Hydrogen Transfer in Slurries of Carbon Supported Catalyst (HPO Process)

The effect of suspended activated carbon on gas/liquid mass transfer is studied for the Pd/C-catalyzed hydrogenation of nitrate to hydroxylamine (HPO process). In a bubble column and in a stirred autoclave, physical mass transfer ($k_L a$) in the concentrated salt solution is improved by more than a factor of three by the catalyst. Chemical absorption enhancement by the zero-order catalytic reaction is insignificant at the employed catalyst diameter (40 μm), but hydroxylamine selectivity depends on the absorption regime.

D. Lindner and M. Werner
Technische Chemie
Universität Oldenburg
D-2900 Oldenburg, West Germany

A. Schumpe
Gesellschaft für
Biotechnologische Forschung
D-3300 Braunschweig, West Germany

Activated carbon is frequently used as the catalyst support material in catalytic hydrogenation. In slurry reactors, suspended activated carbon can considerably increase the gas/liquid mass transfer rate. This has been observed during physical absorption of propane (Kars et al., 1979), as well as O_2 and CO_2 (Alper et al., 1980). In the case of absorption with chemical reaction, higher $k_L a$ values along with chemical absorption enhancement were detected, e.g., for the oxidation of sulfide on activated carbon as the catalyst (Chandrasekaran and Sharma, 1977) and glucose oxidation on Pt/C catalyst (Alper et al., 1980). Physical and chemical absorption enhancement could be observed only if the solid particle size was smaller than the thickness of the liquid side diffusion film. Therefore, the effects were often studied in the stirred cell with plane interface and rather small liquid side mass transfer coefficient k_L. Because of the constant interfacial area in this absorber, higher $k_L a$ value in the presence of suspended activated carbon is referred to higher k_L by adsorption facilitated transport (Alper et al., 1980).

In most industrial processes, on the other hand, high turbulence and coarseness of catalyst particles may render these effects negligible. Quicker et al. (1987) studied the absorption of CO_2 into carbonate buffer solutions with suspended activated carbon powder in a bubble column. The analysis in the form of the Danckwert's plot indicated 1–43% higher liquid side mass transfer coefficient and up to 19% higher interfacial area at the concentration of 9 g/L activated carbon. Studying oxygen transfer in the same bubble column with suspended catalyst support particles, Schumpe et al. (1987) found that $k_L a$ monotonically decreases with increasing concentration of activated carbon in water. The $k_L a$ values were well correlated with suspension viscosity in a single relation for adsorptive and nonadsorptive particles. However, activated carbon suspended in 0.8 M sodium sulfate solution slightly increased the volumetric mass transfer coefficient in spite of the rise in viscosity.

This observation corresponds to previously reported improvement of mass transfer by fine solids suspended in salt solutions. Gopal and Sharma (1983) measured 40% increase of the specific interfacial area in a bubble column with alkaline dithionite solution upon addition of 0.75 wt. % calcium carbonate powder. Similar increase of the gas holdup and the specific interfacial area were observed by Sada et al. (1983, 1985, 1986, 1987) in slurries of magnesium hydroxide (2 μm) or calcium hydroxide (7 μm) in sodium hydroxide solution, and in slurries of aluminium oxide (<3 μm) in sodium chloride or sulfate solution. Suspending aluminum oxide powder in water, on the other hand, gas/liquid mass transfer in the bubble column is not improved (Sada et al., 1986). It seems that fine suspended solids reduce the coalescence rate of small bubbles formed in salt solutions.

A particularly high salt concentration (>5 M) is encountered in the reduction of nitrate to hydroxylamine on Pd/C catalyst:

$$NH_4NO_3 + 2H_3PO_4 + 3H_2 \xrightarrow{Pd/C} (NH_3OH)H_2PO_4 + (NH_4)H_2PO_4 + 2H_2O$$

The catalyst is suspended in a phosphoric acid/dihydrogen phosphate buffer solution (2.2 kmol/m^3) containing ammonium nitrate at a concentration of 3 kmol/m^3. Owing to the low hydrogen solubility in the liquid (about half of that in water), mass transfer resistance may significantly affect the reactor performance. The reaction is carried out industrially in the bubble column slurry reactor at temperatures of 50–60°C and pressures up to 10 bar. It is part of the HPO (hydroxylamine phosphate

---

Correspondence concerning this paper should be addressed to A. Schumpe.

oxime) process of the Dutch State Mines for the production of caprolactam (Loyson and Nunnink, 1972).

