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Oxidative Dehydrogenation of Ethane over Sn-W-O_x Catalysts

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Abstract

The oxidative dehydrogenation of ethane to ethene was investigated over the catalyst composed of tin and tungsten oxides at 923 K under atmospheric pressure. A pure SnO_2 catalyst showed the high ethane conversion but low ethene selectivity (the major product was carbon dioxide). On the other hand, a pure WO_3 catalyst showed the high ethene selectivity while the ethane conversion was relatively low. The remarkable synergetic effect of tin and tungsten was observed when $Sn_2W_3O_8$ was used as catalyst precursor. According to the XRD measurement, $Sn_2W_3O_8$ was found to decompose into SnO_2 and WO_3 after the reaction, however, no significant difference was observed in the XPS analysis for tin and tungsten between the samples before and after the reaction. To clarify the synergism of tin and tungsten in $Sn_2W_3O_8$, the Auger parameter was employed for the surface oxygen atom of the catalyst. The clear relationship was found between the ethene yield and the ionicity of the oxygen atom.

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Keywords: auger parameter, dehydrogenation, ethane, tin oxide, tungsten oxide.

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1. Introduction

Ethene, which is one of the most important raw materials in the chemical industry, is mainly produced by steam cracking of ethane or naphtha at the higher temperatures than 1000 K. Under the reaction conditions of the high temperature and low oxygen concentration, the undesired side reactions, such as coke formation and C-C bond cleavage, take place [1]. The oxidative dehydrogenation of ethane (ODE) can offer a low cost and energy saving process for the ethene production because the reaction is exothermic and suppresses the coke formation.

Molybdenum [2] and vanadium [3] are known as the popular catalyst elements for the ODE and their reaction mechanism and kinetics are investigated in detail [3], [4]. However, the effective catalyst has not been developed due to the difficulty of the C-H bond activation in ethane at low temperatures.

In this study, the ODE over the catalysts composed of tin and tungsten oxides is presented and the catalytic activity is discussed with respect to the electronic state of the surface oxygen atom of the catalyst.

2. Experimental

All chemicals and solvents were of the highest grade where obtainable and were used without further purification.

2.1. Preparation of catalysts

$\underline{Sn/WO_3}$: Tungsten oxide was impregnated with toluene solution of tin octanoate. The solvent was removed at 393 K and the sample was calcined in air at 973 K for 3 h.

$\underline{W/SnO_2}$: Tin oxide was impregnated with an aqueous solution of ammonium tungstate and the sample was calcined in air at 973 K for 3 h.

$\underline{Sn_2W_3O_8}$: The physically mixed tungsten oxide, tin oxide, and tungsten powders were heated in vacuo at 973 K for one week [5].

2.2. Activity test

The activity test was carried out with a flow-type fixed-bed reactor (quartz, 6 mm i.d.) under atmospheric pressure as shown in Figure 1. The length of the heating zone by an electric furnace is 300 mm. The catalyst was placed at the center of the reactor and each reactant gas was supplied through a mass flow controller (MFC).

The catalyst was pretreated with nitrogen gas stream under atmospheric pressure at 973 K for 0.5 h. After enough cooling, a reactant gas mixture (nitrogen/ethane/oxygen=7/2/1) was introduced at SV=30,000 mL g-cat^{-1} h^{-1} and the temperature was set. The effluent gas was analyzed by an on-line gas chromatograph (Porapak Q for CO_2, ethane, and ethene; MS-5A for CO and methane) equipped with a thermal conductivity detector.

2.3. Characterization of catalysts

The X-ray diffraction (XRD) measurement was carried out by using RINT2000 diffractometer (Rigaku Corp., Japan) with Cu Kα radiation. The surface analyses by X-ray photoelectron spectroscopy (XPS) were performed with ESCA-3200 (Shimadzu Corp., Japan) using magnesium radiation (8 kV, 30 mA). After enough cooling, the sample was taken out from the reactor and was set to the sample holder of the XPS instrument. The spectra were recorded after argon-ion etching for 0.5 min (2 kV, 25 mA). The values of binding energy were corrected with that of C(1s) (284.6 eV) for carbon contaminant [6].