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Purification of Waste Water Using Alumina as Catalysts Support and as an Adsorbent

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1. Introduction

Alumina is one of the most widely used adsorbent for removal of dissolved pollutants from waste water. Various chemical species, especially ions, are known to be adsorbed onto alumina. On the other hand, alumina is a typical support for catalysts. Many kinds of metal supported catalysts are prepared using alumina as their support. These two roles of alumina, i.e., as adsorbent and support, are closely related to each other due to two reasons. Firstly, most supported catalysts are prepared by impregnation. Impregnation is the process in which solid alumina is contacted with liquids which contain various metal precursors. Thus, adsorption phenomena play a crucial role in this process. Since a new phase is formed on the surface of the support after the impregnation process, alumina has been reported to have an essential role in the formation of catalysts active sites. Secondly, alumina used as a catalysts support can adsorb reactants in the course of catalytic reaction. Such adsorption onto support must be taken into account when the conversion and selectivity of the catalyst are calculated.
In this chapter, the two roles of alumina and their relationship are discussed in the light of experimental result. Former part of this chapter, behavior of alumina in the process of impregnation is examined and its relationship with the formation of active sites is discussed. Alumina is one of a very active adsorbent for heavy metal ions. This feature is used both in purification of waste water containing heavy metal and preparation of metal supported catalysts. In order to prepare Cu/Al_2O_3 catalyst, alumina was suspended in aqueous solution of $CuSO_4$. This is a typical impregnation process and in the meantime alumina had been thought to be inactive. However, after long contacting time, alumina was found to dissolve even in the neutral pH range. Because alumina did not dissolve in the same experimental condition in the absence of Cu^{2+} ions, the dissolution was found to be induced by contacting with Cu^{2+} ions. Alumina dissolution was observed during impregnation with $PdCl_4^{2-}$ in acid pH range, too. These facts mean that the active site formed on alumina after impregnation can contain significant amount of aluminum, and thus the catalytic performance may different from pure metal particles supported on alumina. In order to examine this possibility, Ru/Al_2O_3 catalyst was prepared by both impregnation and colloidal Ru methods. In the colloidal method, it is possible to minimize support effect by preparing metal particles in the absence of the support, and then deposit them onto the support. Although the two catalysts prepared had same composition, their catalytic

behavior for ammonia synthesis was completely different, and this was attributed to the structure of active site, i.e., contaminated with aluminum or not. These results suggest the importance of adsorption behavior in the process of catalysis preparation, because alumina support is not completely inert in impregnation process.

In the latter part of this chapter, cases in which alumina used as a catalysts support but at the same time behaves as an adsorbent are introduced. Catalytic reduction of NO_3^- and NO_2^- ions are thought to be one of the most promising way to treat contaminated drinking water. This reaction is generally performed by using Pd or Pt-based catalysts supported on Al_2O_3. The conversion of NO_2^- is conventionally calculated from the decrease in NO_2^- concentration of the reacting solution. However, it was found that significant amounts of NO_2^- disappeared from the reacting solution not because of chemical conversion, but because of its adsorption onto alumina which is the support of the catalyst. Furthermore, the equilibrium amount of adsorbed NO_2^- was affected by the size of supported Pt. This result suggests that the adsorption of NO_2^- onto alumina should be considered when the performance of denitration catalysts is evaluated. In addition, utilizing the high adsorption capacity of alumina for NO_2^- may realize its potential as an adsorbent for the removal of NO_2^- ions in waste waters.

2. Adsorption of heavy metal ions onto alumina

Aluminum is a ubiquitous element comprising nearly 8% (w/w) of the earth's crust, and aluminum oxide is a common adsorbent in aqueous electrolyte solutions. The concentration of dissolved metal ions in aqueous systems are controlled to a large extent by the partitioning of solute to solid phases through adsorption and presipication. Therefore, solid-liquid interfacial reactions of heavy metal ions on the surface of alumina has drawn great interest in areas such as water quality and treatment, heavy metal transport, potential bioavailability of aqueous metal species, and biogeochemiscal cycling of metal ions (Trainor et al., 2000). The interfacial reactions on alumina also play an important role in heterogeneous catalyst preparation.

The adsorption phenomena of ions to oxides have been explained mainly by three models: surface complex formation model (ligand model), hydrolysis moderl (ion-solvent interaction model), and crystal field model. Currently, the surface complex formation model seems to be the most general and widely accepted model. Surface complex formation models are chemical models that use an equilibrium approach to describe the formation of complex at the oxide-solution interface (Goldberg, 1991). Unlike empirical models, such as the Langmuir and Freundlich adsorption isotherm equations, chemical models explicitly define surface species, chemical reactions, equilibrium constant expressions, and surface activity coefficient expressions. Additional advantages of the surface complex formation models are inclusion of mass and charge balance equations and consideration of the charge on both adsorbate and the adsorbent. According to the surface complex formation model, the extent of metal ion partitioning and stability of the resulting products is a function of the speciation of the sorbate metals. For example, weakly bound outer-sphere adsorption complex are more rapidly exchangeable than more strongly bound inner-sphere adsorption complexes. This explains so-called *specific adsortpion*, which suggests alumina can adsorb heavy metal ions 1,000 to 10,000 times more readily than alkaline or alkaline earth metal ions (Wada & Abd-Elfattah, 1979).

2.1 Three-steps reaction on the surface of alumina

Surface complex formation between heavy metal ions and aluminol groups (Al-OH) on the surface of alumina has been observed by many researchers using potentiometry,

spectroscopic methods such as EXAFS, and so on. Adsorption experiments of Zn^{2+} onto alumina was performed using a method described by Miyazaki and Tsurumi (1995). Using this potentiometric method, where the ionic strength and pH value of the reacting suspension are kept strictly constant, while the concentration of heavy metal ions in the suspension was increased stepwise. By this method, it is possible to determine the amount of heavy metal ions retained by the solid, and the corresponding amount of H^+ ions released from the surface –OH groups.

Figure 1 shows the result of Zn^{2+} adsorption onto alumina, which was synthesized by hydrolysis of $Al_2(SO_4)_3$ and confirmed to be X-ray amorphous (Miyazaki et al., 2003). In the

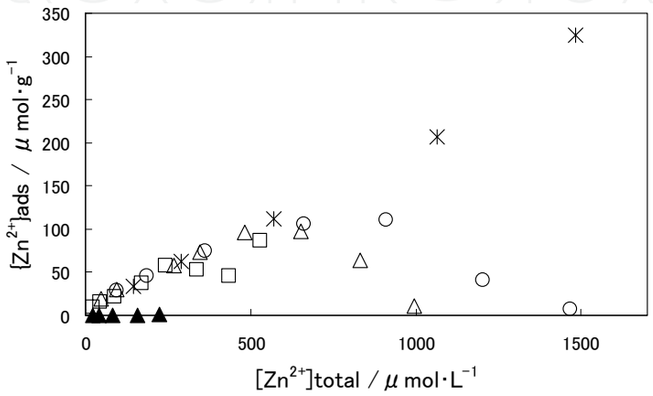
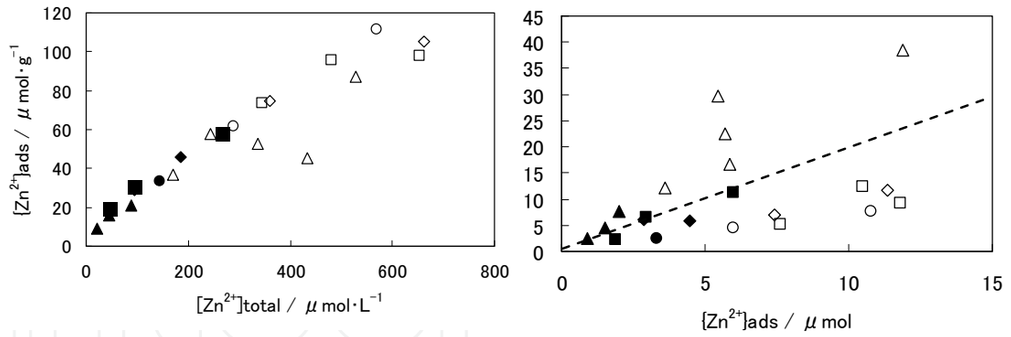


Fig. 1. Adsorption of Zn^{2+} ions onto Al_2O_3. Relationship between the total concentration of Zn^{2+} and amount of Zn adsorbed by 1g of Al_2O_3 is shown. The experiments were performed at constant pH of 6.50 for Zn^{2+} concentrations ranging up to 600 μmol/L(□), 1000 μmol/L(△), 1,500 μumol/L (○), and 3,000 μmol/L (＊). Blank experiment was carried out in the absence of solid (▲).

experiment, the concentration of alumina was kept 1g/L. The ionic strenght of the suspension was maintained at 0.1 by addding $NaNO_3$ and pH was 6.5. The concentration of Zn^{2+} in the suspension was increased from 0 to 600, 1000, 1500 or 3000 μmol/L, by using Zn^{2+} stock solution with different concentrations, and the results of each experiment are represented by different symbols. Each set of symbols represents the measurement at each stepwise increase in the concentration of Zn^{2+} ions in the suspension. From Fig. 1, it can be seen that the adsorption behavior of Zn^{2+} ions differed among the total concentration range of Zn^{2+}. In all cases of experiments shown in Fig. 1, the amount of Zn^{2+} ions adsorbed on the solid increased to a maximum corresponding to the concentration of Zn^{2+} stock solution. Further increase in total Zn^{2+} ions concentration caused a decrease in the propotion of adsorbed Zn^{2+} ions. This means some amount of Zn^{2+} ions adsorbed on the surface of the alumina desorbed.

