Alumina Dissolution Promoted by CuSO₄ Precipitation

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The impregnation of γ-Al₂O₃ with CuSO₄ at 50 °C was investigated at pH 9 and 7 using a dialysis membrane reactor. It was observed that alumina is not inert at pH values close to its isoelectric point when impregnated with CuSO₄. Although the alumina was kept in a membrane bag, the presence of aluminum ions in the copper precipitate, which was formed outside of the membrane bag at pH 9 and 7, was detected by ICP, XRD, XRF, and SEM–EDAX. The molar ratios of Cu to Al in the precipitate formed at pH 9 and 7 were 80.8 and 222, respectively. The total amounts of alumina dissolved at pH 9 (after 240 h) and 7 (after 336 h) were 2.21 mg and 0.51 mg, respectively. It was observed that aluminum ions deriving from the support prefer to accumulate in the copper basic sulfate phase rather than in the CuO (Cu(OH)₂) phase. The dialysis and XANES experiments proved that Cu(OH)₂ is mainly responsible for the alumina dissolution at pH 9. On the other hand, copper basic sulfate, which is the main compound formed at pH 7, was found to be less active in alumina dissolution. It was suggested that the presence of aluminum ions in the copper compound phase may influence the active sites formation of the catalyst by inducing the formation of lattice defects.

Introduction

Copper catalysts supported on alumina are of great interest for many important reactions, including methanol synthesis,[1] steam reforming of methanol,[2] selective reduction of NO$_x$, and adsorption of SO₂.[3] Such catalysts are generally prepared by impregnation of alumina with various precursors.

The impregnation step has been reported to have an essential role for the formation of active sites.[4] 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 attempt to reveal the relationship between the catalyst's preparation and its final activity.[5]

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 precursors but also the supports can contribute to active site formation.[6] Recently, Clauss et al.[7,8] found that alumina, which had been thought to be inert at pH values close to its point of zero charge (PZC), dissolved when it was put in contact with cobalt and nickel compounds. The long time interaction between metal ions and support at pH values close to neutral may lead to the formation of a second phase that contains aluminum originating from the support.

In this paper, we studied the processes associated with the impregnation of aluminum with CuSO₄ at 50 °C and at pH values close to pH$_{ZPC}$. We analyzed the relationship between the pH value of impregnation, the aluminum content of the newly formed phase(s) and the extent of the alumina dissolution. The support participation in the active site formation of catalysts was also discussed.

Methods

Experimental System. All the impregnation experiments were performed with the system shown in Figure 1. The experimental system was designed in reference to the work of Clauss et al.[7] As shown in Figure 1, the experimental system was composed of two parts, and they were separated from each other by a dialysis membrane (Wako/Wiscase Sales Corp., MWCO 12000–14000; pore diameter 25 Å). The tubular shape membrane was closed tightly with a Teflon cap and two Teflon rings. In the following, the membrane tube part will be called "bag", and the two parts of the reactor will be called the inside and outside of the bag. The support, alumina, was placed

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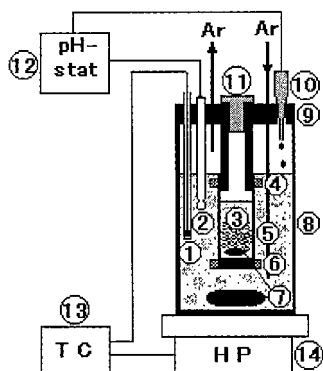(8) Caillerie, J. B. E.; Kermarec, M.; Clause, O. *J. Am. Chem. Soc.* **1995**, *117*, 11471.

Figure 1. Experimental system used for the study of alumina impregnation with $CuSO_4$: (**1**) glass shielded thermocouple; (**2**) pH electrode; (**3**) γ-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.

inside of the bag, and a solution that contains copper ions was placed outside of the bag. Using this system, made it possible to separate the new phase(s), which were to be formed, from the support. In this experimental arrangement, the alumina cannot pass through the membrane, while the ions and the small particles of the newly formed phase can do so. The sealing of the bag was checked by blank experiments at 50 °C using distilled water. Even after 72 h into the experiment, we could not detect aluminum in the solution outside the bag.

