MODELLING OF IMPREGNATION OF γ-ALUMINA WITH COBALT AND MOLYBDENUM SALTS. $Co(NO_3)_2–(NH_4)_2MoO_4$–γ-ALUMINA (CHLORIDE TYPE) SYSTEM

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The kinetics of one-component and two-component impregnation of γ-alumina (prepared from aluminium trichloride) with aqueous solutions of cobalt nitrate and ammonium molybdate were studied and treated in terms of a mathematical model accounting for the simultaneous diffusion and adsorption of the active components. The time-dependent radial concentration profiles of the components across the cylindrical support particle were obtained. The profiles of the cobalt-to-molybdenum atomic ratio were derived from the results. The conclusions are applicable to the development of procedures for the preparation of hydrodesulphuration catalysts for the working of crude oil fractions.

This study is aimed at the investigation of the preparation of cobalt and molybdenum based hydrodesulphurization catalysts, making use of the mathematical model devised previously[1] for the process of support impregnation with salts of the active components. As compared with the previous work[1], a different cobalt compound, *viz.* cobalt nitrate, and a different type of γ-alumina are used.

EXPERIMENTAL

Chemicals. Cobalt nitrate *p.a.* (Lachema, Brno); γ-alumina, development type manufactured at the Chemical Hydrocarbons Exploitation Research Institute in Litvínov by hydrolysis of aluminium trichloride, extrudates 1·74 mm in diameter, average length 7·5 mm, apparent density 1·14 kg l^{-1} (porosity 64%). The other chemicals were as used previously[1].

The experiments were performed with the same apparatus and using the same analytical methods as previously[1].

RESULTS AND DISCUSSION

Measurement of Adsorption Equilibrium

The adsorption data of cobalt nitrate and ammonium molybdate on alumina in aqueous systems could not be described by the Langmuir isotherm for two components. The experimental data were therefore fitted by a 2nd power polynomial

whose constants were obtained by nonlinear regression as

$$n_a = 5\cdot88C_a - 38\cdot1C_a^2 + 5\cdot32C_b - 33\cdot8C_b^2 \qquad (1)$$

$$n_b = 16\cdot2C_b - 120\cdot0C_b^2 + 8\cdot52C_a - 63\cdot7C_a^2, \qquad (2)$$

where a stands for $Co(NO_3)_2$ and b for $(NH_4)_2MoO_4$. The average relative error of the isotherms, constructed from 48 experiments, was 8·7% and 4·7%, respectively. The measurements were performed at concentrations up to 120 mmol l^{-1}.

Modelling of Impregnation with the Individual Components

The kinetics were first examined for the impregnation with the individual components. The time dependences of concentrations of the two salts in the impregnating solution are shown in Figs 1 and 2, respectively. The curves represent the numerical solutions of the partial differential equation for one component[2] using the effective diffusion coefficients that led to the best agreement of the calculation with the experiment, viz. $D_e = 1\cdot5 . 10^{-10}$ m^2 s^{-1} for $Co(NO_3)_2$ and $2\cdot5 . 10^{-10}$ m^2 s^{-1} for $(NH_4)_2MoO_4$. These values were also employed when solving the mathematical model of impregnation with two components.
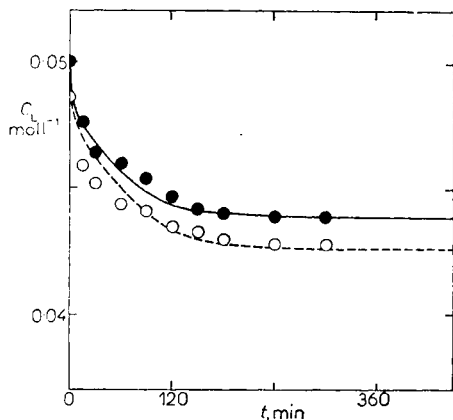