In Fig. 1, every experiment showed the adsorption of Zn^{2+} ions, even if the total concentration was less than 250 μmol/L, which is below the concentration that can form $Zn(OH)_2$ in the bulk solution. Because this concentration range of Zn^{2+} ions was significantly lower than that of the solubility product of $Zn(OH)_2$ (3,000 μmol/L), it is reasonable to suggest that Zn^{2+} ions are retained on the surface of alumina, not by hetrogeneous nucleation on the solid surface, but by some adsorption mechanism. Figure 2(a) illustrates the relationship between the adsorption amount and the total concentration of Zn^{2+} ions (up to 800 μmol/L), as



(a) (b)

Fig. 2. Adsorption of Zn^{2+} ions onto alumina. (a) Relationship between total concentration of Zn^{2+} and adsorbed amount of Zn by 1g of Al_2O_3. The results obtained by using several concentration of Zn stock solutions are depicted with different symbols. The closed symbols are used for the results which seems to fit a line, while open symbols are used for the other. (b) Relationship between absolute amount of adsorbed Zn^{2+} and released H^+, which are calculated for the same experimental data shown in Fig. 2(a). The type of symbols is followed Fig. 2 (a). The line represents a slope 2.

shown previously in Fig. 1. The region in Fig. 2(a), in which the total concentration of Zn^{2+} ions is up to ~ 300 μmol/L, corresponds to the first adsorption region in Fig. 1. Since the results in this adsorption region exhibited good liniarity and reproducibility, it can be assumed that this region exists in an equilibrium state. Figure 2(b) shows the relationship between the absolute amount of adsorbed Zn and the released H^+ ions, corresponding to the same data that was presented in Fig. 2(a). Results in Fig. 2(b) that generally fit the overlaid line (with slope of 2) were designated with solid symbols, which were also assigned to the corresponding data in Fig. 2(a). Similarly, these solid symbols in Fig. 2(b) also showed good liniarity. Since this relationship can be explained as the equilibrium in the formation of a surface complex between two aluminol groups and one Zn^{2+} ion, the first stage of Zn adsorption onto alumina can be defined according to the reaction:

$$2\{\text{Al-OH}\} + Zn^{2+} = \{(\text{Al-O})_2\text{Zn}\} + 2H^+ \quad (1)$$

where { } indicates the chemical species on the surface of solid.
The equilibrium constantt of this reaction was calculated using the data obtained by the potentiometric studies. The equilibrium constant for equation (1) can be expressed as:

$$K=\frac{\left\{(\text{Al-O})_2\,\text{Zn}\right\}\left[H^+\right]^2}{\left\{\text{Al-OH}\right\}^2\left[Zn^{2+}\right]} \quad (2)$$

Where $\{(\text{Al-O})_2\text{Zn}\}$ and $[Zn^{2+}]$ represent the concentrations of Zn^{2+} on the surface of solid (mol/g) and in the liquid phase (mol/L), respectively. This equilibrium constant represents the intrinsic microscopic formation constant for solutions of constant ionic strength. Herein, surface potential was defined as the potential difference between the aluminol site $[(\text{Al-O})_2\text{Zn}]$ and the bulk of solution, and for simplification, this value can be assumed as zero, and therefore, equation (2) does not contain an electrostatic term. Langumuir plots were

obtained using the experimental data, and using the slope of Langumuir plots, the concentration of aluminol sites on the surface of alumina was calculated to be 177 μmol/g. Equilibrium constant log K calculated by this value was log K = -5.67 (standard deviation was 0.0278). The reported equilibrium constant for the surface complexation between the silanol groups and Zn^{2+} ions was log β = -11.6 (Vlasova., 2001). Comparably, the equilibrium constant calculated for alumina was similar.

Figure 1 shows that the Zn^{2+} ions, which were adsorbed onto alumina by surface complexation, were desorbed at higher total concentration of Zn^{2+} ions. This desorption phenomenon did not follow a linear relationship between the total concentration of Zn^{2+} ions and the amount of Zn^{2+} ions adsorbed onto 1 g of solid. As shown in Fig. 2, the desorption behavior of Zn revealed a noticeable deviation from the equilibrium for surface complex formation. The timing for this deviation depended on the experimental conditions, in which the early desorption process seemed to be controlled by the total concentration of Zn^{2+} ions and by the reaction time, which took to increase the concentration of total Zn^{2+} ions. It remains unclear as to why desorption would occur for the Zn^{2+} ions, which initially adsorbed to form the surface complex with aluminol groups at lower total concentration of Zn^{2+} ions. However, as described in next sections, this dissolution phenomenon is not special for Zn^{2+} but general for heavy metal ions adsorbed onto alumina. Moreover, this process is accompanied with dissolution of alumina. The results shown in Fig. 2 suggest that the Zn^{2+} ions, which were desorbed from alumina, can be resorbed onto alumina. This process also included the sorption of Al^{3+} ions.

As it was observed in Fig. 1, the solid-liquid interfacial reaction of Zn^{2+} ions on alumina can be divided into three processes: adsorption, desorption, and re-adsorption. In the adsorption process, one Zn^{2+} ion and two aluminol groups formed a surface complex. This reaction was fast, and the equilibrium constant can be calculated for this surface complexation. The second process, the desorption of Zn, occurred when the surface density of Zn increased above a threshold value. Lastly, the re-sorption process happened as the third and the last process, which may be attributed to the hydroxide coprecipitation of Zn and Al.

2.2 Alumina dissolution induced by Zn^{2+} adsorption

In the process of adsorption of heavy metal ions onto alumina, it has been thought that adsorbed heavy metal ions would never be desorbed and alumina is inert in neutral pH range. However, adsorption experiment described in previous section revealed the Zn^{2+} ions adsorbed on the surface of alumina can be desorbed by increasing of reaction time or Zn^{2+} concentration in the experimental system. Moreover, the existence of Al^{3+} ions was observed at the same time (Miyazaki et al., 2003). This suggests that adsorbed Zn^{2+} ions are not desorbed alone but together with the support. This kind of rearrangement of adsorbed metal ions is reported by some researchers. Trainor et al. (2000) have studied the structure of Zn sorbed on the surface of high-surface-area alumina powders, and found that, at low sorption densities, Zn^{2+} predominantly formed inner-sphere bidentate surface complexes with AlO_6 polyhedra, whereas at high sorption densities, a mixed-metal Zn^{2+}-Al^{3+} hydroxide co-precipitate with a hydrotalcite-type local structure was formed. Based on the Zn^{2+}/Al^{3+} ratios in the precipitate, they have assumed the continuous dissolution of the alumina substrate (or secondary precipitated Al hydroxides), and the rapid re-precipitation of Al^{3+} together with Zn^{2+} for the formation of the mixed metal co-precipitate. Pauliac and Clause (1993) have reported on the formation of zinc-aluminum co-precipitates when 5 g of γ-alumina was in contact with 0.01 mol/L $Zn(NO_3)_2$ (200 mL) for 3 h at near-neutral pH (6.5 <

pH < 8.5). Jacquat et al. (2009) determined the local coordination of Zn in hydroxyl-interlayered smectite (HIS) as a function of Zn loading. They observed a progressive shift from Zn incorporation in the vacancies of gibbsitic Al-polymers to Zn adsorption to incomplete Al-polymers and finally uptake by cation exchange in the polymer-free interlayer space of HIS with increasing Zn loading.

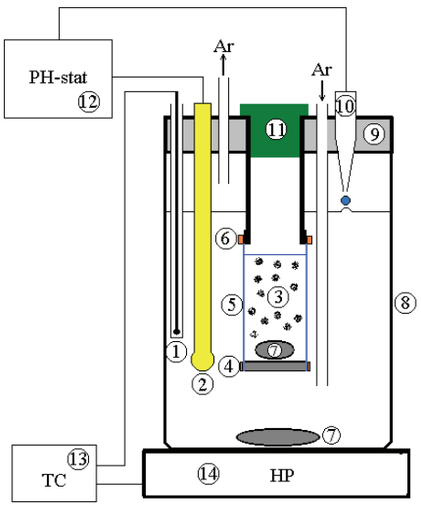


Fig. 3. The experimental system used for the investigation of alumina dissolution at constant pH. (1) glass-shielded thermocouple, (2) pH electrode, (3) alumina, (4, 6) Teflon rings, (5) dialysis bag, (7) Teflon-coated magnetic stirring rods, (8) glass beaker, (9) Teflon cap, (10) buret, (11) Teflon cap with screw, (12) pH-stat, (13) temperature controller, (14) hot plate and stirrer.

