Adhesion of catalyst particles to gas bubbles
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Chapter 1

Introduction

1.1. Slurry bubble column reactors

Slurry bubble column reactors have a wide range of applications in both chemical and biochemical industry. In principle, the chemical reaction takes place on the solid surface of fine catalyst particles dispersed in liquid phase and at least one reactant is present in the gas phase. These reactors have certain advantages:

- Nearly isothermal operation, good heat transfer and temperature control
- Potentially high capacity, greater than 10,000 barrels per day
- Ease of addition and removal of catalyst
- Simple design and construction
- Ideal for high boiling products
- Improved catalyst economy
- Operational flexibility
- Improved selectivity
- Low pressure drop
As disadvantage, it should be mentioned scale-up uncertainty. Therefore, there is in high interest in improvement the design, scale-up and optimisation of slurry bubble column reactors (Krishna and Sie, 2000; Maretto and Krishna, 2001; Krishna et al. 2001; van Baten et al., 2003; Vandu and Krishna, 2004; Omota and Bliek, 2004), as well as the development of more active, selective and stable solid catalysts (Iglesia, 1997; Luo et al., 2003; Ma et al., 2004; de la Peña O'Shea et al., 2004; Xu et al., 2004; Shinoda et al., 2004; Omota et al., 2005).

The slurry bubble column reactor has lots of applications, and one of the most exciting is for development of alternative fuels. Fischer-Tropsch synthesis is one of the applications becoming increasingly important as the price of the crude oil rises (Vosloo, 2001; Dry, 2002). More recently, large-scale production of dimethyl ether (DME) is currently the subject of considerable interest (Lewnard et al., 1990; Adachi et al., 2000; Omata et al., 2002; Ramos et al., 2005). Direct synthesis of DME is possible starting from various resources as natural gas or coal through synthesis gas (CO+H₂). Fig. 1.1 shows the concept of a slurry bubble column reactor for DME synthesis.

Figure 1.1. Concept of a slurry bubble column reactor for dimethyl ether synthesis
Noble metals highly dispersed on an inert support as silica, alumina or activated carbon, are very active catalysts. Many catalytic hydrogenation and oxidation reactions are performed on large-scale in slurry bubble column reactors. Few of them take place in aqueous medium. This thesis focuses on the use of supported noble metal catalysts in slurry bubble column reactors, in aqueous medium. Several examples are given below.

Sorbitol is an intermediate for the production of vitamin C. The catalytic hydrogenation of D-glucose to D-sorbitol in aqueous medium is a large-scale application (Arena, 1992). In 2004, Global Bio-Chem (China) begins the construction of a sorbitol plant of 60,000 metric tonne annual capacity. Crezee et al., (2003) studied this reaction over a 5% Ru/C catalyst at 373–403 K and 4.0–7.5 MPa.

Hydrogenation reaction of aqueous maleic acid to tetrahydrofuran (Thakar et al., 2003) has recent commercial relevance and represents a case where complex multistep catalytic hydrogenation reactions are conducted at 513K and 15 MPa. Ronchin and Toniolo (2001) investigated the hydrogenation of benzene to cyclohexene catalysed by Ru/ZrO₂ in tetra-phase slurry reactor at 423 K and 5 MPa, in the presence of two liquid phases, benzene and an aqueous solution of ZnSO₄ (0.6 mol 1⁻¹). Rode et al. (2001) investigated the kinetics of catalytic hydrogenation of nitrobenzene in acid medium to p-aminophenol in a batch slurry reactor.

The treatment of wastewater by catalytically wet air oxidation in large-scale slurry bubble column is cost effective at high concentration of organic compounds (Schlüter et al., 1992; Béziet et al., 1999; Qin et al., 2001; Shindler et al., 2001; Wu et al., 2003; Cao et al., 2003; Perkas et al., 2005).

