MODELLING OF IMPREGNATION OF γ-ALUMINA WITH COBALT AND MOLYBDENUM SALTS. $CoCl_2-(NH_4)_2MoO_4-\gamma-Al_2O_3$ (ALUMINATE TYPE) SYSTEM

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Adsorption data for the impregnation of alumina with an aqueous solution of cobalt dichloride and ammonium molybdate were treated in terms of the Langmuir adsorption isotherm and compared with a mathematical model set up to describe the kinetics of simultaneous impregnation of a support by two components. The effective diffusion coefficients of the two components at 25°C in a cylindrical particle of alumina were obtained. The validity of the model used was verified qualitatively by comparing the numerical results with the experimental time dependent concentration profiles of the active components in a catalyst particle, measured by electron microanalysis technique.

Hydrodesulphurization catalysts can be prepared in three ways, *viz.* by impregnation, by mixing or by precipitation[1]. The most widely used process is impregnation, carried out either by submerging the support in the impregnating solution[2,3] or by spraying the solution onto the support[4].

The properties of a catalyst depend generally on the method of preparation, kind of active component used (or combination of several components), amount of the active component fixed to the support and its distribution across the particle, kind of support, drying and calcination temperatures, *etc.* The most widely used for hydrodesulphurization processes are cobalt and molybdenum oxide or sulphide based catalysts.

In the present paper, the process of impregnation of support with a solution of compounds of two active catalyst components is treated quantitatively. The treatment is based on the fact that the impregnation is controlled by diffusion and competitive adsorption of the two components inside the support particle.

THEORETICAL

Mathematical Model of Support Particle Impregnation by Two Components

The process of impregnation of a support can be looked upon as consisting of three separate steps, *viz.*

— transport of the active component from the solution to the outer surface of the support particle,

— diffusion of the active component through the inner pores towards the centre of the support particle, and

— adsorption of the active component on the pore surface.

The model was set up making the following assumptions[5,6]: *a*) the particle has a shape of an infinite cylinder; *b*) the impregnating solution has a finite volume and is perfectly stirred so that no concentration gradients occur in it; *c*) the system is in an unsteady state, the concentration of the impregnating solution decreasing with time; *d*) adsorption is considerably faster than diffusion; *e*) only one kind of adsorption sites of support exists and competitive adsorption of the two active components takes place on them; and *f*) the simultaneous presence of the two impregnating components does not affect their individual effective diffusion coefficients.

By eliminating the effect of external mass transport around the catalyst particle, the treatment of the impregnation process simplifies to a treatment of the diffusion and adsorption which, for a simultaneous impregnation by two components, can be described by equations[5,6]

$$D_{e,i}[(\partial^2 C_i/\partial r^2) + (1/r)\,(\partial C_i/\partial r)] - (\varrho_z/\varepsilon)\,(\partial n_i/\partial t) = (\partial C_i/\partial t)\,, \qquad (1)$$

where i stands for the active components a, b.

The first term in Eq. (1) characterizes the diffusion phenomena, the second, adsorption on the inner pore surface. The right side contains the accumulation term only. The time change of the adsorbed amount can be written as

$$\partial n_i/\partial t = (\partial n_i/\partial C_i)\,(\partial C_i/\partial t)\,, \quad i = a, b\,. \qquad (2)$$

The partial derivatives $\partial n_i/\partial C_i$ can be obtained by differentiation of the adsorption isotherm. By insertion and rearrangement in Eqs (1) and (2), the system of partial differential equations

$$\partial C_i/\partial t = \frac{D_{e,i}}{1 + (\varrho_z/\varepsilon)\,(\partial n_i/\partial C_i)}[(\partial^2 C_i/\partial r^2) + (1/r)\,(\partial C_i/\partial r)]\,, \quad i = a, b \qquad (3)$$

is obtained.

For solving this system of equations, the corresponding boundary conditions must be known; these are determined by the assumptions of the model and are as follows:

$$t = 0\,, \qquad 0 \leqq r < R: \quad C_i(r, 0) = 0 \qquad i = a, b \qquad (4)$$

$$t = 0, \qquad r = R: \qquad C_i(R, 0) = C_{0i} \qquad i = a, b \qquad (5)$$

$$t > 0, \qquad r = 0: \qquad \partial C_i(0, t)/\partial r = 0 \qquad i = a, b \qquad (6)$$

$$t > 0, \qquad r = R: \qquad C_i(R, t) = C_{Li}(t) \qquad i = a, b \qquad (7)$$

For a finite volume of the impregnating solution, the time dependence of concentrations of the active components in solution $C_{Li}(t)$ can be obtained from the mass blance of the entire system including both the impregnating solution and the catalyst particles:

$$C_{Li}(t) = C_{0i} - (2\pi h P\varepsilon/V) \int_0^R [(\varrho_z n_i/\varepsilon M_i) - C_i] \, r \, \mathrm{d}r . \qquad (8)$$