During the experiment, the pH value of the solution outside of the bag was monitored with a pH electrode (TOA) and maintained constant (±0.02 pH units) at an adequate pH value with a pH-stat (TOA model AUT-211). The temperature of the system was kept constant at 50 °C. Accurate temperature control of the solution (±0.5 °C) was performed by inserting a temperature controller (Shimazu SR 22) in the heating circuit of a hot plate provided with a magnetic stirrer (Iwaki Glass, PC-351). The temperature was measured with a k-type thermocouple (shielded with a glass tube) placed in the solution. The Teflon-coated magnetic stirring rods, located inside and outside of the bag, minimized the temperature gradients along the vertical axes and maximized the contact surface of the alumina with the liquid phase. The system was purged slowly (3.6 L/h) with argon gas.

General Experimental Procedure. The standard experimental procedure will be described in the following. Any departure from it will be noted in the results section.

A 1 g sample of γ-Al_2O_3 was loaded inside of the membrane bag with 12 mL of 0.1 M K_2SO_4 solution and then sealed tightly from the bulk solution with two Teflon rings. The γ-Al_2O_3 (supplied by Aerosil) 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 experiments was determined to be 8.0 by a mass titration method.[9] Therefore, the impregnation experiments were conducted around the pH_{ZPC}, at pH 7 and 9.

A 250 mL aliquot of a 0.1 M K_2SO_4 solution was poured into a glass beaker, and the membrane bag containing alumina was hung in the beaker. The alumina was equilibrated overnight, with the pH kept constant at 7 or 9 by adding 0.1 M KOH at 50 °C. The concentration of KOH (Fluka, assay 87%) solution was determined by titration with 0.05 M of oxalic acid (Wako) using phenolphthalein as an indicator.

A peristaltic pump was then used to gradually add 3 mL of a 1 M $CuSO_4$ solution to the solution outside of the bag. The $CuSO_4$ aqueous solution was prepared from $CuSO_4 \cdot 5H_2O$ (Wako, assay min. 99.5%). During the impregnation experi-

ment, aliquots of 2 mL were sampled periodically from the solution outside of the bag. The impregnation experiments lasted from 48 h to 336 h. 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.

Analysis. The composition of the solution collected at several time intervals was determined by ICP (Inductively Coupled Plasma Spectroscopy, Seiko SPS 4000). The standard solutions for ICP calibration (Cu and Al) were supplied by Wako. The precipitates obtained outside of the bag and the alumina were analyzed by several methods: X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM−EDAX), and XANES (X-ray adsorption near edge structure).

The X-ray powder diffraction analysis (Cu Kα radiation) was carried out with a Rigaku Geiger Flex RAD-B diffractometer provided with peak assignment software.

The XRF spectra were recorded at room temperature in a vacuum using an SII−Seiko Instruments SEA 2001 L-type apparatus.

The XANES measurements were made with synchrotron radiation using a Si(111) channel-cut monochromator at the beam line 7C of the Photon Factory (PF) at Tsukuba. All the samples were analyzed in the fluorescence detection mode at room temperature. The incident X-ray intensity was measured with a 17 cm-long ionization chamber filled with N_2. For fluorescence detection, a wide-angle collector with an ionization chamber, a Lytle detector (EXAFS Co.), was used after being filled with Ar for Cu Kα.

The standard samples for XANES measurements were prepared as follows.

(a) The $Cu(OH)_2$, was prepared from $CuSO_4$ solution (0.1 M) by adding appropriate amounts of ammonia solution (25%) and then 1 M KOH solution.[10] The $Cu(OH)_2$ precipitate was washed several times with distilled water.

(b) The $[Cu(NH_3)_4]SO_4 \cdot H_2O$ was prepared by adding ammonia solution (25%) in excess to $CuSO_4$ solution (0.1 M) until the color turned blue-violet. Then C_2H_5OH was added in order to obtain a precipitation of $[Cu(NH_3)_4]SO_4 \cdot H_2O$.[10] The crystalline, blue-violet precipitate was filtered and washed several times with C_2H_5OH.

