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The Effect of Sodium on the Catalytic Activity of ZnO-Al2O3/ZSM-5 and SnO-Al2O3/ZSM-5 for the Transesterification of Vegetable Oil with Methanol

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The Effect of Sodium on the Catalytic Activity of ZnO-Al$_2$O$_3$/ZSM-5 and SnO-Al$_2$O$_3$/ZSM-5 for the Transesterification of Vegetable Oil with Methanol

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Abstract

In order to elucidate the effect of sodium on the activity of ZSM-5 supported metal oxides catalysts (ZnO-Al$_2$O$_3$/ZSM-5 and SnO-Al$_2$O$_3$/ZSM-5) for the transesterification of soybean oil with methanol, ZSM-5 supported metal oxides were prepared with and without sodium hydroxide by impregnation. The metal compositions of the ZSM-5 supported metal oxide catalysts and the metal concentrations dissolved from the catalysts to the methylester phase were measured by SEM-EDS and inductive coupled plasma spectroscopy, respectively. The catalytic activity of ZnO-Al$_2$O$_3$/ZSM-5 and SnO-Al$_2$O$_3$/ZSM-5 containing sodium did not originate from surface metal oxides sites, but from surface sodium sites or dissolved sodium leached from the catalyst surface.

Keywords: ZnO-Al$_2$O$_3$, SnO-Al$_2$O$_3$, metal oxides catalyst, deactivation, transesterification, biodiesel

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1. Introduction

Almost all commercial biodiesel is currently produced by using a homogeneous base catalyzed process. Even though homogeneous catalyzed biodiesel production processes are relatively fast and achieve high conversions, the removal of the homogeneous catalyst after reaction may be a significant problem. This is a concern, since aqueous quenching causes the formation of stable emulsions and saponification, making separation of methyl-esters difficult and resulting in the generation of large amounts of waste water.[1].

In order to minimize or avoid problems associated with the homogeneous catalytic process, attempts have been made to develop heterogeneous catalyst systems [2-7]. The catalytic activity of the heterogeneous base catalyst, in the transesterification of soybean oil, shows a striking correlation with basic strength [5, 8-10]. Thus, most heterogeneous catalysts for biodiesel production contain alkali or alkali earth cations [4, 5, 8, 9, 11-19]. However, most of the catalysts experienced deactivation, by leaching of the alkali species from the heterogeneous catalysts to reaction medium [1, 20]. Several studies reported that Mg–Al hydrotalcites [4, 5, 21] and metal oxides (Al$_2$O$_3$-SnO, Al$_2$O$_3$-ZnO) [22] were active for the transesterification of vegetable oils with methanol at a relatively low reaction temperature. Although sodium hydroxide or sodium carbonate compounds were used in these catalyst preparations, the catalytic activity and deactivation behavior of the metal oxide catalysts were reported as originating from metal oxides (Al$_2$O$_3$-SnO, Al$_2$O$_3$-ZnO) or Mg–Al hydrotalcites sites [4, 5, 21, 22]. As a result, there are conflicting reports of the catalytic activity of the metal oxides catalysts at low temperature for transesterification of vegetable oil and methanol.

In this study, ZSM-5 supported metal oxides (SnO-Al$_2$O$_3$, ZnO-Al$_2$O$_3$) were prepared by impregnation with and without sodium hydroxide. The effects of composition of sodium and metal oxides (ZnO-Al$_2$O$_3$/ZSM-5 and SnO-Al$_2$O$_3$/ZSM-5) on the transesterification reaction were investigated. Metal content changes in the catalysts as a result of a sequential washing process were measured and correlated with the catalytic activity.

2. Experimental

2.1. Reagents

Anhydrous methyl alcohol (99.8%) and sodium hydroxide (99%) were obtained from Mallinckrodt Chemicals (Phillipsburg, NJ). Commercially available, edible grade soybean oil (total acid number of 0.05 mgKOH/g) was obtained from a local retail warehouse (COSTCO). Tetraethylorthosilicate (98%), zinc nitrate hexahydrate (98%), 3-mercaptopropyltrimethoxysilane, and aluminum nitrate nonahydrate (98%) were purchased from Sigma-Aldrich (St. Louis, MO). Tin chloride (98%) and sodium aluminate anhydrous were obtained from Riedel-deHaën (Seelze, Germany) and tetrapropylammoniumhydroxide (1.0 M) was purchased from GFS Chemicals (Powell, OH).

