

Photocatalytic Hydrogen and Oxygen Formation from Water over Ga-modified Zeolite

Chong Heng HE^{1*}, O Bong YANG²

¹Department of Chemical Engineering, East China University of Science and Technology, Shanghai 200237

²School of Chemical Engineering and Technology, Chonbuk National University, Chonju, Chonbuk 561-756, Korea

Abstract: Water could be decomposed into hydrogen and oxygen over Ga-modified ZSM-5 zeolite under UV irradiation. The photocatalytic activity was elevated significantly by supporting the gallium species and was sensitive to the loading amount of gallium species on the ZSM-5 zeolites.

Keywords: Photocatalyst, zeolite, decomposition of water.

A lot of studies have been made in the search of new efficient photocatalysts for water decomposition and considerable progress has been obtained in recent years. For example, the metal oxide with tunnel or layered structure has shown a comparatively high activity for water splitting¹. The spontaneously hydrated layered perovskites with two-dimensional sheets structure are also successful examples of efficient decomposition of water². However, the zeolite with uniform porosity as the photocatalyst for water decomposition has not been reported up to now. Here we describe the results of photocatalytic water decomposition into hydrogen and oxygen over Ga-modified ZSM-5 under UV irradiation.

The ZSM-5 zeolite was purchased from ZEOLYST International Company (SiO₂/Al₂O₃=80). Its nominal cation form is ammonium and the Na₂O weight percent is 0.05%. The Ga-modified ZSM-5 photocatalysts were prepared by impregnating ZSM-5 with gallium nitrate (Aldrich) solution by the incipient wetness impregnation technique for 12 h, followed by drying at 110°C for 24 h. Then the dried materials were calcined in static air at 550°C for 4 h.

Photocatalytic decomposition of water was carried out in an inner irradiation closed gas circulating quartz cell system. The catalyst powder (1.0 g) was dispersed and stirred in 700 mL distilled water. The remained air in the reaction system was excluded completely by Ar gas before reaction. A 450 W high-pressure mercury lamp (Korea) was used as the UV light source. The total irradiation time for each sample was 24 h. The amounts of H₂ and O₂ evolved were detected on-line by gas chromatography

* E-mail: chhe895@online.sh.cn

equipped with a thermal conductivity detector (TCD).

The photocatalytic activity of ZSM-5 for water decomposition was elevated significantly by supporting the gallium species and the photocatalytic activity was sensitive to the loading amount of gallium species on the zeolite. **Table 1** shows the effect of gallium content on the photocatalytic activity. At the low additive content, the activity increased slowly with the increase of Ga₂O₃ amount. However, after the loading amount was over 4wt.%, the activity increased sharply with the additive amount of Ga₂O₃ and reached the maximum yield of hydrogen (42.3 μmol/h) at the 6wt.% Ga₂O₃ content. Then the activity decreased dramatically with increasing Ga₂O₃ over 6wt.%.

Table 1 The effect of additive amount and calcination temperature on activity of water decomposition

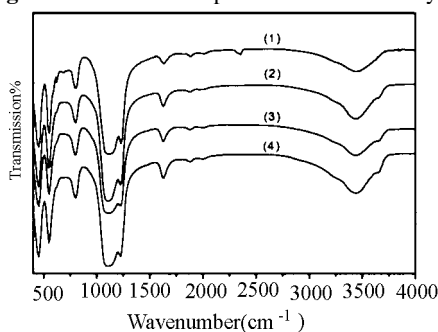
Catalyst	Ga ₂ O ₃ amount (wt.%)	BET area (m ² /g)	Micropore volume (cm ³ /g)	Elevation rate (μmol/h)	
				H ₂	O ₂
H-ZSM-5	0.0	425.00	0.09021	2.84	0.88
Ga/ZSM-5	1.0	422.06	0.09006	14.11	2.25
Ga/ZSM-5	2.0	420.18	0.08977	14.86	2.66
Ga/ZSM-5	4.0	412.32	0.08653	18.75	3.07
Ga/ZSM-5	6.0	403.13	0.08562	42.23	5.52
Ga/ZSM-5	8.0	395.21	0.08464	36.04	4.10
Ga/ZSM-5	12.0	377.94	0.08294	0.86	0.31

