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Integrated Recovery and Recycling of Homogeneous Catalysts by Reverse Flow Adsorption: Selection of Suitable Adsorbents

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Abstract. A promising concept for the recovery of homogeneous catalysts is Reverse Flow Adsorption. In actual homogeneous catalyzed processes, a homogeneous transition-metal catalyst is at equilibrium with its free transition-metal center and ligands. Therefore, to apply Reverse Flow Adsorption, a combination of two adsorbents has to be used to reversibly adsorb: the transition-metal center and its ligands. The transition-metal center can be adsorbed by a suitable ligand immobilized onto a solid carrier, while the ligand is adsorbed by an immobilized transition-metal. Two groups of potential adsorbents were selected by the Hard and Soft Acid and Base (HSAB) theory for the adsorption of Co(II) and PPh_3: (1) phosphor (polymer bound PPh_3), sulfur (polymer bound methylsufanylmethyl) and chloride (polymer bound benzylchloride) functionalized adsorbents and (2) metal (Ag^+, Co^{2+} and Na^+) functionalized Amberlyst 15. The $CoCl_2$ adsorption decreased, as predicted by the HSAB theory, according to: P > S > Cl. Metal functionalized adsorbents adsorbed the PPh_3 with capacities decreasing as predicted by the HSAB theory: $Ag^+ > Co^{2+} > Na^+$. All adsorption interactions proved to be reversible.

Keywords: reverse flow adsorption, process intensification, recovery, recycling, homogeneous catalysts

Introduction

Homogeneous transition-metal catalysts offer a number of advantages (Bhaduri, 2001) when compared to heterogeneous catalysts. Higher selectivities are achieved due to the well-defined and adaptable ligand structures of the homogeneous catalyst. Mass transfer resistances are negligible because of the high degrees of dispersion of the reactants, products and the homogeneous catalyst in one single reaction phase. Consequently, homogeneous catalyzed processes are performed at relative mild reaction conditions in comparison to heterogeneous catalyzed processes.

In spite of these advantages, homogeneous catalysis is still not as common in use as heterogeneous catalysis due to the various draw-backs during the usual methods for the recovery and recycling of homogeneous catalysts. Various processes have been proposed for the recovery of homogeneous catalysts (Bhaduri, 2001): decomposition, distillation, extraction, membrane filtration and—more recently—phase transition by using fluorous media (Behr, 2001). However, these separations include additional solvents and/or are operated at process conditions that negatively influence the stability of the homogeneous catalyst.

Recovery of homogeneous catalysts by adsorption excludes the need for additional solvents. The combination of reversible adsorption with reverse flow technology (Dunnewijk, 2001)—Reverse Flow Adsorption—is a potential method for the integrated recovery and recycling of homogeneous catalysts. The catalyst is separated from the product flow by adsorption downstream the reactor. In the subsequent step, the catalyst is recycled by desorption from the saturated adsorbent by reversal of the process flow (Fig. 1). Preliminary calculations (Dunnewijk, 2004) showed that

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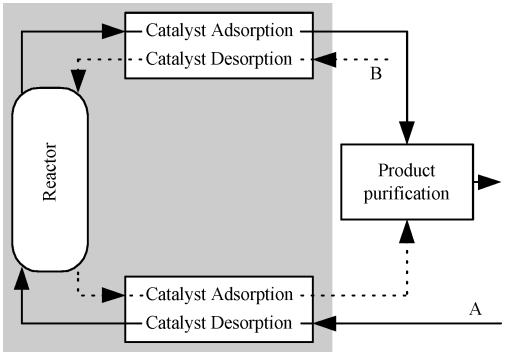


Figure 1. Homogeneous catalyst recycling by Reverse Flow Adsorption (feed alternates between A and B).

the required minimal adsorption bed volumes are sufficiently small to implement Reverse Flow Adsorption into an OXO-synthesis process.

The alternating adsorption and desorption cycles over the adsorption beds in Reverse Flow Adsorption, require adsorbents to be able to reversibly recover the transition-metal based homogeneous catalyst. With the right choice of adsorbent, the stability of the catalyst will be preserved as the recovery can be carried out within the stability constraints of the homogeneous catalyst, for instance at reaction conditions.