Some applications of the oxidation reactions in slurry reactors are further illustrated: removal of sulfur from coal by selective oxidation (Joshi and Shah, 1981; Joshi et al., 1983), oxidation of SO₂ in aqueous slurries of calcium sulphite and sulphate (Pasiuk-Bronikowska and Ziajka, 1989) or in aqueous slurries of activated carbon (Sada et al., 1983), selective oxidation of lactose by O₂ in the presence of Bi promoted Pd/C catalyst (Hendriks et al., 1990), glucose oxidation catalyzed by Pd/SiO2 and Pd/C (Kluytmans et al., 2000; Rathiya et al., 2003), and malonic acid oxidation catalyzed by Pt/graphite (Masende et al., 2005).
Chapter 1

Introduction

1.2. Mass transfer in three-phase systems

Most applications of the multiphase reactors involve a solid catalyst, while the reactants are present in the liquid and gas phases. The chemical reactions take place on the active sites of the catalyst surface. The process is typically limited either by the intrinsic kinetics, adsorption/desorption of one reactant/product, or mass transfer of one reactant/product from the liquid/gas phase to the catalytic sites. Fig. 1.2 depicts the mechanism of a heterogeneously catalysed reaction in three-phase system by a resistances-in-series model. Frequently, the limiting step for the process performances is the liquid-side mass transfer of reactant B through the G-L interface (see Fig. 1.2).

Review papers on mass transfer in slurry reactors have been published by Chaudhari and Ramachandran (1980), Shah et al. (1982), Pandit and Joshi (1984), Pandit and Joshi (1986), Kohler (1986), Beenackers and van Swaaij (1993), Mills and Chaudhari (1997) and Dudukovic et al. (1999).

Figure 1.2. Mechanism of a heterogeneously catalysed reaction in three-phase system
Chapter 1

Introduction

Figure 1.3. Concept of gas absorption enhancement in slurry of small solid particles, explained by higher concentration of gas B at interface $C_{BL}$ than in bulk liquid $C_{BL}$.

The presence of small solid (catalyst) particles may have influence on the G-L mass transfer. If the particles accelerate the gas absorption in the liquid phase, the process is characterised by an enhancement factor $E$, defined as the ratio of mass transfer in the presence of particles, to the mass transfer without particles (Alper et al., 1980; Wimmers et al., 1984; Vinke et al., 1991; van der Zon et al. 1999; Ruthiya et al., 2005). An enhancement of the gas absorption was found during the oxidation of glucose in aqueous solution, catalysed by Pd/C or by an enzyme, glucose oxidase (Lee and Tsao, 1972). A non-uniform distribution and thus a high local concentration of the platinum-on-carbon or the enzyme at the gas-liquid interface have been suggested. It was also suggested that G-L interfacial properties might play a role during the gas adsorption in the slurry. Sada et al. (1977) numerically analyzed and discussed in terms of the enhancement factor the process of gas absorption with a single reaction into slurry containing fine particles. The average diameter of the solid particles was considerably less than the thickness of the liquid film as shown in Fig. 1.3. The concentration of gas is higher in stagnant liquid layer than in the bulk liquid. Thus, overall gas absorption is enhanced due to a higher rate of the gas adsorption on the solid surface, or higher rate of the heterogeneous catalysed reaction.
Alper et al. (1980) found an enhancement of physically oxygen absorption by comparing two types of solid particles, activated carbon and quartz sand. Both solids used were powders, with the particle average size lower than 5 μm. The rate of absorption was significantly higher in the case of activated carbon particles, but it decreases by increasing the stirred speed. It was also found that an increase of the catalyst concentration above 2.5 kg m⁻³ do no longer increase the absorption rate.

Dierendonck et al. (1972) found an enhancement of the rate of hydrogen absorption for the hydrogenation of α-aminocaprolactam in an aqueous solution containing Raney nickel particles and for the hydrogenation of ammoniumnitrate to hydroxylamine in an aqueous solution containing catalyst particles. Wimmers et al. (1984) confirmed the enhancement of gas absorption during the hydrogenation of hydroxilaminephosphate catalysed by small Pd/C particles \(d_p=20 \; \mu m; 10 \; wt\% \; Pd\). The rate of hydrogen absorption from a single bubble partially covered with Pd/C catalyst particles to the liquid
was measured. They proposed an equation for the calculation of the enhancement factor, based on a higher rate of gas absorption through the part of bubble covered by solid particles than through the part of bubble free of adhering particles. Hence, they used the concept of \textit{bubble coverage} defined as the fraction of bubble surface covered with adhering particles (see Fig. 1.4b).