FIG. 1

Concentration changes in the $Co(NO_3)_2$ impregnating solution during the impregnation of γ-alumina. Evacuation pretreatment: ———, ● in impregnating solution, -----, ○ in water
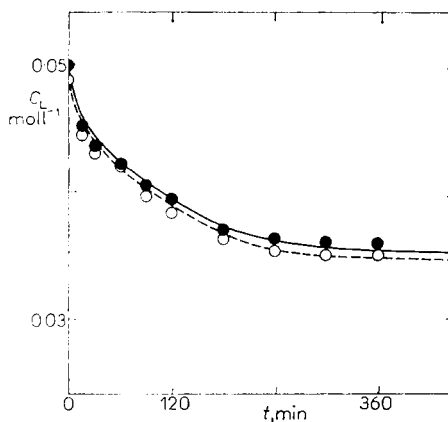
FIG. 2

Concentration changes in the $(NH_4)_2MoO_4$ impregnating solution during the impregnation of γ-alumina. Labelling as in Fig. 1

The calculations and experiments with the impregnation of alumina with the individual components were performed using two methods of support pretreatment, *viz.* removal of air from the pores by evacuation of the particles submerged either in water or in the impregnating solution. The latter variant complies with the boundary condition

$$t = 0, \quad 0 \leqq r \leqq R: \; C_i(r, 0) = C_{0i} \quad i = a, b \,. \tag{3}$$

The course of impregnation was found basically unaffected by the pretreatment method (Figs 1 and 2); the observed and calculated time dependences of the compounds have the same shape, only for the evacuation in water the entire curve is displaced to lower concentrations due to the dilution of the system by the water that is present in the pores at the beginning of impregnation.

The calculated time dependent radial profiles of cobalt and molybdenum, respectively, in the particle pores and on the surface are compared in Figs 3 and 4 for the two support pretreatment procedures. The differences that occur are partly due to
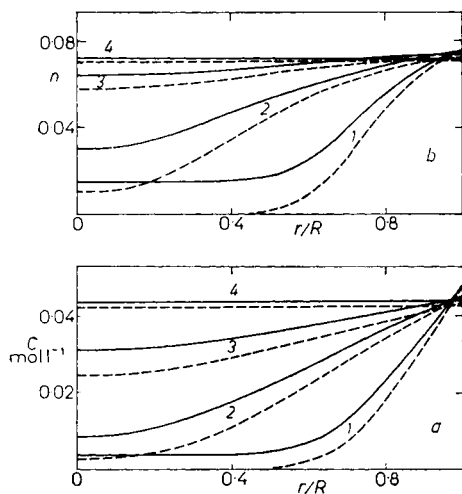
FIG. 3

Time dependences of the radial concentration profiles of cobalt in the support pores (*a*) and adsorbed on the support surface (*b*). Evacuation pretreatment: ——— in impregnating solution, ----- in water. Impregnation time (h): *1* 0·25, *2* 1, *3* 2, *4* 5. *n* is the amount of active component (kg) *per* kg of alumina
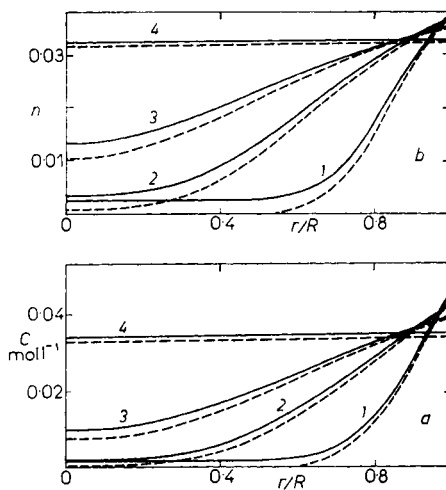
FIG. 4

Time dependences of radial concentration profiles of molybdenum in the support pores (*a*) and adsorbed on the support surface (*b*). Labelling and conditions as in Fig. 3

the fact that the initial concentration of the impregnating solution for the pretreatment by evacuation in water was decreased because of the presence of water in the pores, and partly follow from the assumption of the mathematical model, some amount of the compound of the active component being present in the pores at time $t = 0$ if the pretreatment by evacuation in the impregnating solution has been applied. The mutual shift of the radial profiles for the two pretreatment approaches is not very marked, and it can be concluded that the way of removing air from alumina prior to the impregnation has a negligible effect on the establishment of the equilibrium between the concentrations of the components on the surface of the support and in the solution.