The kinetics of the reaction has recently been investigated by the present authors (Werner et al., 1987a, b). In addition to the formation of hydroxylamine, the parallel reaction to ammonium,

$$NH_4NO_3 + 2H_3PO_4 + 4\,H_2 \overset{Pd}{\rightarrow} 2(NH_4)H_2PO_4 + 3H_2O$$

the consecutive hydrogenation of hydroxylamine,

$$NH_2OH + H_2 \overset{Pd}{\rightarrow} NH_3 + H_2O$$

and, in the absence of hydrogen at the catalyst surface, the catalytic decomposition of hydroxylamine

$$4NH_2OH \xrightarrow{Pd,C} N_2O + 2NH_3 + 3\,H_2O$$

$$3NH_2OH \overset{Pd}{\rightarrow} N_2 + NH_3 + 3H_2O$$

were studied. The reaction system is illustrated in Figure 1. Two reactions involving the catalyst support material, the oxidation of carbon by nitric acid and the catalytic decomposition of ammonium nitrate, occured only at low pH values and high temperatures that are not encountered in the industrial process. Also the catalytic decomposition of hydroxylamine does not take place if a sufficient dissolved hydrogen concentration is maintained. Carefully avoiding any mass transfer limitation, all hydrogenation reactions were shown to be zero order in hydrogen whereas broken reaction orders were reported in the previous literature (de Rooij et al., 1977; van de Moesdijk, 1979) for the hydrogenation of nitrate. The following rate equation was suggested (Werner et al., 1987a,b):

$$r_i = k_i e^{-(53.9\,\mathrm{kJ/mol})/RT}\, c_{Pd} c_{NO_3^-}\, a_{H^+}^{0.62} \tag{1}$$

The value of the constant k_i(kmol$^{-0.62}$ · m$^{4.86}$ · kg^{-1} · s^{-1}) is 1.70 · 10^5 for the formation of hydroxylamine (k_{HA}) and 0.49 · 10^5 for the parallel reaction to ammonia (k_{NH_3}).

It is the purpose of this study to investigate the effect of Pd/C catalyst on gas/liquid mass transfer in the HPO process. The reasons for studying this reaction are its industrial importance and the extremely high salt concentration encountered. Based on the literature survey, a strong effect of the solid on hydrodynamics and mass transfer may be expected. Specifically, the influence on the volumetric mass transfer coefficient k_La and the possibility of absorption enhancement due to the catalytic reaction are considered.

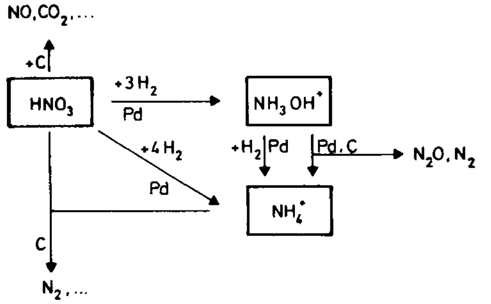

Figure 1. Reactions observed during hydroxylamine production by reduction of nitrate.

Experimental Equipment and Procedure

Activated carbon (Merck), loaded with 10 wt. % Pd (ρ_S = 1,970 kg/m^3) or unloaded (ρ_S = 1,800 kg/m^3), was used. The volume-mean particle size is about 40 μm, the number mean is about 16 μm. The salt solutions studied (2.2 M H_3PO_4 with 0–3 M NH_4NO_3 or KNO_3) had surface tensions in the range of 0.057–0.062 N/m. The *L/S* contact angle (water: 76°) ranged from 79° to 94° depending on the nitrate concentration. This indicates a limited wettability, particularly, at high salt concentration.

The effect of suspended solids on gas/liquid mass transfer was studied in a bubble column and a stirred autoclave. The column reactor is made of glass with an inner diameter of 0.095 m and a height of 1.4 m. A single tube (2 mm ID) served as the gas distributor. The column was operated batchwise at dispersion heights around 1 m. Temperatures in the range of 20–50°C were adjusted by means of a thermostated jacket. The autoclave is made of stainless steel and has a volume of 1.25 L. It was operated batchwise with respect to the slurry and the gas (surface entrainment). The stirrer has a magnetic drive; stirring speed was varied from 300 to 1,800 rpm. By means of a thermostated jacket, temperatures in the range of 20–90°C were adjusted. Details of the reactor are described by Werner et al. (1987a).

The gas holdup in the bubble column was calculated from the change in the dispersion height due to the gas flow. In the covered range of the gas velocity, the axial solids distribution was homogeneous. The volumetric mass transfer coefficient was investigated by dynamic desorption of oxygen from air-saturated slurry into hydrogen gas. The decrease in the liquid phase oxygen concentration was measured with a fast response oxygen electrode (WTW EO 90) inserted horizontally at half the dispersion height. The electrode response time (2 to 3 s, depending on the temperature) needs not to be considered, if the initial part of the response curve (up to 50%) is neglected (Schumpe, 1985). Taking into account quasiinstantaneous oxygen desorption from the solid, the k_La value can be evaluated according to the following relation (Schumpe et al., 1987):

$$\ln C_E = -\frac{k_La/\epsilon_L}{\left(1 + \dfrac{bHc_s}{1-\phi_s}\right)}\, t + \text{const.} \tag{2}$$

For a solution of 2.2 M H_3PO_4 and 3 M KNO_3 at 50°C, Henry's constant H for oxygen is estimated at 4.4 · 10^8 Pa · m^3/kmol (Schumpe et al., 1982) and the adsorption equilibrium constant b at 0.18 · 10^{-10} kmol · Pa^{-1} · kg^{-1} (Li and Deckwer, 1982; Schumpe et al., 1987). Then, at the maximum activated carbon concentration of c_s = 50 kg/m^3, the denominator in Eq. 2 attains its highest value of 1.40. In a few experiments oxygen was absorbed from air into the oxygen-free slurry resulting in about 8% higher k_La values than desorption runs. The difference results from the effect of gas density on k_La as discussed by Öztürk et al. (1987). Obtained under realistic hydrodynamic conditions, the reported k_La values for oxygen desorption into hydrogen might be recalculated for hydrogen transfer by multiplication with the following factor:

$$\frac{k_La(\mathrm{H_2})}{k_La(\mathrm{O_2})} = \left[\frac{D(\mathrm{H_2})}{D(\mathrm{O_2})}\right]^m \approx 2^m \qquad (3)$$

where the exponent m may vary from ½ to ⅔ depending on the bubble size (Calderbank and Moo-Young, 1961).