Vinke et al. (1992) found a maximum of the bubble coverage under stagnant conditions, while under dynamic conditions, the bubble coverage decreases with the shear stress. The bubble coverage was described by a Langmuir type isotherm as shown below:

\[
\frac{\zeta}{\zeta_{\text{max}}} = \frac{Kc_s}{1 + Kc_s} \tag{1.1}
\]

where \(\zeta\) is the bubble coverage under hydrodynamic conditions, \(\zeta_{\text{max}}\) is the maximum bubble coverage under stagnant conditions, \(K\) is a particle-to-bubble adhesion constant, and \(c_s\) is the concentration of particles in the slurry. Further it was shown that the mass transfer coefficient through the covered part of bubble is higher than the mass transfer coefficient through the uncovered part of bubble. Thus, the enhancement factor can be calculated from the bubble coverage:

\[
E = 1 + \zeta \left( \frac{k_{GLS}}{k_{GL}} - 1 \right) \tag{1.2}
\]

The mechanisms of mass transfer enhancement in the presence of particles was explained either by an increase in the G-L interfacial area as result of lower bubble coalescence rate, or by an increase of liquid-side mass transfer coefficient \(k_L\). Ruthiya et al. (2003) discussed four potential mechanisms:

1. Boundary layer mixing – the particles penetrate the boundary layer at the G-L interface and induce a certain degree of turbulence. Consequently, the boundary layer thickness is reduced.
2. Shutting – the particles have strong adsorption properties. In the boundary layer they adsorb gas, while in the bulk liquid the gas is desorbed.

3. Coalescence inhibition – the particles reduce the rate of bubble coalescence and thus increases the G-L interfacial area $a_{L}$.

4. Boundary layer reaction – the particles adhere to the G-L interface. A significant conversion occurs due to the higher concentrations of the reactants and (catalyst) particles than in the bulk liquid.

Physical enhancement (mechanisms 1–3) and reaction enhancement (mechanism 4) were investigated separately by dynamic gas absorption experiments without reaction and pseudo-steady-state gas absorption experiments with reaction, respectively. The mass transfer coefficient in the presence of reaction was found higher in the case of chemical reaction as compared to the case of gas absorption without reaction.

Tinge and Drinkenburg (1992) reported enhancement factors up to 3.5 for the absorption of propane and ethene gas into slurries containing 4 wt% activated carbon in water. These results demonstrate significant enhanced of the gas absorption without chemical reaction, but in agreement with the mechanism proposed in the Fig. 1.4.

More recently, Chen and Hsieh (2002) studied the hydrogenation of nitrobenzene catalysed by nano-sized Ni-B catalysts in a batch reactor. They found an enhancement of the reaction rate in the presence of two types of inert particles, Al$_2$O$_3$ or SiO$_2$. The effect was higher in the case of Al$_2$O$_3$. The reaction conversion increased with increasing stirring speeding until 900 rpm, and then decreased. It was suggested that i) the addition of inert particles prevents the agglomeration of nano-metals, and ii) nano-metals are physically attached on the external surface of the inert particles. These results demonstrate that (nano-) particles may enhance the gas absorption in organic liquids.
1.3. Influence of particles on mass transfer

1.3.1. Particle-to-bubble adhesion

In three-phase slurry bubble columns, the adhesion of catalyst particles to gas bubbles leads to an enhancement of the G-L mass transfer and thus better process performances.

The flotation of small particles in water or electrolyte solutions is well known and practiced on large scale from more than a century ago. There are two important steps in flotation: (a) the collection of the floatable particles by the bubbles, and (b) the transfer of the floated particles from the cell to the product launder via the froth layer. The particles can be captured by air bubbles after random collisions. Mineral particles finer than approximately 10 μm are in general not effectively attached to gas bubbles because of their low inertia. Fine particles are able to follow the hydrodynamic streamline and avoid being captured by the bubble. The particles exceeding a critical size do not adhere to bubbles because of their excessive weight.

1.3.2. Particle agglomeration

In addition to the positive effect of particle-to-bubble adhesion, it was found that the agglomeration of catalyst particles has a negative influence on the process performances. The particles might form large aggregates, which are not able to adhere to the gas bubble due to their excessive weight (Vinke et al., 1992; van der Zon et al., 1999).