Modelling of Simultaneous Impregnation with Two Components

The kinetics of simultaneous impregnation were measured at initial concentrations of 25, 50, and 75 mmol l^{-1}. This concentration region was bounded by the limits of validity of the 2nd power polynomials describing the adsorption equilibria of the two components. The support was pretreated invariably by evacuation in the impregnating solution.
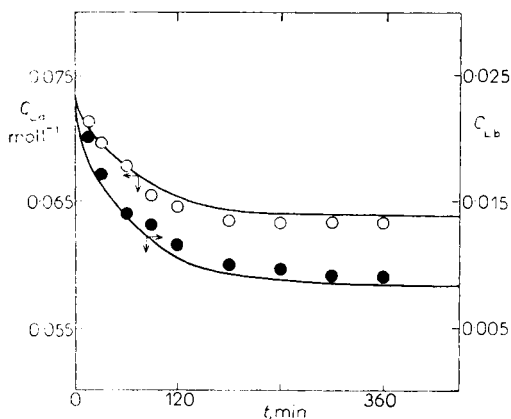

FIG. 5

Concentration changes of Co(NO$_3$)$_2$ and (NH$_4$)$_2$MoO$_4$ in solution during simultaneous impregnation of γ-alumina. ○ Co(NO$_3$)$_2$, ● (NH$_4$)$_2$MoO$_4$; $C_{0a} = C_{0b} = $ = 75 mmol l^{-1}. The curves represent the model solution with $D_e = 1.5 \cdot 10^{-10}$ m^2 . . s^{-1} for Co(NO$_3$)$_2$ and $2.5 \cdot 10^{-10}$ m^2 s^{-1} for (NH$_4$)$_2$MoO$_4$
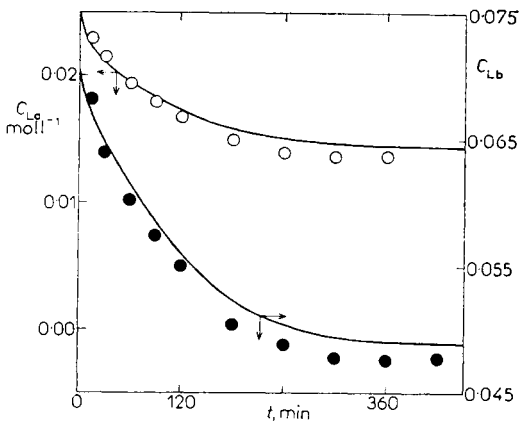
FIG. 6

Concentration changes of Co(NO$_3$)$_2$ and (NH$_4$)$_2$MoO$_4$ in solution during simultaneous impregnation of γ-alumina. $C_{0a} = $ = $C_{0b} = $ 25 mmol l^{-1}, otherwise as in Fig. 5

Examples of comparison of the experimental kinetic data with the mathematical model for two components are shown in Figs 5 and 6. In view of the high sensitivity of the solution of the model to the effective diffusivity values, some inaccuracies in the formal description of the adsorption equilibrium, and errors in the concentration change measurements in the impregnating solution, the agreement of the calculation with the experiment can be regarded as very good.

By comparing the effective diffusion coefficients with the molecular diffusivities determined previously[3], the tortuosity of the alumina used could be determined. For cobalt nitrate the value is 4·69, for ammonium molybdate, 3·07. These values agree with published data[4].

