Remarkably fast and selective recovery of a rhodium-containing catalyst with silica-based (poly)amine ion exchangers

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Three silica-based ion exchangers, containing monoamine (**1**), ethylenediamine (**2**) and diethylenetriamine (**3**) functionalities, have been examined for their capacity to recover the catalyst $RhCl_3$, with emphasis on industrially important factors, such as kinetics and re-usability of the ion exchange materials. Ligand occupations have been found to lie between 40% and 55% (some 40–50 mg Rh per g ion exchanger), suggesting the predominant formation of complexes of the type ML_2. The recovery proved to be most efficient with diluted mineral acids, and the initially adsorbed Rh^{3+} has been removed almost quantitatively (>95%) from **1**. All ion exchangers display excellent recovery kinetics, with $t_{1/2}$ values of adsorption never exceeding 60 s. Successive Rh recovery experiments indicate stable recovery percentages after the first recovery cycle, but show a gradual build-up of residual Rh with ion exchangers **2** and **3**. Rh^{3+} has been extracted with high selectivity up to pH values as high as pH 4 in the presence of other transition metal ions, like Cu^{2+} and Ni^{2+}.

The platinum group metals (Pd, Pt, Rh, Ir, Ru and Os) are widely applied in industry, such as the dental industry, and in electronic and electrical devices and in jewellery. They are also very important as (part of) homogeneous catalysts, used for the improvement of many organic reactions. Their increasing importance in this branch over the years and the fact that they are scarce have caused a dramatic increase in the price of these metals.[1–3] Consequently, the loss of homogeneous catalyst in the product has to be reduced to an absolute minimum. However, the efficient separation of the metal ions after use poses a major problem, as all reagents are generally present in the same liquid phase.[4–6]

Ion exchange has proven to be a highly advantageous method over other traditional methods, such as precipitation, as very low concentrations of metal ions can be removed and a high degree of selectivity in the extraction is possible, when the (coordinating) ligands are well chosen. Another beneficial characteristic of this technique is the ease of separation of the adsorbed metal ions from the product stream.

The focus of this paper is on the recovery of Rh, one of the most expensive platinum group metals and widely used in homogeneous catalysis.[6] More specifically, the present paper deals with the recovery of $RhCl_3$, which is in use both as a catalyst precursor and as a real catalyst.[7–10] Previous investigations with various silica-based ion exchangers, containing ligands with both N and S donor atoms, revealed a high Rh adsorption, selectivity and fast ligand exchange kinetics of these ion exchangers.[11] However, as the Rh elution proved to be problematic,[11] ligands without sulfur functional groups were tried as an alternative, as not only the Rh binding, but also the subsequent Rh recuperation require optimisation of the ligand-to-Rh complex stability.[12,13]

The present study describes our investigations on industrially interesting features concerning Rh metal ion recovery, and has been restricted to ion exchangers containing monoamine (**1**), ethylenediamine (**2**) and diethylenetriamine (**3**) functionalities. The adsorption and desorption kinetics are described. Furthermore, the possibility to re-use the ion exchangers has been examined. Other industrially important factors, such as the influence of pH and the presence of several base metal ions on the rhodium extractability have also been investigated.

Results and discussion

pH-dependent uptake experiments

Some characteristics of the silica-based ion exchangers **1**–**3** are listed in Table 1. As the ligand concentrations vary markedly, it is more correct to not only look at the ligand capacity (*C*, in mmol g^{-1}), but at the ligand occupation as well (L, in %). The latter is defined as follows: $L =$ [uptake capacity for M^{n+} (in mmol per g ion exchanger)]/[ligand concentration (in mmol per g ion exchanger)] *100.

Batch metal-uptake experiments were performed, applying a ligand-to-rhodium molar ratio of 1 : 1, as uptake experiments with an excess of Rh showed hardly any increase in uptake capacity.

