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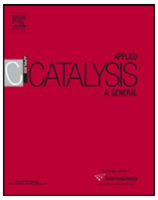

Direct addition of acetic acid to ethylene to form ethyl acetate in the presence of $H_4SiW_{12}O_{40}/SiO_2$

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ABSTRACT

The direct addition of acetic acid to ethylene to form ethyl acetate over $H_4SiW_{12}O_{40}/SiO_2$ using SiO_2 with various surface areas and mesopore sizes was studied. $H_4SiW_{12}O_{40}/SiO_2$ was superior in activity to conventional solid acids including H_3PO_4/SiO_2, Nafion–SiO_2, WO_3–ZrO_2, and unsupported $H_4SiW_{12}O_{40}$. While the selectivity for ethyl acetate was more than 98% regardless of the catalyst, the activities were significantly different. Maximum activity was obtained when SiO_2 having a high surface area and moderate pore size (ave. 6 nm) was utilized. The temperature-programmed desorption of benzonitrile technique and XRD both confirmed that this catalyst had a large amount of acid sites located on the outermost surface due to the high dispersion of $H_4SiW_{12}O_{40}$. In contrast, $H_4SiW_{12}O_{40}/SiO_2$, with SiO_2 of very small mesopores (3 nm) showed a very low activity, despite having the largest amount of acid sites located on the outermost surfaces. On this catalyst, diffusion of the reactant and product were slow due to the very small-sized mesopores. This limited diffusion rate results in its low activity.

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1. Introduction

Ethyl acetate is a useful solvent for the production of lacquers, enamels, inks, adhesives and pharmaceuticals. Recently, aromatic solvents have been replaced with ethyl acetate due to its lower toxicity. Thus the demand of ethyl acetate is increasing at a rate of several percent per year and the current annual demand approaches about 1200 kt throughout the world.

The industrial production of ethyl acetate is accomplished through two main synthetic processes: (1) esterification of acetic acid with ethanol in the presence of liquid acids such as sulfuric acid [1–5] and (2) dimerization of acetaldehyde, the Tischenko reaction, in which aluminum alcoholate is utilized as a catalyst [6]. However, these commercial processes have disadvantages such as the need to separate the catalyst from the product and the generation of a large amount of spent catalyst and waste water due to using homogeneous catalysts. In addition, in order to meet the increase in demand and reduce environmental load, we need to develop new and environmentally benign technologies for the production of ethyl acetate.

Recently, a direct addition of acetic acid to ethylene to form ethyl acetate (Eq. (1)) has attracted much attention, because ideally no by-product is produced with this reaction, i.e., it is a production route of high atom efficiency, if any heterogeneous catalysts with high activity and selectivity can be found.

$$CH_2=CH_2+CH_3COOH \rightarrow CH_3COOC_2H_5 \qquad (1)$$

According to the patent literature of Showa Denko K.K., SiO_2-supported heteropolyacids like $H_4SiW_{12}O_{40}$ are active and selective catalysts for the direct addition of acetic acid to ethylene. By using the SiO_2-supported $H_4SiW_{12}O_{40}$ catalyst, Showa Denko K.K. developed a new commercial process in 1990 that is now going into full-scale operation with 50 kt/year capacity [7]. However, to the best of our knowledge, there have been no academic papers that study this reaction over solid acid catalysts.

In the present study, we compare the catalytic activity and selectivity of $H_4SiW_{12}O_{40}/SiO_2$ in the direct addition of acetic acid to ethylene over typical solid acids as well as over unsupported $H_4SiW_{12}O_{40}$. We systematically prepared $H_4SiW_{12}O_{40}/SiO_2$ using SiO_2 with various surface areas and mesopore sizes, and studied

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the ensuing catalytic reaction. These catalytic properties will be discussed with reference to the surface acidity of $H_4SiW_{12}O_{40}/SiO_2$ assessed by the temperature-programmed desorption of benzonitrile (BN-TPD) technique.

2. Experimental

2.1. Catalyst preparation

Dodecatungstosilicic acid ($H_4SiW_{12}O_{40}$) supported on silica was prepared by the incipient-wetness method using an aqueous solution of $H_4SiW_{12}O_{40}$. The mean pore size, BET surface area, and apparent density of SiO_2 (Fuji Silysia Chemical Ltd., CARiACT Q3, Q6, Q10, Q30, and Q50) are listed in Table 1. The loading amount of $H_4SiW_{12}O_{40}$ was adjusted to 0.1 mol dm^{-3} of SiO_2. Because the apparent densities of SiO_2 were different (Table 1), the loadings of $H_4SiW_{12}O_{40}$ expressed by weight percent (wt%) were different depending on the amount of SiO_2 (Table 2). After the addition of the aqueous $H_4SiW_{12}O_{40}$ solution to SiO_2, the resulting wet solid was dried in an oven at 383 K for 4 h. The concentrations of the $H_4SiW_{12}O_{40}$ solution were adjusted to achieve the intended loadings.

