CO₂ reduction with water over Al₂O₃-supported Ga₂O₃ photocatalysts

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Abstract: Al₂O₃-supported Ga₂O₃ (Ga₂O₃/Al₂O₃) photocatalysts were prepared to improve the photocatalytic activity of Ga₂O₃ for CO₂ reduction with water. Although the CO production activities for 5, 10 and 20 wt% Ga₂O₃/Al₂O₃ samples were lower than non-supported Ga₂O₃, the activity was significantly improved by Al₂O₃-supporting, in particular 40 and 60 wt% of Ga₂O₃ loading. It was revealed that 5, 10 and 20 wt% Ga₂O₃/Al₂O₃ samples were single α-phase Ga₂O₃ while 40 and 60 wt% Ga₂O₃/Al₂O₃ samples consisted of α and γ phases, respectively. Thus, CO production activity of the prepared samples depended on the crystalline structure of Ga₂O₃ loaded on Al₂O₃.

Keywords: Ga₂O₃ loaded Al₂O₃, Ga₂O₃ structural change, photocatalytic CO₂ reduction with water.

1. Introduction

Nowadays photocatalytic reduction of CO₂, which reduces greenhouse gas and creates carbon resources by using clean solar energy, has attracted much attention. Ga₂O₃ is known to work as a photocatalyst for CO₂ reduction with water. However, its photocatalytic activity on CO₂ reduction remains low [1, 2]. In order to improve the photocatalytic activity of Ga₂O₃, in this study, Al₂O₃ was used as support to have large surface area. We have examined photocatalytic activity of synthesized Al₂O₃-supported Ga₂O₃ (Ga₂O₃/Al₂O₃) photocatalysts having different crystalline structures for the photocatalytic CO₂ reduction with water and investigated the relation between the structure of Ga₂O₃ and the CO production activity.

2. Experimental

Ga₂O₃/Al₂O₃ samples were prepared by impregnation of γ-phase Al₂O₃ with aqueous solution of gallium nitrate followed by dry and calcination in air at 823 K for 4 h. The loading amounts of Ga₂O₃ were 5, 10, 20, 40 and 60 wt%. Pure Al₂O₃ and non-supported Ga₂O₃ samples (referred as 0 and 100 wt%, respectively) were also prepared in the similar procedure. The photocatalytic CO₂ reduction with H₂O was carried out for all prepared samples. The synthesized sample (0.1 g) was dispersed in an aqueous solution of NaHCO₃ (0.1M) in the fixed-bed flow reactor cell under CO₂ gas with a flow rate at 3.0 mL/min and irradiated by UV-light (Xe lamp). The reaction products (CO, H₂ and O₂) 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 Ga₂O₃/Al₂O₃. Although all Ga₂O₃/Al₂O₃ except non-supported one showed the photocatalytic activity, both CO production rate and CO selectivity for 5, 10 and 20 wt% Ga₂O₃/Al₂O₃ were lower than the others. 40 and 60 wt% of Ga₂O₃/Al₂O₃ showed higher reaction rate than non-supported one. In particular, the 40 wt% Ga₂O₃/Al₂O₃ 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 Al2O3 from those of Al2O3 supported samples. The patterns depicted that 5, 10 and 20 wt% Ga2O3/Al2O3 were single α-phase Ga2O3, while 40 and 60 wt% Ga2O3/Al2O3 consisted of α and γ phases, respectively. 100 wt% Ga2O3 contained β-phase in addition to the α/γ-mixed phases.

The local structures of Ga2O3/Al2O3 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% Ga2O3/Al2O3 should be corresponding to α-phase Ga2O3 in which the amplitudes of the first and second peaks are almost the same. On the other hand, in RSF of 40 wt% Ga2O3/Al2O3, the first peak is larger than the second one which is similar to that of γ-Ga2O3. Therefore, the γ-Ga2O3 phase would dominate 40 wt% Ga2O3/Al2O3. In the conference, we will discuss why the α/γ-mixed phase Ga2O3 showed high activity for CO production based on the CO2 adsorption experiments and in-situ FT-IR measurements.

4. Conclusions

We have synthesized Al2O3-supported Ga2O3 photocatalysts (Ga2O3/Al2O3) with different Ga2O3 loading. Following the characterization of Ga2O3/Al2O3 with XRD and EXAFS, their photocatalytic activity for CO2 reduction with water was examined. The Ga2O3 loaded samples with more than 40 wt% exhibited higher activity for CO production rate and CO selectivity than non-supported Ga2O3. Among the all samples, 40 wt% Ga2O3/Al2O3 showed the highest CO production activity, and structural analyses by XRD and EXAFS measurements reveal that the appearance of α/γ-mixed phase Ga2O3 is important for CO production.

References