In the stirred autoclave, dynamic absorption of hydrogen into gas-free slurry was observed by the pressure decrease under isochoric conditions using a capacitance sensor (Setra 2001). For physical absorption, the time course of the signal was analyzed as suggested by Albal et al. (1983).

$$\ln(P - P_\infty) = -\frac{P_0}{P_\infty}\frac{k_La'}{1 - \phi_S}t + \text{const.} \qquad (4)$$

Only the mass transfer coefficient with respect to suspension volume (k_La') can be determined since the gas holdup is unknown. From the total pressure decrease ($P_0 - P_\infty$) the hydrogen solubility (and adsorption capacity of solids) can be evaluated. During absorption with chemical reaction on Pd/C catalyst, not only the decrease of the gas pressure was recorded but also the final composition of the gas phase was studied with a gas chromatograph. Liquid samples were analyzed for hydroxylamine and ammonium. Details of the analytical procedures were described by Werner et al. (1987a).

Analysis of Chemical Absorption Runs

Absorption with zero order catalytic reaction in the slurry reactor has been analyzed theoretically by Chaudhari and Ramachandran (1980). The mass balance for pore diffusion with zero order reaction in spherical catalyst particles

$$\frac{D_e}{r^2}\frac{d}{dr}\left[r^2\left(\frac{dc_{H_2}}{dr}\right)\right] = k_0\rho_s \qquad (5)$$

was solved for the boundary conditions

$$r = R, \quad c_{\mathrm{H_2}} = c^s_{\mathrm{H_2}}$$
$$r = \lambda, \quad \frac{dc_{\mathrm{H_2}}}{dr} = 0$$

to obtain the radial concentration profile:

$$c_{\mathrm{H_2}} = c^s_{\mathrm{H_2}} - \frac{k_0\rho_s}{3D_e}\left[\frac{R^2}{2} + \frac{\lambda^3}{R} - \frac{r^2}{2} - \frac{\lambda^3}{r}\right] \qquad (6)$$

In order to avoid mass transfer limitation, the surface concentration $c^S_{\mathrm{H_2}}$ would have to be higher than the critical value obtained by setting $c_{\mathrm{H_2}}$, r and λ to zero in Eq. 6. If the external mass transfer rate

$$R_{\mathrm{H_2}} = (c^*_{\mathrm{H_2}} - c^S_{\mathrm{H_2}})\left(\frac{1}{k_La'} + \frac{1}{k_sa'_s}\right)^{-1} \qquad (7)$$

is insufficient, the hydrogen concentration drops to zero at some radial position $\lambda > 0$ in the catalyst particle. The reaction rate then reduces to

$$R_{H_2} = c_sk_0\left[1 - \left(\frac{\lambda}{R}\right)^3\right]. \qquad (8)$$

Setting $c_{\mathrm{H_2}} = 0$ and $r = \lambda$ in Eq. 6 and introducing the resulting expression for $c^S_{\mathrm{H_2}}$ into Eq. 7, Chaudhari and Ramachandran (1980) finally arrived at the following expression for the absorption rate under mass transfer limitation:

$$R_{H_2} = \left(\frac{1}{k_La'} + \frac{1}{k_sa'_s}\right)^{-1}\left\{c^*_{\mathrm{H_2}} - \frac{k_0\rho_sR^2}{6D_e} \cdot \left[1 - 3\left(\frac{\lambda}{R}\right)^2 + 2\left(\frac{\lambda}{R}\right)^3\right]\right\} \qquad (9)$$

Equations 8 and 9 were used to evaluate the volumetric mass transfer coefficient from the absorption rates measured at various catalyst loadings. The conversion of nitrate to hydroxylamine was kept low (<5%) in these experiments so that the hydrogen consumption by consecutive hydrogenation could be neglected. The kinetics of the hydrogen consumption due to the two parallel reactions with nitrate is calculated from Eq. 1. Considering the stoichiometrics, it holds:

$$k_0c_s = (3k_{\mathrm{HA}} + 4k_{\mathrm{NH_3}})e^{-(53.9\mathrm{kJ/mol})/RT}\,c_{Pd}c_{\mathrm{NO_3}}\cdot a^{0.62}_{\mathrm{H^+}} \qquad (10)$$

The value of (λ/R) is evaluated from Eq. 8 and introduced into Eq. 9. A plot of the absorption rate $R_{\mathrm{H_2}}$ against the parameter group

$$X = \frac{k_0\rho_s}{6}\left[1 - 3\left(\frac{\lambda}{R}\right)^2 + 2\left(\frac{\lambda}{R}\right)^3\right] \qquad (11)$$

allows the sum of the film resistances to be calculated from the intercept. It is estimated that $(1/k_La') \gg (1/k_sa'_s)$ (Ramachandran and Chaudhari, 1983), i.e., the intercept is a measure of the k_La' value. From the slope of the plot, the effective value of R^2/D_e can be calculated.

