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Activated Carbon Supported Silicotungstic Acid Catalysts for Ethyl-*tert*-butyl ether Synthesis

Levent Degirmenci
Chemical and Process Engineering Dept., Bilecik University, 11210 Bilecik, Turkey

Nuray Oktar and Gulsen Dogu
Chemical Engineering Dept., Gazi University, 06570 Maltepe, Ankara, Turkey

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*Vapor phase ethyl-*tert*-butyl ether (ETBE) production was conducted in the presence of Cesium salts of silicotungstic acid (Cs-STA), activated carbon supported silicotungstic acid (AC-STA), and activated carbon supported Cesium salts of silicotungstic acid (AC-Cs-STA) catalysts. Isobutene (IB) conversion to ETBE at 373 K were determined as 0.16 and 0.2 for STA and AC-STA catalysts on constant space time basis. This increase of activity is one of the highlights of this study considering that STA loading in AC-STA catalysts had been adjusted to 40%. IB conversion to ETBE obtained at 373 K in the presence of AC-STA catalyst was found to be close to equilibrium. Stability of the synthesized catalysts were tested by applying a washing procedure with ethanol. Repeated ETBE synthesis with thoroughly washed samples indicated quite stable and active catalyts.* © 2011 American Institute of Chemical Engineers *AIChE J,* 57: 3171–3181, 2011
Keywords: ETBE, activated carbon, STA, Cs-STA, catalyst

Introduction

Detoriation in air quality is being considered as one of the most important environmental problems. Solution to reduce harmful effects of transportation related pollutants was achieved by applying measures such as elimination of lead compounds from gasoline and efficient use of oxygenates as gasoline blending compounds. Improved quality in burning characteristics of gasoline and reduced exhaust emissions had been obtained by oxygenates. Alcohols and tertiary ethers are the oxygenates used as additives in gasoline with their decent properties such as high octane numbers and low CO emissions.[1] Tertiary ethers have attracted increasing attention with their superior properties compared with alcohols. Among the tert-ethers proposed as octane enhancing gasoline blending compounds, ethanol derived oxygenates, such as ethyl-*tert*-butyl ether (ETBE) and tert-amyl ethyl ether (TAEE), attracted major attention of researchers and fuel producers due to their better burning properties and their superiority over MTBE on environmental safety basis.[2–4] ETBE or TAEE production can be achieved by the reaction of ethanol with isobutene or isoamylenes, respectively over acidic macroreticular resin catalysts.[5–8]

ETBE production is achieved in the presence of solid acid catalysts. Zeolites, acidic ion-exchange resins, and recently heteropolyacids (HPA) have been tested as catalysts in ETBE synthesis. Among these catalysts, HPA have attracted major attention of researchers, due to their very high Bronsted acidity. HPA are transition metal-oxygen-anion clusters which are also known as polyoxometalates. They exhibit both acid and redox properties which enable synthesis of various compounds with distinct properties.[9] Dehydrogenation of isobutyric acid and oxidation of methacrolein can be given as examples to applications of heteropolyacid catalysts in oxidation reactions.[10] Acidity of these catalysts was stated to be higher than mineral acids, such as H_2SO_4, HCl,

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Correspondence concerning this article should be addressed to N. Oktar at oktarnuray@gmail.com, or nurayoktar@gazi.edu.tr.

HNO_3.[11] In a work conducted by Thomas et al.,[12] activities of two heteropoly acid catalysts, namely silica supported silicotungstic acid (STA) and tungstophosphoric acid (TPA) were compared by ^1H MAS NMR analysis, in terms of coverage and dehydroxylation temperature. The results of ^1H NMR analysis of TPA after treatment at 300°C, under vacuum indicated disapperance of protons. The ^1H NMR results of STA were found to be quite different, exhibiting a distinct behavior with the evidence of signals that belonged to proton sites even after treatment at 400°C. In a recent research conducted by Degirmenci et al.,[13] the activities of heteropoly acids, namely STA, tungstophosphoric acid-Keggin (TPA-K), and tungstophosphoric acid-Dawson (TPA-D) were compared. Results indicated that STA had exhibited highest activity among the catalysts investigated. Higher activity of STA than TPA and MPA (molybdophosphoric acid) was also reported in a study performed by Varisli et al.,[14] in diethyl-ether production by dehydration of ethanol in a temperature range of 140–250°C.

HPA are considered as highly attractive solid acid catalysts, having superior acidic characteristics. Major disadvantage of HPAs is their very low surface area (less than 1 m^2 g^{-1}) and solubility in the presence of polar solvents. Synthesis of heteropoly acid salts and supported heteropolyacid catalysts are stated to improve the surface area of the parent heteropolyacid.[15–18] Heteropolyacid salts are prepared by exchange of protons of the heteropolyacid with cations of the salt. Cesium based heteropolyacid salts are the most known heteropolyacid salts investigated in the literature. In a study conducted by Soled et al.,[15] highest acidity of heteropolyacid salts had been obtained by exchanging protons of the catalyst in a degree of $x = 2.5$ for Cesium based heteropolyacid salts. A sharp decrease in acidity was observed with further increase in cation number of the compound employed in synthesis of heteropolyacid salt. In a seperate study preformed by Pozniczek et al.,[16] an activity increase with the number of exchanged cations was reported.

Support materials such as TiO_2, SiO_2, γ-Al_2O_3, and activated carbon are being recommended for impregnation of heteropolyacid catalysts. Pizzio et al.,[17] stated stable behavior of carbon and TiO_2 supported TPA up to 425°C. TPA supported on carbon, TiO_2, and SiO_2 were also shown to have higher acidity than bulk catalyst in their study. Activated carbon is accepted as a fine support with surface area values as high as 1000 m^2 g^{-1}. It has the ability to entrap certain amount of heteropolyacid, which enable efficent use of the catalyst in vapor-phase applications. Literature survey on activated carbon supports revealed utilization of catalysts in varying loading amounts. In a study conducted by Chimienti et al.,[18] impregnation of Keggin type TPA and STA catalysts were performed on carbon. Loading amounts as high as 50% were utilized. Activity of the catalysts was tested for isopropanol dehydration reaction. Results indicated an increase in catalyst activity with increasing loading amount up to 30% loading. Filamentous type carbons were employed as support material in the work of Timofeeva et al.[19] In that work, Dawson and Keggin type tungstophosphoric acids were utilized as active materials. Activity of synthesized catalysts were tested in the reaction of 2,6-di-*tert*-butyl-4-methylphenol with toluene. It was stated that the activity of supported catalysts had increased due to the increase in activity of surface protons of the catalysts. In other words, activity of the synthesized catalysts had increased with increasing HPA on the structure. Obalı and Doğu[20] had also prepared activated carbon supported catalysts containing 25 and 31% TPA and tested their activities in etherification reaction of ethanol with iso-amylene. Comparison of activities of these catalysts indicated an increase in fractional converison of isoamylene with increasing TPA loading amount.

Studies on ETBE synthesis in the presence of supported heteropolyacid catalysts are scarce. In the present study, cesium (Cs) based STA salts, STA impregnated activated carbon catalysts (AC-STA) and Cs-STA impregnated activated carbon catalysts (AC-Cs-STA) containing 10–40% STA and 20–40% Cs-STA were prepared and their activities were tested in vapor phase reaction of ethanol with isobutene. Loading amounts were determined based on literature survey conducted for activated carbon supported heteropoly acid catalysts.[18–20] Effect of chemical treatment of the support material was also investigated by comparison of reaction results conducted with H_2O_2 treated and HNO_3 treated, AC-STA and AC-Cs-STA catalysts with different STA loadings.