Complexes of homogeneous transition-metal catalysts are always in equilibrium with their free transition-metal centers and ligands. The metal/ligand equilibrium within a transition-metal based homogeneous catalyst can be used for the separate recovery of the transition-metal and its ligands. By immobilizing a suitable ligand onto a solid carrier, the transition-metal center of the catalyst can be recovered. The recovery of the ligand is then done by contacting the remaining ligands with an immobilized transition-metal.

The goal of this paper is to find adsorbents that are able to reversibly adsorb transition-metal complexes. Potential adsorbents were selected based on the Hard and Soft Acids and Bases (HSAB) theory (Pearson, 1988) which qualitatively predicts the strengths of the interactions between the adsorbents and a transition-metal based homogeneous catalyst. The selected adsorbents have been characterized by batch adsorption experiments on their capacity and ability to reversibly adsorb the transition-metal center or ligands of a transition-metal based homogeneous model catalyst.

Approach

In actual homogeneous catalyzed processes, usually an excess of ligands is added (Bhaduri, 2001) to decrease the amount of free transition-metal which negatively influences the chemical reaction. Therefore, the simplest approach to apply Reverse Flow Adsorption, is to use a combination of two adsorbents for the reversible recovery of the transition-metal center and the excess of ligands.

The HSAB theory gives a qualitative prediction for the interaction strength between a transition-metal – acid – and its ligands – base –. The metal/ligand equilibrium is determined by the ability of the ligands to donate electrons – σ-bond – to an empty d- or p-orbital that is located on the transition metal. This electron donation makes the metal more electron rich, and in order to compensate for this increased electron density, the metal may relieve itself from the added electron density by donating electrons back – π-backbond – to an empty ligand orbital (Cotton, 1999). This equilibrium – σ-bond/π-backbond – also exists between the free transition-metal – or ligand – and its immobilized counterpart (Dunnewijk, 2003) if one of the components is bound to a solid carrier (Fig. 2).

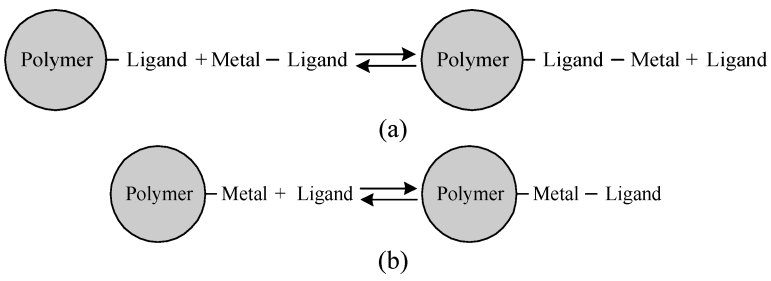


Figure 2. (a) Transition-metal adsorption by an immobilized ligand and (b) ligand adsorption by an immobilized transition-metal.

Table 1. Classification of some selected hard, borderline and soft acids and bases (modified from Cotton, 1999)*.

Hard acids	Borderline acids	Soft acids
$H^+ > Na^+ > Li^+ > K^+$		M^0
$Mn^{2+} > Be^{2+} > Mg^{2+} > Ca^{2+}$	$Ni^{2+} \approx Cu^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+}$	$Cu^+ > Ag^+ \approx Au^+ \approx Hg^+$
$Co^{3+} > Fe^{3+} > Al^{3+}$		$Cd^{2+} \approx Pt^{2+} \approx Hg^{2+} > Pd^{2+}$
Hard bases	**Borderline bases**	**Soft bases**
$H_2O \approx ROH > NH_3 \approx RNH_2$	$(C_6H_5)NH_2 > Cl^-$	$R_2S > R_3As > R_3P$

*arrangement in order of decreasing electronegativity.

Based on the ease of sharing electrons, the HSAB theory classifies both the acids and bases into hard, borderline and soft types (Table 1). Hard acids do not have easily exited outer electrons and are relatively small in size. Hard bases are characterized by a very high electonegativity of a small sized donor atom that results in a nonpolarizable electron cloud surrounding the donor atom. On the other hand, acceptor atoms of the soft acid type are characterized by a relatively large size and have several easily excited outer electrons. Donor atoms that are relatively large in size and having an intermediate to high electronegativity are classified into the group of soft bases. In addition to the fundamental hard and soft categories, two additional categories are useful. Borderline acids and bases are intermediate between hard and soft acids and bases.

Cobalt and triphenylphosphine (PPh_3) ligands are commonly encountered in homogeneous catalyzed processes. Therefore, dichlorobis(triphenylphosphine)cobalt(II) has been selected as a homogeneous model catalyst. In 1-butanol, this complex is in equilibrium with the free $CoCl_2$ and PPh_3 ligands.

