Oxidative Dimerization of 1-Propyne on a 2-Pyridylethyl Copper Complex Fixed Silica Catalyst

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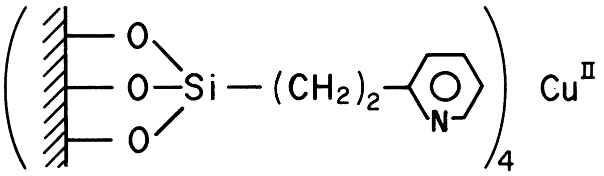
Synopsis. A 2-pyridylethyl copper complex fixed silica catalyst was applied to an oxidative-coupling dimerization reaction of 1-propyne to 2,4-hexadiyne at 100 °C, which is a typical test reaction for Cu-(N base)-complex catalyst in the homogeneous phase. It was found to be highly catalytically active for this reaction compared with a conventional CuO/SiO_2 catalyst. The reaction was deduced to proceed through a redox cycle of copper ions coordinated with the pyridine derivative.

In the presence of pyridine, CuCl has proved to be catalytically active for homogeneous oxidative-coupling reactions of acetylenes,1) aromatic amines,2) or phenols.3) In a previous paper we reported the preparation and spectroscopic characterization of a novel silica-fixed copper catalyst, in which each copper ion is coordinated with four pyridine moietyies of 2-pyridylethyl group fixed on silica as:



and which was denoted as $Cu-Py-SiO_2$. Such copper ions were also subject to an easy reversible redox reaction under vacuum at 200 °C or with molecular oxygen.4)

The present paper is concerned with the application of this catalyst to a heterogeneous oxidative-coupling reaction of 1-propyne, which is a typical test reaction for a Cu-(N base)-complex catalyst in the homogeneous phase, and gives a comparison of its catalytic nature with that of a conventional CuO/SiO_2 catalyst.

Experimental

The $Cu-Py-SiO_2$ catalyst (1.3 wt% of Cu) was prepared and characterized spectroscopically as described in a previous paper.4) It was used after outgassing at 200 °C for 1 h and successive activation under an O_2 atmosphere at room temperature for 24 h. For a comparison, a conventional silica-supported copper catalyst (2.6 wt% of Cu) was used, which was prepared from a tetraamminecopper complex ($[Cu^{II}(NH_3)_4]$) by an ion-exchange method, and calcined with O_2 at 300 °C.5)

A conventional closed recirculating reactor (0.7 l volume) was employed for the catalytic oxidative-coupling reaction of 1-propyne. The partial pressure of 1-propyne, O_2 or CO_2 was monitored with an on-line gas chromatograph. Analysis of the reaction product, 2,4-hexadiyne, was carried out with a Hitachi RMU-6 mass spectrometer.

The states of copper ions were monitored using an ESR or XANES (X-Ray Absorption Near-Edge Structure) spectroscopic technique. ESR spectra were obtained with a Varian E-4 spectrometer at a frequency of 9 GHz. The g-values were calculated relative to DPPH as a standard (g=2.0036). XANES spectra were measured in the transmission mode at the BL10B station of the photon Factory using sychrotron radiation from the 2.5 GeV electron storage ring.6)

The O_2 or 1-propyne gas was of high-purity grade from Takachiho Kagaku Kogyo and was used without further purification.

Results and Discussion

Figure 1A shows the time course of the reaction between 1-propyne and O_2 on $Cu-Py-SiO_2$ at 100 °C. Each reactant decreased monotonously at a ratio of 4–1, respectively, indicating that this reaction proceeded catalytically within the reaction times. The 2,4-hexadiyne has found by mass spectroscopy to be