2.2 Metal oxide catalyst preparation

Nano ZSM-5 zeolite was hydrothermally synthesized with an appropriate mixture of water, sodium hydroxide, sodium aluminate, tetraethylorthosilicate (TEOS), tetrapropylammoniumhydroxide (TPAOH, 1.0 M), and 3-mercaptopropyl-trimethoxysilane (RTOS). The molar composition of the gel mixture was found to be TEOS/RTOS/Al2O3/Na2O/ TPAOH/H2O: 90/10/2.5/3.3/25/2500. The resulting zeolite was washed with de-ionized water, filtered, dried at room temperature, and calcined at 650 ° C for 2 hrs.

ZSM-5 supported metal oxides catalysts were prepared by an impregnation method with an appropriate amount of metal salt solutions. In typical preparations, 1.0 M (aq) solutions of SnCl2, Zn(NO3)2, and Al(NO3)3 were prepared first. Next, 4.0 mmol of the metal salt solution mixture [SnCl2 (1.0 M) and Al(NO3)3 (1.0 M), or Zn(NO3)2 (1.0M) and Al(NO3)3] was added to 2.0 g of nano ZSM-5 particles. The resulting mixture was kneaded thoroughly and aged for 2 hrs at 23 ° C, followed by drying at 23 ° C for 12 hrs. After drying, 4.5 mL of a sodium hydroxide solution (2.0 M) was added to the dried solid according to the method used in reference [22] . The mixture was again kneaded and thereafter aged for 2 hrs at 23 ° C and dried at 23 ° C for 12 hrs. The ZSM-5 supports, now loaded with a metal salt, were heated at a rate of 10 ° C/min to 500 ° C and maintained at 500 ° C for 0.5 hrs. The resulting ZSM-5 supported SnO-Al2O3 catalyst was found to be stable up to a temperature of 600° C. However, the X-Ray diffraction (XRD) peak associated with the ZSM-5 supported ZnO-Al2O3 catalyst significantly decreased after heating above 550° C suggesting the structure did not survive at high temperature. Thus, in order to preserve the mesoporous structure of nano ZSM-5, a lower calcination temperature of 500 ° C was adopted as used in reference [19].

To quantitatively investigate any dissolution of the metals and alkali sodium to the reaction mixture, a washing procedure was used as follows. The calcined solid catalysts were placed into 150 mL of de-ionized water and kept for 12 hrs at 23 ° C to remove the soluble components from the solid catalysts. The mixture was then filtered with 2.5 μm filter paper (Whatman, grade number 42). Most of the unbound components were gradually removed from the solid phases by repeated washing and filtering. The washed solids were dried at 23 ° C and activated at 500 ° C for 0.5 hrs in air before use. In order to investigate the effect of the surface sodium on the catalytic activity of the heterogeneous catalysts, a second set of ZSM-5 supported metal oxide catalysts was prepared with 4.5 mL of ethylenediamine instead of the sodium hydroxide solution. This resulted in ZSM-5 supported catalysts free of surface sodium that could subsequently leach into a reaction mixture and contribute to catalytic activity. All the catalysts were activated at 500 ° C before reaction to minimize possible contamination from ambient moisture and carbon dioxide.