Figure 1 shows the FT-IR spectra of several samples. All the samples show a strong absorption band at 1100 cm⁻¹, which is assigned to internal vibration of TO₄ tetrahedra and the peak at 550 cm⁻¹ assigned to double five-ring vibration. However, we did not find the absorption bands of stretching vibrations of bridged hydroxyls related to tetrahedrally coordinated framework gallium at *ca.* 3615 cm⁻¹ to 3625 cm⁻¹ for any of the gallosilicate structures³, which suggests that the gallium species did not incorporate into the framework tetrahedral sites of ZSM-5. This fact underlines the supposition that nonframework gallium is the actual active species for decomposition of water. An additional shoulder emerges at *ca.* 3670 cm⁻¹ for Ga-modified ZSM-5, it is assigned to the vibration of hydroxyls located at nonframework gallium species⁴ and it increased in intensity with increase of gallium content at the range of low loading amount (2wt.%~6wt.%) and no evident increase is found over 8wt.%.

As we know that the zeolite crystals contain pore and channel systems of molecular dimension with fixed geometry and size. The pores are composed of oxygen rings and the oxygen atoms surround the smaller central atoms of the tetrahedral nearly completely. Therefore, the interior surface of zeolites is nearly entirely composed of oxygen atoms. That means the inside and outside positions of a zeolite pore have different chemical surroundings. Nonframework gallium ions within the pore system can occupy cation positions substituting ammonium ions or protons and coordinate to framework oxygen atoms. These cations can interact with other sorbed molecules, like water, to activate them³. Therefore, we can suppose that the gallium species exchanged at the position of zeolite pore mouth are the active sites for water decomposition under UV irradiation. These sites are different in chemical properties with outside sites, and the photons can ir-

radiate them directly. The ZSM-5 zeolite is classified as the medium-pore zeolite with

Figure 1 The FT-IR spectra of various catalysts



(1) ZSM-5; (2) 4.0wt.% Ga₂O₃/ZSM-5; (3) 6.0wt.% Ga₂O₃/ZSM-5; (4) 8.0wt.% Ga₂O₃/ZSM-5

the ring of 10 oxygen atoms and its pore size is 0.5-0.6 nm. When the loading amount is low, the hydrated Ga³⁺ cations are closely restricted to the outer surface of the zeolite crystals, and they rarely have the chance to gain access to the position inside the zeolite pores⁵. As the loading amount increases, most exchangeable outside sites are occupied and the Ga³⁺ cations have more chance to access to the pores and locate near the mouth of pore. In addition, when the gallium content is high, the gallium species are easier to migrate from outside of zeolite into the zeolite micropores resulting in a highly dispersed gallium phase located close to the acid sites during the activation treatment period by calcination at 550°C⁵. It may be the reason that the activity increased with the increase of loading amount only at the low gallium-load. However, as the loading amount is further increased, the hydrated Ga³⁺ cations have difficulty to find enough way into the pores of zeolite deeply. The extra gallium species will deposit on the outside of zeolite and large aggregates of Ga₂O₃ will block the pores resulting in the decrease of exposed active sites. That is why the activity decreased sharply as the gallium loaded amount increasing over 6.0wt.%. From **Table 1** we can see that the surface areas and the micropore volumes of catalysts decrease with the increase of loading amount. That means some micropores disappeared as supported Ga₂O₃ content increase. In addition, when the loading amount reached 12%, the rate of hydrogen evolution decreased to 0.86 μmol/h (**Table 1**), nearly the same with that of unsupported Ga₂O₃ (0.82 μmol/h). These behaviors supported our deduction about the active sites to a certain extent.

References

1. K. Kudo, K. Sayama, A. Tanaka *et al.*, *J. Catal.*, **1989**, *120*, 337.
2. T. Takata, K. Shinohara, A. Tanaka, A. *et al.*, *J. Photochem. Photobiol. A*, **1997**, *106*, 45.
3. R. Fricke, H. Kosslick, G. Lischke and M. Richter, *Chem. Rev.*, **2000**, *100*, 2303.
4. A. Y. Khodakov, L. M. Kustov, T. N. Bondarenko *et al.*, *Zeolites*, **1990**, *10*, 603.
5. J. F. Joly, H. Ajopt, E. Merlen *et al.*, *Appl. Catal. A*, **1991**, *79*, 249.

Received 17 March, 2003