The pH-dependent Rh uptake is depicted in Fig. 1 and increases from monoamine ion exchanger **1** (NH_2), *via* ethylenediamine ion exchanger **2** (en) to diethylene triamine ion exchanger **3** (dien). This is in agreement with our earlier findings on the complex stability[12] and indicates that the possibility of **2** and **3** to coordinate *via* five-membered chelate rings to the Rh metal ions is favoured over binding in a monodentate fashion.

Table 1 Ion exchanger characteristics

Ion exchanger	Grafted group	Ligand conc.[a]/mmol g^{-1}
1	$–(CH_2)_3NH_2$	1.15
2	$–(CH_2)_3NHCH_2CH_2NH_2$	1.00
3	$–(CH_2)_3NH(CH_2CH_2NH)_2H$	0.90

[a] Based on the N content.

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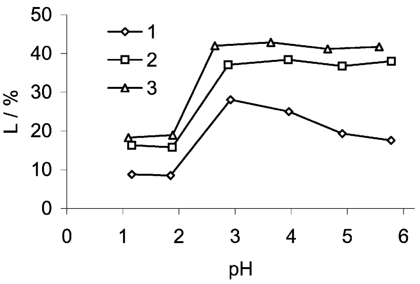


Fig. 1 The ligand occupation of Rh^{3+} as a function of the pH using ion exchangers **1**–**3**.

The large uptake increase, in going from pH 2 to pH 3, can be explained by the use of a different buffer system, containing HOAc–NaOAc at pH 3–6. The absence of chlorides, capable of competing with the ion exchangers for Rh binding, causes a marked increase in adsorption. The inhibiting influence of chloride ions is further demonstrated by a significantly reduced ligand occupation for all three ion exchangers, when the Cl^- concentration is kept constant over the entire pH range tested (see Fig. 2). The uptake capacity of **2** and **3** is enhanced at higher pH, presumably due to decreased protonation of the amine groups, resulting in increased coordination *via* highly stable five-membered chelate rings.[14] Rh is hardly adsorbed by **1** over the entire pH range, due to its much lower complex stability.

Stripping experiments

To design ion exchangers with industrially interesting characteristics such as good recovery kinetics and re-usability of the materials, it is important to find effective stripping agents that do not damage the ion exchangers. Hence, monoamine ion exchanger **1** was loaded with $RhCl_3{\cdot}3H_2O$ in H_2O and subsequently stripped with a range of potential desorbents (Fig. 3). Clearly, elution with mineral acids appears to be the most efficient, and almost quantitative desorption (>95%) has been effected with 2 M sulfuric or 2 M nitric acid or with a combination of hydrochloric acid and $NaClO_3$. Other well known-desorbents,[15,16] such as thiourea and NH_4SCN, were also found to be quite efficient by removing up to 80% of the initially bound Rh^{3+} ions. Other tested ligands, like PPh_3 and ethylenediamine, proved much less efficient.

The high efficiency of the tested mineral acids is due to protonation of the amine groups, leading to sufficient complex destabilisation. Ligands bearing sulfur donor atoms, known to strongly bind to platinum group metal ions, quite efficiently compete with the ion exchanger for Rh binding. Weaker ligands proved much less efficient, especially in comparison with pure water, which already appeared to be capable of removing some 10% of the Rh metal ions. The apparent formation of an equilibrium between bound Rh and Rh metal ions in solution is presumably caused by the relatively weak ligand-to-metal complex of **1**.

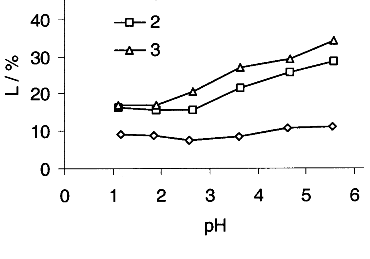


Fig. 2 The ligand occupation of Rh^{3+} as a function of the pH using ion exchangers **1**–**3**, employing a constant 0.6 M chloride concentration.