(c) $3Cu(OH)_2 \cdot CuSO_4$ was prepared from $Cu(OH)_2$ (the preparation of $Cu(OH)_2$ is described in part a) by adding $CuSO_4$ (0.1 M). The green precipitate formed ($3Cu(OH)_2 \cdot CuSO_4$) was filtered and washed several times with distilled water.

The copper oxide was prepared by $Cu(OH)_2$ decomposition at 600 °C for 4 h.

Results and Discussion

Alumina Impregnation with $CuSO_4$ at pH 9. First of all, alumina was impregnated with $CuSO_4$ at pH 9, slightly higher than pH_{ZPC}. While $CuSO_4$ was added to the system at the beginning of the impregnation experiment, a blue-green color precipitate was formed outside of the bag. Then the color progressively became darker, and after 240 h (10 days) the precipitate was black. At the end of the experiment, 0.306 g of precipitate was obtained outside of the bag. Beside the main component, copper (67.68 wt % Cu), the precipitate was found to contain a small amount of aluminum (0.355 wt % Al). The calculated molar ratio of Cu to Al in the precipitate was 80.8. Moreover, a small amount of aluminum (0.08 mg) was found in the filtrate, too. The aluminum presence in the precipitate and the filtrate is consistent with the alumina dissolution. The total amount of

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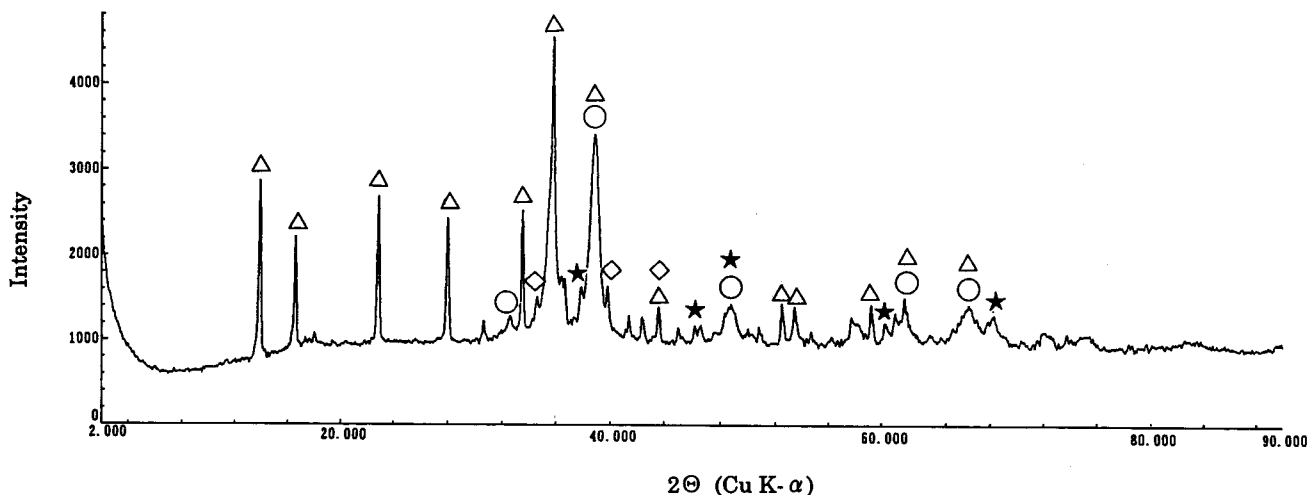
Figure 2. XRD pattern of the precipitate formed outside the bag at pH 9: ($\triangle$) $3Cu(OH)_2 \cdot CuSO_4$; ($\bigcirc$) CuO; ($\star$) Al_2O_3; ($\diamondsuit$) $Cu(OH)_2$.

Table 1. Elementary Composition of the Alumina Inside the Bag after 224 h of Reaction at pH 9 As Estimated by XRF

sample	composition, wt %				
	Al	Cl	S	K	Cu
alumina	86.76	1.80	3.91	6.99	0.52

Table 2. Averaged and Local Compositions of the Precipitate Obtained at pH 9 As Estimated by EDAX

region	Cu (wt %)	Al (wt %)	S (wt %)
average	98.09	0.9	1.01
Region I	98.96	0.79	0.25
region II	99.38	0.51	0.11

alumina dissolved within 240 h of impregnation was 2.21 mg. Copper was not detected in the filtrate.

