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Liquid-phase synthesis of isoprene from MTBE and formalin using cesium salts of silicotungstic acid

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ABSTRACT

A single-stage synthesis of isoprene from methyl tertiary-butyl ether (MTBE) and formalin in an organic-aqueous two-phase system were studied by using Cs-exchanged silicotungstic acid catalysts ($Cs_XH_{4\text{-}X}SiW_{12}O_{40}$, abbreviated as Cs_X-STA). The Cs_X-STA catalysts (x = 2.0, 2.5, 3.0, and 3.5) were prepared using Cs_2CO_3 as Cs source and water as solvent. The catalysts were characterized by using XRF, FTIR, FT-Raman, XRD, N_2 sorption, light scattering, TGA, and potentiometric titration techniques to relate catalytic activities to catalyst properties. The characterization results showed that the Keggin structure and cubic unit cell of all Cs-STA catalyst samples were well preserved. The increase in acid strength and total acid sites with decreasing Cs content (x) resulted in increasing formaldehyde conversion and isoprene selectivity. However, at low Cs content ($x \leq 3.0$), the high contribution of homogeneous catalysis also played a role in the catalytic activities. The highest activity (isoprene formation normalized with total acid sites) of Cs2.5-STA catalyst was found to be attributed to its high surface area. For the organic solvent effect, the Cs2.5-STA catalyst activity increased with the increasing solvent polarity in the order: *n*-hexane < cyclohexane < toluene.

1. Introduction

Methyl tertiary-butyl ether (MTBE) as an oxygenated compound has been widely used as an additive in gasoline to raise the octane number. At present, the growth rate of MTBE consumption has decreased due to the shift to ethyl tertiary-butyl ether (ETBE), ethanol and tertiary-amyl methyl ether (TAME) usage in such developed countries as the United States, Japan and Western Europe. Thus, MTBE is more available and has a high potential to be a new source for high-purity isobutene which can be further converted to a variety of derivative products. One of the interesting isobutene derivative products is the isoprene monomer that could be produced via the Prins condensation reaction of isobutene and formaldehyde. The industrial process using the Prins reaction typically consists of two stages to achieve high yield and purity of isoprene: 1) liquid-phase synthesis of 4,4-dimethyl-1,3-dioxane (DMD) from isobutene and the formaldehyde aqueous solution (formalin) using H_2SO_4 or H_3PO_4 as catalysts; 2) vapor-phase decomposition of the Prins reaction product, DMD, to isoprene over a phosphate catalyst [1]. In this case, a refinery C4 olefin stream or *tert*-butyl alcohol (TBA) or both are normally isobutene sources in the first stage. Formalin as the most economic form of a C_1 aldehyde source is typically used in isoprene synthesis.

To reduce the investment and operating cost of the production process, many efforts have been made on developing a vapor-phase isoprene synthesis via the reaction of MTBE and O_2 or air over mixed oxide catalysts [2,3] and a vapor-phase single-stage synthesis via Prins reaction of isobutene and formaldehyde using various catalysts such as metal oxide catalysts [4], zeolite catalysts [5,6], phosphate catalysts [7], niobium oxide catalysts [8] and silicotungstic acid supported on silica catalysts [9]. Interestingly, a liquid-phase single-stage synthesis from TBA and formalin using inorganic salts as catalysts (such as $AlCl_3$ and $FeCl_2$) [10], MTBE or TBA and formalin using H_3PO_4, H_2SO_4, *p*-toluene sulfonic, and silicotungstic acid catalysts [11,12], isobutene and 1,3-dioxolane using Amberlyst 36 resin catalyst [13], TBA and 1,3,5-trioxane using Granion D001 resin catalyst [14], have been investigated. The use of 1,3-dioxolane or 1,3,5-trioxane as a formaldehyde source was aimed to reduce the high waste water production and energy consumption for the typical two-stage method. Recently, we reported on the isoprene synthesis from MTBE and formalin using Keggin-type heteropolyacids as catalysts, i.e., phosphotungstic acid (PTA), phosphomolybdic acid (PMA), and silicotungstic acid (STA) [15]. It was found that the synthesis in the cyclohexane-water system exhibited the higher isoprene selectivity and yield than in solvent-

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free system while the aqueous phase containing the catalyst was clean and easily separable from the organic phase products. Among the Prins reaction products formed, DMD was the key precursor of isoprene formation.