It has been difficult to monitor the evolution of heavy metal ions and alumina at the same time in the process of solid-liquid interfacial reactions, because of the most of the experimental arrangements utilized by now. Even if metal ions, which were once adsorbed on the surface of alumina, would be desorbed, they will be re-adsorbed immediately on the surface of alumina. Thus, it was difficult to distinguish the solid which was formed secondly by re-adsorption of dissolved aluminum ions and desorbed heavy metal ions, from original alumina and surface complex of heavy metal ions formed on its surface. In order to overcome these difficulties, experimental system using dialysis membrane proposed by Balint et al, (1999) has significant advantages. As shown in Fig. 3, the experimental system was composed of two parts that were separated from each other by a dialysis membrane (Wako/Wiscase Scales Corp., MWCO 12000-14000: pore diameter 25 Å). The tubular membrane was tightly closed with a Teflon cap and two Teflon rings. γ-Alumina (1 g, Aerosil) and 0.1 mol/L $NaNO_3$ aqueous solution (10 mL) were placed in a dialysis bag, then tightly sealed from the bulk solution using two Teflon rings. The γ-Al_2O_3 was produced by flame-hydrolysis of $AlCl_3$. The grains of the fine powder produced were approximately spherical in shape with an average diameter of 13 nm. The pH_{ZPC} of the alumina used in the experiment was determined to be 8.0 by a mass titration method (Subramanian, 1998). The beaker was filled with the solution (240 mL) containing 0.1 mol/L $NaNO_3$ and 1.8 mmol/L $Zn(NO_3)_2$. Before suspending the dialysis bag (containing alumina) in the beaker, the solution outside the bag was adjusted to pH 6.50 by the addition of 0.1 N NaOH. The pH value of the solution was monitored using a pH electrode; 0.1 N NaOH solution was added

using a pH-stat (TOA AUT-211) to maintain pH 6.50. These experimental conditions are corresponding to those adopted in adsorption experiment, whose results are shown in Figs. 1 and 2. Periodically, 2 mL aliquots from the impregnating solution outside the bag were subjected to ICP measurements to determine the concentrations of Al^{3+} and Zn^{2+} ions. The experiments were performed at constant temperature (25 ˚C), and the system was slowly purged (3.6 L/h) using Ar gas.

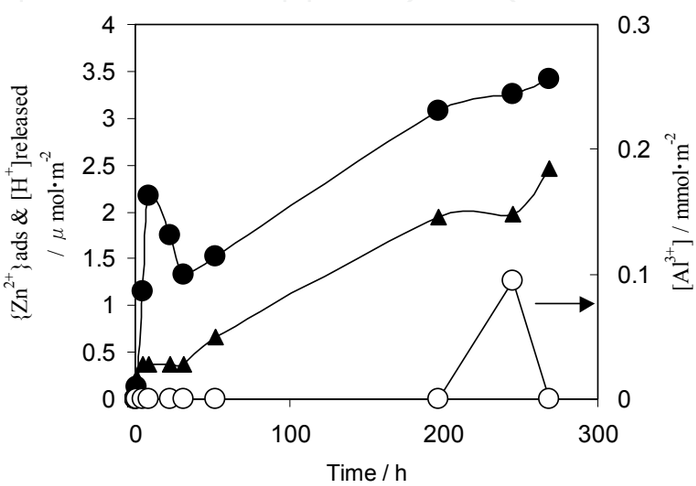


Fig. 4. Alumina dissolution promoted by adsorption of Zn^{2+} ions investigated with the experimental system presented in Fig. 3. The amounts of Zn^{2+} ions adsorbed onto the alumina (●) and the amount of H^+ released from the solid (▲) are shown together with the amount of Al^{3+} observed in the solution outside of the membrane bag (○).

Measured concentration of Zn^{2+} and Al^{3+} ions in the solution outside the dialysis membrane bag, as a function of time, are shown in Fig. 4. Results showed that the amount of adsorbed Zn^{2+} ions increased in 0 to 8 h, which indicated that the Zn^{2+} ions added to the solution (in the beaker) passed through the membrane, and were adsorbed onto the alumina inside the bag. From 9 to 30 h, the adsorbed amount of Zn^{2+} ions decreased, which was attributable to the desorption of the adsorbed Zn^{2+} ions. After 30 h, slow uptake of Zn^{2+} ions was again observed. It is noteworthy that these three steps, as revealed by the membrane separation experiment, are in good agreement, qualitatively, with the result of the adsorption experiments, as shown in Fig 1. However, the time scale for the processes presented in Fig. 1 and Fig. 4 are significantly different. Since the alumina dissolution experiments (Fig. 4) were performed using a dialysis membrane, it is likely that the diffusion of Zn^{2+} ions was relatively restricted.

As for the initial adsorption process (0 to 9 h in Fig. 4), the ratio between the amounts of Zn^{2+} ions adsorbed and H^+ ions released was calculated as 1.8. This result confirmed that the initial adsorption process is the formation of the surface complex between two aluminol groups and one Zn^{2+} ion.

As shown in Fig. 4, the results clearly indicated the formation of Al^{3+} ions after 245 h of the reaction. Since these Al^{3+} ions originated from the alumina that was loaded inside the dialysis membrane, a measurable amount of alumina must have dissolved into the liquid phase during the adsorption of Zn^{2+} ions onto alumina at pH 6.5. A blank experiment without the addition of Zn^{2+} in the solution outside of the membrane confirmed that no Al^{3+} ions was released into the solution outside the bag. Thus, it is clear that the release of Al^{3+} ions was induced by Zn^{2+}.

To reveal the mechanism of this phenomena, $Zn(OH)_2$ was assumed to be the promoter of alumina dissolution. Fendorf et al. (1994) have reported that Cr^{3+} ions form a monodentate surface complex on silica when the surface coverage is below 20%; however, at higher surface coverage, a polynuclear chromium hydroxide surface phase is formed. It is highly possible that $Zn(OH)_2$ - like structure is formed on the surface of alumina, by increasing reaction time and concentration of metal ions on the surface of alumina.

The activity of $Zn(OH)_2$ for the dissolution of alumina was investigated, again by employing the membrane reactor (Fig. 3). In this experiment, $Zn(OH)_2$ was prepared by adding 0.1 mol/L NaOH solution to a $ZnNO_3$ solution, then mixed with alumina, in which the ratio between $Zn(OH)_2$ and Al_2O_3 was adjusted as equimolar (molar ratio = 1). The dialysis membrane bag, which contained the mixture, was suspended in the beaker filled with 0.1 mol/L $NaNO_3$ (pH 6.5).

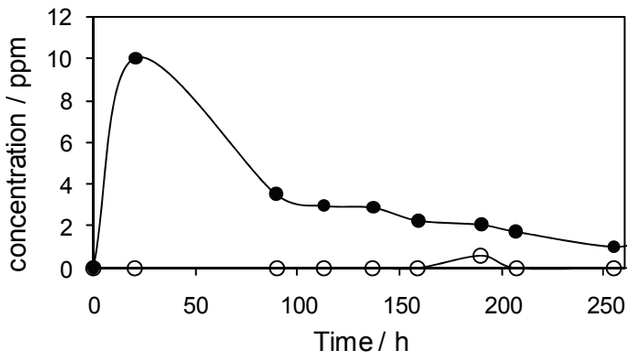


Fig. 5. Alumina dissolution promoted by $Zn(OH)_2$ investigated with the experimental system shown in Fig. 3. The time course of Zn^{2+} (●) and Al^{3+} (○) concentrations in the solution outside of the dialysis membrane.

Concentrations of the Zn^{2+} and Al^{3+} ions in the solution outside the dialysis membrane, as a function of time, are shown in Fig. 5. From 0 to 20 h, the concentration of Zn^{2+} ions in the solution increased dramatically, indicating that some $Zn(OH)_2$ dissolved and diffused into the solution outside the bag. From 20 to 255 h, the concentration of Zn^{2+} ions in the solution constantly decreased due to the re-adsorption of Zn^{2+} ions. Interestingly, after 190 h, the presence of Al^{3+} ions was observed in the solution outside the dialysis membrane bag. Comparatively, the time line for the formation of Al^{3+} ions is in good agreement with the results as described above (Fig. 4). In both cases, Al^{3+} ions were formed during the Zn^{2+} ion resorption process. The results presented in Figs. 4 and 5 proved that the formation of $Zn(OH)_2$ was mainly responsible for the dissolution of alumina. The $Zn(OH)_2$ phase, which is formed by increasing surface coverage, may possibly promote the dissolution of alumina.