For determining time functions of the adsorbed components on the catalyst particle surface, the shape of the adsorption isotherm for the two components must be known. If the solutes adsorb more strongly than the solvent, the adsorption in diluted solutions can be described by the Langmuir adsorption isotherm[7,8]. Assuming that the adsorption centres of the support are available to both components, *i.e.* no centres exist where only one component is adsorbed, the Langmuir equation is

$$n_a = K_{1a}C_a/(1 + K_{2a}C_a + K_{2b}C_b), \qquad (9)$$

$$n_b = K_{1b}C_b/(1 + K_{2a}C_a + K_{2b}C_b). \qquad (10)$$

The adsorption constants in the two isotherms were determined by nonlinear regression of adsorption data using the Newton–Raphson method[9,10]. The system of equations $(3)-(8)$ was solved numerically by the finite difference method using the explicit computation procedure[9,10]. The differences in the space and time coordinates were $\Delta r = 0.09$ mm and $\Delta t = 1$ s. The calculations were performed on an EC 1030 computer.

EXPERIMENTAL

Chemicals. Cobalt dichloride hexahydrate *p.a.*, ammonium molybdate *purum*, 4-(2-pyridylazo)-resorcinol, phenylhydrazine, hydrochloric acid *p.a.* 35% (all Lachema, Brno) were used. The catalyst support was aluminate type CHEROX 33-00 alumina (Chemical Works, Litvínov), extrudates 1·8 mm in diameter, average length 7 mm; their apparent density was $1·24 \text{ kg l}^{-1}$ (porosity 59·6%).

Apparatus and procedure. The thermostatted reaction vessel, where both the adsorption equilibria and the impregnation process were examined at 25°C, accomodated a Teflon basket with a fixed support layer through which the impregnating solution (0·4 l) was pumped by means of a turbine pump. Prior to measurement, air was removed from the pores of the support by evacuation in water.

Samples for analysis were taken from the vessel in preselected time intervals. In this manner the attaining of the adsorption equilibrium was also monitored. The support batch was invariably 15 g. The initial concentrations of the active components in the impregnating solution were $5-50$ mmol l^{-1}. After the equilibrium established (in 6·5 h for the highest concentrations), the concentrations of the active components in solution were measured and the adsorbed amounts established by balance calculations.

The concentrations of the active components in the solution were determined by absorption photometry measurements[11] on a Spekol instrument (Carl Zeiss, Jena). Cobalt was determined using 4-(2-pyridylazo)resorcinol with which it forms a red complex at pH $6-9$, exhibiting the absorption maximum at 510 nm; the concentration region was $0·1-1$ ppm. Molybdenum was determined as molybdate using phenylhydrazine hydrochloride, with which it forms a red solution with the absorption maximum at 505 nm in acid medium.

After sample calcination at 300°C for 6 h, the concentrations of the two metals on the cross section of the catalyst extrudates were measured by the electron microanalysis technique[14] using a JEOL JSM electron microscope equipped with an EDAX 711 analyzer.

RESULTS AND DISCUSSION

Adsorption Equilibrium of Cobalt Dichloride and Ammonium Molybdate on Alumina in Aqueous Systems

The adsorption equilibrium measurements for the simultaneous impregnation of alumina with an aqueous solution of cobalt dichloride and ammonium molybdate afforded the Langmuir isotherm in the forms of

$$n_a = 2·76 C_a/(1 + 69·59 C_a + 198·48 C_b) \tag{11}$$

for $CoCl_2$, and

$$n_b = 17·16 C_b/(1 + 69·59 C_a + 198·48 C_b) \tag{12}$$

for $(NH_3)_2MoO_4$. The average error between the experimental and calculated adsorbed amouts was 12·5% and 4·7% for the two compounds, respectively. Thus, the Langmuir relation fits better the adsorption equilibrium of ammonium molybdate; this is also demonstrated by Figs 1 and 2 showing the adsorption data in the linearized coordinates of the isotherms. The straight lines constructed for constant equilibrium concentrations of the other component are parallel, their slopes being the adsorption constant ratios K_{2a}/K_{1a} for $CoCl_2$ and K_{2b}/K_{1b} for $(NH_4)_2MoO_4$. Some deviations of the experimental data from the linear dependences are due to the fact that the experiments were performed at constant initial concentrations of the other component rather than constant equilibrium concentrations.