Experimental Section

Chemicals and catalysts

Ethanol (EtOH) and isobutene (IB) employed in ETBE synthesis were purchased from Merck and Air Products, respectively. STA and cesium salt (Cs_2CO_3) were obtained from Sigma-Aldrich. Activated carbon (AC) used as support material was purchased from KUREHA (Japan).

Preparation of heteropolyacid salt and supported catalysts

Cs-STA catalyst was prepared by dropwise addition of Cs_2CO_3 solution into the ethanol solution of STA. The resulting solution was stirred at room temperature for 18 h and then heated up to 50°C to vaporize ethanol. Vaporization of ethanol was completed by drying in oven at 50°C. Molar ratio of Cs_2CO_3 and STA was adjusted to obtain a heteropoly acid salt with a molecular formula of $H_{4-x}Cs_xSiW_{12}O_{40}yH_2O$ where $x = 2.5$.

AC was washed with 0.1M solutions of NaOH and HCl, respectively for the removal of possible impurities. Following the washing step, an activation step was conducted by treatment with 30% HNO_3 solution at 70°C in a reflux system, for 2 h, before being utilized as support material. The pretreated activated carbon was then impregnated by STA with loading amounts of 10, 20, and 40%.

AC-Cs-STA catalysts were prepared by a two-step synthesis method. Cs was first impregnated on AC by dropwise addition of Cs_2CO_3 solution on AC. Ethanol in the solution was evaporated by drying in the oven at 50°C. In the following step, STA in ethanol solution was added dropwise on Cs impregnated AC. The synthesized AC-Cs-STA catalyst was dried at 50°C. Loading amounts of Cs-STA was determined as 20 and 40%. Unless otherwise stated the phrases AC-STA and AC-Cs-STA were referred for the catalysts, with the support material being chemically treated by HNO_3.

A separate activated carbon treatment procedure, besides HNO_3 treatment, was applied in the synthesis of some of the catalysts. In that case, treatment was achieved by activation of AC with H_2O_2, followed by STA or Cs-STA impegnation. AC was washed with 0.1M solutions of NaOH and HCl prior to synthesis as in AC-STA and AC-Cs-STA. Loading amount was adjusted as 40% for STA and Cs-STA in the H_2O_2 treated catalysts.

The stability of impregnated catalysts was tested by washing the synthesized catalysts with EtOH. In these experiments, AC-STA and AC-Cs-STA catalysts with a loading amount of 40% STA or Cs-STA were throughly washed with EtOH for 8 h before being tested in ETBE synthesis.

Reaction experiments

IB and EtOH were used as reactants in vapor phase ETBE synthesis. Reaction experiments were conducted in the presence of Cs-STA, AC-STA, and AC-Cs-STA catalysts in a temperature interval of 353–523 K and with a IB/EtOH molar ratio of 0.17, in a fixed bed flow reactor. A set of reaction experiments were also performed with ethanol as the sole reactant in feed, to determine the effect of IB absence on product distribution at temperatures exceeding 373 K. These experiments were performed in the presence of H_2O_2 treated AC-STA catalysts. A catalyst amount of 0.1 g was used in all experiments, and total volumetric flow rate of reactants and helium was adjusted to 113 ml min^{-1} during the course of the experiments. A gas chromotograph (Agilent 6890N) equipped with a flame ionization detector and containing Chromosorb AW column (15% FFAB) was connected on-line to the system to analyze outlet stream composition.

Characterization studies

Thermogravimetrical analysis (TGA) of AC-STA and AC-Cs-STA catalysts were conducted with a Dupont 921 Thermal analyzer. Temperature range was selected as 293–873 K. Analyses were performed at a heating rate of 10°C min^{-1}, in the presence of nitrogen.

Single point Brunauer, Emmett and Teller (BET) surface areas of the samples were measured by a Quantachrome sorptometer. Pore size distributions and average pore diameter of supported catalysts were determined by nitrogen adsorption-desorption isotherms in Quantachrome Autosorb-1-C/MS device.

FT-IR analyses of HNO_3 and H_2O_2 treated AC-STA and AC-Cs-STA samples were also conducted to validate the presence of catalyst structure on the support material. Analyses were performed in a Thermo Nicholet 8700 instrument.

X-ray fluorescence analysis (XRF) was conducted in a PAN ANALYTICAL AXIOS ADVANCED Model WDS XRF device (4 kW, Max 160 mA). Activated carbon supported catalysts synthesized with 40% STA/Cs-STA loading amount were analyzed for the Cs/W ratio by XRF.

X-ray photoelectron spectra (XPS) of AC-Cs-STA catalysts were recorded using a SPECS instrument. Analyses were conducted with a MgKα anode operating at 300 W. The C1s peak with a binding energy of 284.6 eV was employed to correlate sample charging effects.[21,22]

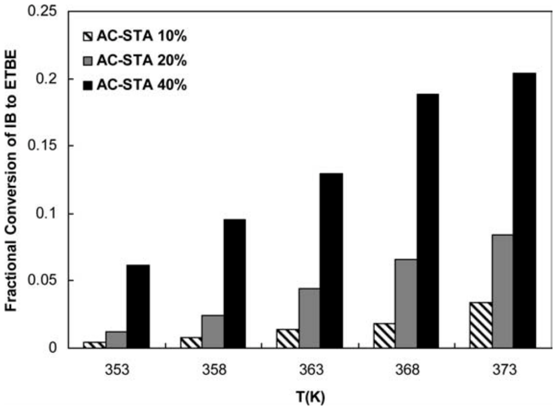

Figure 1. Effect of STA loading on the activity of AC-STA catalysts.

The acidic nature of supported catalysts was determined by Diffuse-Reflectance FT-IR (DRIFTS) analyses performed with pyridine adsorbed samples in a Perkin Elmer Spectrum One device. Analyses were carried out at room temperature by mixing 0.02 g of sample with 0.07 g KBr. A wavelength interval of 400–4500 cm^{-1} was investigated to detect acidic sites.

Results and Discussion

Reaction experiments

ETBE synthesis was conducted in a temperature interval of 353–523 K, in a fixed bed flow reactor. Loading amount of STA on AC supported catalysts was varied between 10–40% in these experiments. Effect of STA loading on conversion of IB to ETBE was illustrated in the presence of AC-STA catalysts, in Figure 1. As seen in this figure, an increase in conversion of IB to ETBE with temperature and STA loading amount was observed. Results indicated that highest conversions to ETBE was obtained with a catalyst containing 40% STA. IB conversion to ETBE obtained at 373 K (about 0.2) was found to be close to equilibrium, with the catalyst containing 40% STA. IB conversion was reported as 0.16 using pure STA at the identical experimental conditions in our earlier publication.[13] These results showed the improvement in catalyst activity as a result of impregnation of STA in AC. Based on constant space time, the conversion value of 0.20 obtained in the presence of AC-STA (40% STA loading) gave 20% higher conversion to ETBE than pure STA. This result is considered to be due to the increased surface area of STA by impregnation into activated carbon.