Physical Mass Transfer in the Bubble Column Slurry Reactor

Oxygen desorption into hydrogen gas could be carried out only with Pd-free activated carbon as the solid. Therefore, in a few runs oxygen was absorbed from air into initially gas-free suspensions of activated carbon and Pd/C catalyst. The volumetric mass transfer coefficients for both types of solid agreed very well.

Some results of the desorption runs are plotted in Figure 2. At the high phosphoric acid concentration encountered in the process liquid, the volumetric mass transfer coefficients without solids are smaller than in water. They decrease with an increase in the nitrate concentration. Usually, dissolved salt is found to increase the volumetric mass transfer coefficient (Schumpe et al., 1987). This is not observed in the presence of phosphoric acid, perhaps, owing to the higher viscosities of the solutions. Even more surprising is the spectacular increase of the volumetric mass transfer coefficient by addition of only 5 g/L activated carbon. In the carbon slurries, the k_La value does not depend on the nitrate concentration. The relative increase due to activated

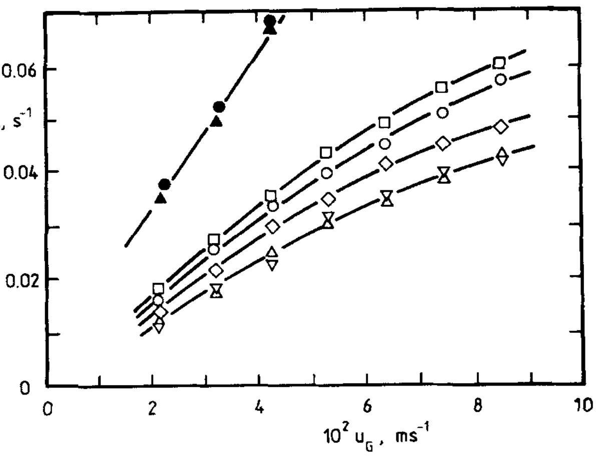

Figure 2. Volumetric mass transfer coefficients for oxygen in the bubble column (with and without activated carbon) at 50°C.

□ Water, ○ 2.2 M H_3PO_4; ◇ 2.2 M H_3PO_4 + 1 M KNO_3; △ 2.2 M H_3PO_4 + 3 M KNO_3; ▽ 2.2 M H_3PO_4 + 3 M NH_4NO_3; ● (as ○) with 5 g/L C; ▲ (as △) with 5 g/L C

carbon is by more than a factor of 3 in the most concentrated solution and still by factors of 2–2.5 in phosphoric acid.

The gas holdups plotted in Figure 3 show very similar trends to the mass transfer coefficients at lower sensitivity. This indicates an additional variation of the mean bubble diameter. The holdups in the solid-free solutions are only slightly different. Much higher gas holdup is observed in the presence of activated carbon due to foaminess of the HPO slurry as reported also by de Rooij et al. (1977). Although foaming causes some difficulty in column operation and scale-up, the high volumetric mass transfer coefficients are an important asset to the process, as discussed later.

The effect of the activated carbon concentration on mass transfer is systematically studied in a solution of 2.2 M H_3PO_4 and 3 M KNO_3 at 50°C. Figure 4 is a plot of the relative increase of the volumetric mass transfer coefficient as compared to the solid-free liquid. Even at very small carbon loadings there is an increase by a factor of three. At higher concentrations, the relative increase of the k_La value is by up to a factor of 4. Concentrations less than 1 kg/m^3 could not be adjusted reliably since the solids tend to stick to the wall of the reactor. There is no significant effect of the superficial gas velocity in the covered range (0.02–0.085 m/s) on the relative k_La increase. The present results may be compared to the measurements of Schumpe et al. (1987) in salt-free activated carbon slurries. As indicated by the dotted line in Figure 4, they observed a slight decrease of k_La owing to the increasing slurry viscosity ($k_La \propto \mu_{eff}^{-0.39}$). There was no adsorption-facilitated absorption enhancement in spite of an even smaller particle size (number mean: 5.4 μm) than used in this study. Therefore, the observed effect is attributed to reduced coalescence of small bubbles formed in the HPO process slurry but not in water.

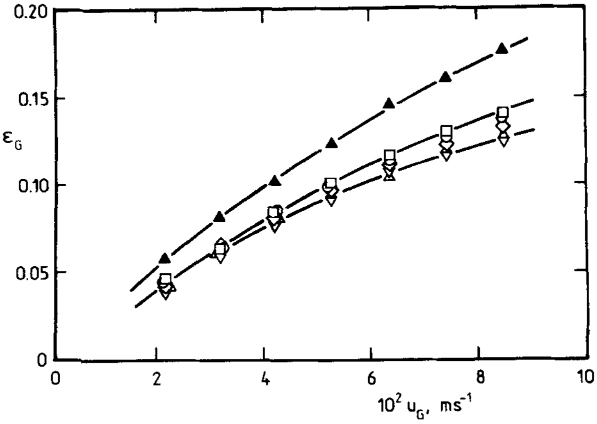

Figure 3. Hydrogen holdups in the bubble column at 50°C.

