Phi_S$

The intraparticle diffusion has a large influence on the rate which can be expressed by the equation:

$$r_m = \eta \cdot k_m \cdot C_H = \frac{3}{R_p} \cdot \sqrt{\frac{D_{eff} \cdot k_m}{\rho_p}} \cdot C_H \tag{11}$$

The cases *(a)* and *(b)* are illustrated by the lines *a* and *b* on the Arrhenius plot (Fig. 2). Hence, by taking into account the temperature dependence of the reaction rate constant for the reaction-controlled kinetic range:

$$k_m = k_{m,0} \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{12}$$

the apparent activation energy for the intraparticle diffusion-controlled rate should be:

$$E_{a,ap} = \frac{E_a}{2} \tag{13}$$

which is the case for the kinetic constants which belong to the line *(b)* of the Arrhenius plot. Indeed, the equations that are describing the temperature dependence of the experimental determined rate constants are:

a) for T < 576.7 K

$$\ln k_m = 15.5596 - \frac{59.87 \text{kJ/mol}}{RT} \tag{14}$$

b) for T > 576.7 K

$$\ln k_m = 11.3120 - \frac{46.66 \text{kJ/mol}}{RT} \tag{15}$$

(the points were fitted numerically using a least squares procedure).

At the intersection point *S* of the lines *(a)* and *(b)* we have:

$$k_{m,S} = \frac{3}{R_p} \cdot \sqrt{\frac{D_{eff} \cdot k_{m,S}}{\rho_p}} \tag{16}$$

This means that the effective diffusion coefficient of the catalyst particle can be calculated on the base of the rate constant corresponding to the turning point *S* on the Arrhenius plot:

$$D_{eff} = \frac{k_{m,S} \cdot \rho_p \cdot R_p^2}{9} \tag{17}$$

The experimentally determined D_{eff} together with the calculated $D_{m,H}$, $D_{k,H}$, and D_P are listed in Table 2.

Table 2.

Calculated and experimentally determined diffusion coefficients of hydrogen in a 0.4 mm diameter $LaMn_{0.8}Cu_{0.2}O_3$ pellet[a)] at 596.7 K and 1 atm.

$D_{m,H}$, cm^2/s	$D_{K,H}$, cm^2/s	D_P, cm^2/s	D_{eff}, cm^2/s
2.52	0.402	0.347	0.0423

[a)] the textural characteristics are listed in Table 1

Using equation (4), a value of

$$\tau = 3.925$$

for the tortuosity factor can be achieved, which is in accordance with those given in the literature for porous oxides ($1 < \tau < 6$) [1].

CONCLUSIONS

Kinetic measurements allow the delimitation of reaction-controlled and intraparticle diffusion- controlled working regimes and the turning point temperature for a certain catalyst and reaction in specific conditions.

At the same time, kinetic studies yield an indirect value for the effective diffusion coefficient, which is perhaps the most meaningful taking into account that ordinary methods for determining it refer to conditions where no reaction can occur (usually, at room temperature). Using the experimentally determined effective diffusion coefficient and porosity and the calculated pore diffusion coefficient, the tortuosity factor can be also calculated. This value can then be used to evaluate the effective diffusion coefficient for pellets of the same catalyst having other sizes, but the same textural characteristics.

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LIST OF SYMBOLS

C_H	concentration of H_2 in the reaction mixture, mol·cm^{-3}
$D_{m,H}$	diffusion coefficient for bulk ("molecular") diffusion of H_2 in a mixture of H_2 and air, cm^2·s^{-1}
$D_{K,H}$	Knudsen diffusion coefficient for a straight round pore, cm^2·s^{-1}
D_{eff}	effective diffusion coefficient for a porous pellet, cm^2·s^{-1}
D_P	pore diffusion coefficient (combined molecular and Knudsen diffusion), cm^2·s^{-1}
E_a	true activation energy, kJ·mol^{-1}

$E_{a,ap}$	apparent activation energy, $kJ \cdot mol^{-1}$
k_m	intrinsic reaction-rate constant (specific rate) per unit mass of catalyst pellet, $cm^3 \cdot g^{-1} \cdot s^{-1}$
$k_{m,0}$	frequency factor in Arrhenius equation, $cm^3 \cdot g^{-1} \cdot s^{-1}$
M_A, M_H	molecular weights of air and hydrogen, respectively, $g \cdot mol^{-1}$
P	total pressure, atm
r_m	reaction rate per unit mass of catalyst pellet, $mol \cdot g^{-1} \cdot s^{-1}$
r_P	pore radius, cm
$\bar{r}_P$	average pore radius, cm
R_p	pellet radius, cm
R	gas constant, ($R = 8.314\ J \cdot mol^{-1} \cdot K^{-1}$)
S_{BET}	surface area of porous solid, $cm^2 \cdot g^{-1}$
T	absolute temperature, K
v_A, v_H	diffusion volumes of air and hydrogen, respectively
ψ	porosity (void fraction in the porous pellet), $cm^3 \cdot cm^{-3}$
η	effectiveness factor of the catalyst
ρ_p	apparent (grain) density of catalyst, $g \cdot cm^{-3}$
ρ_r	true (skeletal) density of catalyst, $g \cdot cm^{-3}$
τ	tortuosity factor
Φ_S	Thiele modulus for a spherical catalyst particle
ε, σ	Lnnard-Jones force constants
Ω_D	collision integral for diffusion

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