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Effect of zirconia phase on the reduction behaviour of highly dispersed zirconia-supported copper oxide

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Abstract

Reduction processes of copper oxide supported both on tetragonal and on monoclinic zirconia were investigated by means of hydrogen temperature-programmed reduction (H_2-TPR). Results show that there exists apparent difference between the reduction behaviour of highly dispersed CuO supported on these two-phase zirconia; while two reduction peaks appear in the H_2-TPR profile of monoclinic zirconia-supported monolayer CuO, only one reduction peak at low temperature is developed for tetragonal zirconia-supported counterpart.
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1. Introduction

The zirconia phases were shown to influence the catalytic performance [1–6], the acidic features [7] and CO, CO_2 adsorption [8] for zirconia-based catalysts. For CO hydrogenation reaction, Li et al. [1] observed that monoclinic zirconia (MZ) has high selectivity to butene, while on tetragonal zirconia (TZ) the main products are methane, ethene, propene. In 1999, Yori and Parera [2] reported that the larger the fraction of the tetragonal phase of zirconia in Pt/WO_3-ZrO_2, the higher the activity of n-butane isomerization and the lower the metallic activity of Pt. Recently, while both Stichert et al. [3,4] and us found that the monoclinic sulfated zirconia is less effective compared to tetragonal sulfated zirconia for n-butane isomerization, Jung and Bell's [5] results of methanol synthesis from CO/H_2 and CO_2/H_2 on Cu/ ZrO_2 show that MZ is the better support (4.5–7.5 times more active) than TZ. Zhao et al. [6] evaluated their

zirconia-supported Mo-based hydrodesulfurization catalysts and found that, as a support, MZ is superior to TZ if catalysts with equal surface area were used. While both Brønsted acid sites and Lewis acid sites exist on MZ, only Lewis acid sites measurable by IR spectroscopy after pyridine adsorption are found on TZ; and the former possesses more acid sites than the latter [7]. The CO adsorption capacity of MZ has been found 5- to 10-fold higher than that of TZ [8]. Considering the apparent structural difference between TZ and MZ (Zr^{4+} is octacoordinated in TZ, heptacoordinated in MZ), which has resulted in distinctness in many features for zirconia-based catalysts, some difference in reduction behaviour is expected for reducible metal oxide supported on these two ZrO_2 phases.

As zirconia-supported CuO is a kind of promising catalyst for methanol synthesis [5,8–11] as well as for NO_x reduction by CO (forming N_2 and CO_2 at 100–200 °C) [12] etc., studies relevant to the catalyst preparation, the catalytic performance and the mechanism have been made [13–15]. Research on the reduction kinetics of CuO in CuO/ZnO/ZrO_2 systems has shown that the dispersion of Cu increases with a decrease in the CuO

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content in $CuO/ZnO/ZrO_2$ [11]. Here, the reduction properties of highly dispersed CuO on ZrO_2 with different crystal phases were evaluated by TPR technique, and a significant difference in the reduction processes of such highly dispersed CuO was observed.

2. Experimental

2.1. Sample preparation

The preparation of tetragonal zirconia and monoclinic zirconia supports was the same as reported previously [7], and the specific surface areas for them are 120 and 65 $m^2 g^{-1}$, respectively. MZ was prepared by a reflux-hydrolysis route. A 0.4 $mol\,dm^{-3}$ aqueous solution of $ZrOCl_2$ was digested under open reflux at a slightly boiling state for 96 h. Then ammonia was added to the resulting sol until pH 9.3 was reached. The precipitate was washed till the negative test for chloride, separated, dried overnight at 383 K, and finally calcined in static air at 773 K for 4 h. TZ was prepared by 50 h refluxing the fresh precipitate from $ZrOCl_2$ and ammonia solution at pH of 9.3. After washed, separated and dried, the solid was calcined in air at 873 K for 4 h. As-prepared zirconia supports are monoclinic zirconia and tetragonal zirconia, identified by both XRD (bulk) and LRS (surface) measurements [7], respectively.

The loading of Cu was performed by impregnating the supports with a $Cu(NO_3)_2$ solution, followed by rotary evaporation at 313 K and calcination at 623 K in static air. The experimental monolayer dispersing capacity of CuO on tetragonal ZrO_2 is 1.44 mmol 100 m^{-2} [16], which agrees well with the theoretical value (1.42 mmol 100 m^{-2}) according to the "incorporation model" based on the available vacant sites (i.e. the sites above each surface Zr^{4+}, as the size of Cu^{2+} is comparable with the size of Zr^{4+}) on its preferentially exposed (1 1 1) plane [17]. Since the Zr^{4+} density on the preferential planes of MZ is comparable with that of TZ [7], the dispersing capacity of CuO on TZ is adopted here for MZ in the case of no such value for MZ available. Thus for samples of monolayer CuO supported on TZ and on MZ, the mass contents of CuO are 12 and 7 wt%, respectively.

