

Vapor-phase oxidant-free dehydrogenation of 2,3- and 1,4-butanediol over Cu/SiO₂ catalyst prepared by crown-ether-assisted impregnation

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Experimental

Estimation of Cu surface area

In a classical measurement of Cu dispersion (D), the consumption of N₂O has been measured by pulse N₂O titration using chromatographic separation [S1,S2] and monitoring TCD signal without separating N₂O and N₂ [S3]. Although it had been believed that only the surface of Cu particles could be oxidized by N₂O, oxidation of bulk Cu particles actually proceeded even at room temperature during the N₂O oxidation [S4,S5]. Thus, the distinction of oxidation between the surface and the bulk of Cu particles is necessary to estimate the Cu surface area. One of the authors has previously developed a back titration of a copper surface oxidized with N₂O for the estimation of copper surface area as well as D value using a combination of a temperature-programmed reduction (TPR) and a diffusion theory of oxide species in bulk Cu particles [S4]. It is preferable that the oxidation of Cu particles through N₂O exposure is operated at a low temperature of 50 °C or lower because of the low diffusion speed in the bulk oxidation of Cu particles [S1]. The procedure of the experiment using a self-made apparatus equipped with an N₂O flow line described in the previous paper [S4] was as follows:

1. At first, a TPR profile was obtained by reducing the copper oxide of the unreduced catalyst with a mixture of H₂/N₂ (=1/9) at a flow rate of 10 cm³ min⁻¹, while the temperature was increased from room temperature to 300 °C at a heating rate of 10 °C min⁻¹. Afterward, the temperature was kept at 300 °C for 1 h. The total number of Cu (A_1) is the peak area of this TPR profile.
2. The metallic Cu produced in the previous step was oxidized by N₂O gas at a flow rate of 3.0 cm³ min⁻¹ together with a H₂/N₂ (=1/9) mixture of 10 cm³ min⁻¹ at 50 °C for a prescribed time (t).
3. The back titration of the oxidized surface was performed by conducting the TPR in which the oxidized Cu species obtained in step 2 was reduced with the H₂/N₂ (=1/9) mixture of 10 cm³ min⁻¹, while the temperature was increased up to 250 °C. The amount of surface Cu (A_2) is the peak area of this TPR. The Cu₂O fraction, D^* , at an oxidation time (t) was then obtained using the following equation:

$$D^* = \frac{2A_2}{A_1}$$

Several D^* values were obtained by repeating the above steps 2 and 3 with different t several times. The TPR profiles for the back titration of Cu_2O formed by N_2O oxidation, as shown in Fig. 2 of Ref. [S4].

Because the oxidation of Cu particles proceeded not only on the surface but also in the bulk of Cu particles, we removed the contribution of bulk oxidation by using Fick's law. According to Fick's law, the apparent dispersion, D^* , is expressed as the total of true dispersion, D , and bulk oxidation, which is represented as a product of the function of time, $t^{1/2}$, and proportional coefficient, B . The correlation of those quantities is expressed by the following equation:

$$D^* = D + B(t)^{1/2}$$

Therefore, by plotting D^* against $t^{1/2}$, the true dispersion of D could be obtained as the intercept, as shown in Figs. 4 and 5 of Ref. [S4]. The Cu metal surface area per unit weight of catalyst, SA_{Cu} , was calculated as the following equation: $SA_{\text{Cu}} (\text{m}^2 \text{ g}_{\text{cat}}^{-1}) = \bar{D} N_A C_{\text{Cu}} / 100 N_{\text{Cu}} W_{\text{Cu}}$, where N_A , C_{Cu} , N_{Cu} and W_{Cu} are Avogadro constant, Cu content in the catalyst (wt.-%), number of surface Cu atoms in unit surface area, $1.7 \times 10^{19} \text{ m}^{-2}$, and atomic weight of Cu (63.5 g mol^{-1}), respectively [S2].

[S1] Dvořák, B.; Pašek, J.; Determination of the specific copper surface area by chromatographic technique, *J. Catal.* **1970**, 18, 108–114.

[S2] Evans, J.W.; Wainwright, M.S.; Bridgewater, A.J.; Young, D.J.; On the determination of copper surface area by reaction with nitrous oxide, *Appl. Catal.* **1983**, 7, 75–83.

[S3] Chinchin, G.C.; Hay, C.M.; Vandervel, H.D.; Waugh, K.C.; The measurement of copper surface areas by reactive frontal chromatography, *J. Catal.* **1987**, 103, 79–86.

[S4] Sato, S.; Takahashi, R.; Sodesawa, T.; Yuma, K.I.; Obata, Y.; Distinction between surface and bulk oxidation of Cu through N_2O decomposition, *J. Catal.* **2000**, 196, 195–199.

[S5] Jensen, J.R.; Johannessen, T.; Livbjerg, H.; An improved N_2O -method for measuring Cu-dispersion, *Appl. Catal. A Gen.* **2004**, 266, 117–122.

[S6] Hosaka, S.; Kurniawan, E.; Yamada, Y.; Sato, S.; Vapor-phase dehydrogenation of 1-decanol to decanal over Cu/SiO_2 catalyst prepared by organic additives-assisted impregnation, *Appl. Catal. A Gen.* **2023**, 653, 119079.

Table S1. Detail quantity for the preparation of Cu/SiO₂ catalysts

Catalyst	Cu content / wt%	Cu(NO ₃) ₂ ·3H ₂ O / g	Organic additive / g	SiO ₂ support / g
None-Cu/SiO ₂	2.00	0.152	-	1.96
	5.00	0.380	-	1.90
	10.0	0.760	-	1.80
	15.0	1.14	-	1.70
	20.0	1.52	-	1.60
12C4-Cu/SiO ₂	2.00	0.152	0.110	1.96
	5.00	0.380	0.277	1.90
	10.0	0.760	0.555	1.80
	15.0	1.14	0.832	1.70
	20.0	1.52	1.11	1.60
15C5-Cu/SiO ₂	2.00	0.152	0.139	1.96
	10.0	0.760	0.693	1.80
18C6-Cu/SiO ₂	2.00	0.152	0.166	1.96
	10.0	0.760	0.831	1.80
CA-Cu/SiO ₂	2.00	0.152	0.132	1.96
	10.0	0.760	0.661	1.80
TEG-Cu/SiO ₂	10.0	0.760	0.473	1.80

Table S2. SA_{Cu} values of Cu/SiO₂ catalysts used in Figs. 5 and 7.

Organic additive	Cu content /wt.-%	Dispersion, D^a	SA_{Cu}^a /m ² g _{cat} ⁻¹	D_{Cu}^a /nm
None	5.0	0.166	4.62	7.2
	10	0.203	11.3	5.9
	15	0.237	19.8	5.1
	20	0.0904	10.1	13.3
12C4	5.0	0.434	12.1	2.8
	10	0.468	26.1	2.7
	15	0.476	39.8	2.5
	20	0.502	56.0	2.4
15C5	10	0.478	26.6	2.5
18C6	10	0.316	17.6	3.8
TEG	10	0.450	25.1	2.7
CA	10	0.302	16.8	4.0

^a Estimated by N₂O titration, and the data are cited from Ref. [S6]. A mean particle size of Cu, D_{Cu} , was calculated by the following equation: $D_{Cu} = 6 C_{Cu}/100 d SA_{Cu}$, assuming that the Cu particles are spherical or cubic, where C_{Cu} and d are the Cu content (wt.-%) and the density of Cu ($d = 8.96$ g cm⁻³), respectively.