Activity of Cs-STA was also tested with AC-Cs-STA catalysts prepared by 20 and 40% Cs-STA loading. Results are given in Figure 2. It can clearly be seen from this figure that IB conversion also increased by increasing the amount of Cs-STA in the AC supported catalyst. Conversion values obtained for AC-Cs-STA catalyst with 40% Cs-STA loading exceeded the corresponding IB conversion values obtained with pure Cs-STA, for the reactions conducted at 368 and 373 K. These results indicated an improvement in activity for constant space time. It can be implied from the reaction results that loading amounts as high as 40% could have been

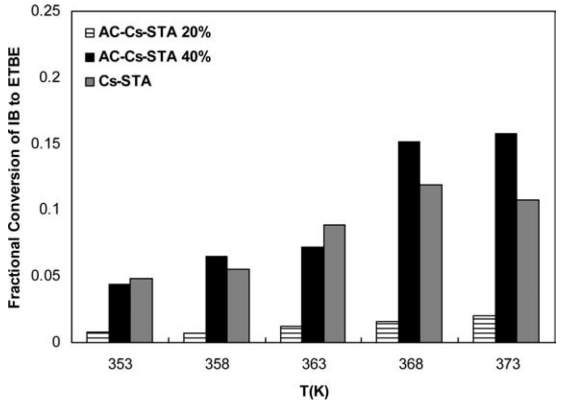

Figure 2. Activity comparison of Cs-STA loaded AC catalysts with pure Cs-STA.

impregnated on support material without loss in catalyst activity. However, the activity of Cs-STA impregnated AC catalysts was less than the activity of STA impregnated AC catalysts. This was considered to be due to less acidity of the Cs-STA than STA. Reaction results obtained in the presence of AC supported catalysts indicated highest catalytic activity with 40% loading of STA/Cs-STA. Consequently, catalysts synthesized with 40% loading amount were employed on the proceeding experiments.

Side product formation was also observed in the course of experiments. Possible reactions which might take place during ETBE synthesis are:

$IB + EtOH \Leftrightarrow ETBE$ (ETBE synthesis)
$2EtOH \Leftrightarrow DEE + H_2O$ (Formation of diethyl ether)
$2IB \Leftrightarrow DIB$ (Formation of di-isobutene)
$DIB + IB \Leftrightarrow TRIIB$ (Formation of tri-isobutene)
$3IB \Leftrightarrow TRIIB$
$EtOH \Leftrightarrow ETHYLENE + H_2O$ (Ethanol dehydration to form ethylene)
$EtOH \Leftrightarrow AA + H_2$ (Ethanol dehydrogenation to form acetaldehyde)

Due to ethanol dehydration, formation of side products, such as diethyl ether (DEE) and ethylene were also observed during the course of experiments conducted in the presence of AC-STA catalyts, at temperatures exceeding 423 K. Ethylene was observed at higher temperatures over 473 K. Trace amounts of di-isobutene, tri-isobutene, and acetaldehyde were also observed above 423 K. Product distributions in the presence of AC-STA (40% STA loading) and H_2O_2 treated AC-STA were illustrated in terms of ETBE, DEE and ethylene selectivities and fractional conversions of IB to ETBE and EtOH to DEE and ethylene in Figures 3a, b and 4a, b, respectively, in the temperature range of 353–523 K. A stable 100% ETBE selectivity was observed between 353

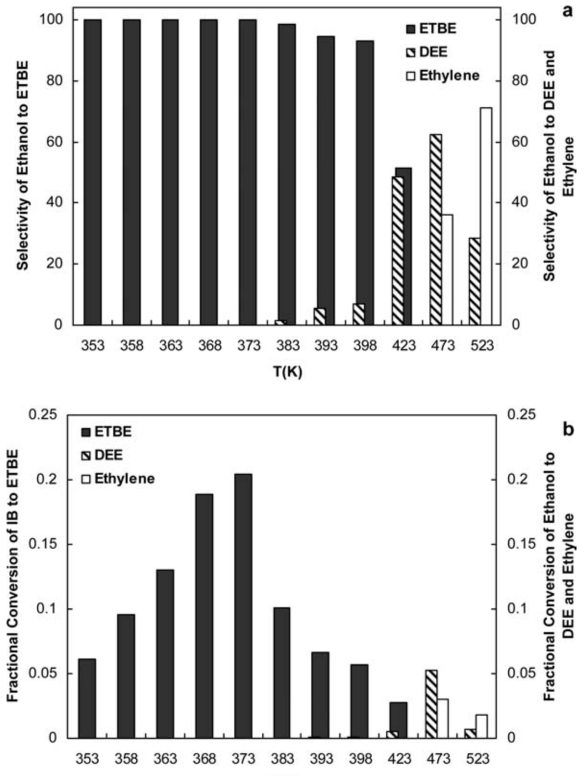

Figure 3. Product distributions in the presence of AC-STA catalyst (containing 40% STA).

(a) Effect of temperature on the selectivities of ETBE, DEE, and ethylene, based on EtOH. (b) Effect of temperature on fractional conversions of IB to ETBE and on the fractional conversion of ethanol to DEE and ethylene.

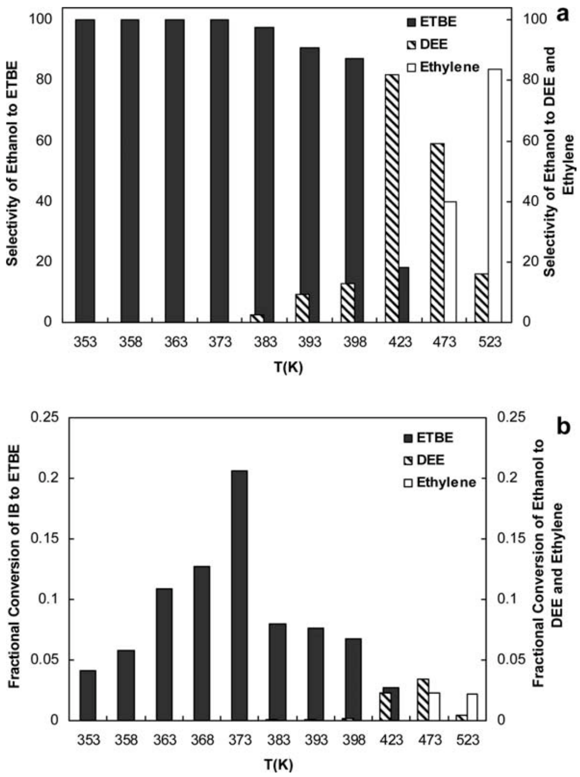

Figure 4. Product distribution in the presence of H_2O_2 treated AC-STA catalyst (containing 40% STA).

(a) Effect of temperature on the selectivities of ETBE, DEE and ethylene, based on EtOH. (b) Effect of temperature on fractional conversions of IB to ETBE, and on the fractional conversion of ethanol to DEE and ethylene.