2.3 Catalyst structure characterization

In order to characterize the structure and composition of the each prepared catalyst, several techniques were employed. Powder X-ray diffraction (XRD) patterns were taken with a Rigaku RU2000 rotating anode powder diffractometer equipped with CuKα radiation (40 kV, 200 mA) to determine the structure and identify individual elements. Microscopic images of the catalysts were taken with a scanning electron microscope (Hitachi S-2400). The metal composition of the catalysts were measured with a scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS). The sodium ion concentration dissolved from the catalyst was measured with inductively coupled plasma spectrometry (Optima TM 2100 DV ICP-OES system, Perkin-Elmer). BET surface area and pore size estimates of the catalysts were calculated from nitrogen adsorption isotherms obtained at -196 ° C using a Quantachrome AS-1MP volumetric adsorption analyzer. However, before adsorption measurements were taken, all the samples were out-gassed for 12 hrs at 350 ° C. Finally, x-ray photo-electron spectroscopy (XPS) analyses of catalyst surfaces were conducted on a PHI 5500 Spectrometer (Perkin Elmer, Wellesley, MA) equipped with an aluminum Kα X-ray radiation source (1486.6 eV) and AugerScan system control (RBD Enterprises, Bend, OR).

2.4 Transesterification procedure and analysis methods

For this work, Erlenmeyer flasks (25 mL) containing soybean oil, methanol, and catalyst, were used as batch reactors. In most of the studies, 10.0 g of soybean oil and 4.55 mL of methanol were pipetted into a flask; thereafter, 0.8 g of catalyst was added. The flasks containing reaction mixtures were sealed with rubber stoppers to prevent methanol vaporization. Because methanol and soybean

oil are immiscible, they formed two distinct layers while the solid catalyst resided at bottom of the flask. At this point, the transesterification reaction can be regarded as negligible and inactive. To initiate the transesterification reaction, the sample flasks were first heated to 62 ° C for 20 min at 0 rpm in a shaking bath (Series 25 incubator, New Brunswick Scientific Co.). The reaction time was considered to have started with the shaking of the flasks at a speed of 450 rpm. Sampling was conducted as described in reference [2]. At the appropriate sampling time, a 0.5 mL of sample was collected from the reaction mixture and dried in flowing air. Since the dried oil phase contained essentially fatty acid methyl ester (FAME) and unreacted soybean oil, the biodiesel yield (%) was defined as the total weight of FAME divided by the weight of the total oil phase. The weights of FAME in the samples were quantified using a gas chromatograph-mass spectrometer (GC-MS, Clarus 500 GC-MS, Perkin-Elmer) with a capillary column (Rtx-WAX catalog number 12426). Ethyl arachidate (Nu-Chek Prep, Inc., Elysian, Minnesota) was used as an internal standard.

3. Results and Discussion

3.1 Metal oxide loading

The XRD patterns of nano-ZSM-5 and SnO-Al2O3/ZSM-5 are shown in Figure 1. The results show the crystal size of the nano ZSM-5 calculated by the Scherrer equation was about 10 nm. The particle size of the nano ZSM-5 was about 0.5 µm. Several diffraction peaks related to the supported ZnO-Al2O3 structure (ZnO-Al2O3/ZSM-5 calcined at 500° C) were observed at two theta degrees of 16.48, 31.92, 34.66, and 36.46 (Figure 1).
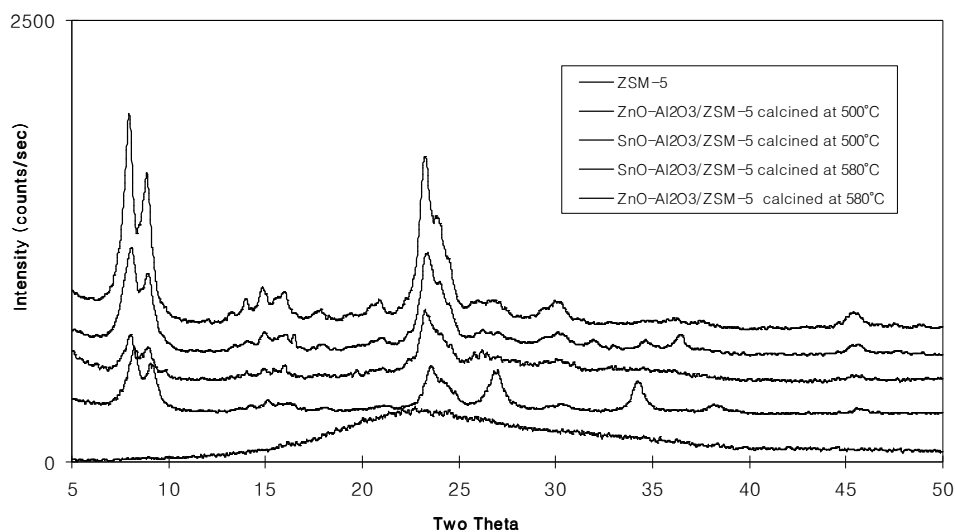