The calculated adsorption constants indicate that on the alumina used, the molybdenum salt adsorbs more strongly than the cobalt salt, the K_1 and K_2 constants being 6 and 2·8 times, respectively, lower for the latter than for the former.
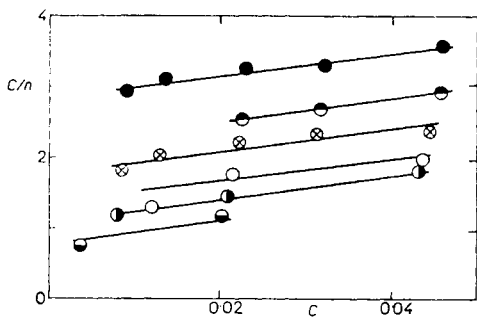
FIG. 1

Adsorption data of cobalt dichloride in co-ordinates of linearized Langmuir isotherm; $c_{(NH_4)_2MoO_4}$ (mmol l^{-1}): ◒ 5, ◓ 10, ○ 15, ⊗ 25, ◓ 35, ● 50
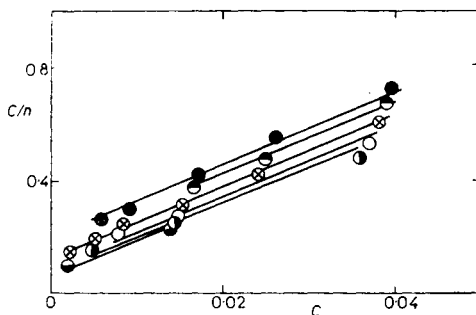

FIG. 2

Adsorption data of ammonium molybdate in coordinates of linearized Langmuir isotherm; c_{CoCl_2} (mmol l^{-1}): ◒ 5, ◓ 10, ○ 15, ⊙ 25, ◓ 35, ● 50
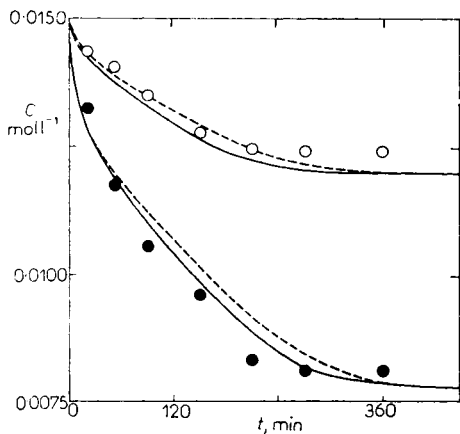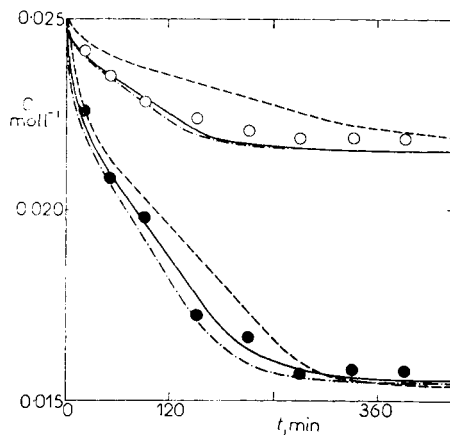

FIG. 3

Determination of effective diffusion coefficients by comparison of the solution of the mathematical model with experiments; ○ CoCl$_2$, ● (NH$_4$)$_2$MoO$_4$. D_e (10^{-9} m^2 s^{-1}): —— 0·28 and 0·58, respectively; - - - - 0·23 and 0·52, respectively

FIG. 4

Determination of effective diffusion coefficients by comparison of the solution of the mathematical model with experiments; ○ CoCl$_2$, ● (NH$_4$)$_2$MoO$_4$. D_e (10^{-9} m^2 s^{-1}): —— 0·23 and 0·52, - - - - 0·11 and 0·40, –·–·– 0·25 and 0·60, respectively

Solution of the Mathematical Model of the Process of Simultaneous
Impregnation of Alumina with Cobalt and Molybdenum Salts