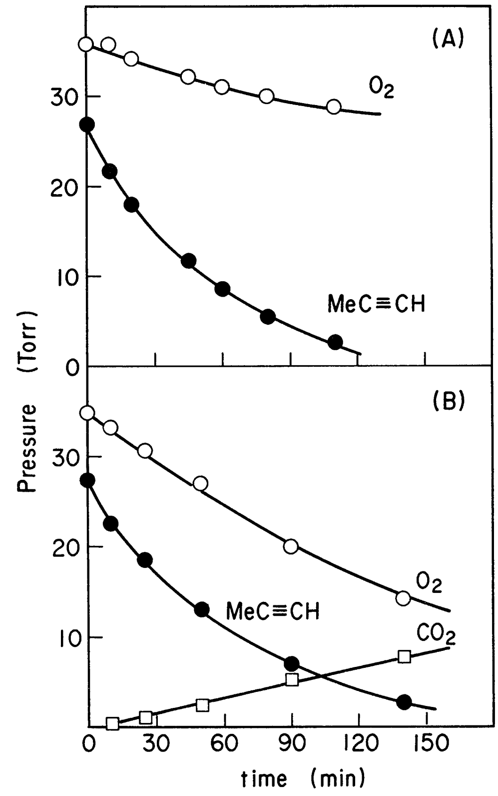


Fig. 1. Time course of reaction between 1-propyne and oxygen. (A) $Cu-Py-SiO_2$ at 100°C; (●): 1-propyne; (○): O_2, (B) CuO/SiO_2 at 200°C; (●): 1-propyne; (○): O_2; (□): CO_2.

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the main product derived from the dimerization of 1-propyne, though its amount could not be followed quantitatively because of its low vapor pressure. Neither CO_2 nor CO was detected. Therefore, the following reaction stoichiometry can be proposed:

$$2\ CH_3\text{-}C{\equiv}C\text{-}H + 1/2\ O_2 \longrightarrow CH_3\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_3 + H_2O. \qquad (1)$$

The activity of the CuO/SiO_2 catalyst, on the other hand, was too low to follow the reaction at 100 °C, indicating that $Cu\text{-}Py\text{-}SiO_2$ is specifically effective for this reaction. Fig. 1B shows the time course at 200 °C on CuO/SiO_2. As can be seen from these results, the kinetic behavior was different from that on $Cu\text{-}Py\text{-}SiO_2$. CO_2 was detected as one of the reaction products in addition to 2,4-hexadiyne, showing that a complete oxidation of 1-propyne proceeded other than by dimerization as:

$$CH_3\text{-}C{\equiv}C\text{-}H + 4\ O_2 \longrightarrow 3\ CO_2 + 2\ H_2O. \qquad (2)$$

The $Cu\text{-}Py\text{-}SiO_2$ catalyst activated under an O_2 atmosphere had a dark-green color, and exhibited an ESR signal with parameters of $g_{/\!/}=2.24$, $g_{\perp}=2.04$, $A_{/\!/}=170$ G and $A_N=15$ G (Fig.2a); these are characteristic of Cu(II) ions. When the sample was exposed to 100 Torr of 1-propyne at 100 °C for 3 h (1 Torr= 133.322 Pa), it turned to a gray color and the ESR signal showed a considerably weakened intensity (Fig. 2B), indicating that 1-propyne reduced a large part of the Cu(II) ions on the catalyst. When the sample was exposed again to 100 Torr of O_2 at 50 °C after outgassing at room temperature, it turned back to a dark-green color and restored the ESR signal completely in its intensity (Fig. 2C). The copper ions were oxidized again under these conditions. This redox cycle was confirmed to be reversible by repeating the above-mentioned experiment several times.

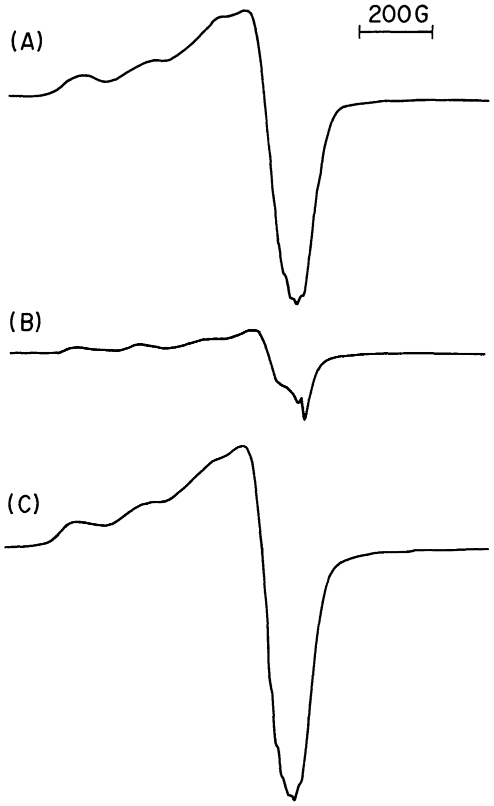

Fig. 2. ESR spectra of $Cu\text{-}Py\text{-}SiO_2$. (A) after activation under O_2 atmosphere, (B) after exposure to 100 Torr of 1-propyne at 100 °C for 3 h, (C) after exposure to 100 Torr of O_2 at 50 °C overnight after outgassing at room temperature. Spectra were observed at room temperature.

