CO_2 reduction with water over Al_2O_3-supported Ga_2O_3 photocatalysts

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Abstract: Al_2O_3-supported Ga_2O_3 (Ga_2O_3/Al_2O_3) photocatalysts were prepared to improve the photocatalytic activity of Ga_2O_3 for CO_2 reduction with water. Although the CO production activities for 5, 10 and 20 wt% Ga_2O_3/Al_2O_3 samples were lower than non-supported Ga_2O_3, the activity was significantly improved by Al_2O_3-supporting, in particular 40 and 60 wt% of Ga_2O_3 loading. It was revealed that 5, 10 and 20 wt% Ga_2O_3/Al_2O_3 samples were single α-phase Ga_2O_3 while 40 and 60 wt% Ga_2O_3/Al_2O_3 samples consisted of α and γ phases, respectively. Thus, CO production activity of the prepared samples depended on the crystalline structure of Ga_2O_3 loaded on Al_2O_3.

Keywords: Ga_2O_3 loaded Al_2O_3, Ga_2O_3 structural change, photocatalytic CO_2 reduction with water.

1. Introduction

Nowadays photocatalytic reduction of CO_2, which reduces greenhouse gas and creates carbon resources by using clean solar energy, has attracted much attention. Ga_2O_3 is known to work as a photocatalytst for CO_2 reduction with water. However, its photocatalytic activity on CO_2 reduction remains low [1, 2]. In order to improve the photocatalytic activity of Ga_2O_3, in this study, Al_2O_3 was used as support to have large surface area. We have examined photocatalytic activity of synthesized Al_2O_3-supported Ga_2O_3 (Ga_2O_3/Al_2O_3) photocatalysts having different crystalline structures for the photocatalytic CO_2 reduction with water and investigated the relation between the structure of Ga_2O_3 and the CO production activity.

2. Experimental

Ga_2O_3/Al_2O_3 samples were prepared by impregnation of γ-phase Al_2O_3 with aqueous solution of gallium nitrate followed by dry and calcination in air at 823 K for 4 h. The loading amounts of Ga_2O_3 were 5, 10, 20, 40 and 60 wt%. Pure Al_2O_3 and non-supported Ga_2O_3 samples (referred as 0 and 100 wt%, respectively) were also prepared in the similar procedure. The photocatalytic CO_2 reduction with H_2O was carried out for all prepared samples. The synthesized sample (0.1 g) was dispersed in an aqueous solution of $NaHCO_3$ (0.1M) in the fixed-bed flow reactor cell under CO_2 gas with a flow rate at 3.0 mL/min and irradiated by UV-light (Xe lamp). The reaction products (CO, H_2 and O_2) were analyzed with gas chromatography. The samples were characterized with XRD and Ga K-edge EXAFS.

3. Results and discussion

Fig.1 compares production rates of CO and CO selectivity for all synthesized Ga_2O_3/Al_2O_3. Although all Ga_2O_3/Al_2O_3 except non-supported one showed the photocatalytic activity, both CO production rate and CO selectivity for 5, 10 and 20 wt% Ga_2O_3/Al_2O_3 were lower than the others. 40 and 60 wt% of Ga_2O_3/Al_2O_3 showed higher reaction rate than non-supported one. In particular, the 40 wt% Ga_2O_3/Al_2O_3 showed the highest CO production rate and CO selectivity.

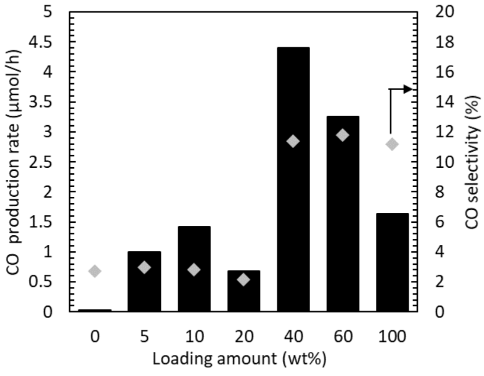

Fig.1 CO production rates and CO selectivity for prepared samples after 5 h

Fig.2 compares difference XRD patterns for all prepared samples which were given by subtracting the XRD intensity of pure Al_2O_3 from those of Al_2O_3 supported samples. The patterns depicted that 5, 10 and 20 wt% Ga_2O_3/Al_2O_3 were single α-phase Ga_2O_3, while 40 and 60 wt% Ga_2O_3/Al_2O_3 consisted of α and γ phases, respectively. 100 wt% Ga_2O_3 contained β-phase in addition to the α/γ-mixed phases.