After 240 h of reaction, the alumina inside of the bag had a light blue color. The alumina was dissolved in a mixture of HF:HClO:HNO, and then the composition was determined by ICP. The determined copper loading of the alumina was 0.1 wt %. This means that some of the added copper diffused through the membrane and adsorbed on the alumina surface. The composition of the alumina was estimated by XRF and listed in Table 1. The presence of a significant amount of chlorine may be explained by the preparation method of the alumina used in this experiment (flame-hydrolysis of $AlCl_3$). The XRF method has limitations at low concentration. This explains the differences observed between the ICP results (0.1% Cu) and the XRF result (0.52% Cu).

To confirm the copper-promoting effect on alumina dissolution, a blank experiment was performed under the same conditions (50 °C, pH 9) but without addition of $CuSO_4$. Neither the formation of precipitate nor the release of aluminum ions into the solution outside the bag was observed, even after 220 h of reaction. The blank experiment confirmed that the alumina dissolution at pH 9 is related to the presence of $CuSO_4$. Therefore, we assumed that a certain copper compound-(s) adsorbed onto the alumina promotes the dissolution of the alumina.

The XRD pattern of the precipitate formed outside of the bag is presented in Figure 2. It can be seen that the main components of the precipitate formed at pH 9 are 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. As we can see in Figure 2, some of the reflection peaks for Al_2O_3 are broad, due to its low crystallinity.

The precipitate formed outside of the bag was observed by SEM–EDAX. The average composition obtained by EDAX was in agreement with that obtained

by ICP after dissolution of the precipitate. However, the precipitate is not homogeneous according to EDAX measurement. As shown in Table 2, the precipitate consists of two phases: one contains a relatively high amount of aluminum (0.79 wt %), and the other has lower aluminum content (0.51 wt %). The higher aluminum phase also had higher S (SO_4^{2-}) content. According to the XRD data (Figure 2), these two regions of the precipitate should correspond to $3Cu(OH)_2 \cdot CuSO_4$ and CuO. The nonuniform distribution of aluminum in the precipitate may be explained by the difference in the affinity of aluminum ions to these two phases. It can be said that copper basic sulfate, $3Cu(OH)_2 \cdot CuSO_4$, has a higher affinity to aluminum than copper oxide, CuO. This difference in affinity will be discussed later in detail.

The alumina inside of the bag was also analyzed by XRD (the spectrum is not presented here). Broad reflections were observed, but it was not possible to ascertain whether they were due to CuO or $3Cu(OH)_2 \cdot CuSO_4$.

Alumina Impregnation with CuSO4 at pH 7. A similar experiment was conducted at pH 7, slightly lower than pH_{ZPC}. The experiment lasted for 336 h. As $CuSO_4$ was slowly added, a green precipitate formed outside of the bag. At the end of experiment, a small amount of aluminum (0.101 wt %) was detected again in the precipitate along with the main component of Cu (52.855 wt %). 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). In the filtrate, the presence of aluminum or copper could not be detected. The total amount of alumina dissolved in 336 h was 0.51 mg, only 23% of the amount of alumina dissolved at pH 9 (2.21 mg).