Symbols as in Figure 2.

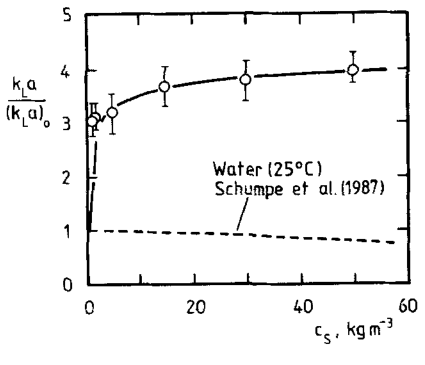

Figure 4. Relative increase of the volumetric mass transfer coefficient in the bubble column by adding activated carbon.

2.2 M H_3PO_4 + 3 M KNO_3, 50°C

Physical Mass Transfer in the Stirred Autoclave

The volumetric mass transfer coefficients for hydrogen determined in the stirred autoclave are higher by an order of magnitude than those in the bubble column at the high stirring speeds employed. A comparison is given in Fig. 5 by the temperature effect in various solid-free liquids. Increasing temperature lowers liquid viscosity and thus improves mass transfer because of the higher gas diffusivity, higher surface renewal rate and, possibly, smaller bubble size. Apparently linear dependencies are observed; note that different scales are used depending on the reactor type. Similarly high mass transfer coefficients at ambi-

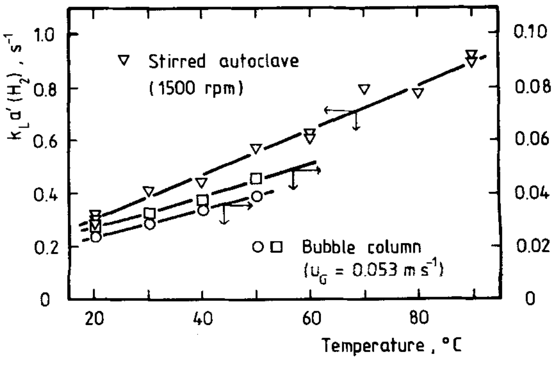

Figure 5. Temperature effects on mass transfer in the column reactor and stirred autoclave.

Symbols as in Figure 2

ent temperature have been reported by Ledakowicz et al. (1983) for the same type of autoclave. As in the bubble column, the volumetric mass transfer coefficient for hydrogen in the absence of suspended solids decreases with an increase in the nitrate concentration but it has no effect in the slurries (results not shown).

Most experiments in slurries were carried out at concentrations of 2.2 M H_3PO_4 and 3 M NH_4NO_3, Figure 6. The temperature was only 20°C in these runs since at higher temperature the absorption rate in the slurries became too high to be measured reliably. The volumetric mass transfer coefficients are higher than in the solid-free system by more than a factor of 3 even at the lowest studied carbon concentration (1 kg/m^3). There is no significant effect of the solid concentration (2 to 30 kg/m^3) and the stirring speed (800–1,800 rpm) on the relative increase of k_La'.

Overall, a very similar trend is observed as in the bubble column, and it is suggested that also in the stirred autoclave mainly the coalescence-hindering effect is responsible for the high volumetric mass transfer coefficients. It is surprising, however, that the well known coalescence hindering effect of dissolved salt is not observed unless activated carbon is added. To check whether adsorption of liquid impurities on activated carbon plays a role in reducing the coalescence rate, a few runs were carried out with liquid filtered off from the carbon slurry. The same behavior as in the case of untreated liquid disproved this explanation. A possible mechanism of coalescence hindering is by enrichment of moderately wettable carbon particles at the bubble surface. This might also explain that the increase of the k_La value is observed already at very small average carbon concentrations. This explanation is supported by the recent results of Wimmers and Fortuin (1988a). They studied the fractional surface coverage of single hydrogen bubbles by solid particles. A strong influence of both solid and liquid properties was found. Activated carbon particles (10 μm) led to higher surface coverage than aluminium oxide powder (5 μm). Particularly, in a liquid of similar composition as the HPO process liquid, a KH_2PO_4 solution in phosphoric acid, much stronger adhesion between carbon particles and bubbles was found.

The effects on interfacial area and liquid side mass transfer coefficient could not be determined individually in the HPO slurry. Higher liquid side mass transfer coefficient k_L by adsorption facilitated transport at the rigid surface of small bubbles with a correspondingly thick liquid side diffusion film might add up to the coalescence hindering effect of activated carbon which is obvious from the higher gas holdup, Figure 2. If the film thickness were sufficiently large for adsorption facilitated transport, there should be also some absorption enhancement due to the catalytic reaction. This was checked in the stirred autoclave.