Figure 1. XRD diffraction patterns of nano-ZSM-5, SnO-Al2O3/ZSM-5 and ZnO-Al2O3/ZSM-5 prepared with NaOH and calcined at 500℃and 580℃, respectively.

However, the nano ZSM-5 supported ZnO-Al2O3 catalyst (ZnO-Al2O3/ZSM-5) completely collapsed to an amorphous structure when it was heated to 580 ° C. Conversely, one diffraction peak related to SnO-Al2O3 structure (SnO-Al2O3/ZSM-5 calcined at 500° C) appeared at a two theta of 8.92 degree. This suggests that some crystal structures involving the metal oxides started to form or were formed on the support when the catalysts were heated at 500° C for 30 min. In this case though, upon further heating to 580° C, the nano ZSM-5 supported SnO-Al2O3 catalyst (SnO-Al2O3/ZSM-5), remained relatively stable. Several diffraction peaks at 27.00, 34.22, and 38.20 related to SnO-Al2O3 crystal structure were observed after heating to 580° C suggesting that a crystalline structure was still present.

The specific BET surface area of the nano ZSM-5 was measured as 566 m2/g. The N2 adsorption-desorption isotherms for nano ZSM-5 showed a type-IV isotherm similar to the mesoporous silica materials (Figure 2). A distinct increase of N2 adsorption in the region 0.4 < P/P0 < 0.9, which is interpreted as capillary condensation in mesopore void spaces, was observed. After incorporation of the metal oxides (SnO-Al2O3 and ZnO-Al2O3) onto the nano ZSM-5 support, the BET surface areas decreased to 315 and 197 m2/g, respectively. This fact could be explained by both the partial blocking of the porous network by the metal oxides and by filling of the pores [12].
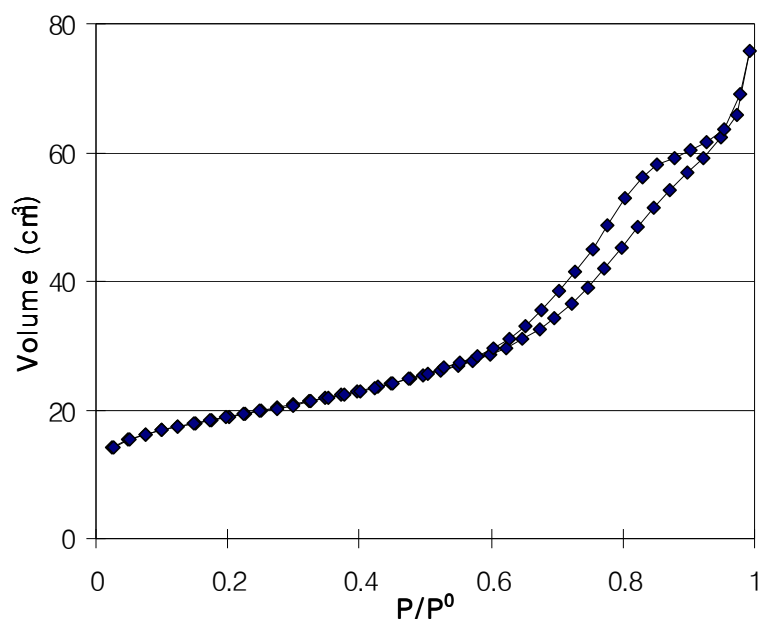

Figure 2. N2 adsorption-desorption isotherms of nano ZSM-5.