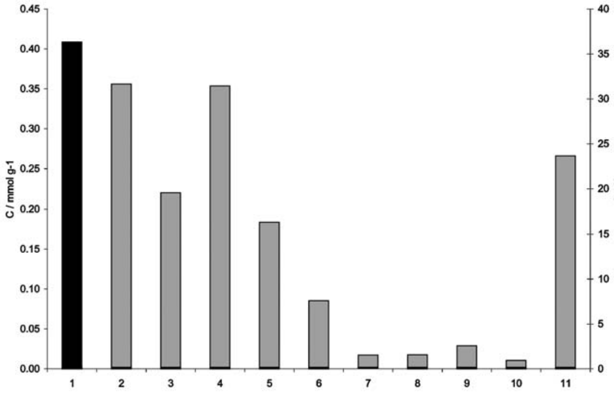


Fig. 3 Regeneration experiments of $RhCl_3{\cdot}3H_2O$-loaded **1** (entry 1). Entries 2–11 indicate the residual amount of Rh^{3+} after stripping with water (2), 0.5 M Na_2H_2EDTA (3), 0.1 M PPh_3–DCM (4), 1 M NH_4SCN (5), 1 M $(NH_2)_2CS$ (6), 2 M H_2SO_4 (7), 2 M HNO_3 (8), 5 M HCl (9), 5 M HCl–0.4 M $NaClO_3$ (10) and 0.1 M ethylenediamine (11).

The desorption pattern for ion exchangers **2** and **3** (not shown) was comparable to the results of ion exchanger **1**, depicted in Fig. 3. Again, the most effective desorption has been effected with mineral acids, with maximum desorptions for both ion exchangers of about 50% using 2 M HNO_3. The combination of hydrochloric acid with the strong oxidant $NaClO_3$ proved to be an even better desorbent, but re-adsorption tests indicated that the ion exchanger is severely damaged when this method is applied.

Based on the results, as depicted in Fig. 3, nitric acid was chosen as an eluent for all further desorption experiments. Solutions as diluted as 0.5 M proved to be almost equally efficient, but 2 M solutions were employed as a standard method to ensure maximum desorption, without damaging the materials.

Recovery kinetics

As lock-up of the precious Rh metal ions on the ion exchangers is undesired, fast recovery of the metal ions is of paramount importance, and therefore the kinetics of both the rhodium adsorption and desorption have been investigated (Figs. 4 and 5). Clearly, the adsorption is very fast for all the ion exchangers used, and $t_{1/2}$ values (the time needed for loading half of the total amount of Rh^{3+}) never exceed 60 s. The ligand occupation reaches its maximum after approximately 15 min and even shows a slight decrease in the case of **1** when a longer loading time is applied (see Fig. 4), presumably due to the low stability of the complexes of the monoamine ligand. The ligand occupation levels off between 40% and 55% (some 40–50 mg Rh per g ion exchanger), and this suggests the predominant formation of complexes of the type ML_2. Further support for the formation of these complexes comes from the fact that Rh-to-ligand ratios as high as 10 : 1 led to hardly any increase in the occupation level (%*L*).

Subsequent desorption using 2 M HNO_3 proved to be almost as fast as the adsorption. However, the relative desorptions have been found to range from almost quantitative (>95%) for **1**, *via* 42% for **2** to a mere 35% for triamine ion exchanger **3**. The ease of desorption is apparently strongly dependent on the type of complex formed, as has been reported previously.[12]

An important issue is the necessity to perform the desorption directly after the adsorption, because drying of the loaded samples at elevated temperatures, prior to elution, drastically decreases the desorption. This is presumably due to

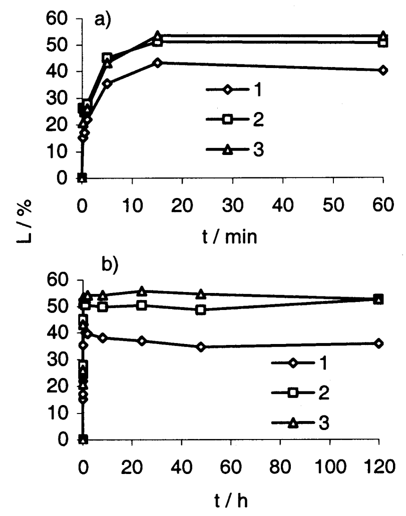


Fig. 4 Kinetic Rh^{3+} adsorption behaviour of ion exchangers **1**–**3** in water during (a) the first 60 min. and (b) five days.