The basic parameters of the model are the diffusion coefficients of the two components. The effective diffusion coefficient values for cobalt dichloride and ammonium molybdate on alumina were determined by comparing the experimental concentration changes of the active components in the impregnating solution with the numerical solution of the mathematical model of the simultaneous impregnation process. Three measurements of concentration changes in the impregnating solution were performed at different initial concentrations of the two components within the region of $15-35$ mmol l^{-1}. The fit of the calculated curves to the experimental points, for some values of effective diffusion coefficients, is shown in Figs $3-5$. The fit is very good for all the three concentrations of $CoCl_2$, which gives evidence that
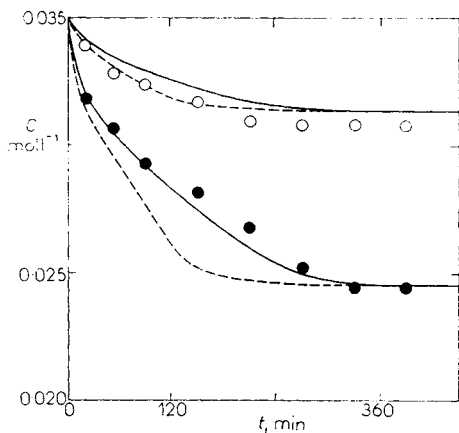

FIG. 5

Determination of effective diffusion coefficients by comparison of the solution of the mathematical model with experiments; $\circ$ $CoCl_2$, $\bullet$ $(NH_4)_2MoO_4$. D_e $(10^{-9}$ m^2 s$^{-1})$: —— 0·2 and 0·4, ----- 0·25 and 0·6, respectively
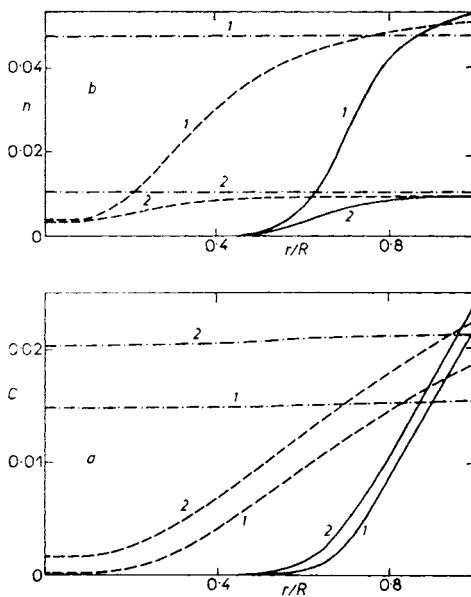
FIG. 6

Time dependences of the concentration profiles of components in support pores (*a*) and adsorbed on support surface (*b*). $C_{0a} = C_{0b} = 25$ mmol l^{-1}; $D_e = 2·5 . 10^{-10}$ $(CoCl_2)$ and $6 . 10^{-10}$ m^2 s^{-1} $((NH_4)_2$.$MoO_4)$. *1* $(NH_4)_2MoO_4$, *2* $CoCl_2$. Time of impregnation: —— 0·5 h, ----- 2 h, $-\cdot-\cdot-$ 6 h

the effective diffusion coefficient of this compound, amounting to $2·5 . 10^{-10} m^2 s^{-1}$, is concentration independent. This is in agreement with our previous experiments[12], where the molecular diffusion coefficients were measured by the diaphragm method.

The likely value of the effective diffusion coefficient of ammonium molybdate, on the other hand, decreases from $6·5 . 10^{-10} m^2 s^{-1}$ to $4·0 . 10^{-10} m^2 s^{-1}$ with increasing concentration. This is probably a consequence of some solvation effects whose recognition would call for additional experimental effort.

Based on the knowledge of the molecular[12] and effective diffusion coefficients, the tortuosity of the alumina used, which is defined as

$$\tau = D\varepsilon/D_e \qquad (13)$$

can be estimated. For cobalt dichloride this value is $2·6$, for ammonium molybdate the value varies over the region of $1·1 - 1·8$ for concentrations of $15 - 35$ mmol l^{-1}. These values agree well with published data[13] reporting them to be within the region of $1·5 - 4$.