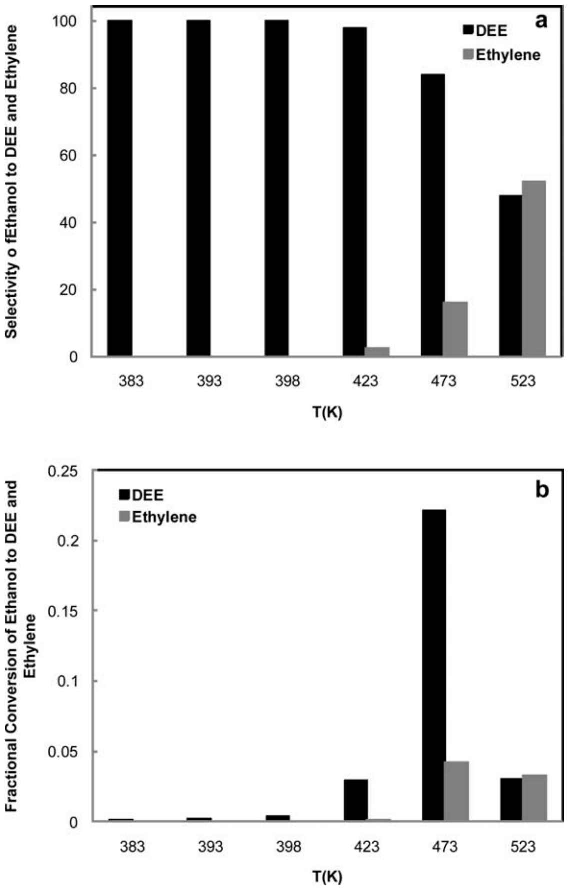

Figure 5. Product distribution in the presence of H_2O_2 treated AC-STA catalyst with pure EtOH in the feed composition.

(a) Effect of temperature on the selectivities of DEE and ethylene. (b) Effect of temperature on fractional conversions of EtOH to DEE and ethylene.

and 373 K, as seen from Figure 3a. At exceeding temperatures ETBE selectivity decreased with increasing temperature, as a result of DEE formation. DEE was the major side product until 423 K. At exceeding temperatures, ethylene formation also occurred due to decomposition of DEE. Selectivity of ethylene reached to a maximum at 523 K. Fractional conversion of IB to ETBE increased up to 373 K. Conversion values decreased above 373 K basically due to thermodynamic limitations. A maximum in DEE selectivity was obtained at 473 K. At exceeding temperatures DEE selectivity decreased with an increase in ethylene formation (Figure 3b). Product distributions observed in the presence of H_2O_2 treated AC-STA catalyst were found to follow a similar behavior with a distinction in temperature of highest DEE selectivity, which was obtained at 423 K, as seen from Figure 4.

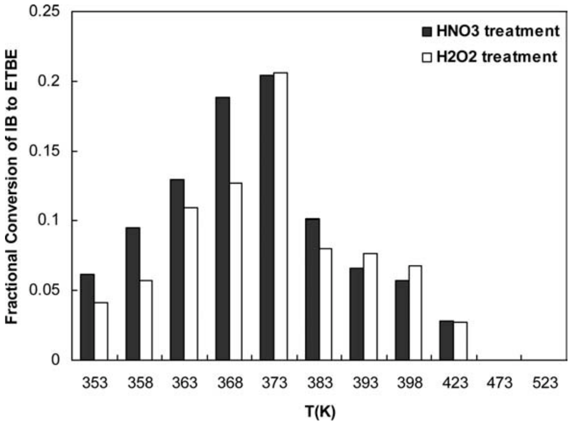

Figure 6. Effect of chemical treatment on IB conversion to ETBE in the presence of AC-STA catalyst (IB/EtOH: 0.17).

Etherification reaction in the presence of H_2O_2 treated AC-STA catalyst was also performed in identical experimental conditions using EtOH as the sole reactant in the feed stream. Results of these experiments were illustrated in terms of DEE and ethylene selectivities and fractional conversions of EtOH (Figure 5). Formation of DEE and ethylene were observed only at temperatures higher than 373 K. Almost 100% DEE selectivity values were obtained between 373 and 393 K. At exceeding temperatures, DEE selectivity decreased due to ethylene formation. Fractional conversion of EtOH to DEE had reached its highest value of 0.22 at 473 K. Comparison of applied feed compositions for fractional conversion of ethanol to DEE and ethylene revealed an increase for DEE and ethylene in the case of EtOH being the sole reactant which indicated the inhibiting effect of IB in dehydration reaction of EtOH.

The change in activity with chemical treatment of support material with H_2O_2 and HNO_3 was discussed by evaluation of reaction experiments conducted in the presence of AC-STA catalysts containing 40% STA. Results are given in Figure 6, in terms of fractional conversion of IB to ETBE and in Figure 7, in terms of EtOH conversion to DEE and ethylene between 353 and 523 K. At temperatures exceeding 423 K, ETBE formation was not observed. Comparison of activities revealed that at temperatures lower than 373 K, higher conversions were obtained in the presence of HNO_3 treated AC-STA catalysts when compared with H_2O_2 treated catalyst. Conversion to ETBE reached its highest value at 373 K (Figure 6). As discussed in the previous paragraphs,

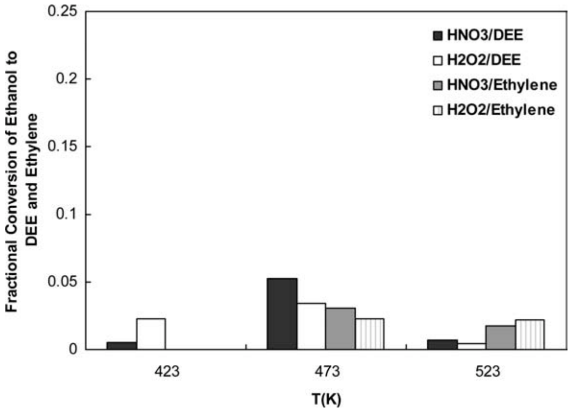

Figure 7. Effect of chemical treatment on ethanol conversions to DEE and ethylene in the presence AC-STA catalysts (IB/EtOH: 0.17).

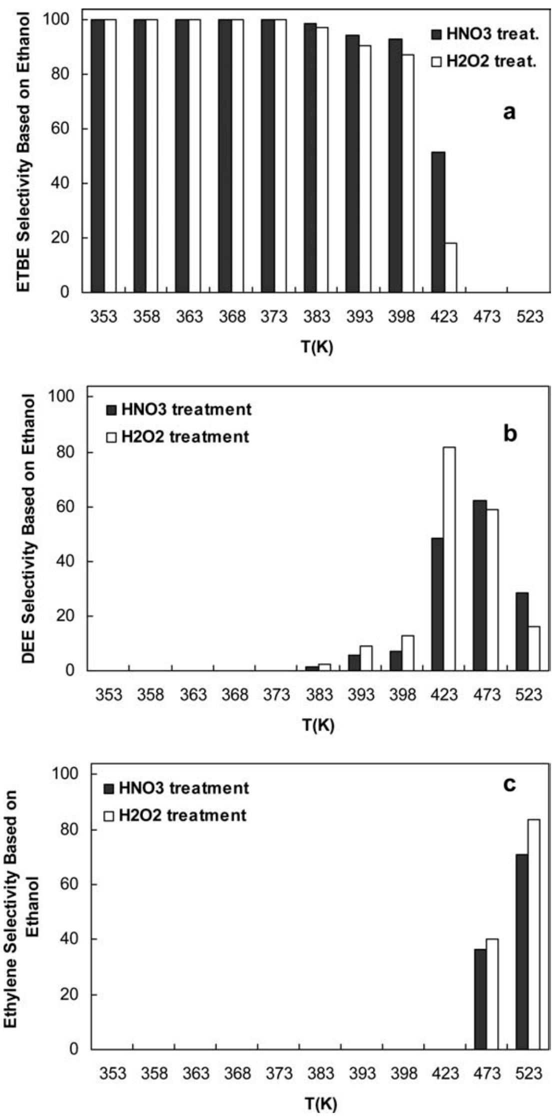

Figure 8. Effect of chemical treatment of AC-STA on the selectivities of (a) ETBE, (b) DEE, and (c) Ethylene.

the conversions obtained with both of these catalysts were higher than the conversion values determined in the presence of pure STA, for identical space times. Chemical treatment of the catalysts had no significant effect on conversions to ethylene, as seen from Figure 7.