1.3.3. Bubble coalescence

Bubbles occur frequently in chemical and mineral processing plants. It is of interest to know the factors that will retard or accelerate the coalescence process that occurs when two bubbles come close together. In pure liquids, the coalescence of two bubbles occurs almost instantaneous. In aqueous systems, it is well known that surface active molecules or even simple substances like common salt can have a strong effect on the rate of bubble coalescence. Numerous studies demonstrated that the presence of solid particles has influence on the bubble coalescence and thus on the gas hold-up in bubble columns. Despite a large number of publications regard to the influence of particular solid particles on the gas hold-up, the mechanism of bubble coalescence is still ambiguous.
1.4. Scope of this thesis

The aim of this thesis is to study the adhesion of catalyst particles to gas bubbles and particle agglomeration, and further, the influence of particle-to-bubble adhesion on the bubble coalescence and mass transfer, for the improvement of bubble slurry reactor performances.

1.5. Main contributions

The theoretical and experimental results of this thesis cover two areas of high interest in chemical engineering: i) improvement of the performances of noble metal catalysts in slurry bubble column reactors, by simple modification the support properties, and ii) improvement of the design and scale-up of slurry bubble column reactors, by exploiting particle-to-bubble adhesion, particle agglomeration and bubble coalescence in the presence of small solid particles.

This thesis brings the following contributions to the fundamental knowledge of microscopic phenomena which take place in slurry bubble column reactors:

- A generalised model explaining the adhesion of particles to gas bubbles, taking into account the particle-particle and particle-bubble interactions. The model correlates the adhesion and cohesion forces with the bubble coverage angle and the thickness of particle aggregates adhering to a gas bubble. Previous models explain the adhesion of particles to gas bubbles only as monolayer. These models cannot be satisfactorily applied to small hydrophobic particles, as for example activated carbon.

- Understanding the three-phase contact angle of rough and porous particles adhering to gas bubbles. The intrinsic contact angle is usually defined as the three-phase contact angle on smooth surfaces and cannot be applied to catalyst particles adhering to gas bubbles. In liquid, non-porous particles with rough surfaces adhere to gas bubbles, the effective contact angle being equal to the receding contact angle. In air, the same particles adhere to liquid droplets and the effective contact angle is equal to the advancing contact angle. Porous particles adhering to gas bubbles show an extremely low effective contact angle comparing to the intrinsic contact angle.
The mechanism of bubble coalescence in the presence of solid particles. High speed video imaging combined with high resolution optical microscopy allowed the identification of several stages and their durations during the collision and coalescence of two bubbles in the presence of (adhering) particles. Generally, the particles prevent coaxial coalescence of two approaching bubbles. However, the coalescence takes place when small particles remain entrapped in a thin liquid film between two bubbles and by the friction between the two bubbles.

The preparation and characterisation of a partially hydrophobised Pd/SiO₂ catalyst, suitable for the use in aqueous media. The catalytic performances for the hydrogenation reactions in aqueous medium was studied by comparing two Pd/SiO₂ catalysts with the same particle size, porosity, specific surface area and noble metal content, by varying only the support hydrophobicity. Previously, the hydrophobicity was investigated by comparing different catalyst supports.

General recommendations for design and scale-up of slurry bubble column reactors, and for the manufacture of modified supported catalysts with improved activity, as result of better adhesion to gas bubbles in slurry reactors.

Notations

\( \zeta \) fraction of the bubble area covered with particles under dynamic conditions, -

\( \zeta_{\text{max}} \) fraction of the bubble area covered with particles under stagnant conditions, -

\( K \) equilibrium constant for the attachment and detachment of particles at the G-L interface under dynamic conditions (Vinke et al., 1992), kg\(^{-1}\) m\(^3\)

\( c_S \) concentration of particles in bulk liquid, kg m\(^{-3}\)

\( E \) enhancement factor, -

\( k_{GL} \) liquid-side mass transfer coefficient of the G-L interface free of particles, m s\(^{-1}\)

\( k_{GLS} \) liquid-side mass transfer coefficient of G-L interface covered by solid particles, m s\(^{-1}\)
Chapter 1

Introduction

References


Chapter 1

Introduction


Chapter 1

Introduction