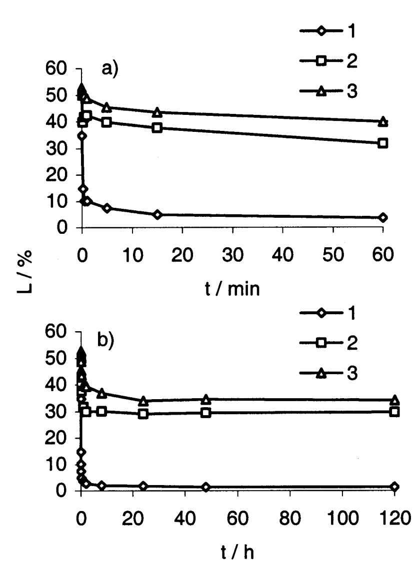


Fig. 5 Kinetic Rh^{3+} desorption behaviour of ion exchangers **1**–**3** in 2 M HNO_3 during (a) the first 60 min. and (b) five days.

Table 2 Successive recovery of Rh^{3+}. Adsorption is performed in water and subsequent desorption is done in 2 M HNO_3, with adsorption and desorption times of 15 min

Cycle	Relative amount of Rh^{3+}/ %[a]		
	1	**2**	**3**
1 Adsorption	100.0	100.0	100.0
Desorption	12.6	29.2	39.8
2 Adsorption	86.1	85.3	99.2
Desorption	17.6	39.2	58.3
3 Adsorption	85.5	94.5	122.2
Desorption	17.4	48.7	62.2
4 Adsorption	85.6	98.7	116.1
Desorption	19.0	50.6	60.5
5 Adsorption	88.2	101.6	111.2
Desorption	22.0	53.7	64.5

[a] The adsorption in the first cycle is set to 100%.

partial reduction of the Rh^{3+} metal ions to Rh^0, as witnessed by a slight colour change of the dried loaded samples, which cannot be recovered under these circumstances.

Successive extraction

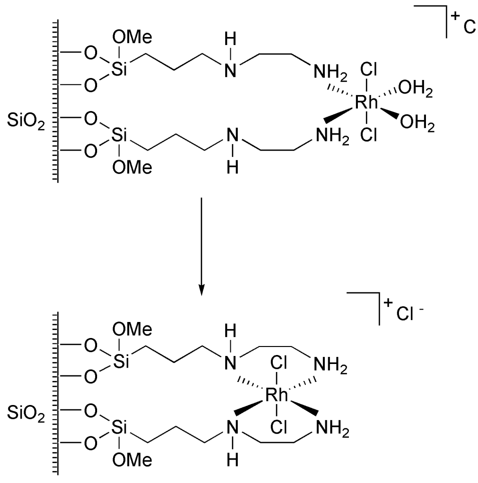
The performance of the ion exchangers in five successive Rh^{3+} recovery cycles is listed in Table 2. The relative amounts of Rh are compared with the amount adsorbed in the first cycle. The ligand occupations, corresponding to the 100% adsorption values, are similar to the adsorption percentages observed after 5 days (Fig. 4).

The most important recovery observations are: (1) The adsorption on ion exchanger **1** drops some 10–15% after the first cycle. This can be explained by the detachment of some of the ligands under the desorption conditions, as confirmed by elemental analysis. After the first cycle, about two-thirds of the Rh metal ions are consistently desorbed, leading to a small build-up of residual rhodium. (2) The recovery pattern for ion exchangers **2** and **3** is similar. Both show a gradual build-up of residual Rh in time. The relative desorption of **2** remains constant after the first cycle at some 50%. The Rh recovery using ion exchanger **3** appears as somewhat more capricious, but after several cycles the relative desorption appears to stabilise at about 50%.