As the PPh_3 ligands are classified to be of the soft base type and the HSAB theory states that soft bases prefer to interact with soft acids, Table 1 can be used for the selection of a suitable immobilized counterpart. Here, Ag^+ – a soft acid –, Co^{2+} – a borderline acid – and Na^+ – a hard acid – functionalized adsorbents have been selected to investigate the PPh_3 adsorption. The HSAB theory predicts the trend in the strength of their interaction, which is a measure of adsorption capacity, with PPh_3 to decrease according to:

$$Ag^+ > Co^{2+} > Na^+$$

These metal functionalized adsorbents were prepared by immobilizing Ag^+, Co^{2+} and Na^+ by ion-exchange onto a solid carrier, for which Amberlyst 15 has been selected.

Co(II) is a transition-metal that has been classified as a borderline acid. Phosphorous, sulfurous and chloride functionalized adsorbents have been selected to investigate the adsorption of Co(II). The phosphor and sulfur containing ligands are both classified as soft bases. The chloride containing ligands are classified as borderline bases. The HSAB theory predicts that the strength of the interaction follows the trend of increasing electronegativity: Group V > Group VI > Group VII. It is therefore expected that the capacity of the Co(II) adsorption onto adsorbents that are functionalized with a group V, VI or VII elements, decrease according to:

$$P > S > Cl$$

Materials and Experimental

Amberlyst 15 (Fluka) is a macroreticular sulfonated cation exchange resin with a polystyrenic – crosslinked by divinylbenzene – backbone. It has been selected as a carrier because of its large pore diameter of approximately 100 (nm). These macropores ensure the accessibility for the relatively large PPh_3 ligands. Amberlyst 15 was rinsed with de-ionized water (Millipore) in a column set-up. The functionalization of the Amberlyst 15 was done by contacting the resin with either 0.1 (mM) of $AgNO_3$ (extra pure, Sigma-Aldrich), $CoCl_2$ (anhydrous, Fluka) or NaOH (p.a., Sigma Aldrich) aqueous solutions. During the ion-exchange, the hydrogen of the Amberlyst 15 was exchanged for one of the selected cations. The exchange was done until the pH of the feed and residual solutions were equal and thus complete exchange was reached.

In the washing step all functionalized Amberlyst 15 adsorbents and polymer bound

triphenylphosphine (Sigma Aldrich), polymer bound methylsulfanylmethyl (Sigma Aldrich) and polymer bound benzylchloride (PolymerLabs) were rinsed with de-ionized water. These latter three adsorbents are gel-type resins of polystyrene crosslinked with 2 (%) divinylbenzene. The water was then rinsed out of the resin with methanol (p.a., Merck). The remaining methanol was rinsed with 1-butanol (p.a., Merck). The adsorbents (Table 2) thus prepared were taken from the column set-up and used in the adsorption experiments.

The adsorption characterizations of the various adsorbents were done via batch adsorption experiments. The series of phosphorous, sulfurous and chloride functionalized adsorbents ($m_{\text{ads,wet}} \approx 0.3$ (gr)) were contacted in erlenmeyer flasks with 10 (ml) of $CoCl_2$ at various concentrations of 1, 2, 4 and 8 (mM). The Ag^+, Co^{2+} and Na^+ functionalized adsorbents were conctacted with 10 (ml) PPh_3 (99 (%), Sigma Aldrich) solutions of 2, 4, 8 and 16 (mM) under Argon (grade 5.0, Hoekloos). The erlenmeyer flasks were then equilibrated at 90 (°C) in a thermostated shaking water bath for 15–16 (hr) (approximately 5 times the real equilibration time). The liquid phases were decanted and analyzed. UV/Vis spectroscopy (Varian Cary 300) was used for the determination of the PPh_3 concentrations at 265 (nm). The Co(II) concentrations have been analyzed by AAS (Varian Specrtaa 110). Note that adsorption of PPh_3 over the phosphorous, sulfurous and chloride functionalized adsorbents has not been observed.