By solving the impregnation model, the radial profiles of concentrations and adsorbed amounts of the active components across the catalyst particles could be determined. The calculated time dependent concentration profiles of the two components in the pores of alumina and the radial profiles of the adsorbed components on the support surface are shown in Fig. 6. It is clear that ammonium molybdate is
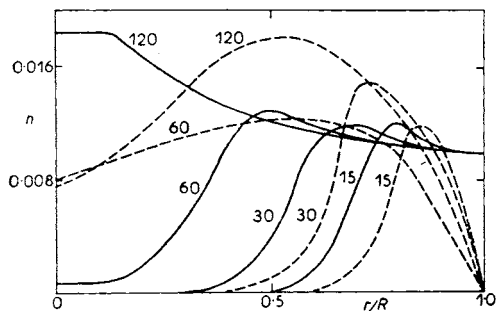

FIG. 7

Comparison of experimental and calculated time dependent radial profiles of cobalt dichloride across the support particle. $C_0 = 50$ mmol l^{-1}, $D_e = 2·5 . 10^{-10} m^2 s^{-1}$, m/V = 37·5 g l^{-1}, $t = 15$, 30, 60, and 120 min; ——— calculation, ––––– experiment
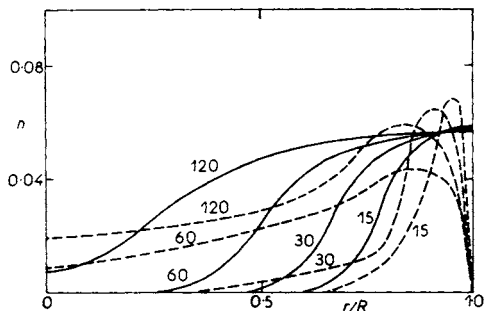
FIG. 8

Comparison of experimental and calculated time depended radial profiles of ammonium molybdate across the support particle. $C_0 = 50$ mmol l^{-1}, $D_e = 3·5 . 10^{-10} m^2 . s^{-1}$, m/V = 37·5 g l^{-1}, $t = 15$, 30, 60, and 120 min; ——— calculation, ––––– experiment

adsorbed more strongly than cobalt dichloride. Fig. 6 demonstrates that the calculated concentration of cobalt dichloride in the pores of the particle is higher than that of ammonium molybdate while the adsorbed amount of the latter is multiply higher than that of the former.

The shape of the calculated concentration profiles of the active components across the catalyst particle was confronted with the results of measurements of the concentrations of cobalt and molybdenum on the cross section the catalyst extrudates prepared by impregnation of the support with a solution of the cobalt and ammonium salts. The results are presented in Figs 7 and 8, showing the time dependent radial concentration profiles of cobalt dichloride and ammonium molybdate, respectively, acrosss the alumina particle within the first 2 hours of impregnation; the curves are the smoothed electron microscope records. The pitfall of this method is in the precise vertical sample positioning and consequently, a precise establishment of the extrudate section edge. The experimental curves thus start in the point of zero signal corresponding to the given element, which is localized on the sample holder in its immediate vicinity. Still, it is apparent that during the impregnation of the support, the components permeate gradually towards the particle centre. The observed and calculated dependences are also seen to be in a qualitative agreement, which gives evidence that the mathematical model is adequate.

The calculated curves of radial profiles of adsorbed cobalt shown in Fig. 7 are somewhat different from the profiles shown in Fig. 6. The difference arises from the different initial concentration of the two components in the impregnating solution, which were one-half for Fig. 6. This indicates a sensitivity of the solution of the model to the initial concentration values. It is interesting, though, that this effect only manifests itself for the component that adsorbs less strongly on the support surface; the radial profiles of molybdenum (Figs 6 – 8) are virtually identical in the two cases.

The results obtained show that for the system under study, a uniform radial profile of cobalt and molybdenum establishes across the catalyst particle in a sufficiently long time of impregnation, hence, the ratio of the two active components is identical at each site of the catalyst particle.

LIST OF SYMBOLS

C concentration of active component in solution, mol l^{-1}
C concentration of active component in the inner pore of support (mol l^{-1}) in the impregnation process modelling
C_0 initial concentration of active component in solution, mol l^{-1}

C_L time variable concentration of active component in impregnating solution, mol l^{-1}
D molecular diffusion coefficient, $m^2 s^{-1}$
D_e effective diffusion coefficient, $m^2 s^{-1}$
h mean length of support extrudate, m
K_1 Langmuir isotherm constant, $1 \ kg \ mol^{-1} \ kg_{alum}^{-1}$
K_2 Langmuir isotherm constant, $1 \ mol^{-1}$
m support mass, kg
M_i molecular weight of component i
n adsorbed amount of component on the inner surface of support, $kg_{act \ comp} \ kg_{alum}^{-1}$
P number of particles impregnated
r radial coordinate, m
Δr step in the radial coordinate, m
R particle radius, m
Δt step in the time coordinate direction, s
V volume of impregnating solution, m^3
ε porosity
ϱ_z apparent density of support, $kg \ m^{-3}$
τ tortuosity

Subscripts

a, b active component (Co and Mo, respectively)

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