The build-up of residual Rh can be attributed to the formation in time of more stable complexes. The 70% desorption, observed for **2** after the first adsorption, is some 30% higher than the desorption found in the kinetics experiment (see Fig. 5). The adsorption time in that experiment was 5 days (to ensure adsorption equilibrium), during which time presumably very stable metal complexes had formed on the ion exchangers, next to the more readily extractable species. A change in coordination with time, as for instance depicted in Scheme 1, could be the basis for the formation of these more stable complexes. Such very stable complexes do not form, apparently, with monoamine ion exchanger **1**, as the residual amount of Rh metal ions on the ion exchanger hardly increases.

Selectivity

The Rh extraction selectivity has been assessed in the presence of the divalent base metal ions Cd^{2+}, Zn^{2+}, Ni^{2+} and Cu^{2+}(see Fig. 6). Clearly, a very strong preference of all three ion exchangers for Rh^{3+} is displayed, especially at low pH, with Rh^{3+}-to-total M^{2+} ratios of over 50 : 1. Above pH 3–4, Cu^{2+} is increasingly adsorbed. Somewhat surprisingly, Rh and Cu are co-extracted to a considerable extent at higher pH values,



Scheme 1 Suggested formation of a more stable ML_2 complex in time, as depicted for ethylenediamine ion exchanger **2**.

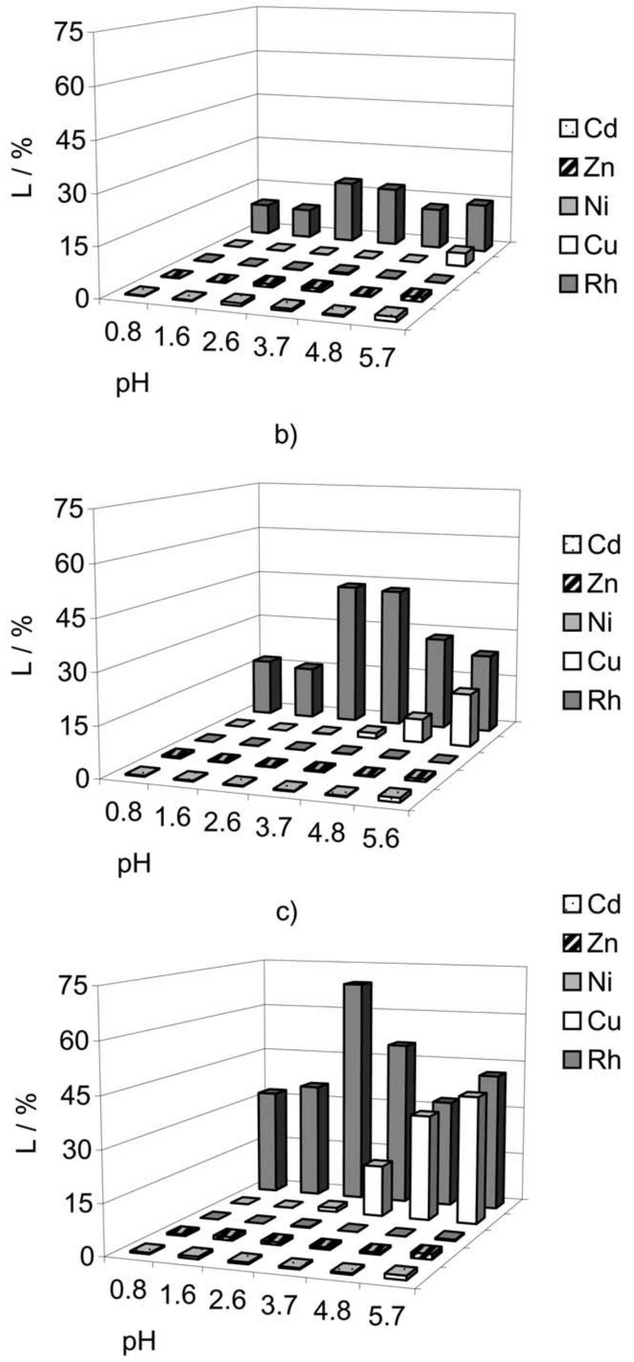


Fig. 6 pH-dependent competitive metal ion uptake behaviour of (a) ion exchanger **1**, (b) ion exchanger **2** and (c) ion exchanger **3**.