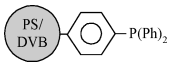
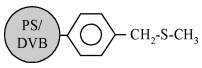
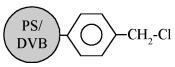
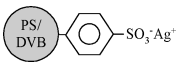
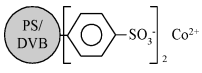
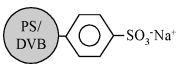
After adsorption, all equilibrated samples were contacted with 10 (ml) of fresh 1-butanol for 15–16 (hr) at 90 (°C) to investigate the reversibility of the adsorption. The equilibrium concentrations after desorption of the relevant components were measured as described above. The desorption results have been corrected for the remaining $CoCl_2$ concentration in the pores of the adsorbents after the adsorption experiments.

The amounts adsorbed were calculated from the differences in initial and equilibrium amounts. The loading (q) of the adsorbents after adsorption and desorption are expressed with respect to the number of functional sites – P, S, Cl, Ag^+, Co^{2+} or Na^+ – in the adsorbents.

Experimental Results and Discussion

The results of the Co(II) adsorption and desorption experiments over the polymer bound **P**$(Ph)_2$, **S**(Me) and **Cl** adsorbents are respectively presented in Figs. 3(A) and (B). The Co(II) loadings onto these selected adsorbents are represented as a function of the equilibrium concentration of Co(II) in the liquid phase. The

Table 2. Overview of the selected adsorbents for the adsorption of $CoCl_2$ or PPh_3.

Adsorbent type	Adsorbent structure	Number of adsorption sites (mmol sites/g dry)
Adsorbents for $CoCl_2$ adsorption		
Polymer bound PPh_3 **P**$(Ph)_2$		3.0[a]
Polymer bound methylsulfanylmetyl **S**(Me)		3.0[a]
PL-CMS Resin **Cl**		2.0[a]
Adsorbents for PPh_3 adsorption		
Ag$^+$ loaded Amberlyst 15		4.3[b]
Co^{2+} loaded Amberlyst 15		4.2[b]
Na$^+$ loaded Amberlyst 15		4.3[b]

[a]Given by PolymerLabs and Sigma Aldrich.
[b]Calculated from H^+ form.

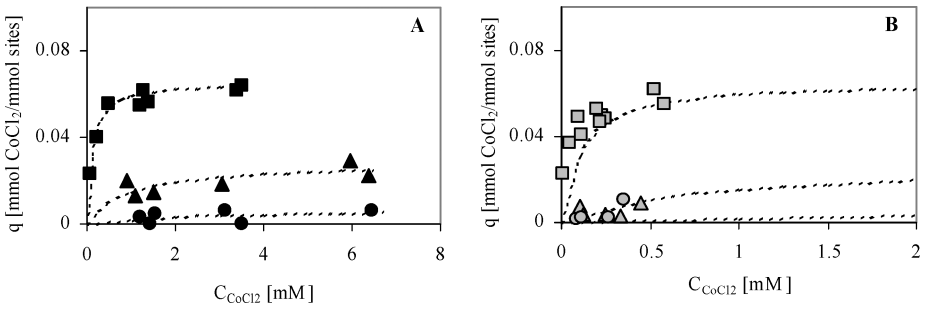


Figure 3. $CoCl_2$ adsorption (A) and desorption (B) over polymer bound **P**$(Ph)_2$ (squares), **S**(Me) (triangles) and **Cl** (circles) from 1-butanol at 90 (°C).

second-order isotherms that are fitted on the adsorption data are shown as dashed lines in both the adsorption (Fig. 3(A)) and desorption (Fig. 3(B)) plots.

The adsorption capacity of $CoCl_2$ onto polymer bound **P**$(Ph)_2$ is stronger in comparison to the polymer bound **S**(Me), which is in its turn adsorbs stronger as the polymer bound **Cl**. The observed trend is in agreement with the HSAB theory and decreases with the increase in electronegativity of the functional group which indicates that the sharing of electrons decrease according to the:

$$\text{Group V (}\mathbf{P}\text{)} > \text{Group VI (}\mathbf{S}\text{)} > \text{Group VII (}\mathbf{Cl}\text{)}$$

The $CoCl_2$ adsorption proves to be reversible, as after the addition of fresh 1-butanol a certain amount of the previously adsorbed Co(II) increased its concentration in the liquid phase.

Because the immobilized $\mathbf{Ag}^+$ and $\mathbf{Na}^+$ can be exchanged for Co(II) from the homogeneous model catalyst, the metal functionalized adsorbents have only been contacted with PPh_3 solutions. The experimental results of the PPh_3 adsorption and desorption on the transition metal – $\mathbf{Ag}^+$ and $\mathbf{Co}^{2+}$ – functionalized adsorbents are shown in Figs. 4(A) and (B) as a function of the equilibrium PPh_3 concentration.