It can be observed from SEM and TEM_images that ZSM-5 particle was formed with agglomerated nano ZSM-5 crystals. Metaloxides can be supported on the outer surface and void spaces between the crystals. Thus, there was no obvious difference between the SEM image of nano ZSM-5 and those of the SnO-Al2O3/ZSM-5 and ZnO-Al2O3/ZSM-5 (Figure 3), suggesting amorphous metal oxides on the nano ZSM-5.
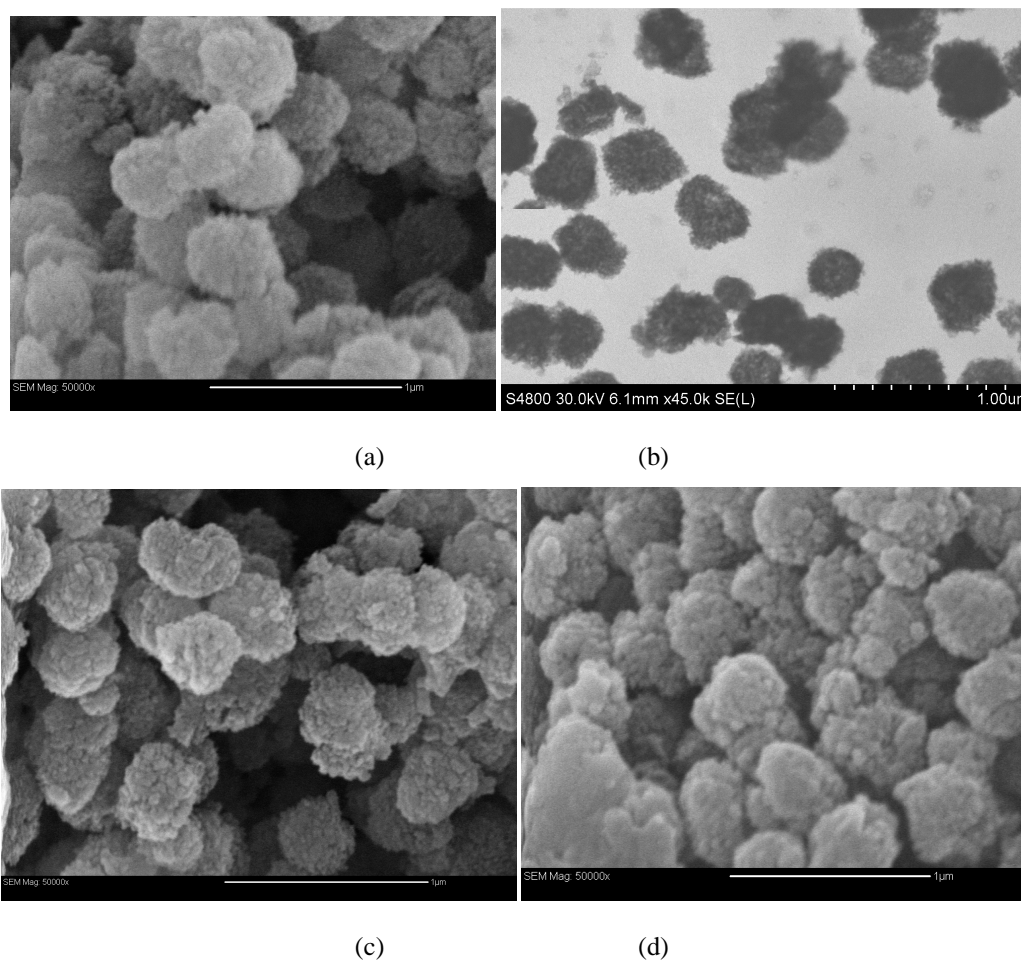

(a)　　　　　　　　　　(b)

(c)　　　　　　　　　　(d)

Figure 3. SEM and TEM images of nano ZSM-5 and ZSM-5 supported metal oxides: (a) SEM image of the nano-ZSM-5, (b) TEM image of nano ZSM-5, (c) SEM images of SnO-Al2O3/ZSM-5 prepared with NaOH, (d) SEM image of ZnO-Al2O3/ZSM-5 prepared with NaOH