The alumina inside of the bag had smaller copper loading (0.054 wt % Cu) than that obtained at pH 9 (0.1% Cu). The composition of the alumina inside of the bag and the precipitate outside of the bag was deter-
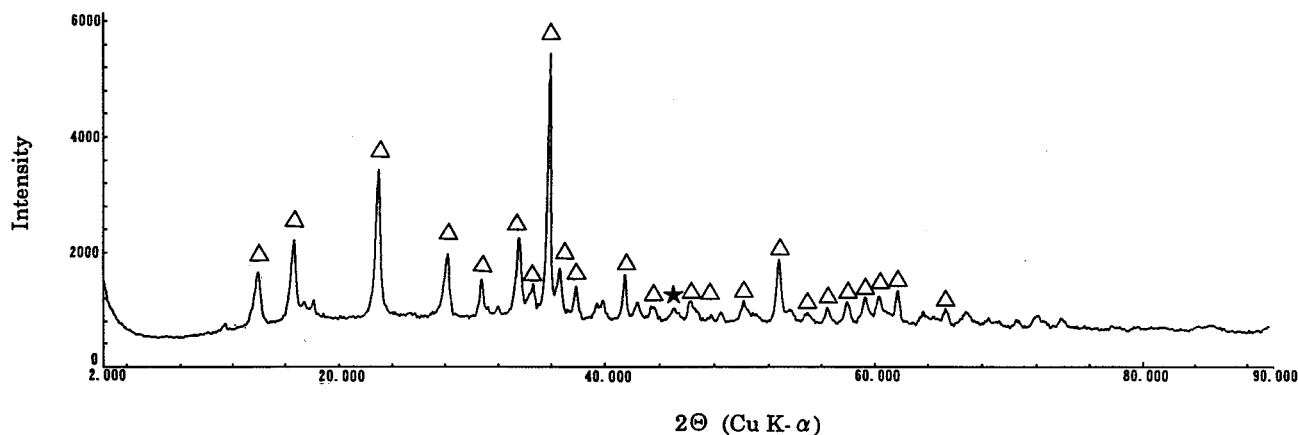
Figure 3. XRD pattern of the precipitate formed outside the bag at pH 7: (△) $3Cu(OH)_2 \cdot CuSO_4$; (★) Al_2O_3.

Table 3. Elementary Composition of the Alumina Inside the Bag and the Precipitate Formed outside the Bag at pH 7 after 336 h of Reaction as Estimated by XRF

	composition, wt %				
sample	Al	Cl	S	K	Cu
alumina	44.54	1.97	19.95	33.38	0.15
precipitate			10.651		89.35

mined by XRF, too. The results are presented in Table 3. The difference between the copper loading determined by XRF (0.15%) and ICP (0.05%) could be explained by the difference in the detection limits of these two methods.

The XRD pattern of the precipitate formed outside of the bag is shown in Figure 3. The well-crystallized copper basic sulfate, $3Cu(OH)_2 \cdot CuSO_4$, was identified as the main component of the precipitate. Other small peaks were assigned to $Cu(OH)_2$ and Al_2O_3.

Alumina Dissolution Promoted by Cu(OH)2. From the impregnation experiments conducted at pH 7 and 9, it is clear that $CuSO_4$ promotes alumina dissolution at a pH value near to pH_{ZPC}. To reveal the mechanism of this phenomena, we assumed $Cu(OH)_2$ and $3Cu(OH)_2 \cdot CuSO_4$ to be the main promoters of alumina dissolution, an assumption based on the composition of the precipitate 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.[10] Heavy metal sulfates are known to stabilize $Cu(OH)_2$ as a basic sulfate. First, the interaction of copper hydroxide with the alumina was examined in order to assess its activity in alumina dissolution.

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 (10^{-3} mol) of wet $Cu(OH)_2$ was added to the alumina inside of the bag. The $Cu(OH)_2$ was prepared as follows. First, 2 mL of 1 M KOH solution was added slowly to 1 mL of 1 M $CuSO_4$ solution at room temperature with constant stirring. Then the light blue precipitate ($Cu(OH)_2$) obtained was washed several times with distilled water and mixed with alumina quickly in order to avoid hydroxide decomposition. The experiment lasted for 74 h.

The concentration of aluminum released in the solution outside of the bag increased progressively over time (Figure 4). Figure 4 shows that the aluminum concentration in the solution was 3.3 ppm at the end of the
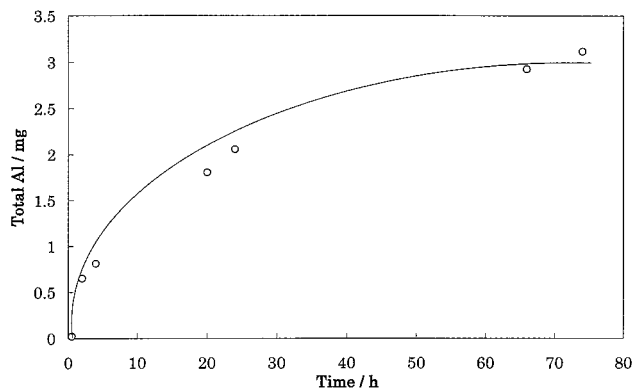

Figure 4. Aluminum ion release in the solution outside the bag during $Cu(OH)_2$ interaction with alumina.