The adsorption data of the $\mathbf{Na}^+$ loaded Amberlyst 15 is not shown, because no adsorption of PPh_3 has been observed for this type of adsorbent. The dashed lines in both figures represent the second-order isotherms fitted on the adsorption data.

As predicted by the HSAB theory, Fig. 4(A) demonstrates that the interaction of PPh_3 with the $\mathbf{Ag}^+$ functionalized Amberlyst 15 is larger compared to the immobilized $\mathbf{Co}^{2+}$. In combination with the fact that no adsorption of PPh_3 over $\mathbf{Na}^+$ loaded Amberlyst 15 has been observed, it can be stated that the adsorption of the soft base PPh_3 is predicted by the HSAB theory to be the strongest with a soft acid:

$$\mathrm{Ag}^+(\text{soft acid}) \gg \mathbf{Co}^{2+}(\text{borderline acid}) > \mathrm{Na}^+(\text{hard acid}) \approx 0$$

Besides the weaker interactions of PPh_3 with Co^{2+}, the large difference in the adsorption capacities between the $\mathbf{Ag}^+$ and $\mathbf{Co}^{2+}$ functionalized Amberlyst 15

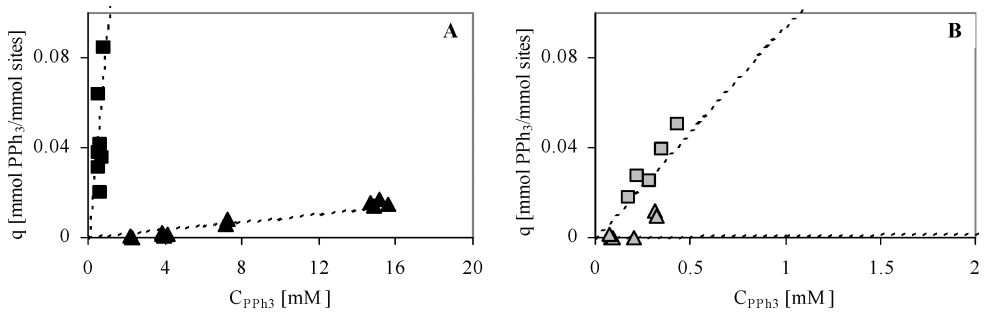


Figure 4. PPh_3 adsorption (A) and desorption (B) over $\mathbf{Ag}^+$ (squares) and $\mathbf{Co}^{2+}$ (triangle) loaded Amberlyst 15 from 1-butanol at 90 (°C).

is attributed by the less accessible $\mathbf{Co}^{2+}$ coordination sphere as two SO_3^- groups interact with the relatively large PPh_3. During the preparation of the Amberlyst 15, one $\mathbf{Co}^{2+}$ is immobilized onto two SO_3^- groups.

The experimental results indicate that the PPh_3 adsorption over the transition-metal functionalized adsorbents is reversible as shown in Fig. 4(B).

Conclusion

To apply Reverse Flow Adsorption, a combination of two adsorbents has to be used for the reversible adsorption of a homogeneous transition-metal catalyst. While the transition-metal center can be adsorbed by a suitable ligand immobilized onto a solid carrier, the ligand, in its turn, can be recovered by an immobilized transition-metal.

Based on the predictions of the HSAB theory on the interactions with the Co(II) transition-metal center or PPh_3 ligands, various functionalized adsorbents were selected. Two groups of adsorbents have been characterized by batch adsorption experiments:

- Phosphor, sulfur and chloride functionalized adsorbents showed the trends in the reversible adsorption of Co(II) as predicted by the HSAB theory:

$$\text{Group V } (\mathbf{P}) > \text{Group VI } (\mathbf{S}) > \text{Group VII } (\mathbf{Cl})$$

- The soft base PPh_3 is adsorbed – as predicted by the HSAB theory – by $\mathbf{Ag}^+$, $\mathbf{Co}^{2+}$ and $\mathbf{Na}^+$ functionalized adsorbents according to:

$$\begin{aligned} &\text{Ag}^+ \text{ (soft acid)} \gg \text{Co}^{2+} \text{ (borderline acid)} \\ &> \text{Na}^+\text{(hard acid)} \approx 0 \end{aligned}$$

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