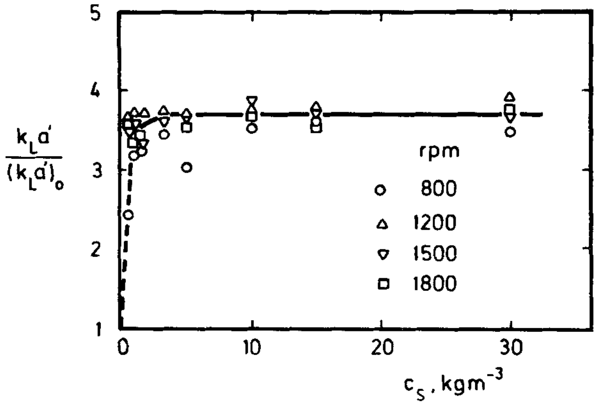

Figure 6. Increase in volumetric mass transfer coefficient in the stirred autoclave by adding activated carbon.
2.2 M H_3PO_4 + 3 M NH_4NO_3, 20°C

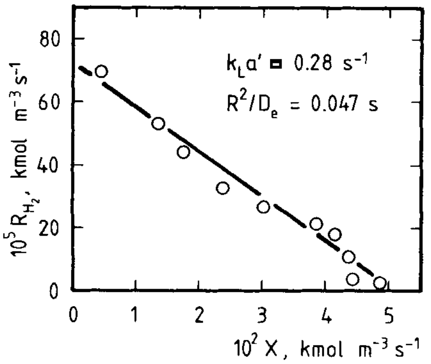

Figure 7. Evaluation of k_La' under reactive conditions (800 rpm).

Chemical Absorption in the Stirred Autoclave

The volumetric mass transfer coefficient for hydrogen in the stirred autoclave was determined also under reactive conditions. At appropriately small stirring speeds (600 and 800 rpm), hydrogen absorption rates (at 2 and 5.5 bar, respectively) were measured in the transition regime from kinetic to diffusional absorption control. Varying the catalyst concentration in a wide range, the value of λ/R characterizing the hydrogen depleted core region ranged from 0.35 to 0.83 (Eq. 8). A plot of the absorption rate as to Eq. 9 is given in Figure 7 for the data at 800 rpm. A straight line is obtained. This is possible only since the k_La' value is constant in a wide range of catalyst concentration, Figure 6. Nevertheless, some deviation might have resulted from the nonspherical shape and the non-uniform size of the catalyst. The effective values of R^2/D_e calculated from the slope agree well for the two stirring speeds, Table 1. The volumetric mass transfer coefficients k_La' calculated from the intercepts compare well with the results of physical absorption runs under the same hydrodynamic conditions in the presence of activated carbon instead of Pd/C catalyst. It is concluded that high mass transfer coefficients due to the presence of suspended carbon prevail also under reactive conditions.

At still higher rate of chemical reaction or lower volumetric mass transfer coefficient, hydrogen absorption might be enhanced by the reaction on the catalyst particles in the liquid side diffusion film. To check on chemical absorption enhancement,

Table 1. Parameter Values Evaluated by Eq. 9 from the Rates of Absorption with Zero-Order Catalytic Reaction*

N, rpm	R^2/D_e, s	k_La', s^{-1}
600	0.051	0.14 (0.15)**
800	0.047	0.28 (0.34)**

*2.2 M H_3PO_4 + 2 M KNO_3, pH = 1.8, 50°C.

**k_La' from physical absorption rate into slurries of Pd-free activated carbon (Eq. 4).

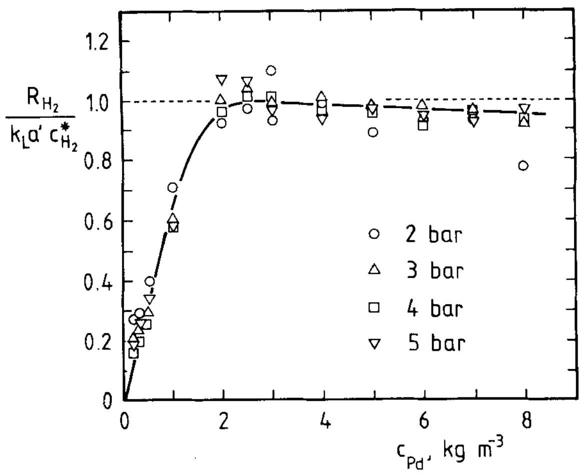

Figure 8. Check for absorption enhancement due to the catalytic reaction.
2.2 M H_3PO_4 + 2 M KNO_3, pH = 1.8, 50°C, 600 rpm

nitrate hydrogenation was carried out at a stirring speed of 600 rpm and catalyst concentrations in the range of 2–80 kg/m^3. The absorption regimes are identified in a plot of the hydrogen absorption rate (referred to the product of the estimated equilibrium concentration $c^*_{H_2}$ and the volumetric mass transfer coefficient $k_L a'$) against the palladium concentration, Figure 8. After the linear increase in the kinetic absorption regime, the parameter group levels off at a value of about 1 as expected for the diffusional absorption regime. There is no further increase at still higher catalyst concentration, i.e., no significant absorption enhancement occurs. This result is quite expected at a catalyst particle size exceeding the thickness of the liquid side diffusion film (Alper et al., 1980). It may then further be concluded that adsorption facilitated transport does not significantly contribute to the high $k_L a$ values in HPO slurry.

This result disagrees with the recent paper of Wimmers and Fortuin (1988b). For the hydrogenation of hydroxylamine on Pd/C catalyst (20 μm), they reported enhancement factors of 3 to 4 at a catalyst concentration of only 1 kg/m^3 (0.1 kg/m^3 Pd). The discrepancy may result from the fact that Wimmers and Fortuin calculated the enhancement factor by relating the rate of absorption with chemical reaction to the physical absorption rate into the particle-free liquid. In this way the effect of activated carbon on the volumetric mass transfer coefficient is overlooked which is just of the same magnitude as the apparent enhancement factors reported.