Among acid catalysts, heteropolyacids (HPAs), the acidic form of polyoxometalates, have been extensively employed in many acid-catalyzed reactions [16,17] such as Prins cyclization of styrene [18], oxidation of alcohol [19], veratrole benzoylation [20] and dehydration of glycerin [21]. HPAs inherently possess a very strong Brønsted type acidity and tunable acid-base and redox properties. The best known HPAs are the Keggin-type $H_{8-n}XM_{12}O_{40}$, where X is the hetero atom (usually P, Si, Ge, and As), n is the oxidation state of X and M is the addenda metal atom of element in high oxidation state (usually V, Mo, W, Co, and Zn). The Keggin anion, $XM_{12}O_{40}{}^{n-8}$, is composed of a central tetrahedron XO_4 surrounded by a shell of twelve edge- and corner- sharing metal-oxygen octahedral MO_6 [22]. In general, HPAs are highly soluble in polar media which their acid sites could effectively be utilized; however, the number of accessible acid sites in vapor-phase reaction, or non-polar liquid-phase reaction where they are insoluble, is low owing to their low intrinsic specific surface area (< 5 m^2/g). Salts of HPAs that protons could be substituted by large monovacant cations (such as $NH_4{}^+$, K^+, Cs^+), for example, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ had high specific surface area (c.a. 130 m^2/g) and high hydrophobicity [23], in other words, higher water-tolerable property [24] than the parent acid. For Cs-exchanged PTA ($Cs_XH_{3\text{-}X}PW_{12}O_{40}$, abbreviated as Cs_X-PTA), Cs2.0-PTA or particularly Cs2.5-PTA with large number of accessible surface acid sites was the efficient catalyst in liquid phase alkylation reaction of *m*-xylene or trimethylbenzene with cyclohexene [25], hydrolysis of ethyl acetate in excess water, hydration of olefin in excess water [26], and liquid phase transesterification of triglycerides with methanol and vapor-phase dehydration of ethanol [27]. For Cs-exchanged STA ($Cs_XH_{4\text{-}X}SiW_{12}O_{40}$, abbreviated as Cs_X-STA), Cs2.0-STA was also the active catalyst in heterogeneous etherification of hydroxymethylfurfural [28] whereas Cs0.8-STA was the efficient catalyst in C_4 and C_8 triglyceride transesterification, and palmitic acid esterification with methanol due to high acid properties and contribution of homogeneous catalysis [29]. For the structure of the cation-exchanged HPAs, the model proposed by Okuhara et al. was the Cs-PTA core-shell structure consisting of the fully-exchanged Cs3.0-PTA microcrytstallite core covered by the $H_3PW_{12}O_{40}$ layer [30]. The aggregate of the microcrstallites formed the secondary particle whereas the hydrogen-form PTA was also acting as a cement.

Isoprene synthesis over HPAs had been earlier reported both in a heterogeneous vapor phase [9,31] and homogeneous liquid phase reaction [11,12,15]. In this study, we report on a single-stage isoprene synthesis from MTBE and formalin in organic-aqueous two-phase system using Cs-exchanged silicotunstic acids or Cs_X-STA as catalysts. The catalysts were characterized by various techniques to investigate its surface, structural and acidic properties, relating to the catalytic activities. The effect of Cs content (x = 2.0, 2.5, 3.0, and 3.5) and solvent type on isoprene yield and selectivity were elucidated.