2.3 Alumina dissolution induced by Cu^{2+} adsorption

Alumina dissolution induced by adsorption of heavy metal ions is deeply related to heavy metal behavior in environment and catalyst preparation. Support impregnation with metal(s) precursor(s) solution is a widespread method for catalysts preparation. The impregnation step has been reported to have an essential role for the formation of active sites (Foger, 1984). After the process of impregnation, a new phase is formed on the surface

of the support and it is likely to contain the precursor(s) of the active sites. Therefore, the impregnation process has been the focus of a large number of studies that attempted to reveal the relationship between the catalyst's preparation and its final activity (Zhang et al. 1992). The process of active site formation is not well-known, because the amount of the new phase formed is very small compared to the bulk, i.e., the support. However, it is important to acknowledge that not only the precursor but also the supports can contribute to active site formation. The alumina dissolution observed by Zn^{2+} adsorption strongly supports this possibility. In order to see if alumina dissolution is not a special phenomena observed by Zn^{2+} adsorption but general phenomena induced by other metal cations, solid-liquid interfacial reaction between alumina and Cu^{2+} was studied. Copper was selected because copper catalysts supported on alumina are of great interest for many important reactions, including methanol synthesis, steam reforming of methanol (Agaras et al, 1998), selective reduction of NO_x, and adsorption of SO_2 (Katheuser, et al, 1991). Such catalysts are generally prepared by impregnation of alumina with various precursors.

The processes associated with the impregnation of alumina with $CuSO_4$ at 50°C and at pH values close to pH_{ZPC}, i.e., pHs 7 and 9, were studied. All the experiments were performed with the system shown in Fig. 3. A 1 of γ-Al_2O_3 (Aerosil) was loaded inside of the membrane bag with 12 mL of 0.1 mol/L K_2SO_4 solution. A 250 mL of 0.1 mol/L K_2SO_4 solution was poured into a glass beaker, and the membrane bag containing alumina was suspended in the beaker. The alumina was equilibrated overnight, with the pH kept constant at 7 or 9 by adding 0.1 mol/L KOH at 50°C. A peristaltic pump was then used to gradually add 3 mL of a 1 mol/L $CuSO_4$ solution to the solution outside of the bag. At the end of the experiment, the precipitate formed outside of the bag was collected by filtration, washed several times with distilled water, and then dried at 100°C. The alumina inside of the bag was treated in the same way.

Impregnation experiment at pH 9 lasted 240 h and formed 0.306 g of black precipitate, which contained 67.9 wt% of Cu and 0.355 wt% of Al. The XRD pattern of the precipitate formed outside of the bag suggested that the main components of the precipitate were CuO and $3Cu(OH)_2 \cdot CuSO_4$. The presence of a small amount of $Cu(OH)_2$ and Al_2O_3 in the precipitate was observed, too. A blank experiment without addition of $CuSO_4$ resulted neither the release of Al^{3+} ions nor the formation of the precipitate, even after 220 h.

On the other hand, impregnation experiment at pH 7, slightly lower than pH_{ZPC}, formed green precipitate after 336 h. The molar ratio between Cu and Al (Cu/Al) was 222, and this is smaller than the value observed at pH 9 (Cu/Al = 80.8). The total amount of alumina dissolved was 0.51 mg, and this corresponds to 23% of the amount of alumina dissolved at pH 9 (2.21 mg).

From the impregnation experiments conducted at pHs 7 and 9, it is clear that $CuSO_4$ promotes alumina dissolution at pH value near to pH_{ZPC}. To reveal the mechanism of this phenomena, $Cu(OH)_2$ and $3Cu(OH)_2 \cdot CuSO_4$ were assumed to be the main promoters of alumina dissolution. This assumption was based on the composition of the precipitates formed outside of the bag: CuO and $3Cu(OH)_2 \cdot CuSO_4$ at pH 9 and $3Cu(OH)_2 \cdot CuSO_4$ at pH 7. It is well-known that $Cu(OH)_2$ rapidly decomposes into oxide in the presence of excess hydroxyl ions, due to spontaneous dehydration (Massey, 1973). Heavy metal sulfates are known to stabilize $Cu(OH)_2$ as a basic sulfate. Thus, the interaction of copper hydroxide with the alumina was examined in order to assess its activity in alumina dissolution. The experiment was performed in the same way to alumina dissolution by $Zn(OH)_2$. A 1 g sample of γ-Al_2O_3 kept inside of the bag was equilibrated with 0.1 M K_2SO_4 solution at pH 9, 50°C for 12 h. Then, 0.127 g ($1 \cdot 10^{-3}$ mol) of wet $Cu(OH)_2$ was added to the alumina inside of the bag. The $Cu(OH)_2$ was prepared

by adding KOH solution to $CuSO_4$ solution at room temperature with constant stirring. The light blue precipitate obtained was washed several times with distilled water and mixed with alumina quickly in order to avoid hydroxide decomposition.

Figure 6 shows that the concentration of aluminum released in to solution outside of the bag increased progressively over time. It can be seen that the aluminum concentration in the

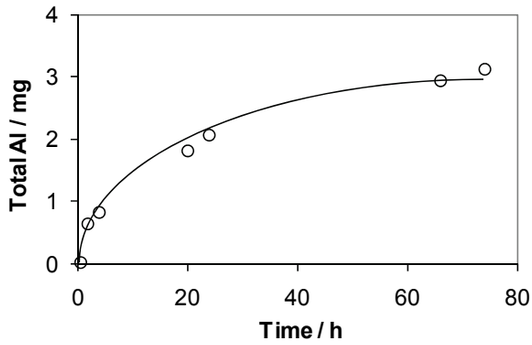


Fig. 6. Aluminum ion released in the solution outside the bag during $Cu(OH)_2$ interaction with alumina.

solution was 3.3 ppm at the end of the experiment. The total amount of alumina dissolved after 74 h of experiment was calculated to be 6.06 mg from the aluminum content of the solution. This amount of alumina dissolved is significantly higher than when alumina was impregnated with $CuSO_4$ at pH 9 for 240 h. The presence of copper was not detected in the solution outside of the bag. The color of $Cu(OH)_2$ inside of the bag did not change even after 74 h of experiment. Therefore, it can be said that $Cu(OH)_2$ did not decompose (at pH 9, 50°C) when it was mixed in a slurry with an appropriate amount of alumina. On the basis of the above observations, additional experiments were performed to determine the adsorption capacity of γ-Al_2O_3 for $Cu(OH)_2$.

A 0.1 g sample of alumina was added to the fresh $Cu(OH)_2$ precipitate (0.127 g) under stirring, and the pH was adjusted to 9 at temperature of 50°C. It was observed that the amount of alumina, 0.1 g was too small to stabilize the $Cu(OH)_2$ completely, because some of the $Cu(OH)_2$ had decomposed into CuO and the color of the slurry had turned black. The amount of added alumina was increased gradually in 0.05 g increments. Ultimately it was found that 0.6 g of the alumina was necessary to completely stabilize 0.127 g of $Cu(OH)_2$. The alumina adsorption capacity for copper was calculated to be ~$1.66 \cdot 10^{-5}$ mol $Cu \cdot m^{-2}$. This value is almost completely in agreement with the value reported by Dumas et al., (1989); $3.3 \cdot 10^{-6}$ mol $Cu \cdot m^{-2}$ in a basic medium and $0.7 \cdot 10^{-5}$ mol $Cu \cdot m^{-2}$ in an acidic medium.

On the other hand, activity of copper basic sulfate, $3Cu(OH)_2 \cdot CuSO_4$ was assessed. A 0.204 g ($2 \cdot 10^{-3}$ mol) of alumina (in the bag) was equilibrated at 50°C, pH 7, with 0.1 M K_2SO_4 solution. Then, $3Cu(OH)_2 \cdot CuSO_4$ was added into the bag. The experiment lasted for 371 h. $3Cu(OH)_2 \cdot CuSO_4$ was prepared from $Cu(OH)_2$ by adding $CuSO_4$ (0.1 mol/L). $3Cu(OH)_2 \cdot CuSO_4$ was obtained as green precipitate, then filtered and washed several times with distilled water.

At the end of the experiment, no precipitate had formed outside of the bag. Furthermore, neither aluminum nor copper was detected in the solution outside of the bag. This result suggests two possibilities: one is that it is not $3Cu(OH)_2 \cdot CuSO_4$ that promotes the alumina dissolution, and the other possibility is that aluminum ions resulting from alumina dissolution were trapped by the $3Cu(OH)_2 \cdot CuSO_4$ phase and could not diffuse outside the bag. The latter hypothesis was checked by another experiment, which is described briefly as follows.