In the absence of mass transfer enhancement, there is no advantage in operating the reactor under mass transfer control but a loss of hydroxylamine selectivity is encountered since in the hydrogen-depleted bulk of the slurry the catalyzed decomposition of the desired product is the only reaction taking place. In the experiments, the effective selectivity was reduced by up to 20%. The observed pressure decrease had to be corrected for the effect of N_2 and N_2O evolution by the decomposition reaction. In the industrial process, the formation of these gaseous byproducts required an unnecessarily high purge of the hydrogen recycle stream. For these reasons, operation in the mass transfer controlled absorption regime is rather undesirable. The increase of the volumetric mass transfer coefficient in the presence of activated carbon greatly assists in maintaining kinetic control.

Conclusions

The effect of suspended activated carbon and Pd/C catalyst, respectively, on gas/liquid mass transfer in a bubble column and a stirred autoclave is studied for the conditions of hydroxylamine production by reduction of nitrate (HPO process). Physical desorption of oxygen and physical and chemical absorption of hydrogen are investigated. The results of the different experimental techniques are in good agreement. The solids are found to reduce the bubble coalescence rate and increase the volumetric mass transfer coefficient $k_L a$ in the concentrated (>5 M) salt solution employed in the HPO process. The relative increase of the $k_L a$ value is by factors of 3 to 4 as compared to the solid-free liquid. Thus high mass transfer rates can be achieved, which allows operation in the kinetic absorption regime. There is no absorption enhancement at higher catalyst concentrations. It may then be concluded that adsorption facilitated transport does not significantly contribute to the high $k_L a$ values in the HPO slurry. Operation in the mass transfer controlled regime is discouraged by the absence of chemical absorption enhancement and by catalytic decomposition of hydroxylamine in the hydrogen-depleted bulk of the slurry. This leads to lower selectivity than in the kinetically controlled absorption regime and to the formation of undesirable gaseous byproducts.

Acknowledgment

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

Notation

a_{H^+} = proton activity, kmol · m^{-3}
b = adsorption constant, kmol · Pa^{-1} · kg^{-1}
c_E = reading of the oxygen electrode in arbitrary units
$c_{H_2}(c^*_{H_2})$ = liquid phase hydrogen concentration (in equilibrium to the gas phase), kmol · m^{-3}
$c^s_{H_2}$ = hydrogen concentration at the outer surface of the catalyst particles, kmol · m^{-3}
c_{Pd} = palladium concentration, kg · m^{-3}
c_S = solid concentration, kg · m^{-3}
D = diffusivity, m^2 · s^{-1}
D_e = effective pore diffusion coefficient, m^2 · s^{-1}
H = Henry's constant, Pa · m^3 · kmol^{-1}
k_i = kinetic constant in Eq. 1, kmol$^{-0.62}$ · m$^{4.86}$ · kg^{-1} · s^{-1}
k_0 = zero-order reaction rate constant, Eq. 10, kmol · kg^{-1} · s^{-1}
$k_L a$ = G/L mass transfer coefficient referred to slurry ($G/L/S$) volume, s^{-1}
$k_L a'$ = G/L mass transfer coefficient referred to suspension (L/S) volume, s^{-1}
$k_s a'_s$ = S/L mass transfer coefficient referred to suspension (L/S) volume, s^{-1}
N = stirring speed, s^{-1}
P = pressure, Pa
r = radial coordinate in the catalyst particle, m
r_i = reaction rate, kmol · m^{-3} · s^{-1}
R = particle radius, m
R_{H_2} = hydrogen absorption rate, kmol · m^{-3} · s^{-1}
t = time, s
T = Temperature, K
X = parameter group defined in Eq. 11, kmol · m^{-3} · s^{-1}

Greek letters

ϵ = phase holdup
λ = radial coordinate at which the hydrogen concentration becomes zero, m
ρ = density, kg · m^{-3}
ϕ_s = solid volume fraction in the gas-free suspension

Indices

G = gas
L = liquid
S = solid
0 = solid-free system
∞ = final value ($t \rightarrow \infty$)

Literature Cited

Albal, R. S., Y. T. Shah, A Schumpe, and N. L. Carr, "Mass Transfer in Multiphase Agitated Contactors," *Chem. Eng. J.*, **27,** 61 (1983).

Alper, E., B. Wichtendahl, and W.-D. Deckwer, "Gas Absorption Mechanism in Catalytic Slurry Reactors," *Chem. Eng. Sci.*, **35,** 217 (1980).

Calderbank, P. H., and M. Moo-Young, "The Continuous Phase Heat and Mass Transfer Properties of Dispersions," *Chem. Eng. Sci.*, **16,** 39 (1961).

Chandrasekaran, K., and M. M. Sharma, "Absorption of Oxygen in Aqueous Solutions of Sodium Sulfide in the Presence of Activated Carbon as Catalyst," *Chem. Eng. Sci.*, **32,** 669 (1977).