As references, H_3PO_4/SiO_2, Nafion–SiO_2, WO_3–ZrO_2, and unsupported $H_4SiW_{12}O_{40}$ were utilized as catalysts. Nafion–SiO_2 (Nafion SAC-13) was purchased from N.E. CHEMCAT. H_3PO_4/SiO_2 and WO_3–ZrO_2 were prepared according to the methods described in the literature [8].

2.2. Characterization

Temperature-programmed desorption of ammonia (NH_3-TPD) was carried out with a multitask TPD system (BEL Japan Inc.) equipped with a quadrupole mass spectrometer. After the sample was pretreated in a He flow at 373 K for 0.5 h, it was exposed to NH_3 (100 Torr) for 2 h at 373 K. The chamber was subsequently purged with a He flow at 373 K for 0.5 h to remove physisorbed NH_3. The temperature of the sample was increased at a rate of 10 K min^{-1} to 973 K, and the desorption rate of NH_3 was monitored at $m/z = 16$ for NH_3. In order to remove the interference of water desorbed from the sample, we also measured TPD spectra in a similar manner but without adsorption of NH_3, and the resultant TPD spectrum was subtracted from the original one obtained with the adsorption process.

The benzonitrile-TPD (BN-TPD) profile was obtained using a custom made TPD system equipped with an FID detector [9]. After the sample was pretreated under a flow of N_2 at 523 K for 2 h, it was exposed at 373 K for 1 h to a N_2 flow bubbled through a saturator of BN at room temperature. During the adsorption process of BN, the changes over time in the concentration of BN at the outlet of the cell were monitored on the FID detector to confirm the achievement of adsorption equilibrium. The excess BN was then removed under a flow of N_2 at 373 K for 1 h and then at 393 K for 1 h. The temperature of the sample was increased at a rate of 10 K min^{-1} to 973 K under a N_2 flow while the concentration of BN in the gas-phase was monitored by the FID detector.

The surface area was estimated by the BET method using the adsorption isotherm of N_2 at 77 K taken by an automatic adsorption apparatus (ASAP2010, Micromeritics) after evacuation of the sample at 423 K for 5 h. Mesopore size distribution was calculated by the BJH method using the desorption isotherm of N_2. XRD patterns were recorded on an X-ray diffractometer (M18XHF22-SRA, MacScience) after the samples were dried at 373 K.

2.3. Catalytic reaction

The gas-phase reaction for the formation of ethyl acetate from acetic acid and ethylene was performed in a continuous flow reactor (SUS316L tube, 21.4 mm inside diameter) at 0.8 MPaG and 438 K. The pelletized catalysts (40 cm^3) were fixed in the reactor and treated under a flow of a gas mixture consisting of acetic acid (37%), water (21%), and N_2 (42%) at a total rate of 60 dm^3 h^{-1} (STD) at 428 K for 0.5 h. After the temperature was increased to 438 K, the reactant gas mixture [acetic acid (8%), ethylene (78.5%), water (4.5%), and N_2 (9%)] was fed into the reactor at a total flow rate of 60 dm^3 h^{-1} (STD).

At the outlet of the reactor, ethyl acetate, ethanol, diethyl ether, and acetic acid were collected in a trap cooled to about 280 K for 1–2 h. The amounts of each trapped product were determined using a FID-GC (Shimadzu GC-14B) equipped with a capillary column (TC-WAX, 0.25 mm × 30 m), and the amount of the trapped water was determined by a Karl Fischer titration (Type KF-07, Mitsubishi Chemicals Co.). The products (ethyl acetate, ethanol, and diethyl ether) that slipped through the sampling trap were periodically extracted using a syringe and analyzed using FID-GC (Shimadzu GC-14B) equipped with a glass column (Span80, 3 mm × 2 m).

Table 1
Physical properties of silica used in the present study

Grade of SiO_2	Mean pore size (nm)	Pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	Apparent density[a] (kg dm^{-3})
Q3	3	0.25	632	0.85
Q6	6	0.61	384	0.60
Q10	11	1.04	345	0.42
Q30	29	0.94	107	0.42
Q50	26	0.59	73	0.42

[a] From a technical description of Fuji Silysia Chemical Ltd.

Table 2
Physical properties of $H_4SiW_{12}O_{40}/SiO_2$

Catalyst	Loading amount[a] (wt%)	Mean pore size (nm)	Pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})
$H_4SiW_{12}O_{40}$/Q3	26	3	0.11	183
$H_4SiW_{12}O_{40}$/Q6	33	6	0.30	211
$H_4SiW_{12}O_{40}$/Q10	42	11	0.48	195
$H_4SiW_{12}O_{40}$/Q30	42	31	0.40	76
$H_4SiW_{12}O_{40}$/Q50	42	39	0.18	54

[a] Loading amount of $H_4SiW_{12}O_{40}$ for all catalysts was 0.1 mol per 1 dm^3 of SiO_2.

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