A 5 g sample of copper basic sulfate was equilibrated with 250 mL of 0.1 mol/L $Al_2(SO_4)_3$ solution at 50°C for 44 h. During the experiment, the colorless solution outside of the bag turned blue as a result of $CuSO_4$ formation. At the end of the experiment, the new compound that had formed inside of the bag consisted of 9.13% of Al and 32.27 % of Cu. The molar ratio between Cu and Al was 1.5. This means that the $CuSO_4$ units were replaced completely by $Al_2(SO_4)_3$ units in the copper basic sulfate structure:

$$Al_2(SO_4)_3 + 3Cu(OH)_2 \cdot CuSO_4 \rightarrow 3Cu(OH)_2 \cdot Al_2(SO_4)_3 + CuSO_4 \quad (3)$$

This result clearly shows that $Cu(OH)_2$ has a higher affinity to $Al_2(SO_4)_3$ than $CuSO_4$ in forming basic sulfate. This provides a convincing reason for the absence of aluminum in the solution outside of the bag when aluminum interacted with copper basic sulfate in the bag. The small amount of aluminum ions formed were trapped by $3Cu(OH)_2 \cdot CuSO_4$ to form $3Cu(OH)_2 \cdot Al_2(SO_4)_3$.

From the above experiments, the processes that occur during alumina impregnation with $CuSO_4$ may be explained as follows. First, copper ions outside of the bag diffuse into the bag and precipitate on the surface of the alumina as $Cu(OH)_2$ and/or $3Cu(OH)_2 \cdot CuSO_4$. Then, the $Cu(OH)_2$ precipitate strongly adsorbed on the surface of the alumina and promote alumina dissolution. The aluminum ions released from the alumina dissolution diffuse outside of the bag, and they are preferentially trapped in the $3Cu(OH)_2 \cdot CuSO_4$ phase by coprecipitation or ion exchange. Another parallel reaction which should be considered is the coprecipitation of aluminum ions and copper ions outside of the dialysis bag. The aluminum uptake by the copper precipitate is limited. At pH 9, the amount of aluminum ions formed was too high to be taken up completely by the precipitate. Therefore, the presence of aluminum was detected in the solution, too.

The experimental results demonstrate that the impregnation step in catalyst preparation can be thought of as a complex chemical solid-liquid interfacial reaction. The support should be considered as an active participant with a specific reactivity dependent upon the experimental conditions, in the formation process of the active phase during the impregnation step. The presence of the ions dissolved from the support may have an important effect on the formation of active site in catalysts. The presence of small (0.51 Å) and high charge-carrying aluminum ions in the catalyst active phase may induce strong local perturbation in the host lattice as a result of defects formation (Balint & Aika, 1997). Therefore, the aluminum presence in the copper active phase should be taken into consideration in explaining the active site formation and the catalytic activity of Cu/Al_2O_3.

2.4 Alumina dissolution in the presence of $PdCl_4^{2-}$

In the former sections, it was shown that adsorption of heavy metal cations, i.e., Zn^{2+} and Cu^{2+}, onto alumina can induce alumina dissolution. Hydroxides of heavy metals, which were formed on the surface of alumina after some amount of coverage was accomplished, are found to be responsible for alumina dissolution. Such alumina dissolution induced by heavy metal adsorption must be paid great attention because of various reasons. For example, aluminum is known to be toxic to a wide range of aquatic organisms under conditions of low pH and hardness (Dobbs, et al., 1989). Oxide of aluminum, i.e., alumina, is known to be one of the most effective adsorbent to remove heavy metal ions from aqueous phase (Bold & Van Riemsdijk, 1987). Thus, dissolved aluminum, produced in the process of heavy metal removal, may have great impact on aquatic environment. On the other hand,

alumina dissolution induced by heavy metal adsorption may have significant effect on active site formation on catalysts prepared by impregnation.

It was shown that alumina dissolution is induced by heavy metal cations. However, many heavy metals, especially platinum group metals used in catalysts, exist in aqueous solution forming anions. Therefore, it is of great importance to see whether alumina dissolution can be induced by adsorption of heavy metal anion, too. The possibility of alumina dissolution in the course of Pd/Al_2O_3 catalysts preparation was studied by using $PdCl_4^{2-}$ ion (Balint et al., 2001). $PdCl_4^{2-}$ was selected because palladium is one of the mostly used metals in heterogeneous catalysts and $PdCl_4^{2-}$ ions have good stability and solubility in the acid pH range. Pd/Al_2O_3 catalyst prepared using $PdCl_4^{2-}$ and activated properly has reported to have high activity for reactions such as, methane oxidation (Burch, 1990).

To find out the influence of $PdCl_4^{2-}$ on alumina dissolution in the acid pH range, the following procedure was applied. First, the proton-promoted dissolution of alumina was investigated, in the absence of any additional ligand, at pH 3.5, 4 and 5. Then, the dissolution of alumina in the presence of $PdCl_4^{2-}$ was studied in similar conditions. In this manner, the differences observed would be due to the presence of $PdCl_4^{2-}$. All the impregnation experiments were performed with the system shown in Fig. 3.

Alumina dissolution was observed at pH 3.5 and 4. At pH 3.5, the total amount of dissolved alumina during 74 h of experiment, calculated from the concentration of Al^{3+} in solution, was 1.07 % of the initial amount of alumina. The rate of Al^{3+} formation was 0.0603 μmol m^{-2} h^{-1}. It was evidenced that the dissolution rate for alumina was lower (0.0353 μmol m^{-2} h^{-1}) when $PdCl_4^{2-}$ was present in the system. The amount of dissolved alumina after 96 h of experiment was 1.47%. The amount of $PdCl_4^{2-}$ adsorbed on the alumina surface, calculated from the decrease in palladium concentration in the impregnating solution, increased rapidly to 0.32 μmol m^{-2} in the first 2 h of impregnation. Then, the rate of adsorption of $PdCl_4^{2-}$ decreased to reach finally (after 46 h of impregnation) an equilibrium value at ~ 0.68 μmol m^{-2}. After impregnation, alumina was dissolved in a mixture of HF : $HClO_4$: HNO_3 and then the composition was determined by ICP-AES. There was a fair agreement between the palladium coverage estimated from the impregnation experiment and from ICP-AES analysis. The adsorption densities of $PdCl_4^{2-}$ on alumina obtained were close to those obtained by classic impregnation methods. The densities of $PdCl_4^{2-}$ on alumina range depending upon the condition of impregnation, between 0.8 and 1.2 μmol m^{-2} (Caillerie et al., 1995, Santhanam et al., 1994, Contescu & Vass, 1987).

The proton consumption in time during the impregnation of alumina with $PdCl_4^{2-}$ and adsorption density of $PdCl_4^{2-}$ is shown in Fig. 7 (a) and (b), respectively. As it can be seen in Fig. 7 (a), the proton consumption at pH 3.5 decreased progressively. This is same as in the case of proton-promoted dissolution of alumina. From the result shown in Fig. 7 (a), the rate of proton consumption was calculated to be ~ 0.206 μmol m^{-2} h^{-1}. This value roughly corresponds to ~ 5.8 protons for each Al^{3+} released into solution. For a longer impregnation time (t > 32 h), the rate of proton consumption decreased to ~ 0.108 μmol m^{-2} h^{-1} (Fig. 7 (a)). A simple calculation shows that 3.05 protons were consumed for the formation of one Al^{3+}. The amount of $PdCl_4^{2-}$ adsorbed on the alumina surface calculated from the decrease in palladium concentration in the impregnation solution, increased rapidly to 0.32μmol m^{-2} in the first 2 h of impregnation (Fig. 7 (b)). Then, the rate of adsorption of $PdCl_4^{2-}$ decreased to reach finally (after 46 h of impregnation) an equilibrium value at ~ 0.68 μmol m^{-2}.

In the first 2 h of impregnation, the quick adsorption of $PdCl_4^{2-}$ takes place parallel to alumina dissolution. As the surface of alumina became saturated in $PdCl_4^{2-}$, the rate of

palladium adsorption decreased below that of alumina dissolution. The amount of $PdCl_4^{2-}$ on alumina is limited by the (i) strong electric forces of adsorbed species and (ii) dissolution of alumina. However, it is clear that some amount of the adsorbed $PdCl_4^{2-}$ is detached together with Al^{3+} during the dissolution process. Therefore, it can be assumed that one important consequence of alumina dissolution, in addition to the effect of ionic strength, is the retardation of $PdCl_4^{2-}$ adsorption.