Since sodium hydroxide was used as a neutralizing agent for the acidic metal salts, the ZSM-5 supported metal oxides catalysts (SnO-Al2O3/ZSM-5 and ZnO-Al2O3/ZSM-5) inevitably contain sodium oxide residue. In order to investigate the extent of sodium dissolution, the metal compositions of the supported catalysts were determined as shown in Table 1. It should be noted that a beam of high energy electrons (SEM-EDS) can penetrate as deep as 1µm to provide an estimate of the   bulk composition [23]. With this in mind, we have found for this work that surface

compositions (XPS) and bulk compositions (SEM-EDS) show significant differences. The surface concentrations of dissolvable species were much lower than the bulk concentrations. This result can be attributed to most of the catalyst material residing in the internal porous structure of the support. Additionally, it appears that supported metal oxides can be stabilized within the pore system of the nano ZSM-5 structure.

Samples	Number of wash cycle	Sn or Zn atomic % (by XPS)	Na atomic % (by XPS)	Al atomic % (by XPS)	Si atomic % (by XPS)
SnO-Al$_2$O$_3$/ZSM-5	2	7.6	10.0	8.1	74.3
	3	7.9 (4.2)	10.2 (8.2)	7.8 (10.0)	74.1 (77.6)
	4	8.1	8.7	7.1	76.1
	5	7.7 (3.9)	7.5 (5.8)	7.2 (13.2)	77.6 (77.1)
ZnO-Al$_2$O$_3$/ZSM-5	2	6.6	15.6	7.1	70.7
	3	6.9 (3.7)	15.4 (11.2)	7.4 (12.4)	70.3 (72.7)
	4	7.0	13.7	6.7	72.6
	5	7.1(3.3)	13.1 (9.6)	6.4 (17.7)	73.4 (77.7)

Table 1. Metal compositions of the ZSM-5 supported metal oxides prepared with NaOH and determined with SEM-EDS and XPS (Composition obtained by XPS)

Using SEM-EDS, we found the concentrations of SnO and ZnO remained constant as a function of washing cycles within the error limit (±0.3) (Table 1). However, the measured sodium content in the SnO-Al2O3/ZSM-5 samples decreased from 10.0% to 7.5% after 5 washing cycles. On the other hand, the sodium content remained higher in ZnO-Al2O3/ZSM-5 samples than in SnO-Al2O3/ZSM-5 samples, although the same preparation procedure and washing process were used. This can be attributed to a stronger interaction of sodium to ZnO-Al2O3 structure than SnO-Al2O3 structure.