although each metal ion is theoretically capable of occupying all binding sites.

The high Rh selectivity at low pH values can be explained in the following way: at low pH (<2), the amines are predominantly protonated[17,18] and binding will presumably proceed *via* an ion association pathway, with positively charged amine ligands binding in an ionic fashion to negatively charged $[MCl_x]^{n-x}$ complexes.[16,19] Rh^{3+} readily forms complexes of the type $[RhCl_{6-n}(H_2O)_n]^{(3-n)-}$ (with n generally 0–2),[20] but the other transition metals form much weaker anionic complexes.[16,21] As the pH increases, binding takes place *via* N-donor coordination and Cu^{2+}, capable of forming very stable complexes with ligands that contain chelating amine groups,[14,22] is readily adsorbed as well.

The pH range of selectivity is much broader with monoamine ion exchanger **1**, due to lower complex stability, as already mentioned. Hence, by varying the ligand, the pH range of selective extraction can be tuned. Although the Rh^{3+} ligand occupation of **1** is smaller then with the other ion exchangers, its efficiency of elution (see Fig. 5) more than compensates this drawback.

Concluding remarks

Maximum Rh^{3+} adsorption is achieved within 15 min. Furthermore, over 50% of the maximum Rh^{3+} adsorption and subsequent desorption takes place in *less than 5 min.* The Rh recovery percentages of all three ion exchangers remain constant after the first recovery cycle, although a gradual Rh build-up in time occurred with some ion exchangers. A very high selectivity for Rh^{3+} over Cd^{2+}, Zn^{2+}, Ni^{2+} and Cu^{2+} at values up to pH 3 has been observed.

If only a good extraction is required, then the ion exchangers **2** and **3**, with strong chelating functionalities, are preferred. If an almost quantitative desorption is desired, then the ion exchanger **1** is preferred. These features, together with the excellent kinetic characteristics, Rh selectivity and stability under various desorption conditions, qualifies these silica-based (poly)amine ion exchangers as suitable candidates for application in a continuous system. The only problem that needs to be solved, before large-scale application is feasible, is the gradual build-up of rhodium on the ion exchangers, especially when the chelating ion exchangers **2** and **3** are applied.

Experimental

Reagents and analytical methods

All reagents and solvents were purchased from commercial sources and were used without further purification unless stated otherwise. As $RhCl_3$ shows extensive aquation (the formation of kinetically rather inert aquochloro complexes) in time, freshly prepared $RhCl_3$ solutions (< 10 min old) were always used. Unless stated otherwise, a 1 : 1 rhodium-to-ligand molar ratio was applied in all Rh uptake experiments.

The ion exchangers **1**–**3** were synthesised as described elsewhere.[23] Metal analyses were performed on a Perkin–Elmer 3100 atomic absorption (AAS) and flame emission spectrometer using a linear calibration method. Elemental analyses (C, H, N) were carried out by the Micro Analytical Laboratory of the University College in Dublin.

pH-dependent uptake experiments

The non-competitive uptake behaviour was studied as a function of the pH, employing 0.6 M NaCl–HCl buffer solutions (pH 1–2) and 0.6 M NaOAc–HOAc buffer solutions (pH 3–6), respectively, and for the pH-dependent uptake behaviour with constant chloride concentration, NaCl was additionally added to the pH 3–6 buffer solutions to a final concentration of 0.6 M Cl^-. To a solution of $RhCl_3 \cdot 3H_2O$ in 25 mL of demineralised H_2O, 25 mL of the appropriate buffer solution was added, followed by the addition of 100 mg of ion exchanger.