2. Experimental

2.1. Materials

Cs_2CO_3 (99% wt, Aldrich), STA ($H_4SiW_{12}O_{40}\cdot nH_2O$) (> 99.9% wt, Sigma-Aldrich), and de-ionized water were used to synthesize Cs-STA catalysts. Formalin (formaldehyde 37% wt, methanol 10% wt, Merck) and MTBE (> 99% wt, Bangkok Synthetic Co., Ltd.) were used as raw materials. Cyclohexane (99.5% wt, RCI Lab-Scan), *n*-hexane (> 99% wt, Merck), toluene (99.5% wt, Merck), and de-ionized water were used as solvents for isoprene synthesis. Acetonitrle (> 99.9% wt, Sigma-Aldrich) and *n*-butylamine (99.5%, Sigma-Aldrich) were used for potentiometric titration. All chemicals were used as received.

2.2. Catalyst preparation

Cesium exchanged silicotungstic acid catalysts ($Cs_XH_{4\text{-}X}SiW_{12}O_{40}$ abbreviated as Cs_X-STA, x = 2.0, 2.5, 3.0 and 3.5) were prepared according to the literature method [32]. The stoichiometric amount of an aqueous Cs_2CO_3 solution (0.03 M) was added dropwise (c.a. 0.03 mL/s) into an aqueous STA solution (0.05 M) under stirring at room temperature. For example, Cs2.5-STA was prepared from dropping 104 mL of Cs_2CO_3 solution (Cs^+ = 6.25 mmol) to 50 mL of STA solution (Keggin anion = 2.5 mmol) to achieve the desired Cs cation/Keggin anion ratio of 2.5. The white colloidal solution was aged overnight at room temperature, and subsequently evaporated to dryness at 100 °C on a hot plate for 12 h. After calcination at 300 °C for 3.5 h, the white powder obtained was stored in a desiccator cabinet. All Cs-STA and STA catalysts were used for isoprene synthesis without any drying treatment or thermal activation.

2.3. Catalyst characterization

The elemental analysis for the actual Cs content (x) per Keggin anion of Cs_X-STA catalysts was determined using the wavelength dispersive X-ray fluorescence (WDXRF) technique (Bruker S8 Tiger). Thermogravimetric measurements were made on a thermogravimetric analyzer (Shimadzu TGA-50) and the catalyst sample was heated from room temperature to 550 °C at a constant heating rate of 10 °C/min with N_2 flow rate of 20 mL/min. Transmission FT-IR spectra (ATR mode) were recorded on a Perkin Elmer spectrometer (Paragon 500) in the 650–1850 cm^{-1} range at resolution of 4 cm^{-1} with 32 scans. The X-ray diffraction patterns were performed on a Bruker D8 Advance diffractometer by using the Cu/K-α1 radiation source (λ = 1.5406 Å) at 40 KV, 40 mA, step time of 15.5 s, step size of 0.02°, and 2θ range of 5–80°. All catalysts were dried at 100 °C in an oven prior to the XRD and FTIR analysis. FT-Raman spectra were measured on a Perkin Elmer spectrometer (Spectrum GX), equipped with a Nd-YAG laser source (λ = 1064 nm), over the 200–3500 cm^{-1} range at resolution of 4 cm^{-1} with 1000 scans.

The porosimetry data on specific surface area and average pore diameter were obtained from Quantachrome Autosorb-1. The specific surface areas were calculated using the multipoint BET method over the P/P_0 range of 0.05-0.30. All Cs-STA catalyst samples were degassed at 300° C prior to construction of N_2 sorption isotherms. The colloidal particle size of Cs-STA catalysts was also measured by using light scattering technique (particle analyzer – DelsaNano S). Before the measurement, the fresh catalyst powders were suspended in water (0.1% wt) and stirred for 15 min; whereas the used catalyst samples from an aqueous colloidal product were also diluted with water at appropriate amount.

The acid strength and the total number of acid sites of catalysts were determined using a potentiometric titration method [33]. For a typical experiment, 0.1 g of fresh catalyst sample was suspended in 90 mL of acetonitrile and stirred for 3 h. Then, the suspension was titrated against 0.05 M solution of *n*-butylamine in acetonitrile at dosing rate of 0.05 mL/min. The potential variation was measured with an automatic titrator (SI Analytics TitroLine7000) using an N 6480 eth electrode. The first reading of electrode potential (E_i) indicated the maximum strength of the acid sites and the value from which the plateau was reached (mmol of *n*-butylamine per g of cat-