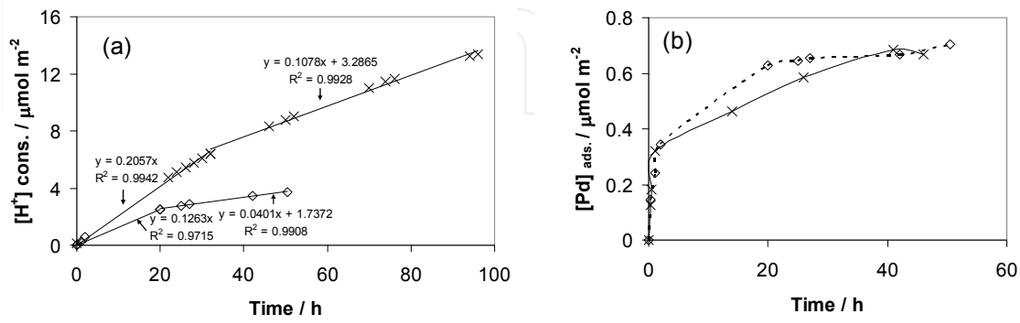


Fig. 7. Time course of (a) proton consumption and (b) adsorption density of $PdCl_4^{2-}$ on alumina, during the impregnation of γ-Al_2O_3 with $PdCl_4^{2-}$ at pH 3.5 (x) and pH 4 (◊).

To find out whether the proton consumption is affected by $PdCl_4^{2-}$ adsorption, the ratio between $[H^+]_{cons.}$ and $[Al^{3+}]_{sol.}$ is analyzed in Table 1. From Table 1, it is clear that $PdCl_4^{2-}$ does not promote alumina dissolution, because the rate between $[H^+]_{cons.}$ and $[Al^{3+}]_{sol.}$ remained practically constant (~ 4.2), regardless of whether $PdCl_4^{2-}$ was present or not in the solution. If $PdCl_4^{2-}$ would promote alumina dissolution, the proton consumption should decrease significantly in comparison to the amount of Al^{3+} formed. In practice, only the rate of alumina dissolution was affected by $PdCl_4^{2-}$. It is likely that one of the reasons for the retardation of $PdCl_4^{2-}$ adsorption is alumina dissolution.

$[H^+]_{cons.}/[Al^{3+}]_{sol.}$	experiment time/h	pH	system
3.99	72	3.5	$Al_2O_3 + H^+$
4.24	74	3.5	$Al_2O_3 + H^+ + PdCl_4^{2-}$
4.23	70	4.0	$Al_2O_3 + H^+$
4.19	50.5	4.0	$Al_2O_3 + H^+ + PdCl_4^{2-}$

Table 1. Influence of $PdCl_4^{2-}$ on $[H^+]_{cons.}/[Al^{3+}]_{sol.}$ ratio at pH 3.5 and 4

In the course of $PdCl_4^{2-}$ impregntion, three types of simultaneous process could be analyzed: (I) alumina dissolution, (II) proton consumption, and (III) adsorption density of $PdCl_4^{2-}$ on the surface of alumina. It was observed that some amount of support was mobilized in the liquid phase during impregnation. The amount of dissolved alumina depends on the pH of the solution as well as on the nature of the impregnating ion ($PdCl_4^{2-}$). It was demonstrated that the protons are consumed in two distinct processes, i.e., reversible adsorption of H^+ (Langmuir-type adsorption) and irreversible adsorption of H^+ (leading to dissolution of alumina). A clear distinction between the reversible and irreversible adsorbed proton has been made for the first time.

Alumina dissolution during impregnation may have significant consequences on the formation of the catalytic active phase. It is expected that aluminum ions, originating from

the support, will always be present in the catalytic phase (i.e., palladium phase), inducing the formation of lattice defects (Balint & Aika, 1997). Therefore, the aluminum presence in the palladium active phase should be taken into consideration in explaining the catalytic behavior in a chemical reaction.

3. Alumina as catalytic support

3.1 Effect of support on active site formation

Alumina is frequently used as a support for metal catalysts due to its high surface area and good thermal stability. However, as shown above, alumina can be dissolved during the process of impregnation. The dissolution of alumina is induced by adsorption of heavy metal ions. Then, dissolved aluminum species may be included in the newly formed phase on the surface of the support, which is the precursor of active site. It is highly possible that such contamination of active site by aluminum may have significant effect on catalyst performance. In order to assess the effect of possible aluminum inclusion in the active site, Ru/Al_2O_3 catalysts were prepared by two different methods; one is conventional impregnation and the other is metal colloid synthesis and supporting them onto alumina support (Miyazaki et al, 2001). Then, their performance in ammonia synthesis was compared (Balint & Miyazaki, 2007).

Ruthenium is known to have one of the highest catalytic activities for ammonia synthesis (Aika, 1994). Typically, the conventional Ru catalysts are prepared by impregnation of the

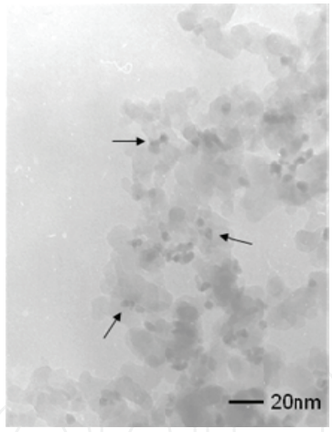


Fig. 8. TEM image of 6.3% Ru/Al_2O_3. Some typical Ru particles are indicated by arrows.

oxide support either with and aqueous solution of $RuCl_3 \cdot 3H_2O$ or with $Ru_3(CO)_{12}$ dissolved in tetrahydrofuran (Murata & Aika, 1992a, b). When catalysts are prepared by impregnation of alumina with $RuCl_3$, the metal particles, after drying, calcinations, and reduction, are not uniform in size and shape. It is well known that the catalytic activity of a supported metal is strongly related to the morphology of the particle, i.e., size and shape (Ahmadi, et al., 1996). However, the conventional preparation of catalysts, consisting of the impregnation of a support with an aqueous solution of a soluble metal precursor, makes it difficult to control the final size and shape of the supported metal particles. Additionally, it is highly possible that the support has a great influence on the catalytic activity of the metal when the catalyst is prepared by impregnation. An alternative method to obtain supported catalysts with well-defined metal particles is the preparation of supported catalysts from metal colloids.

The great advantage of the colloid method is that it provides relatively monodispersed metal particles. Moreover, it is shown that not only the particle size but also the crystal structure of the metal nanoparticles can be controlled to some extent by using appropriate structure-directing polymers for colloid preparation (Miyazaki, et al., 2000).
Ru colloid was prepared by reducing $RuCl_3 \cdot nH_2O$ in ethylene glycol. The average diameter of the particle measured by TEM was 5 nm. The colloid particles were supported on γ-Al_2O_3 (Aerosil) to realize the Ru loading of 6.3 wt%. Figure 8 shows the TEM image of Ru/Al_2O_3. EPMXA measurement proved that the black spots corresponded to ruthenium particles. It can be seen that the Ru particles was uniform in size and shape, and they were dispersed well on the surface of γ-Al_2O_3. The particle size of Ru obtained by TEM was 4.2 nm. This value agreed well with the values obtained by H_2 and CO chemisorption; 4.8 and 5.4 nm, respectively. It is noteworthy that by using colloid method, Ru particles can be supported without affecting the particle size and dispersion, even when the metal loading was increased up to 6.3%.

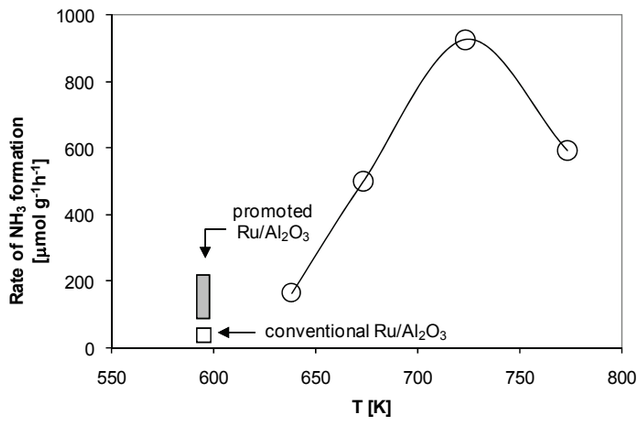


Fig. 9. Temperature dependence of the rate of ammonia synthesis over Ru/Al_2O_3 (6.3 wt%). The rates over conventional Ru/Al_2O_3 catalysts are also shown for comparison.

