Synthesis of acetaldehyde and acetic acid by the gas phase oxidation of ethanol over gold and vanadia catalysts

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Introduction

Biomass has been receiving much attention in the world as a renewable resource to replace fossil fuel. Bioethanol is mostly used for blending into gasoline as a renewable fuel, while it can also be transformed into valuable chemicals such as acetaldehyde and acetic acid. Major industrial production of acetic acid is based on the carbonylation of methanol, whereas acetaldehyde production uses ethylene as a source. Owing to the gradual shift from fossil to renewable resources in chemical industry, the transformation of ethanol into valuable chemical feed stocks has attracted growing concerns [1]. We have investigated the oxidation of ethanol with O_2 in gas phase using gold and vanadium oxides as catalysts and have found that either acetaldehyde or acetic acid can be selectively produced.

Experimental

Supported gold catalysts were prepared by coprecipitation(CP), deposition precipitation(DP), or solid grinding(SG) method. $HAuCl_4$ was used as a starting reagent of Au for CP and DP methods, while $(CH_3)_2Au(C_5H_7O_2)$ was used for SG method. The precursors were calcined in air at 573 K. Vanadium catalysts were prepared by incipient wetness impregnation(IW) method, where NH_4VO_3 was used as a reagent of vanadium. The precursors were calcined in air at 573-773 K.Catalytic activities were measured by a continuous-flow fixed-bed quartz reactor. The reactant gas was passed through the catalyst bed (150 mg) under a total pressure of 1 atm and at a space velocity of 20,000 ml h^{-1} g_{cat}^{-1} at temperatures of 373-553 K. The composition of the feed gases used as $C_2H_5OH/O_2/N_2$= 1/3/126. The effluent gas was analyzed by using a FID gas chromatograph and TCD gas chromatographs equipped with an automatic gas sampling system.

Results/Discussion

Metal oxides as support for gold can be classified into three groups. The first group leads to complete oxidation of ethanol into CO_2 and is represented by p-type semi-conductive oxides, which are active for the complete oxidation of CO and hydrocarbons. The second group is represented by n-type semi-conductive metal oxides, which show medium catalytic activity for the complete oxidation so that acetaldehyde oxidation directly to CO_2 might be depressed. Therefore, when gold nanoparticles are deposited, products are a mixture of acetic acid and acetaldehyde. The third group is represented by basic or strongly acidic metal oxides such as La_2O_3 and MoO_3, which are inactive for the oxidation of ethanol at temperatures below 573 K. This group of metal oxides can provide high selectivities and yields to acetaldehyde above 95% and above 80%, respectively, when gold nanoparticles are deposited on them (Fig. 1).

It was also found that vanadium oxides can provide high yields to acetic acid or acetaldehyde depending on their crystalline structure and supports (Fig. 2).

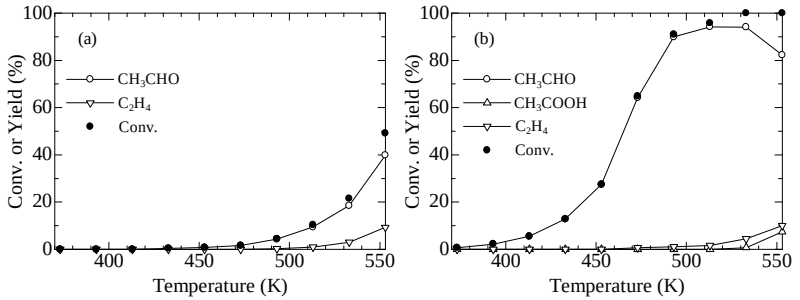

Figure 1. Ethanol conversion and product yields as a function of reaction temperature over MoO_3(a) and Au/MoO_3(b). Reaction conditions : SV=20,000 ml h^{-1} g_{cat}^{-1}, $C_2H_5OH/O_2/N_2$= 1/3/126.

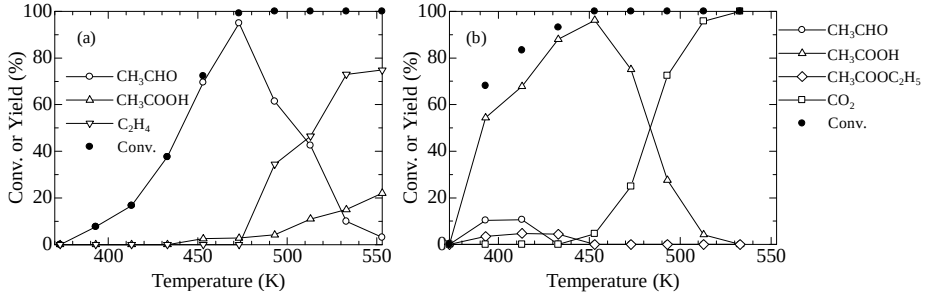

Figure 2. Ethanol conversion and product yields as a function of reaction temperature over V_2O_5(a) and V_2O_5/anataseTiO_2(b). Reaction conditions : SV=20,000 ml h^{-1} g_{cat}^{-1}, $C_2H_5OH/O_2/N_2$= 1/3/126.

References.

1. T. Takei, N. Iguchi, M. Haruta, *Catal. Surv. Asia,* (2011) doi:10.1007/s10563-011-9112-1