The different strength of adsorption of the two compounds is seen in Fig. 7, showing the calculated time dependent radial concentrations of the components across the support particle during the simultaneous impregnation. With the equimolar ratio of the two components at the beginning of the impregnation (C_{0i} = 75 mmol . . l^{-1}), the amount of ammonium molybdate is about twice as high as that of cobalt nitrate in any time of impregnation and at any site of the support particle.
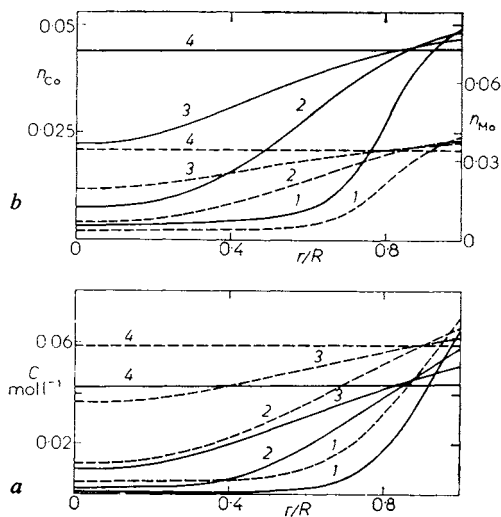
FIG. 7

Radial concentration profiles of cobalt and molybdenum across the catalyst particle (a) and the adsorbed amounts of active components (kg) per kg of alumina (b). - - - - - $Co(NO_3)_2$, C_0 = 75 mmol l^{-1}, ———— $(NH_4)_2MoO_4$, C_0 = 75 mmol l^{-1}. Impregnation time (h): 1 0·25, 2 1, 3 2, 4 5
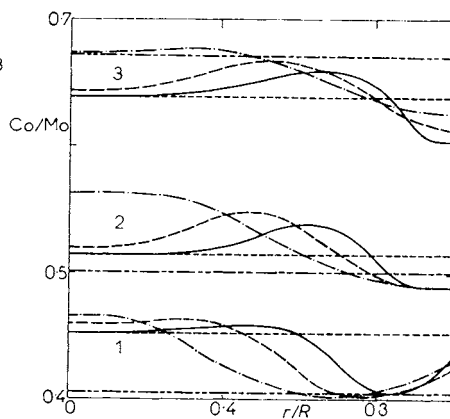
FIG. 8

Time dependent radial profiles of the Co/Mo ratio across the catalyst particle. Initial concentrations of Co and Mo (mmol l^{-1}): 1 25, 75; 2 50, 50; 3 75, 25. Impregnation time (h): - - - - - 0, ———— 0·25, - - - 1, - · - · - 2, - ··· - 5

The results indicate that for the system under study subjected to impregnation for a sufficiently long time, a uniform radial profile of both cobalt and molybdenum establishes across the catalyst particle. This conclusion derived from the solution of the mathematical model is in agreement with the experimental radial concentration profiles measured by the electron microscopy technique.

The time variable radial profiles of the cobalt-to-molybdenum atomic ratio across the catalyst particle obtained by solving the mathematical model of simultaneous impregnation are shown in Fig. 8. The model was solved using boundary conditions corresponding to the particle pretreatment by evacuation in the impregnating solution. The cobalt-to-molybdenum atomic ratio is seen to depend on the initial concentration ratio of the respective compounds. For equimolar $Co(NO_3)_2$–$(NH_4)_2$. .MoO_4 mixtures (75, 50, and 25 mmol l^{-1}) the radial profiles of the atomic ratio are virtually identical. During the impregnation, the maximum of the Co/Mo ratio displaces gradually from the outer surface of the cylindrical particle towards its axis. This gives evidence that cobalt nitrate passes into the particle bulk faster than ammonium molybdate which is more strongly adsorbed. The displacement of the maximum is fastest if ammonium molybdate has been added in excess. After the adsorption equilibrium has established, the radial profile of the cobalt-to-molybdenum ratio remains constant at each site of the catalyst particle.

CONCLUSIONS

The solution of the impregnation model has provided insight into the radial profiles of concentrations of the active components across the support particle. It was found that the atomic ratio of the two elements at a site of the support does not remain constant during the impregnation. This fact might be made use of during the preparation of hydrodesulphurization catalysts where a defined radial profile of cobalt and molybdenum is desired. Further study should be aimed at the investigation of the relation between the radial profile of the active component across the catalyst particle and the catalytic activity of the latter. The results of the study will be applicable to the preparation of catalysts with the active components distributed near the outer surface of the particle, which suit well to the liquid-phase hydrodesulphuration of high-boiling oil fractions.

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