2.2. Characterization

XRD patterns were recorded with a D/MAX-2500 diffractometer (Rigaku, Japan) using Cu $K\alpha$ radiation.

The TPR experiments were carried out in a self-made system with a TCD detector. An amount of 10 mg sample was mounted in an U-shaped quartz tube and treated in N_2 atmosphere at 573 K for 1 h, and then cooled to room temperature in N_2 flow. After that the N_2 carrier gas was changed to a H_2–N_2 mixture with a

H_2:N_2 ratio of 1:10 and the total flow rate of 20 ml min^{-1}. The temperature ramp-rate was 12 K min^{-1}.

3. Results and discussion

Fig. 1 shows the TPR profiles of CuO supported on zirconia. For TZ-supported samples with CuO loading less than the monolayer dispersing capacity, only one reduction peak at the temperature about 460 K (α) was observed, as shown in Fig. 1 for TZ-supported CuO with monolayer loading (MTZ) and half monolayer loading (HTZ). Two peaks at 448 K (peak α) and 513 K (peak β) appeared in the TPR profile of MZ-supported monolayer CuO (MMZ). For TZ-supported double monolayer CuO (DTZ) sample, two peaks (at 450 and 511 K) similar to those of MMZ were developed, which may be ascribed to the dispersed CuO (peak α) and microcrystal CuO (peak β), respectively. As a matter of fact, it's well known that highly dispersed copper oxide is more easily reduced, which means it can be reduced at lower temperature as compared with bulk CuO [18]. In fact, the H_2-TPR peak for bulk CuO (prepared from $Cu(NO_3)_2$ decomposition at 623 K) is at the temperature about 653 K at the present conditions, about 200 K higher than peak α.

XRD result of the monolayer CuO supported on monoclinic ZrO_2, sample MMZ, indicates that there hardly exist diffraction lines corresponding to CuO, as shown in Fig. 2. Taking into consideration that CuO is highly dispersed on supports with its loading less than the monolayer, the single reduction peak in the case of TZ should be assigned to such uniformly dispersed CuO. The similarity of reduction features for CuO in MMZ and in DTZ poses a problem: is the reduction peak of MMZ resulted from the local microcrystal
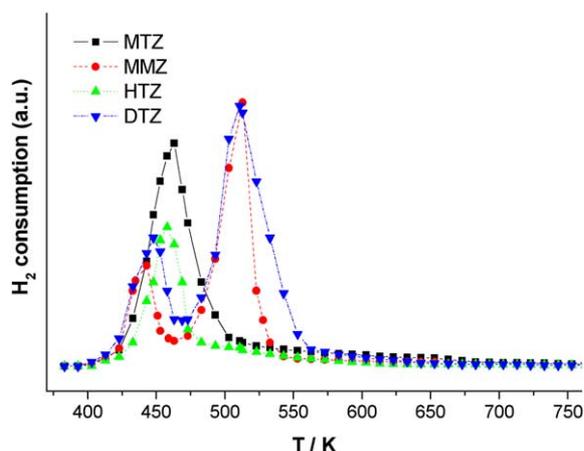

Fig. 1. TPR profiles of ZrO_2-supported CuO. MTZ = monolayer CuO on tetragonal ZrO_2 (TZ), MMZ = monolayer CuO on monoclinic ZrO_2 (MZ), HTZ = half monolayer CuO on TZ, DTZ = double monolayer CuO on TZ.
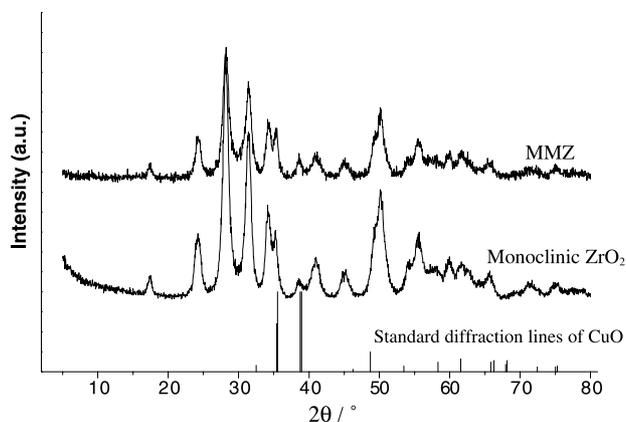
Fig. 2. XRD patterns of monolayer CuO supported on monoclinic zirconia (MMZ) after calcined at 623 K and of the monoclinic zirconia support.