The local structures of Ga_2O_3/Al_2O_3 were investigated by the EXAFS measurement of Ga K-edge spectra. The Fourier transform was performed on each EXAFS spectrum in the range from 3 $Å^{-1}$ to 12 $Å^{-1}$ and the radial structure function (RSF) was obtained as shown in Fig. 3. In the RSFs, the first peak appeared at 1-2Å is assigned to the backscattering from adjacent oxygen atoms (Ga-O bond) and the second peak around 2.7Å shows the presence of the second-neighboring gallium atoms (Ga-Ga bond) [3-5]. Considering XRD results, the RSF of 20 wt% Ga_2O_3/Al_2O_3 should be corresponding to α-phase Ga_2O_3 in which the amplitudes of the first and second peaks are almost the same. On the other hand, in RSF of 40 wt% Ga_2O_3/Al_2O_3, the first peak is larger than the second one which is similar to that of γ-Ga_2O_3. Therefore, the γ-Ga_2O_3 phase would dominate 40 wt% Ga_2O_3/Al_2O_3. In the conference, we will discuss why the α/γ-mixed phase Ga_2O_3 showed high activity for CO production based on the CO_2 adsorption experiments and in-situ FT-IR measurements.

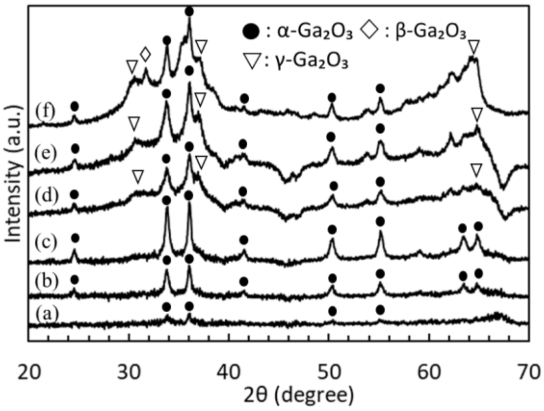

Fig.2 Difference XRD patterns of Ga_2O_3/Al_2O_3 and Ga_2O_3 samples. The loading amount of Ga_2O_3 is (a) 5 wt% (b) 10 wt% (c) 20 wt% (d) 40 wt% (e) 60 wt% and (f) 100 wt%.

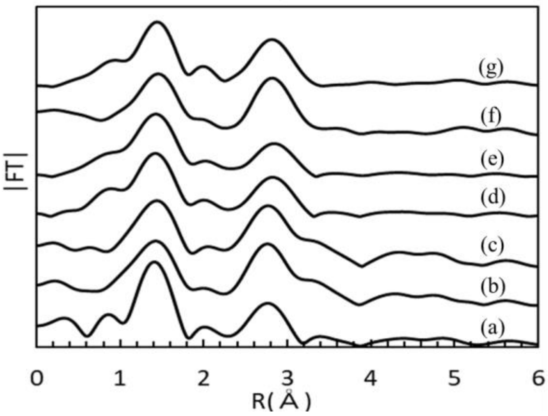

Fig.3 Fourier transfer Ga K-edge EXAFS spectra of (a-e) Ga_2O_3/Al_2O_3 samples and (g) γ-Ga_2O_3. The loading amount of Ga_2O_3 is (a) 5 wt% (b) 10 wt% (c) 20 wt% (d) 40 wt% (e) 60 wt% and (f) 100 wt%.

4. Conclusions

We have synthesized Al_2O_3-supported Ga_2O_3 photocatalysts (Ga_2O_3/Al_2O_3) with different Ga_2O_3 loading. Following the characterization of Ga_2O_3/Al_2O_3 with XRD and EXAFS, their photocatalytic activity for CO_2 reduction with water was examined. The Ga_2O_3 loaded samples with more than 40 wt% exhibited higher activity for CO production rate and CO selectivity than non-supported Ga_2O_3. Among the all samples, 40 wt% Ga_2O_3/Al_2O_3 showed the highest CO production activity, and structural analyses by XRD and EXAFS measurements reveal that the appearance of α/γ-mixed phase Ga_2O_3 is important for CO production.

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