

Complete Oxidation of Chlorinated Aromatic Compounds over Metal Oxide Composite Aerogel Catalysts

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Introduction

Many of polychlorinated aromatic compounds such as dioxins and furans have been designated as human carcinogenic substances. Thermal disposal of wastes containing chlorinated hydrocarbons often generates these man-made toxic substances. Demand for detoxification of chlorinated compounds has gradually increased, but still sufficient removal efficiency has not been achieved due to their chemical stability and resistance to degradation.

Photodegradation and biodegradation are relatively slow. Complete thermal decomposition [1] consumes a great deal of energy. Hydrogenation [2] or oxidation [3] produce unwanted byproducts such as aromatics or carbon monoxide. Up to now, a commercial-scale disposal process has not been optimized in a either liquid or gaseous state. This study concentrates on the disposal efficiency for catalytic oxidation of 1,2-dichlorobenzene through a gaseous reaction over high-surface-area aerogel catalysts.

The unique properties of aerogels make them attractive as effective catalysts for the oxidation of high molecular substances [4,5]. Here, we have conducted a gas-phase oxidation of 1,2-dichlorobenzene that is one of the chemical precursors of 2,3,7,8-dioxin using vanadia-titania and manganese oxide-titania composite aerogel catalysts.

Materials and Methods

V₂O₅-TiO₂ and MnO_x-TiO₂ composite aerogels were synthesized by the gelation of metal components in ethanol solutions, and followed by aging, supercritical drying, and calcination. The resulting aerogels exhibited high porosity and high specific surface area with highly dispersed metal oxides. Characteristics were observed by BET, Raman, XRD, and TPR, and reactions were conducted with 1,000 ppm of 1,2-dichlorobenzene at GHSV, higher than 10,000 hr⁻¹ that gives the disposal capacity of 15 kg-Cl/kg-cat.·day for aerogels.

Results and Discussion

Titania synthesized by sol-gel methods hardly loses its anatase crystallinity even after 777K calcination. This enhances the reaction activity for vanadia and manganese oxides due to the intrinsic oxidation ability and interacted strength with other metal oxides. Physical characteristics such as high specific surface area and large pore diameter also overcome the diffusion limited reaction that often occurs with large molecules.

Each metal oxide has shown its unique reaction selectivity to carbon oxides; vanadia to CO and manganese oxides to CO₂. Decomposition ability is higher on vanadia catalysts while complete oxidation is better on manganese oxides, that possibly caused by the

enthalpy strength between chlorine and metal components (V-Cl, 477±63 kJ/mol; Mn-Cl, 360.7±9.6 kJ/mol).

Table 1. BET Surface area (S_{BET}), total pore volume (V_p), and average pore diameter (D_p) of V₂O₅-TiO₂ and MnO_x-TiO₂ composite aerogels calcined at 773K.

Catalyst	S _{BET} (m ² /g)	V _p (cc/g)	D _p (nm)
10 wt.% V ₂ O ₅ -TiO ₂	127	0.83	25.3
10 wt.% MnO _x -TiO ₂	166	0.79	19.0

High specific surface area and mesoporosity would be of great benefits to conduct the catalytic oxidation of high molecular compounds.

Significance

Most of chemical plants inevitably discharge chlorinated materials originated from petrochemical substances. Catalytic oxidation is relatively facile in order to cope with stringent environmental regulations for the disposal of chlorinated aromatic compounds.

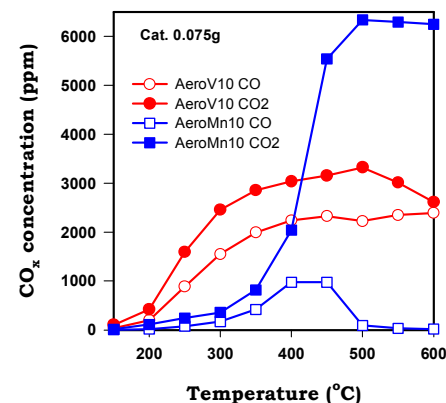


Figure 1. Reaction selectivity to carbon oxides for the 1,2-dichlorobenzene oxidation over 10 wt.% V₂O₅-TiO₂ (AeroV10) and 10 wt.% MnO_x-TiO₂ (AeroMn10) composite aerogels.

References

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