The catalytic activity of Ru/Al_2O_3 was measured for ammonia synthesis. The catalytic tests were performed at atmospheric pressure in a stainless steel reactor containing 0.4 g of 6.3 wt % Ru/Al_2O_3. Prior to the catalytic tests, the Ru/Al_2O_3 was pelletized, crushed, and then sieved. The fraction, from 335 to 1000 μm, was collected and loaded into the reactor. Before the test, the sample was reduced in H_2 flow at 550˚C for 2 h. The catalytic activity tests were carried out at a flow rate of the reaction mixture 60 cm^3/min STP (45 cm^3/min H_2 and 15 cm^3/min N_2). The rate of ammonia synthesis was measured in a 365 to 500˚C temperature range. The produced ammonia was trapped by $1 \cdot 10^{-3}$ mol/L solution of sulfuric acid, and the rate of ammonia formation was determined from the decrease in the conductivity of the solution.
The catalyst which was prepared by supporting the Ru colloid on γ-Al_2O_3 showed a remarkably high activity for ammonia synthesis. The reaction rates expressed as micromoles per gram-hour as a function of temperature are shown in Fig. 9. Figure 9 shows that the rate of ammonia synthesis over 6.3 wt% of Ru/Al_2O_3 increased progressively with an increase in temperature, reaching a maximum at 723 K. Above this temperature, the reaction is thermodynamically limited and therefore the overall rate decreased. The highest reaction rate of 923 μmol g^{-1} h^{-1} was observed at 723 K. The reproducibility at each reaction temperature was within the range of experimental error (± 25 μmol g^{-1} h^{-1}). Apparent activation energy of 76.9 kJ/mol was estimated, and this value agreed well with the previously published data. For

example, the apparent activation energies determined for promoted and nonpromoted Ru/Al_2O_3 catalysts range between 44 and 101 kJ/mol (Murata & Aika, 1992a,b).

From the above results there are two points that are worthy of note. One is the temperature of highest activity for ammonia synthesis. The highest activity of the conventional Ru/Al_2O_3 catalysts was observed at 315˚C (Murata & Aika, 1992), whereas the catalyst prepared from the Ru colloid had a maximum activity at a higher temperature, 450˚C (723 K). From industrial point of view, it is preferable for ammonia synthesis to have a catalyst that is more active at a lower temperature. Thermodynamically, the increase in temperature is not favourable for ammonia synthesis reaction. Therefore, it is of great interest to obtain the higher equilibrium conversions at lower temperatures.

The other point is that Ru/Al_2O_3 catalysts prepared from the Ru colloid showed unusually high activity although it was not promoted. The conventional Ru/Al_2O_3 catalysts are known to exhibit quite low activities for ammonia synthesis, and this has been attributed to the acidity of alumina. The addition of alkaline or lanthanide promoters was reported to be an effective way of enhancing the catalytic activity (Murata & Aika, 1992a). The highest catalytic activities of the promoted and nonpromoted Ru/Al_2O_3 catalysts prepared by conventional methods using $RuCl_3$ or $Ru_3(CO)_{12}$ as precursors together with the activity of the catalyst prepared from the Ru colloid are shown in Fig. 9. The reported activity of the nonpromoted conventional Ru/Al_2O_3 catalysts is very small, ranging from 10 to 60 μmol g^{-1} h^{-1}. It was reported that the nonpromoted catalysts prepared from $RuCl_3$ exhibited significantly lower activities as compared to those obtained from $Ru_3(CO)_{12}$.

The acidity of alumina has been considered to be the main reason for the low activity of the conventional Ru/Al_2O_3 catalysts for ammonia synthesis. The addition of alkaline (Cs, Rb, K) or rare earth (La, Ce, Sm) elements to Ru/Al_2O_3 leads to a significant increase in the catalytic activity (Murata & Aika, 1992b, Moggi, et al., 1995). Typically, the activity of the promoted Ru/Al_2O_3 catalysts ranges from 130 to 250 μmol g^{-1} h^{-1} (Fig. 9). The Ru/Al_2O_3 catalyst prepared from the Ru colloid showed a significantly higher activity than that from promoted catalysts. A notable exception is the K^+-promoted Ru/Al_2O_3 catalyst, prepared from $Ru_3(CO)_{12}$, whose catalytic activity for ammonia synthesis was reported to be 2470 μmol g^{-1} h^{-1} under conditions comparable to those shown in Fig. 9 (0.4 g catalyst, 60 ml min^{-1}) (Moggi, et al., 1995). However, the activity of the conventionally prepared Ru catalysts strongly depend on the conditions of preparations. Slight changes of the preparation variables result in significant changes in catalytic activity.

The differences observed between the Ru/Al_2O_3 catalysts prepared by the conventional impregnation methods and the catalyst obtained via colloid deposition raise problems regarding the role that supports play in the formation of catalytically active phases. In the former part of this chapter, we reported that the support (alumina) plays an essential role in the formation of the active phase(s) when the catalysts were prepared by the impregnation method. The impregnation process can be regarded as complex sequences of chemical reactions taking place at the solid (the support)-liquid (solution of the metal salt) interface. During the impregnation process, the metal particles, i.e., the active site of the catalysts, are contaminated more or less by the supports. In this case, the acid or base character of the supports plays an important role in determining the final catalyst activity. In contrast to the impregnation method, metal colloid deposition onto a support gives metal particles that are uncontaminated by the support. Therefore, the influence of the support on the metallic active phase is minimized. The Ru/Al_2O_3 catalyst prepared by Ru colloid, is supposed to have Ru nanoparticles that do not interact significantly with the support, and this should be the reason for the remarkably high catalytic activity demonstrated for ammonia synthesis.

3.2 Support as adsorbent

Nitrate and nitrite ions are one of the world's major pollutants of drinking-water resources. In order to remove nitrate and nitrite ions in drinking water, physicochemical methods (e.g. ion exchange, reverse osmosis, and electrodialysis) and biological denitration methods have been studied (Fanning, 2000). However, these methods have disadvantages, in that they are consuming, complex, and sometimes require costly post-treatment of the effluent. The catalytic reduction of nitrate and nitrite in the liquid phase with hydrogen over a solid catalyst has recently been confirmed to be a promising method for the treatment of drinking water (Corma, et al., 2004). The most widely used catalyst is Pd-Cu/Al_2O_3. On the other hand, the catalytic performance of the Pt-Cu/Al_2O_3 catalyst is comparable to that of Pd-Cu/Al_2O_3 (Gauthard, 2003). Alumina is a typical support used in this reaction. The reduction of nitrate is known to proceed in two reaction steps, i.e., reduction of nitrate to nitrite and further reduction of nitrite to N_2 (desired product) and/or NH_4^+ (byproduct). Epron et al., (2001) found that two metal components of the catalyst are active for distinct reasons. Less noble metals, such as Cu, are catalytically active for the reduction of nitrate to nitrite, whereas the nitrite is reduced on the surface of noble metals, i.e., Pd or Pt. However, the two reactions do not seem to be completely independent of each other. Gao et al., (2003) reported that the bimetallic Pd-Cu catalyst (especially in the case of Pd:Cu = 2:1 molar ratio) exhibits much higher activity for nitrite reduction compared with the monometallic palladium catalyst.

In studies of the catalytic reductions of nitrate and nitrite, the catalytic activity is generally calculated from the decrease in the concentration of nitrate or nitrite ions in the reaction solution. In practice, the nitrate and nitrite ions that disappear from the reaction solution are presumed to be converted to N_2 and NH_4^+, without taking the possibility of adsorption onto the catalyst into account. In fact, there is very little information regarding to the nitrate and/or nitrite adsorption onto alumina; however, there have been recent reports regarding such adsorption (Handa et al., 2001, Kney et al., 2004, Ebbesen, et al., 2008). If significant amounts of nitrate or nitrite ions are adsorbed onto an alumina support, then such adsorption phenomena should be taken into consideration when the catalytic activity of denitration is calculated, especially for batch experiments. Measurement of the actual catalytic activity for liquid phase reduction of nitrate is an important issue, due to the potential application of this method. Conversion over denitration catalyst must be significantly high to overcome the regulation limits, and this is one of the critical point that would allow or prevent practical applications. Therefore, it is necessary to evaluate the amounts of nitrate and nitrite ions removed from the reaction solution, not only by reaction, but also by adsorption. Therefore, adsorption of nitrite onto alumina and Pt/Al_2O_3 was focused (Miyazaki et al., 2009). Nitrite was selected because it is the reaction intermediate of the nitrate reduction reaction, and because its toxicity is higher than nitrate.

NO_2^- catalytic reduction experiments were performed in a four-neck flask. The necks were used for the Ar (inert gas) inlet, H_2 (reduction gas) inlet, and gas outlet, and for sampling of the liquid phase, respectively. One hundred and fifty milliliters of the 2 mmol/L $NaNO_2$ solution was stirred in a flask with a magnetic stirrer and the solution was kept at 25˚C using a water bath. γ-Al_2O_3 (Aerosil) or Pt/Al_2O_3 (0.3 g) was then added to the nitrite solution. Prior to the reduction, dissolved air in the suspension was removed by bubbling Ar gas for 20 min. H_2 gas was then bubbled into the solution with a flow rate of 10 min/min. Two milliliter aliquots of the reaction solution were sampled periodically and filtered immediately. The concentrations of NO_2^- and NH_4^+ ions in the solution were measured using a UV-vis spectrophotometer.

On the other hand, adsorption experiments were performed in the same manner as the reduction experiments, excepting H_2 flow. Ar gas was continuously bubbled in the suspension, so that no NO_2^- loss by reduction was presumed to occur, due to the absence of reductant H_2 gas.