Effect of chemical treatment of catalyst support with H_2O_2 and HNO_3 on product selectivities was investigated by evaluation of reaction data. Results are illustrated in terms of ETBE, DEE, and ethylene selectivities in Figure 8. ETBE selectivities remained as 100% between 353 and 373 K, indicating no side product formation in this temperature interval. At 383 K, a decrease in ETBE selectivity was observed. Comparison of selectivities obtained with chemically treated catalysts revealed that AC-STA catalyst treated with HNO_3 was more convenient for ETBE production (Figure 8a). Selectivities of DEE and ethylene were observed to be higher in the presence of H_2O_2 treated AC-STA catalyst, at the temperatures of 423 K (for DEE) and 523 K (for ethylene) (Figures 8b, c).

Considering that STA was soluble in polar media, ETBE synthesis was repeated with thoroughly washed AC-STA and AC-Cs-STA catalysts to investigate the effect of chemical treatment on catalyst stability. IB conversions to ETBE obtained for thoroughly washed catalyst samples are shown in Figure 9 for HNO_3 treated catalysts and in Figure 10 for H_2O_2 treated catalysts. A minor activity loss of about 10% was observed following the washing step of AC-STA catalysts treated with HNO_3 and H_2O_2, at 373 K. The decreasing trend of the activity by the applied procedure was determined to be independent of chemical treatment, as seen in Figures 9 and 10. Similar behavior in activity loss was observed in the presence of HNO_3 and H_2O_2 treated AC-Cs-STA catalysts. However, in this case activity loss was more significant. Results obtained with EtOH washed samples imply synthesis of a reasonably stable and active catalyst to be employed in ETBE synthesis. These catalysts are especially suitable for vapor phase reactions.

Characterization studies

TGA analysis of AC-STA and AC-Cs-STA were conducted to determine thermal stability of synthesized catalysts. Samples were heated with a heating rate of 10°C $\min^{-1}$ between 293 and 873 K, in the presence of nitrogen. TGA curves of AC-STA and AC-Cs-STA were illustrated in

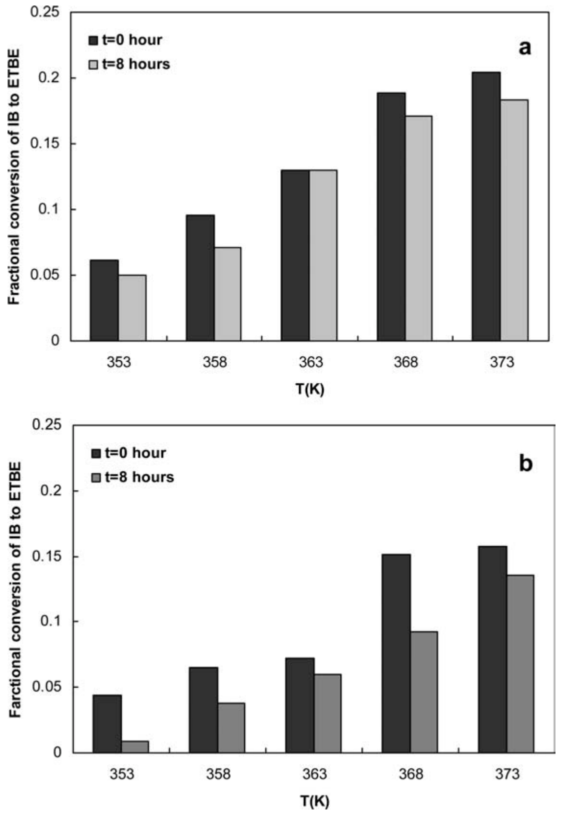

Figure 9. Effect of washing on the stability of HNO_3 treated (a) AC-STA catalysts and (b) AC-Cs-STA catalysts.

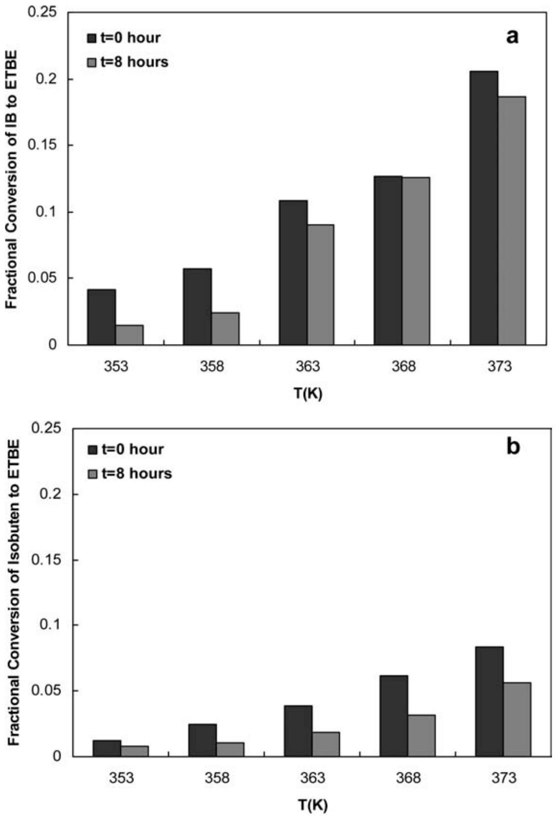

Figure 10. Effect of washing on the stability of H_2O_2 treated (a) AC-STA catalysts and (b) AC-Cs-STA catalysts.

comparison with TGA curve of STA conducted in our earlier studies[23] (Figure 11). TGA curve of AC-STA and AC-Cs-STA revealed a weight loss between 293 and 363 K, which corresponded to desorption of physically adsorbed water. It was thought that the weight loss detected between 363 and 800 K for activated carbon supported catalysts had occurred due to cleavage of oxygenated carbon surface groups[24] as well as removal of water from the crystal structure of STA. At temperatures exceeding 800 K decomposition of molecular structure of STA had occurred. In the case of AC-STA catalyst, decomposition of structure occurred at about 800 K, which was 150°C higher than pure STA,[23] indicated an improvement in thermal stability of STA upon impregnation onto support material. Similar improvement was obtained in the work of Obalı and Doğu[20] Similar decomposition behavior was observed with AC-Cs-STA.