Such an easy reversible redox behavior was not observed for CuO/SiO_2 upon exposure to either 1-propyne or O_2. Therefore, this must be related to the low catalytic activity of CuO/SiO_2 for the above-mentioned reaction.

The following reaction mechanism has been suggested for the oxidative-coupling reaction of acetylenes in an aqueous alkaline solution,[1]

$$2\ R\text{-}C{\equiv}C\text{-}H \longrightarrow 2\ R\text{-}C{\equiv}C^- + 2\ H^+ \qquad (3)$$

$$2\ R\text{-}C{\equiv}C^- + 2\ Cu^{2+} \longrightarrow 2\ R\text{-}C{\equiv}C\cdot + 2\ Cu^+ \qquad (4)$$

and

$$2\ R\text{-}C{\equiv}C\cdot \longrightarrow R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}R, \qquad (5)$$

and from (3) + (4) + (5)

$$2\ R\text{-}C{\equiv}C\text{-}H + 2\ Cu^{2+} \longrightarrow R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}R + 2\ H^+ + 2\ Cu^+. \qquad (6)$$

Here, the first step consists of the ionization of acetylenic compounds, the second one is a single-electron transfer from ethynyl anions to Cu(II) ions to lead the formation of ethynyl radicals, and the last one is the dimerization of ethynyl radicals.

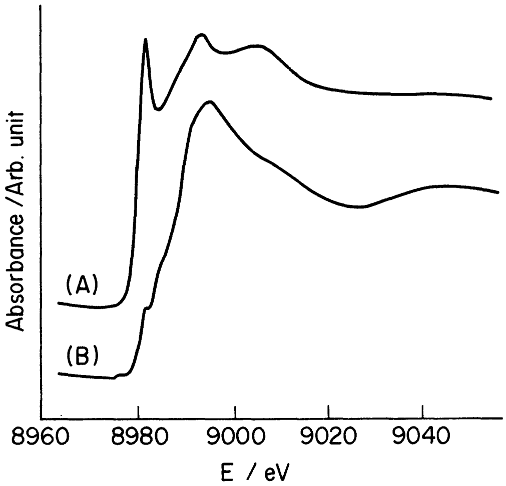

Fig. 3. XANES spectra of $Cu\text{-}Py\text{-}SiO_2$. (A) reduction by outgassing at 200 °C for 1 h, (B) exposure to 100 Torr of O_2 at room temperature for 24 h after observing spectrum (B).

The copper ions in Cu–Py–SiO_2 were found to be easily reduced with 1-propyne or to be oxidized with O_2, as described previously. Furthermore 1-propyne and O_2 were found to be decreased at a 4–1 ratio, as previously expressed by the stoichiometry of (1). These facts seem to indicate that the above reaction mechanism is also operative on the Cu–Py–SiO_2 catalyst, even though ethynyl radicals could not be detected by ESR spectroscopy.

Thus, the copper–pyridine derivative complex fixed on silica was proved to be active for the catalytic oxidative-coupling reaction of 1-propyne, in which the redox cycle of copper ions plays an important role.

Finally, the redox process of Cu–Py–SiO_2 was studied using XANES spectroscopy, which is usefull in distinguishing the oxidation state of copper ions; Cu(0), Cu(I) or Cu(II). In Fig.3 are shown the Cu–K edge XANES spectra of the sample. In its oxidized form, a small peak was observed around 8976 eV, which is due to the $1s \rightarrow 3d$ transition and is characteristic of Cu(II) ions. The sample which was outgassed at 200 °C, on the other hand, exhibited a quite different spectrum: the 8976 eV peak disappeared and a more intense one was observed around 8982 eV, which is due to $1s \rightarrow 4p\pi$ transition and is characteristic of Cu(I) complex with a small coordination number.[7]

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