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 $Cu(OH)_2$ does not decompose (at pH 9 and 50 °C) when it is 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 ~1.66×10^{-5} mol $Cu \cdot m^{-2}$. This value is almost completely in agreement with the values reported by Dumas et al.:[11] 3.3×10^{-6} mol $Cu \cdot m^{-2}$ in a basic medium and 0.7×10^{-5} mol $Cu \cdot m^{-2}$ in an acidic medium.

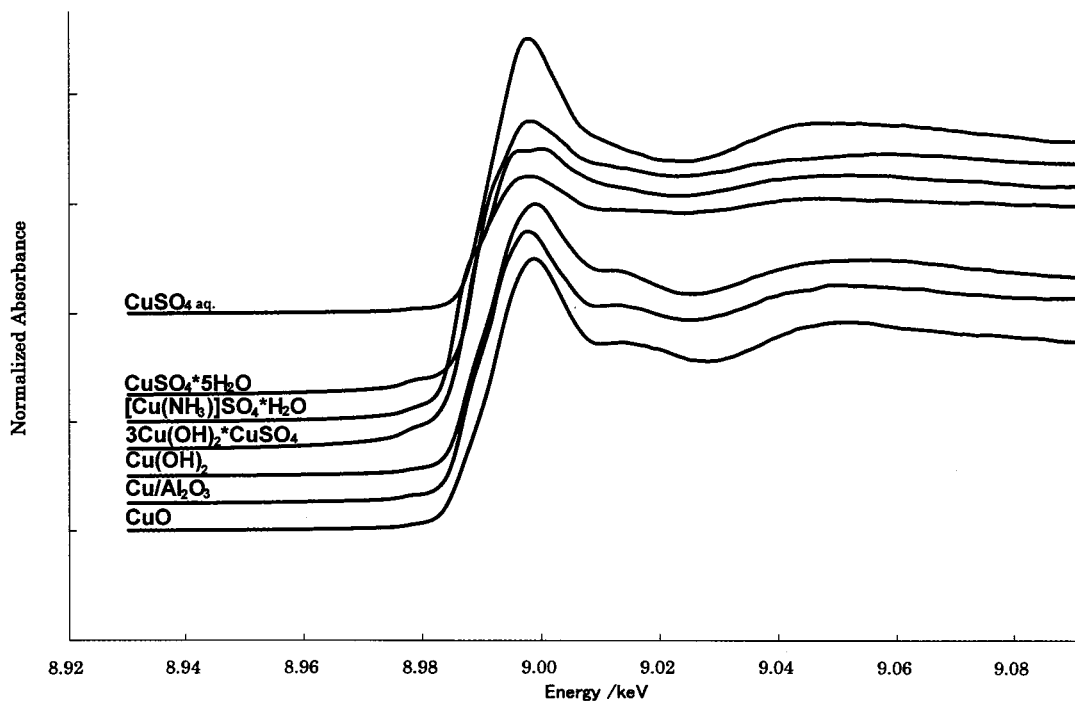(11) Dumas, J. M.; Geron, C.; Kribbi, A.; Barbier, J. *Appl. Catal.* **1989**, *47*, L9.

Figure 5. Normalized XANES spectra of copper adsorbed on alumina at pH 9 (Cu/Al_2O_3) compared to those for the model compounds selected.