Chaudhari, R. V., and P. A. Ramachandran, "Influence of Mass Transfer on Zero-Order Reaction in a Catalytic Slurry Reactor," *Ind. Eng. Chem. Fund.*, **19,** 201 (1980).

de Rooij, A. H., C. Dijkhuis, and J. T. J. van Goolen, "A Scale-Up Experience: The DSM Phosphate Caprolactam Process," *Chem. Technol.*, **7,** 309 (1977).

Gopal, J. S., and M. M. Sharma, "Mass Transfer Characteristics of Low H/D Bubble Columns," *Can. J. Chem. Eng.*, **61,** 517 (1983).

Kars, R. L., R. J. Best, and A. A. H. Drinkenburg, "The Sorption of Propane in Slurries of Active Carbon in Water," *Chem. Eng. J.*, **17,** 201 (1979).

Ledakowicz, S., R. Kokuun, A. Brehm, and W.-D. Deckwer, "Einfluß suspendierter inerter Partikeln auf die Stoffübergangs-Charakteristik eines Rührkessels," *Chem.-Ing.-Tech.*, **55,** 648 (1983).

Li, Z., and W. D. Deckwer, "Adsorption von Gasen an suspendierter Aktivkohle," *Chem.-Ing.-Tech.*, **54,** 669 (1982).

Loyson, S. J., and G. H. J. Nunnink, "Caprolactam via HPO Process," *Hydroc. Proc.*, 92 (Nov., 1972).

Öztürk, S., A. Schumpe, and W.-D. Deckwer, "Organic Liquids in a Bubble Column: Holdups and Mass Transfer Coefficients," *AIChE J.*, **33,** 1473 (1987).

Quicker, G., E. Alper, and W.-D. Deckwer, "Effect of Fine Activated Carbon Particles on the Rate of CO_2 Absorption," *AIChE J.*, **33,** 871 (1987).

Ramachandran, P. A., and R. V. Chaudhari, "Three-Phase Catalytic Reactors," Gordon and Breach Science Publishers, New York (1983).

Sada, E., H. Kumazawa, and C. H. Lee, "Chemical Absorption in a Bubble Column Loading Concentrated Slurry," *Chem. Eng. Sci.*, **38,** 2047 (1983).

Sada, E., H. Kumazawa, C. H. Lee, and N. Fujiwara, "Gas-Liquid Mass Transfer Characteristics in a Bubble Column with Suspended Sparingly Soluble Fine Particles," *Ind. Eng. Chem. Process Des. Dev.*, **24,** 255 (1985).

Sada, E., H. Kumazawa, and C. H. Lee, "Influences of Suspended Fine Particles on Gas Holdup and Mass Transfer Characteristics in a Slurry Bubble Column," *AIChE J.*, **32,** 853 (1986).

Sada, E., H. Kumazawa, C. H. Lee, and H. Narukawa, "Gas-Liquid Interfacial Area and Liquid-Side Mass Transfer Coefficient in a Slurry Bubble Column," *Ind. Eng. Chem. Res.*, **26,** 112 (1987).

Schumpe, A., G. Quicker, and W.-D. Deckwer, "Gas-Liquid Interfacial Areas in a Bubble Column with Suspended Solids," *Chem. Eng. Sci.*, **39,** 179 (1984).

Schumpe, A., "Zur Ermittlung von Stoffübergangszahlen auf der Basis von Gelöstsauerstoff-Messungen," *Chem.-Ing.-Tech.*, **57,** 501 (1987).

Schumpe, A., A. K. Saxena, and L. K. Fang, "Gas/Liquid Mass Transfer in a Slurry Bubble Column," *Chem. Eng. Sci.*, **42,** 1787 (1987).

van de Moesdijk, C., "The Catalytic Reduction of Nitrate and Nitric Oxide to Hydroxylamine: Kinetics and Mechanism," *Thesis*, TH Eindhofen (1979).

Werner, M., D. Lindner, and A. Schumpe, "Kinetik der Pd/C-katalysierten Hydrierung von Nitrat zu Hydroxylamin," *Chem.-Ing.-Tech.*, **59,** 72 (1987a).

Werner, M., D. Lindner, and A. Schumpe, "The Production of Hydroxylamine by Hydrogenation of Nitrate on Suspended Pd/C Catalyst: Kinetics and Mass Transfer," *Recent Trends in Chemical Reaction Engineering*, B. D. Kulkarni, et al., eds. **2,** 502, Wiley Eastern, New Delhi (1987b).

Wimmers, O. J., and J. M. H. Fortuin, "The Use of Adhesion of Catalyst Particles to Gas Bubbles to Achieve Enhancement of Gas Absorption in Slurry Reactors: I. Investigation of Particle-to-Bubble Adhesion Using the Bubble Pick-Up Method," *Chem. Eng. Sci.*, **43,** 303 (1988a).

Wimmers, O. J., and J. M. H. Fortuin, "The Use of Adhesion of Catalyst Particles to Gas Bubbles to Achieve Enhancement of Gas Absorption in Slurry Reactors: II. Determination of the Enhancement in a Bubble Containing Slurry Reactor," *Chem. Eng. Sci.*, **43,** 313 (1988b).

Manuscript received Jan. 25, 1988, and revision received May 19, 1988.