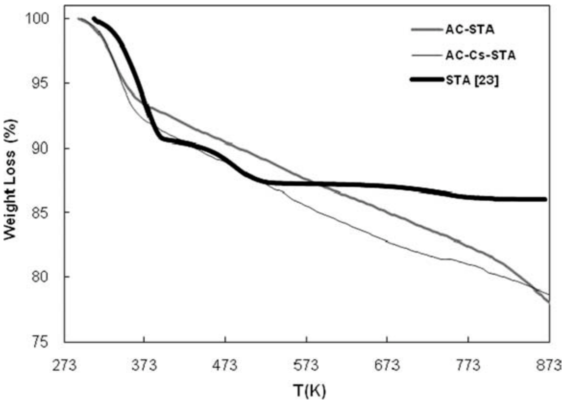

Figure 11. Comparison of TGA curves obtained with STA, AC-STA, and AC-Cs-STA catalysts.

Some physical properties of AC supported STA and Cs-STA catalysts were illustrated in Table 1. Single point BET analyses of the samples were conducted by Quntachromo sorptometer. BET surface areas were determined as 502, 350, 550, and 430 m^2 g^{-1} for HNO_3 pretreated AC-STA, HNO_3 pretreated AC-Cs-STA, H_2O_2 pretreated AC-STA and H_2O_2 pretreated AC-Cs-STA, respectively. Surface areas of Cs-STA impregnated catalysts were found to be lower than STA impregnated ones, which occurred as an expected result due to interaction of the support material with large Cs cations. Fractional conversion of IB to ETBE was also obtained to be higher in the presence of AC-STA than AC-Cs-STA, which was expected considering higher BET surface area and higher acidity of AC-STA when compared with AC-Cs-STA.

Pore size distributions and pore diameters of catalysts were determined by evaluation of nitrogen adsorption-desorption isotherms. Nitrogen adsorption-desorption isotherms and pore size distributions of synthesized catalysts are given in Figure 12. Isotherms can be considered as Type 1 according to IUPAC classification and indicate a microporous structure. In fact, pore size distributions also indicated presence of micropores having diameters smaller than 2 nm. It was interesting that these materials had also some mesopores in the order of about 4 nm.

Total pore volumes of AC-STA and AC-Cs-STA catalysts were reported in Table 1. Pore volumes of H_2O_2 treated AC-STA and AC-Cs-STA were found to be higher than HNO_3 treated catalysts. It was thought that corrosive effect of H_2O_2 had increased pore volume.

FTIR analyses of AC-STA and AC-Cs-STA catalysts treated with HNO_3 and H_2O_2 were also conducted to determine any distortions in the FT-IR pattern of STA upon supporting on AC. Results are shown in comparison with FT-IR analysis of STA conducted in our earlier studies[23] (Figure 13). FT-IR analyses of AC-STA and AC-Cs-STA catalysts revealed the presence of undecomposed STA molecule which had been evidenced with a series of peaks observed between 700 and 1200 cm^{-1}. The observed peaks attributed to W-O_d terminal with a wavenumber of 980 cm^{-1}, W-O_b-W edge shared with a wavenumber of 923 cm^{-1} and W-O_c-W with a wavenumber of 779 cm^{-1}, respectively, which had been identified in accordance with literature.[23,25] The fact that the characteristic bonds between W-O had remained unchanged regardless of treatment had implied preservation

Table 1. Physical Properties of the Catalysts

	Surface Area (m^2/g)		Total Pore Volume (cc/g)	Average Pore Diameter (nm)
Sample ID	BET	BJH	BJH ads.	BJH ads.
AC-STA/HNO_3	502	462	0.19	1.2
AC-STA/H_2O_2	550	542	0.21	1.2
AC-Cs-STA/HNO_3	350	415	0.17	1.2
AC-Cs-STA/H_2O_2	430	571	0.23	1.2

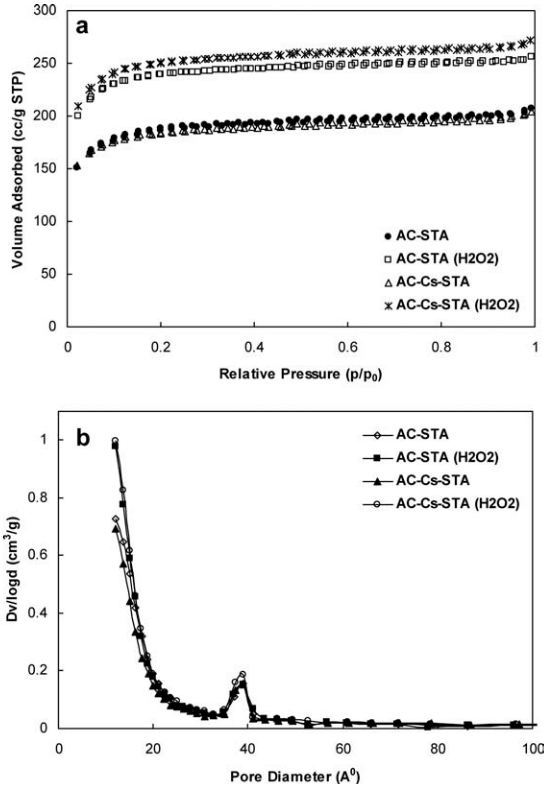

Figure 12. Nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) of HNO_3 and H_2O_2 treated AC-STA and AC-Cs-STA catalysts (Loading amount: 40% STA, 40% Cs-STA).

of the primary structure of heteropolyacid on catalyst surface. However, the intensities of the IR peaks observed with the HNO_3 treated catalysts were higher than those observed with H_2O_2 treated catalysts. The peaks obtained with STA sample designated with wavenumbers of 3130 and 1720 cm^{-1} corresponded to proton structure of the catalyst.[23,25] The disappearance of the stated peaks with impregnation on support implied bondage occurred between H^+ of STA and AC.

XRF analyses of AC-Cs-STA catalyst indicated that atomic ratio of Cs to W was 0.202, which was quite close to the theoretical value of Cs/W ratio (0.208) according to the synthesis conditions.

XPS analyses conducted with HNO_3 and H_2O_2 treated AC-Cs-STA catalysts are given in Figures 14–17. Peak values obtained in the course of analyses are illustrated in comparison with reference values, in Table 2. A major peak with a maximum of 284.5 eV was observed in C 1s XP spectrum of AC-Cs-STA catalysts revealing graphite as the main state. XPS spectra of C 1s, W 4f, O 1s, and Cs $3d_{5/2}$ were fitted and analyzed in detail. In the case of C 1s, two additional peaks were obtained indicating C-O and C=O formation,[26–28] respectively (Figure 14). The W 4f spectrum of AC-Cs-STA revealed a well-resolved spin-orbit doublet defining W $4f_{7/2}$ and W $4f_{5/2}$, which are typical of the presence of W(VI) structure[21] (Figure 15). XP spectrum of O 1s indicated the presence of W-O-W bonds[21] along with the presence of C-O moieties in the catalyst structure[26–28] (Figure 16). XP spectrum of Cs $3d_{5/2}$ revealed two regions identifying terminal and bridge Cs structures (Figure 17). Analysis of the structures revealed two coordination environments corresponded to proton exchange between Cs and $H_5O_2^+$ together with Cs^+-O^-=W coordination.[29] As a result of proton exchange, it was thought that a decrease in the activity of the catalyst had occurred compared with AC-STA which had been emphasized in reaction experiments.