The XANES method was used to investigate the chemical state of the copper on the alumina surface. The XANES spectra of the alumina impregnated with $CuSO_4$ at pH 9 was measured together with five reference compounds: $Cu(OH)_2$, CuO, $3Cu(OH)_2 \cdot CuSO_4$, $[Cu(NH_3)]SO_4 \cdot H_2O$, and an aquatic solution of $CuSO_4$,

The XANES spectra shown in Figure 5 suggest that the chemical state of copper on the alumina has features in common with $Cu(OH)_2$ and CuO. In Figure 5, we can observe that the spectra for copper adsorbed on alumina (Cu/Al_2O_3) lies between those of CuO and $Cu(OH)_2$. This may suggest that the hydrogen atoms of $Cu(OH)_2$ bond directly to the oxygen atoms of alumina, the copper first coordination shell becomes poorer in hydrogen, and the copper state approaches ever closer to CuO as a consequence of hydrogen (hydroxyl) displacement toward the alumina surface.
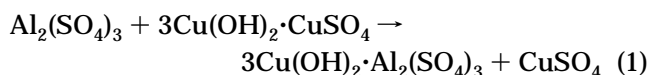
Alumina Interaction with Copper Basic Sulfate. From the above experiment, $Cu(OH)_2$ was found to promote the dissolution of alumina at pH values close to $pH_{ZPC.}$ Another possibility is that copper basic sulfate, $3Cu(OH)_2 \cdot CuSO_4$, may also promote alumina dissolution. A small amount of aluminum was identified in the precipitate formed by impregnation at pH 7, and the main component of the precipitate was copper basic sulfate. Therefore, the ability of $3Cu(OH)_2 \cdot CuSO_4$ to promote alumina dissolution was investigated in an additional experiment.

A 0.204 g (2×10^{-3} mol) of the 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.

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 possibility 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 dissolu-

tion are trapped by the $3Cu(OH)_2 \cdot CuSO_4$ phase and cannot diffuse outside the bag. The second 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 M $Al_2(SO_4)_3$ 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% Al and 32.27% 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:

$$Al_2(SO_4)_3 + 3Cu(OH)_2 \cdot CuSO_4 \rightarrow$$
$$3Cu(OH)_2 \cdot Al_2(SO_4)_3 + CuSO_4 \quad (1)$$

This result shows clearly 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 alumina 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 $3Cu(OH)_2 \cdot Al_2(SO_4)_3$.

As we saw in Tables 1 and 2, the precipitates formed during alumina impregnation with $CuSO_4$ at pH 7 and 9 contained significantly different amounts of aluminum. The precipitate formed at pH 9, whose main components were CuO and $3Cu(OH)_2 \cdot CuSO_4$, had a higher aluminum content than the precipitate formed at pH 7, whose main component was $3Cu(OH)_2 \cdot CuSO_4$. This result can be explained by the higher affinity of aluminum to $3Cu(OH)_2$ than to $3Cu(OH)_2 \cdot CuSO_4$.

Reactions Associated with Impregnation of Alumina with $CuSO_4$. In conclusion, the processes that occur during alumina impregnation with $CuSO_4$ may be explained as follows.
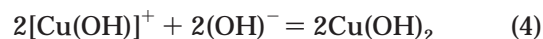
First, copper ions outside of the bag diffuse into the bag and precipitate on the surface of the alumina as $Cu(OH)_2$ and/or $3Cu(OH)_2 \cdot CuSO_4$. Then the $Cu(OH)_2$ precipitate strongly adsorbs on the surface of the alumina and promote alumina dissolution. The aluminum ions released from the alumina 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 is too high to be taken up completely by the precipitate. Therefore, the presence of aluminum was detected in the solution, too.

It was found that $3Cu(OH)_2 \cdot CuSO_4$ has a lower activity in dissolving alumina than does $Cu(OH)_2$, due to weaker interaction with alumina. To some extent the strong adsorption of $Cu(OH)_2$ on alumina can be compared to stabilization of $Cu(OH)_2$ by heavy metals in basic sulfates.

