



Styrene epoxidation over V-SBA-15 with alkaline-earth metal ion promotion under photo-assisted conditions

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ABSTRACT

The photo-assisted epoxidation of styrene over V/SBA-15 modified by alkaline-earth metal ions was investigated with hydrogen peroxide at room temperature. The results indicated that the isolated VO₄ tetrahedron dispersed on the SiO₂ was the photo-assisted catalytic active site for the formation of styrene oxide, while V⁵⁺ polymer species in V/SBA-15 with highly loaded V species caused deep oxidation of styrene oxide. Among the catalysts modified by alkaline-earth metal ions, Mg-V/SBA-15 displayed the best catalytic performance. It was probably due to the fact that the metallic character of Mg was weaker in alkaline-earth metals, so it was easier to disperse V⁵⁺ polymer species and the dispersion effect was especially obvious in the comparatively high loading weight of vanadium oxide. Moreover, addition of alkaline-earth metals decreased the acidic sites of V/SBA-15, inhibiting the ring-opening reaction on which the deep oxidation occurred. The structures of all catalysts were thoroughly investigated using different characterization techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), NH₃-temperature programmed desorption (TPD), H₂ temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS), etc. A possible catalytic mechanism was proposed.

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1. Introduction

Styrene epoxidation was of interest to both academic and commercial fields for the synthesis of two important products—styrene oxide and benzaldehyde [1–3]. From the environmental and economic viewpoints, hydrogen peroxide was an ideal oxidant to olefins epoxidation with the aid of light and heterogeneous photocatalyst. It is difficult, however, to control partial oxidation of olefins for conventional bulk semiconductor metal oxides, such as TiO₂ which brought about non-selective photooxidation of olefins to carbon dioxide even with a low conversion [4]. On the other hand, highly dispersed titanium oxide species on SiO₂ promoted the photoepoxidation of propene by molecular oxygen [5]. For the analogous state, such as Nb₂O₅ [6], MgO [7], CrO₃ [8], and ZnO [9], a high dispersion of corresponding species also exhibited better photoepoxidation performance than that of bulk metal oxides.

Then for vanadium-based catalysts, in order to obtain higher active and selective for epoxidation of olefins, it is clear that a high dispersion of the vanadium oxide species should be achieved as high as possible. Great efforts have therefore been made to detect the potential applications of high surface area materials which can be used as the supports for dispersing the vanadium oxide

species [10–12]. Since the discovery of periodic mesoporous silica M41S materials, much attention has been attracted to their application using as catalyst supports [13–15]. Very recently, the synthesis of a new ordered mesoporous material, SBA-15, was achieved using a triblock copolymer as structure-directing agent under strongly acidic conditions [16,17]. SBA-15 material has a high surface area (600–1000 m² g⁻¹) and is formed by hexagonal arrays of uniform tubular channels with pore diameters in the range of 5–30 nm [18,19] which are significantly larger than those of MCM-41 (3–8 nm). In addition, due to a thicker pore wall (31–64 Å), SBA-15 provides a higher thermal and hydrothermal stability compared with MCM-type mesoporous materials [16,20].

For silica-supported vanadium oxide deep oxidation generally happens especially in V₂O₅ high loading. However, the control of partial oxidation is the key for industry benefit which relates to selective oxidation. Yoshida, S. et al. [21,22] have reported the photooxidation of propene over V₂O₅/SiO₂ with O₂ under UV irradiation in a closed circulation reactor, but propene oxide was not detected as a product. Afterwards, Fumiaki Amano et al. [23] suppressed the decomposition of the unstable PO intermediate by adopting a flow reactor system instead of a closed reactor system to obtain a short contact time between the substrates and the catalysts, and observed the formation of propene oxide over V₂O₅/SiO₂ for the first time. It is known that polymeric species and even crystalline V₂O₅ species containing V–O–V entities have been suggested as the active sites for the deep oxidation, which is still a

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