True surface STA contents of the AC-Cs-STA catalysts were evaluated via XPS analysis. Surface STA content was determined in terms of W/C atomic ratio. XPS analysis of H_2O_2 pretreated AC-Cs-STA gave a W/C ratio of 0.20. In the case of HNO_3 pretreated AC-Cs-STA catalyst this ratio was determined as 0.12. The theoretical atomic W/C ratio of the synthesized materials was also estimated from the STA loading amount into AC. The theoretical value of W/C atomic ratio (about 0.016) was an order of magnitude smaller than the W/C ratios obtained from XPS analysis. These results indicated that most of STA was deposited near the external surface of the AC support material. In the case of H_2O_2 treated AC, W/C ratio evaluated from XPS was higher than the corresponding value for HNO_3 treated AC. It was thought that due to surface corroding (etching) effect of H_2O_2, deposition of Cs-STA had occurred mostly on the surface of the support material. In the case of HNO_3 pretreated AC-Cs-STA, lower value of W/C evaluated by XPS than the

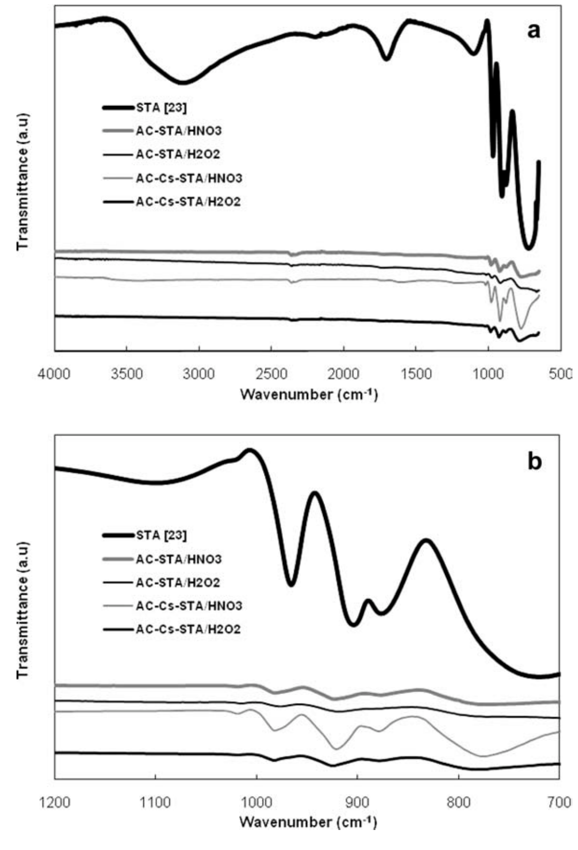

Figure 13. FT-IR analyses of AC-STA and AC-Cs-STA catalysts in a wavenumber of (a) 500–4000 cm^{-1} and (b) 700–1200 cm^{-1}.

Table 2. The Assignment of XPS Peaks Obtained with Deconvolution Results of AC-Cs-STA Catalysts Treated with HNO_3 and H_2O_2, respectively

Species	Peak (eV) This Work	Peak (eV) Reference	FWHM(eV)	Surface Group	Ref.
C1s					
1	284.5 (NA, HP)	284.5 ± 0.1;284.2–284.9;284.4 ± 0.2	2.26	C	26,27,28
2	285 (NA) 285.6 (HP)	286.1 ± 0.1;285.4–286.3;285.5 ± 0.5,	4.18	C-O-	26,27,28
3	287.9 (NA) 287.7 (HP)	288.7 ± 0.1;287.2–287.9;287.2 ± 1.0,	3.89	C=O	26,27,28
W4f					
1	35.6 (NA) 35.7 (HP)	35.7	1.76	W $4f_{7/2}$	21
2	37.6 (NA, HP)	37.7	2.53	W $4f_{5/2}$	21
O1s					
1	531 (NA,HP)	531.2	2.25	W-O-W	21
2	533 (NA) 533.5 (HP)	533.5 ± 0.2;533.2–533.8, 532.9 ± 0.4	2.03	C-O	26,27,28
Cs $3d_{5/2}$					
1	724 (NA) 723.6 (HP)	724.3, 724.1	3.73	Terminal Cs	22,29
2	724.5 (NA) 724.3 (HP)	724.8, 725.1	1.60	Bridge Cs	22,29

NA: HNO_3 treated catalyst.
HP: H_2O_2 treated catalyst.

theoretical value may be due to better penetration of some STA into the micropores of AC.

DRIFTS analyses conducted on pyridine adsorbed samples revealed the presence of Bronsted and Lewis acid sites. The bands observed in 1536 and 1439 cm^{-1} corresponded to pyridinium ion adsorbed on Bronsted acid sites and CN vibration for coordinatively bonded pyridine molecules on Lewis acid sites, respectively. Physically adsorbed pyridine was also determined in 1486 cm^{-1} wavelength.[13] A decrease in intensity of Bronsted sites was observed within AC-Cs-STA catalysts regardless of the kind of treatment. Reaction results conducted in the presence of AC-Cs-STA catalysts indicated a decrease in activity compared with AC-STA catalysts supporting the results obtained with XPS and DRIFT analyses (Figure 18).

As stated above BET surface areas of AC-Cs-STA catalysts was lower than AC-STA catalysts which was explained

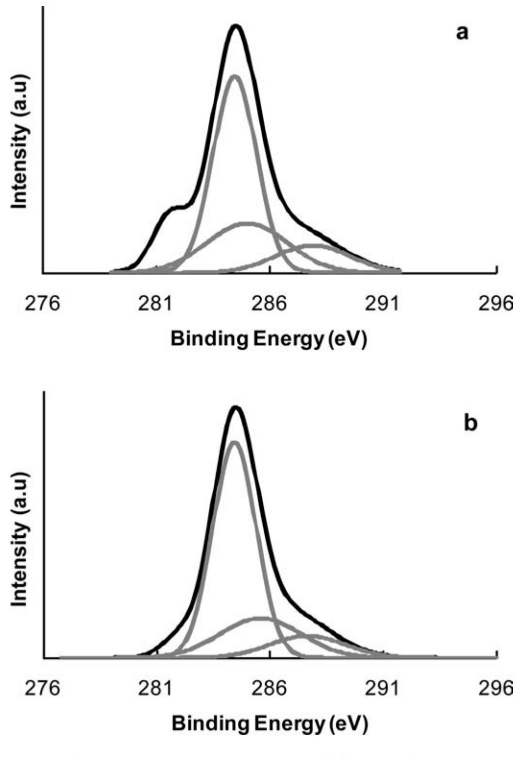

Figure 14. C 1s XP spectra of (a) HNO_3 treated and (b) H_2O_2 treated AC-Cs-STA catalysts.

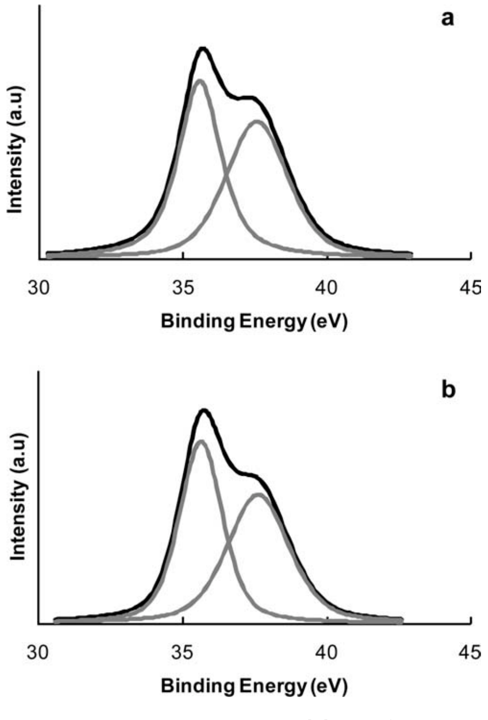

Figure 15. W 4f XP spectra of (a) HNO_3 treated and (b) H_2O_2 treated AC-Cs-STA catalysts.