Our blank experiment showed that γ-alumina is inert in the pH range 7–9. The alumina was mobilized in solution only when $CuSO_4$ was added slowly at a constant pH (7 or 9), and a copper precipitate was formed. Additional experiments, which are not described in this paper, showed that the addition of $CuSO_4$ to a slightly acidic medium (pH 5.5–6) did not promote alumina dissolution. It therefore follows that near pHzpc the Cu^{2+}, SO_4^{2-}, OH^-, or H^+ ions are not directly promoting alumina dissolution. The activity of the copper compounds formed at pH 7–9 (copper basic sulfate and $Cu(OH)_2$) in alumina dissolution was checked in separate experiments, as described in detail in this paper. Surprisingly, when mixed directly with alumina, $Cu(OH)_2$ showed remarkable activity in alumina dissolution (Figure 4), while copper basic sulfate had considerably lower activity. These facts are in perfect agreement with the experimental results obtained for alumina impregnation at pH 7 and 9; i.e., the low amount of alumina dissolved at pH 7 is due to the low dissolving activity of copper basic sulfate, which is the main component of the precipitate formed at pH 7. At pH 9, where $CuSO_4$ precipitates as a mixture of $Cu(OH)_2$ (partially decomposed to CuO) and copper basic sulfate, the amount of aluminum found in the precipitate as well as in the solution (outside the bag) is significant. The experimental results presented in this paper are strong evidence that $Cu(OH)_2$ is remarkably active in alumina dissolution.

As for the mechanism of alumina dissolution by $Cu(OH)_2$, it does not seem likely that this is attributable to the weakening of Al–O bonds by proton loss from hydroxyl groups of $Cu(OH)_2$. If there is proton consumption (at pH 7 or 9), the same amount of protons should be supplied to the system by the pH-stat to keep the pH constant. In fact, we observed OH^- consumption over time ranging between 1 and 2 for every aluminum ion mobilized from the alumina.

At the present stage, the mechanism of alumina dissolution by $Cu(OH)_2$ is still unclear. We assume that the adsorption of $Cu(OH)_2$ on alumina gives rise to a high local concentration of hydroxyl, and this, in turn, dissolves the alumina by the following mechanism:

$$2Cu(OH)_2 = 2[Cu(OH)]^+ + 2(OH)^- \qquad (2)$$

$$Al_2O_3 + 2(OH)^- + 3H_2O = 2Al(OH)_4^- \qquad (3)$$

$$2[Cu(OH)]^+ + 2(OH)^- = 2Cu(OH)_2 \qquad (4)$$

The $Cu(OH)_2$ adsorbed on the alumina surface undergoes a partial dehydroxylation (eq 2), a process also revealed by XANES spectra (partial dehydroxylation of $Cu(OH)_2$). The high local concentration of hydroxyl groups on alumina surface gives rise to a synergetic effect and brings on the alumina dissolution (eq 3). The copper hydroxide is regenerated by OH^- groups (from KOH) present in the solution.

In reality, the processes which occur during alumina impregnation are likely to be more complex than depicted by eqs 2–4. It is clear that $Cu(OH)_2$ has strong interaction with alumina (see the XANES spectra shown in Figure 5). This is the reason that we considered $Cu(OH)_2$ to be the source of the OH^- which weakens Al–O bonds. In fact, it is well-known that at high pH values alumina reacts with OH^- to form aluminates, and this is another reason for the mechanism proposed in this paper. The nature and structure of aluminates is a problem, but in light of the experimental conditions, we assume that the main species is a polymer with octahedral Al and OH bridges or tetrahedral $Al(OH)_4^-$ ions.[12] The $(Al)_n$-$(OH)_m$ polymer removed from the alumina surface should be smaller than 25 Å (the diameter of the membrane pore) to diffuse through the dialysis membrane. Then the $(Al)_n(OH)_m$ units are embedded in the copper precipitate. Only a small amount of free aluminum was identified in solution after the impregnation experiment at pH 9. We could not identify a constant ratio between Cu and Al in the precipitate. Further RMN and EXAFS experiments may give more information about the local structure of Al in the copper precipitate and clarify the mechanism of alumina dissolution.

The experimental results demonstrate that the impregnation step in catalyst preparation can be thought of as a complex chemical reaction between a solid (the support) and a metal compound (precursor). 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 (precursor) during the impregnation step.

The presence of the ions dissolved from the support may have an important effect on the formation of active sites 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.[13] 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.

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(13) Balint, I.; Aika, K. *J. Chem. Soc.: Faraday Trans.* **1997**, *93*, 1797.