CuO out of the detection sensitivity of XRD, or from dispersed CuO located in different coordination environment?

To make the problem mentioned above clear, the double-peak fitting treatment was carried out for the TPR profile of MMZ. A Lorenz function was used to fit the TPR profile. The fitting result shows that the percentage of the peak β area ($\beta/(\alpha + \beta)$) is 73.9% (Fig. 3), about 3/4. If this high-temperature peak may be ascribed to the reduction of microcrystal CuO, it will disappear or be very weak when only a quarter of monolayer CuO was dispersed on MZ (QMZ) by the same method. Fitting the TPR profile of the QMZ sample gives that the peak β still occupies approximately the 3/4 area, as shown in Fig. 4. This result suggests that the peak β does not result from CuO microcrystal.

Zhou et al. [18] had evaluated a series of zirconia-supported CuO catalysts by H_2-TPR. They found that three TPR peaks (ascribed to highly dispersed copper oxide species by them) at about 450, 493 K (a very weak shoulder of the first peak) and 508 K, were developed
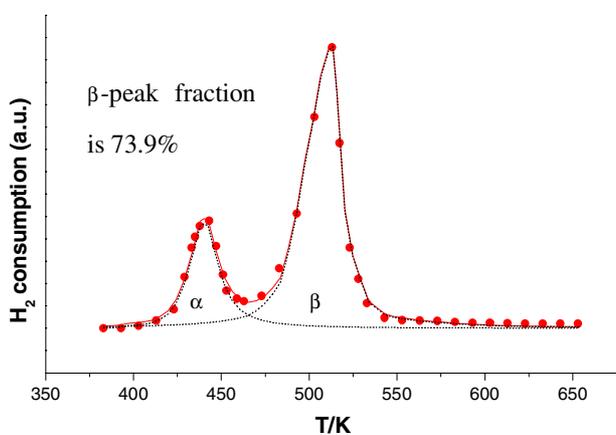

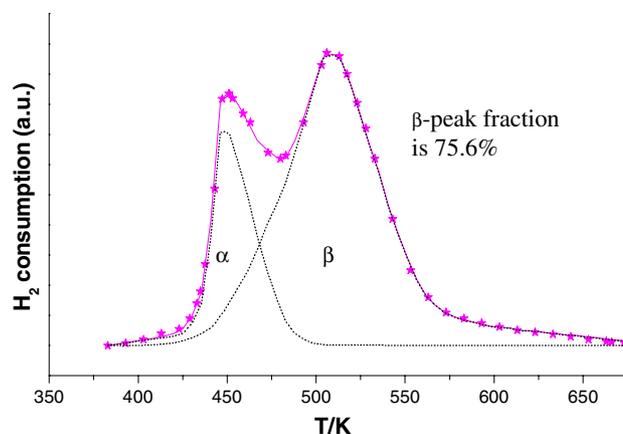Fig. 3. Fitting result of TPR profile of monolayer CuO supported on monoclinic CuO.

when the catalyst with the CuO loading of 5 wt% was calcined at 773 K. The temperatures of the first and the third TPR peaks are well consistent with our results here. The zirconia support Zhou used has a BET surface area of 63 $m^2 g^{-1}$. Thus the 5 wt% loading of CuO on Zhou's zirconia equals to 1.0 mmol CuO 100 m^{-2}, which is less than the monolayer dispersing capacity of zirconia [17]. Because of no clear information about the crystal phases of zirconia supports (especially the surface phase structure characterized by LRS, etc.) available, Zhou's results from XRD and TPR measurements are not expected to lead to a relationship between the reduction behaviour of supported CuO and the structure of zirconia support.

It is well known that the O^{2-} is tetracoordinated in tetragonal zirconia, whereas in monoclinic zirconia the O^{2-} is either tri- or tetracoordinated [19], indicating that there are one and two types of O^{2-} in tetragonal zirconia and in monoclinic zirconia, respectively. Accordingly, one and two TPR peaks are developed for monolayer CuO supported on tetragonal zirconia and on monoclinic zirconia, respectively. Thus, the peak β in the TPR profiles of MZ-supported CuO with the loading less than the monolayer dispersing capacity, such as sample MMZ and sample QMZ, is likely due to the reduction of CuO located in the unique environment consisting of tricoordinated O, which exists only in monoclinic ZrO_2. The strong interaction between the low-coordinated O^{2-} and Cu^{2+} may make the reduction of such Cu^{2+} more difficult, and thus account for the high-temperature reduction of such CuO.

Fig. 4. TPR profile of a quarter of monolayer CuO supported on monoclinic ZrO_2 and the fitting result.

Acknowledgements

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