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An EXAFS Study on CuCl/NaY and CuCl/ γ -Al₂O₃ Systems

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Abstract. XAFS evidence shows that the dispersed Cu⁺ ions of CuCl/ γ -Al₂O₃ or CuCl/NaY have changed their coordination structure. Below the maxima of dispersion amounts (thresholds) with increase of contents, O neighbors of Cu decrease and Cl neighbors increase. When the loadings get to the thresholds, the coordination numbers of Cu-O and Cu-Cl of the dispersed phase keep constant values. The results combining the adsorption behavior of systems indicate that although when CuCl disperses on γ -Al₂O₃ or NaY, Cu tends to coordinate with O on the surface of the support first, and the coordination mode has been changed, it has no influence to the adsorption ability and the key to improving the adsorption behavior is to increase the surface area and the dispersion amount.

1. Introduction

The CuCl dispersion system on supports with high specific surface area such as γ -Al₂O₃ or NaY zeolite is not only an excellent adsorbent of ethylene or carbon oxide, but also an important catalyst or catalyst precursor in petroleum chemistry or environmental science. CuCl/NaY (CuY) and CuCl/ γ -Al₂O₃ (CuAl) systems have been studied by XAFS which gives information of coordination species and factors affecting coordination structure.

2. Results and Discussion

Samples were prepared in dried N₂ flow by mixing and grinding of CuCl and supports. Then they were enclosed in hardy glass tube under vacuum and baked at 623K for 24 hours. The maximum dispersed amounts (thresholds) of CuCl/NaY and CuCl/ γ -Al₂O₃ systems, obtained by XRD Phase Quantitative Analysis are 0.579 gCuCl/gNaY, 0.16 gCuCl/g γ -Al₂O₃. The specific surface areas of the two supports are 192 m²/g and 851 m²/g, respectively. The XAFS data of Cu K-edge were acquired repeatedly at BSRF XAFS station and Photon Factory in Japan.

Figure 1 and Figure 2 show the Fourier transform of $\chi^2 K^2$ (2.5 Å⁻¹ to 16.2 Å⁻¹). A triple peak can be found from 1.00 to 2.50 Å. Compared with FT figures of CuCl and Cu₂O, it can be supposed that the first two and the last one attribute to Cu-O and Cu-Cl coordination shells respectively. In the two systems, the coordination peaks of Cu-O reduce and the coordination peak of Cu-Cl get larger with the increase of content. Below the threshold, the coordination peaks of Cu-O are higher than those of Cu-Cl and it is reversed when the loadings are more than the threshold.

Figure 1: The Fourier transform of CuCl/ γ -Al₂O₃ system

From left to right: CuAl10, CuAl8, CuAl6, CuAl4, CuAl2, the content of Cu decreases

Figure 2: The Fourier transform of CuCl/NaY system

From left to right: CuY9, CuY7, CuY5, CuY4, CuY2, the content of Cu decreases

Fourier Filter was taken (0.997 Å to 2.429 Å) for the triple peak to obtain the mixing EXAFS functions of the three coordination shells, then the three shell fitting was carried out. The standard amplitude and phase shift function were got from coordination shell (0.997 Å - 1.994 Å) of Cu-O of Cu_2O , coordination shell (1.099 Å - 2.020 Å) of Cu-O of CuO and coordination shell (1.355 Å - 2.429 Å) of Cu-Cl of CuCl, respectively. The following isolation formula [1, 2] is used to get the true Cu-Cl coordination in the dispersed phase, $(N_{\text{Cu-Cl(appeant)}} - 4.0) \times (N_{\text{Cu-Cl(dispersed)}} - 4.0) \times \text{Th}$ (x content, Th threshold). The results are shown in table 1 and table 2. Below the threshold, the O neighbors of Cu^+ decrease and the Cl neighbors increase with increase of content of CuCl. It indicates that while CuCl was dispersed on $\gamma\text{-Al}_2\text{O}_3$ or NaY, Cu tends to coordinate with O in the support surface first and they maybe located discretely each other as CuCl_2 , CuBr_2 disperse on $\gamma\text{-Al}_2\text{O}_3$ [3, 4]. The samples with higher Cu loadings have higher Cl-coordination number. It is very reasonable, since the content of CuCl, the density of Cl on the surface of support and the opportunity sharing a common Cl increase, when CuCl loading increases. When the content of Cu-Cl is more than the threshold, the coordination numbers of Cu-O and Cu-Cl in the dispersion phases are unchanged. The results combining the adsorption behaviors of the systems, it can be seen that coordination modes (in Cu-O or Cu-Cl) of dispersed Cu^+ ions have no marked influence on the adsorption. Cu^+ in NaY or alumina has similar coordination structure, but the adsorption ability of former is two times of later. It shows that high specific surface of support and the dispersion amount of CuCl is the key to improve the adsorption ability of these adsorbents.

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Table 1: The isolation results of CuCl/NaY

Sam.	Load.*	$N_{\text{Cu-O(appe.)}}$	$N_{\text{Cu-O(dis.)}}$	$N_{\text{Cu-Cl(appe.)}}$	$N_{\text{Cu-Cl(dis.)}}$
CuY2	0.202	3.70	3.70	1.10	1.10
CuY3	0.342	2.75	2.75	1.42	1.42
CuY4	0.348	2.92	2.92	1.50	1.50
CuY5	0.489	2.46	2.46	2.08	2.08
CuY6	0.550	2.32	2.32	2.09	2.09
CuY7	0.640	2.10	2.31	2.47	2.28
CuY8	0.703	2.02	2.39	2.60	2.27
CuY9	0.851	1.68	2.31	2.80	2.21
CuY10	0.989	1.48	2.27	3.03	2.32
CuY11	1.007	1.47	2.29	2.98	2.20

Table 2: The isolation results of CuCl/ $\gamma\text{-Al}_2\text{O}_3$

Sam.	Load.*	$N_{\text{Cu-O(appe.)}}$	$N_{\text{Cu-O(dis.)}}$	$N_{\text{Cu-Cl(appe.)}}$	$N_{\text{Cu-Cl(dis.)}}$
CuAl2	0.166	2.92	3.01	1.97	1.89
CuAl3	0.260	2.01	3.02	2.72	1.92
CuAl4	0.312	1.72	2.97	2.96	1.97
CuAl6	0.490	1.25	3.00	3.26	1.73
CuAl8	0.688	0.97	2.85	3.50	1.85
CuAl9	0.776	0.94	3.02	3.56	1.87
CuAl10	0.850	0.89	3.00	3.62	1.98

* The unit of loading is gCuCl/g support

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