For the determination of the competitive pH-dependent uptake behaviour, 100 mg of ion exchanger was added to a solution of 5.0 mL $RhCl_3 \cdot 3H_2O$ together with 5.0 mL of standard metal chloride solutions of copper, cadmium, nickel and zinc and pH 1–6 buffer solutions (25 mL) were prepared, maintaining a ligand-to-metal molar ratio of 2 : 1 for each metal ion.

All samples were subsequently treated according to the following general procedure.

General procedure. The suspensions were agitated in polyethylene bottles mounted on a shaker for 48 h at room temperature. After shaking, the samples were filtered and the residue was washed with H_2O, EtOH and Et_2O (3 ×), respectively, and dried *in vacuo* at 50 °C until constant weight. Samples for metal analysis were prepared by heating *ca.* 100 mg of loaded samples overnight in 5 mL of concentrated H_2SO_4. Subsequently, concentrated HNO_3 was added dropwise until the solutions became clear. After dilution in volumetric flasks the solution was filtered over a glass filter (P4) to remove residual, undigested silica. The filtrate was collected and analysed by AAS.

Blank uptake experiments with $RhCl_3$ using pure silica have been performed under various acidic conditions up to 5 M HCl, under neutral conditions and using the above-mentioned buffer system. No significant uptake was detected. Hence, all uptake capacity can be contributed to the supported ligand systems.

Stripping experiments

Prior to the regeneration, 1.1 g of ion exchanger was loaded over a period of 2 days in a solution of 50 mL of $RhCl_3{\cdot}3H_2O$–H_2O. After filtration and washing with water, ethanol (absolute) and diethyl ether, 100 mg samples were added to the following stripping solutions (50 mL) in water: 0.5 M Na_2H_2edta, 1 M NH_4SCN, 1 M thiourea, 2 M H_2SO_4, 2 M HNO_3, 5 M HCl, 5 M HCl–0.4 M $NaClO_3$, 0.1 M ethylenediamine. Furthermore, both water and a solution of 0.1 M PPh_3 in CH_2Cl_2 were tested as stripping agents. After 48 h, the samples were filtered, washed, dried and prepared for analysis following the general procedure (see above).

Kinetic behaviour

For the determination of the rhodium-uptake kinetics, 100 mg of ion exchanger was agitated in a solution of $RhCl_3{\cdot}3H_2O$ in water (50 mL) for 10 s, 30 s, 1 min, 5 min, 15 min, 1 h, 2 h, 8 h, 24 h, 48 h and 120 h, respectively. The loaded ion exchangers were filtered, washed and dried as described in the general procedure.

The desorption kinetic experiments were conducted in the following way: 1.2 g of ion exchanger was loaded for 5 days in a solution of 50 mL of $RhCl_3{\cdot}3H_2O$–H_2O. After filtration and washing with water, EtOH and Et_2O, 100 mg was held apart as the adsorption reference. Samples of approximately 100 mg were added to a solution of 2 M HNO_3 and agitated for 10 s, 30 s, 1 min, 5 min, 15 min, 1 h, 2 h, 8 h, 24 h, 48 h and 120 h, respectively. The suspensions were filtered, washed and dried. All samples were then analysed according to the general procedure.

Successive extraction

Ion exchanger (1.0 g) was loaded for 15 min in a solution of 50 mL of $RhCl_3{\cdot}3H_2O$–H_2O. After filtration and washing with water, ethanol (absolute) and diethyl ether, 900 mg of the loaded sample was desorbed for 15 min in 2 M HNO_3 (50 mL) in water. The suspension was filtered and washed and about 800 mg of the stripped ion exchanger was reloaded with $RhCl_3{\cdot}3H_2O$. This procedure was repeated 4 times. After drying and preparation for analysis in the usual way, the Rh content of both the adsorbed and the desorbed samples was established.

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