A catalytic reduction experiment was performed using γ-Al_2O_3 without Pt in the presence and absence of H_2 flow. The concentration of NO_2^- decreased, even though there was no noble metal on the support (Fig. 10). In the catalytic reduction of nitrate, the reduction of nitrite by H_2 to N_2 and/or NH_4^+ is reported to take place on the surface of supported noble

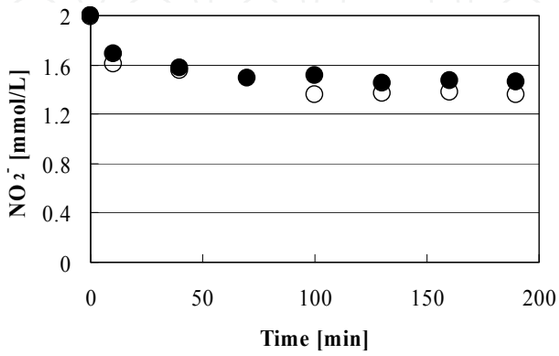


Fig. 10. Time course of nitrite concentration in the reacting solution. Experiment was performed with H_2 flow (●) and without H_2 flow (○).

metal particles. It is generally assumed that the catalytic activity can be ascribed only to the supported metal (i.e., Pd and Pt), and that the support (i.e., alumina, silica, carbon, etc.) is completely inert (Epron, 2002). Therefore, the decrease of NO_2^- in the presence of H_2 may not be due to catalytic conversion. To confirm this, the same experiment was performed without the reductant (H_2 gas). Interestingly, a decrease in NO_2^- concentration was also observed as shown in Fig. 10. In both cases, no formation of NH_4^+ (product) was observed. Thus, the decrease in NO_2^- concentration was not due to reduction, i.e., alumina was completely inert toward NO_2^- reduction. Therefore, the disappearance of NO_2^- is attributed to adsorption on alumina. The result showed that around 30% of the initial amount of NO_2^- was absorbed after 100 min of reaction time.

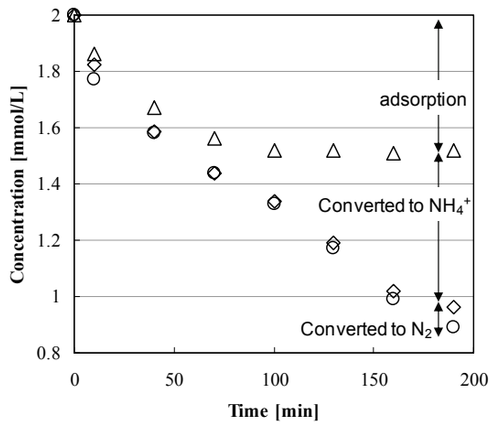


Fig. 11. 2 mmol/L $NaNO_2$ was reduced by H_2 gas on 0.1 wt% Pt/Al_2O_3 catalyst. The decrease of NO_2^- (○) was found to be caused by catalytic conversion to N_2 or NH_4^+, and by adsorption onto alumina (Δ).

Because a significant amount of NO_2^- was found to be adsorbed onto alumina, the adsorption experiment was performed using a 1 wt% Pt/Al_2O_3 catalyst, in order to determine whether the same adsorption phenomena occurred on Pt supported catalyst. Figure 11 shows the result of both the adsorption and reduction experiment on 1 wt% Pt/Al_2O_3 catalyst. The Pt/Al_2O_3 catalysts were prepared by impregnation using aqueous solution of K_2PtCl_4. The Pt/Al_2O_3 catalysts were pelletized, crushed, and then sieved. The fraction of powder with size from 335 to 1000 μm was collected. The adsorption experiment was carried out in the absence of H_2, whereas the catalytic reduction was performed under H_2 flow. The H_2 flow induces the reduction of NO_2^- over Pt; therefore, it is not possible to evaluate the amount of adsorbed NO_2^- under H_2 flow. In the absence of a H_2 flow, the concentration of NO_2^- was decreased with the 1wt% Pt/Al_2O_3 catalyst. The adsorption behaviour of NO_2^- onto 1wt% Pt/Al_2O_3 catalyst was similar to that on alumina without Pt. For both cases, the adsorption equilibrium was reached after 100 min of reaction time. As much as 24% of the NO_2^- was adsorbed on the 1wt% Pt/Al_2O_3 catalyst.

The calculation of NO_2^- conversion and selectivity to N_2 can be subjected to significant error if adsorption by the support is not taken into consideration. There are very few papers discussing the adsorption of NO_3^- or NO_2^- on the support, as well as possible influence of the supporting metal on the metal catalytic activity. If adsorption of NO_2^- onto the catalyst occurred during the reduction experiment, the actual amount of NO_2^- catalytically converted should be obtained as the difference between the amount of NO_2^- removed by catalytic reduction and by adsorption. According to this assumption, NO_2^- conversion with 1wt% Pt/Al_2O_3 was calculated to be 31.5% at 190 min, but 55.5% if adsorption is not considered. Adsorption of NO_2^- onto the catalyst has an even more dramatic effect on the selectivity to N_2 production. Generally, the catalytic reduction of NO_3^- and NO_2^- is monitored by analyzing the species in the liquid phase, i.e., by measuring the concentration of NO_3^-, NO_2^- and NH_4^+ ions in the reaction solution. In most cases, the gaseous products (i.e., N_2) are not quantitatively determined (Epron, 2001). If adsorption is not considered, then the selectivity to N_2 on 1wt% Pt/Al_2O_3 is calculated to be 49.5%, while the selectivity is only 11.1% if adsorption is taken into account. In the reduction experiment on 1wt% Pt/Al_2O_3, an attempt was made to detect gaseous N_2 by gas chromatography; however, the detectable amounts were negligible. The mass balance suggested that the decrease of NO_2^- in the reaction solution can be ascribed to either adsorption onto the catalyst or conversion to N_2 and NH_4^+.

NO_2^- adsorption on Pt/Al_2O_3 is of great practical importance, because Pt/Al_2O_3 is one of the most common catalysts used to reduce NO_2^- and NO_3^- in waste waters by reduction with H_2. Thus, it is necessary to make a clear distinction between the NO_2^- ions removed from a reaction solution by catalytic reaction (reduction) and those removed by adsorption. One the other hand, alumina has a possible application as NO_2^- scavenger in the treatment of waste water, due to its relatively high adsorption capacity for NO_2^- ions.

4. Conclusion

Two aspects of alumina, i.e., heavy metal adsorbent and catalysts support, were discussed and it was shown that they are closely related each other. Alumina is one of the most frequently used adsorbent to remove heavy metal ions from waste water. The adsorption process of heavy metal cations onto alumina is not a simple phenomenon but a complex process composed by three main steps, i.e., adsorption, desorption and re-sorption. The first adsorption step can be explained as surface complexation between heavy metal cation and

surface aluminol groups. However, the adsorbed heavy metal cations can be desorbed by accomplishing some surface coverage. It was shown that the formation of hydroxide of the heavy metal is the reason for this process. In the desorption process, alumina was found to be dissolved, too. Then, in the third step, aluminium ions dissolved from alumina may coprecipitate with desorbed heavy metal cations. Alumina dissolution was proved to be induced not only heavy metal cations (Zn^{2+} and Cu^{2+}), but also anions, $PdCl_4^{2-}$ in acid pH range.

Alumina dissolution induced by heavy metal adsorption must have significant impact for heavy metal behaviour in natural aquatic systems and catalyst active site formation. Actually, Ru/Al_2O_3 catalysts prepared by impregnation and colloid showed quite different activity for ammonia synthesis. The difference must be caused by the composition of active site. In the case of colloid, ruthenium particles do not contain aluminium, but the active site of the catalyst prepared by impregnation must include aluminium, which was dissolved in the process of impregnation. On the other hand, alumina used as catalyst support can play a role of adsorbent, too. When NO_2^- was reduced on the surface of Pt/Al_2O_3 catalyst, significant amount of NO_2^- was found to be adsorbed on the support. Thus, in order to adequately evaluate conversion and selectivity of the catalyst, it is necessary to take into account the adsorption.

The two different aspect of alumina, i.e., adsorbent and support, are closely related to each other and both are quite important for waste water treatment. Therefore, in near future, it is very necessary to study the relation between these two roles of alumina and apply it to waste water treatment.

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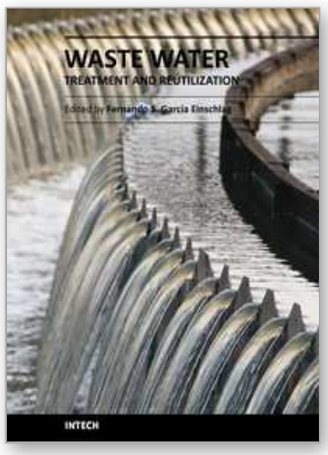
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