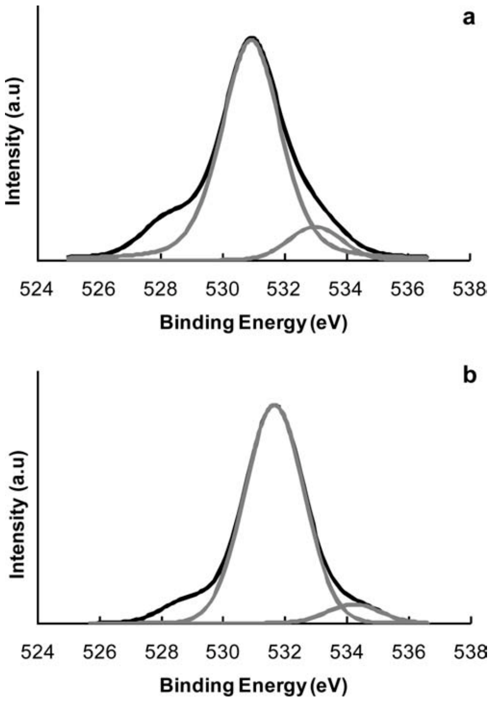

Figure 16. O 1s XP spectra of (a) HNO_3 treated and (b) H_2O_2 treated AC-Cs-STA catalysts.

with addition of a large Cs cation on catalyst structure. XPS analyses of AC-Cs-STA catalysts indicated that the interaction between Cs and STA had occurred principally between Cs and $H_5O_2^+$ of heteropolyacid. This interaction resulted as a decrease in the acidity of AC-Cs-STA catalysts also evidenced by a decrease in Bronsted acid sites in DRIFTS analyses and decrease of fractional conversion of IB to ETBE in reaction experiments regardless of the applied treatment procedure.

Summary and Conclusion

Vapor phase ETBE synthesis was conducted in the presence of active carbon supported STA, Cs-STA along with pure Cs-STA catalysts. Effect of temperature on product distribution was determined by evaluation of experiments conducted between 353 and 523 K. Reaction results revealed side product formation which were determined as DEE at temperatures above 423 K and ethylene at temperatures above 523 K. DEE exhibits properties similar to ETBE and can be used as an additive in gasoline. Ethylene obtained at high temperatures implied the possibility of production of a petrochemical feedstock from ethanol. HPA are known to exhibit high activity in vapor phase tertiary ether production. However, their low surface area is a major drawback in application. This problem was overcome by impregnating STA and Cs-STA on activated carbon in varying loading amounts (10–40%) and stability of synthesized catalysts was investigated by comparing various treatment procedures applied on the support material. Results indicated 20% increase in the conversion of IB to ETBE conversions in the presence of AC-STA with 40% STA loading, when compared with the conversion achieved with pure catalyst.

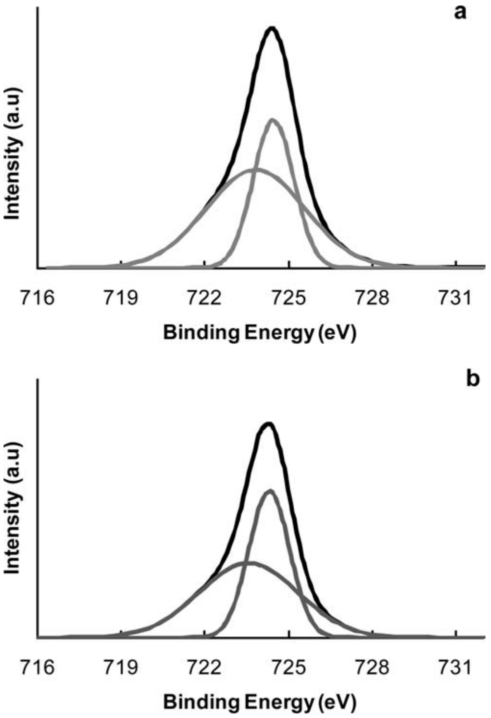

Figure 17. Cs $3d_{5/2}$ XP spectra of (a) HNO_3 treated and (b) H_2O_2 treated AC-Cs-STA catalysts.

Reaction experiments conducted in the presence of AC supported catalyst with ethanol as the sole reactant in the feed composition revealed inhibiting effect of IB on fractional conversion of ethanol to DEE. Reaction experiments conducted in the presence of supported catalysts indicated a significant modification of STA activity via impregnation.

BET surface areas of AC-STA and AC-Cs-STA catalysts revealed a decrease in the surface area by Cs impregnation which had been due to location of large Cs cation on the support material. The decrease in the surface area and decrease of Bronsted acidity of the catalysts by Cs impregnation was thought to be the cause of the decrease in the fractional conversion of IB to ETBE.

FT-IR analyses conducted with supported catalysts revealed the presence of heteropolyacid structure evidenced

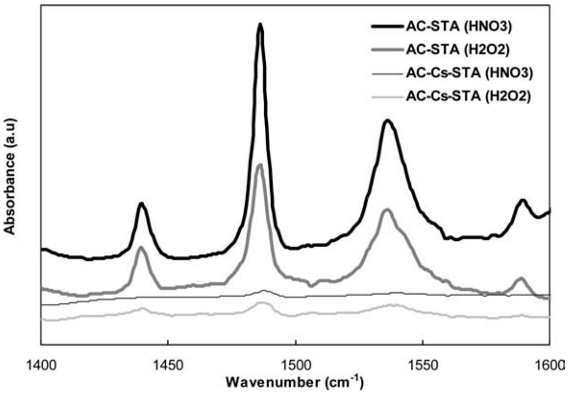

Figure 18. DRIFT analyses of pyridine adsorbed catalysts treated with HNO_3 and H_2O_2.

with existing W-O bands. FT-IR analyses also revealed disappearance of OH bands by impregnation which was due to bonding between STA and activated carbon. XPS analyses indicated well-resolved W 4f peaks defining STA structure. XP spectra of Cs 3d5/2 showed existence of an interaction between Cs cation and $H_5O_2^+$ of STA resulted in proton exchange between Cs and STA during synthesis. DRIFT analyses conducted with supported catalysts showed a decrease in Bronsted acid sites hence activity in the presence of AC-Cs-STA catalysts regardless of the kind of treatment, validating the proton exchange as stated by FT-IR and XPS analyses.

Stability of impregnated catalysts was investigated by applying a washing procedure in the presence of EtOH. Successive reaction experiments were conducted in the presence of catalysts treated by EtOH in an 8 h basis. A decrease of 10% in activity of the catalyst at 373 K was observed in the presence of both HNO_3 and H_2O_2 treated AC-STA catalysts which implied improvement in stability considering severe washing conditions. The decreasing trend in activity was found to be independent of the applied treatment procedure on the support material.

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