To verify this interaction effect, the binding energies of Na, Zn, and Sn were measured by XPS analysis. The intrinsic binding energy of Na (1s) in the ZnO-Al2O3/ZSM-5 was higher than Na (1s) in the SnO-Al2O3/ZSM-5 (Figure 4). Also, the binding energy peak for Na (1s) in the ZnO-Al2O3/ZSM-5 increased with washing cycles. However, the binding energy associated with Na (1s) in the SnO-Al2O3/ZSM-5 decreased with additional washing. Therefore, these data suggested that the loosely bonded Na in the SnO-Al2O3/ZSM-5, having a binding energy range of 1070~1071 eV, washes off. Also, the binding force of the Zn (2p3/2) in the ZnO-Al2O3/ZSM-5 increased with further washing, while the binding energy of Sn (3d5/2) in SnO-Al2O3/ZSM-5 decreased with additional washing. In summary, the binding energy of Sn (3d5/2) to the catalyst surface was weaker than the
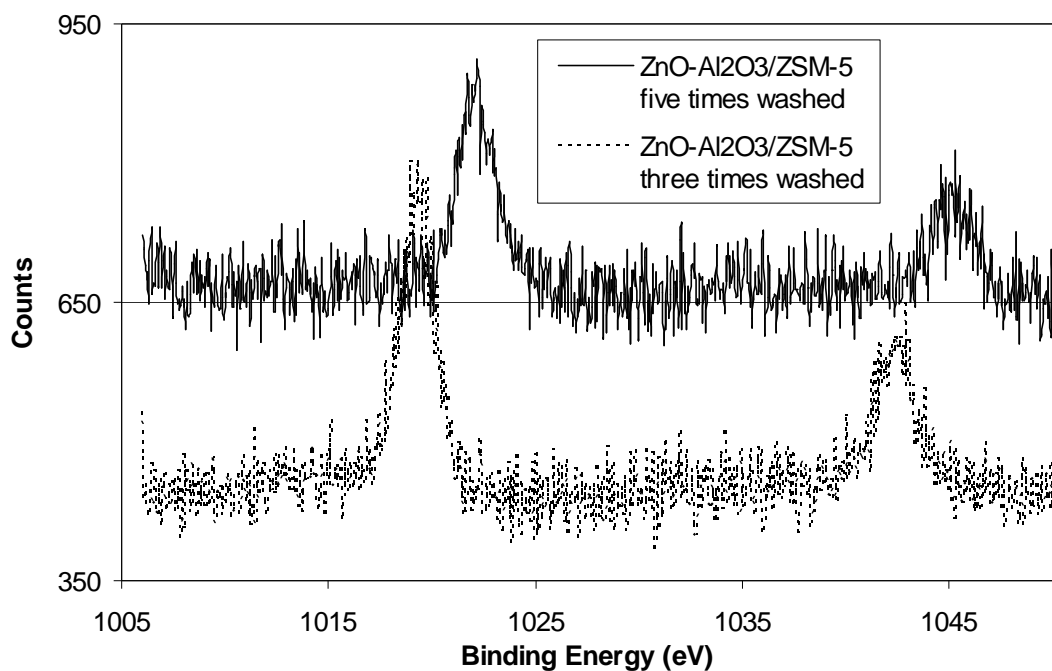
binding energy of SnO (3d5/2, 486.4 eV) and the binding energy of ZnO to the ZnO-Al2O3/ZSM-5 was higher than that of ZnO (2p3/2, 1021.7 eV).
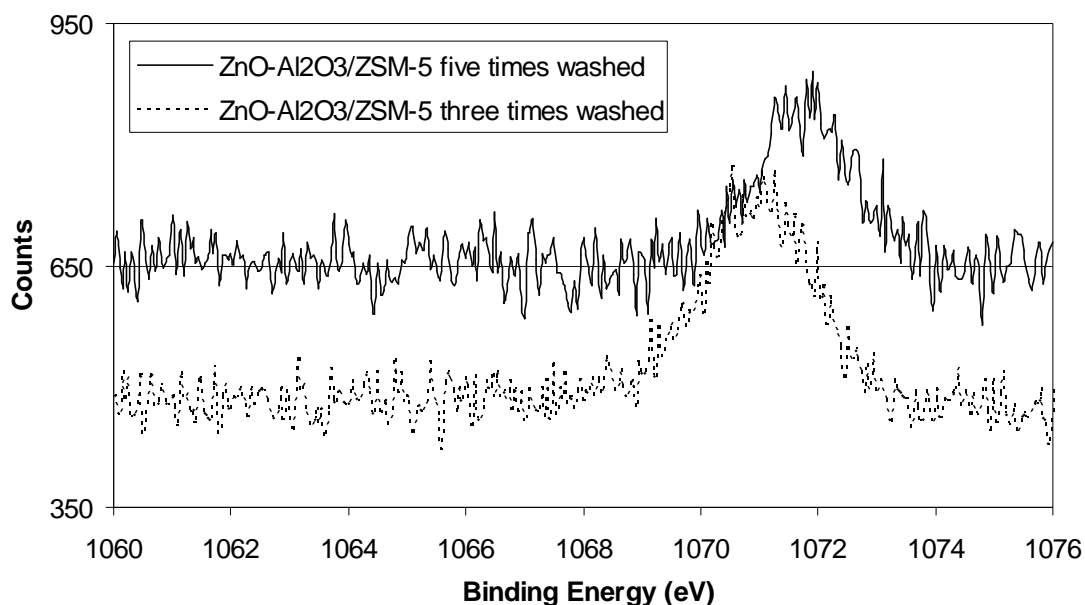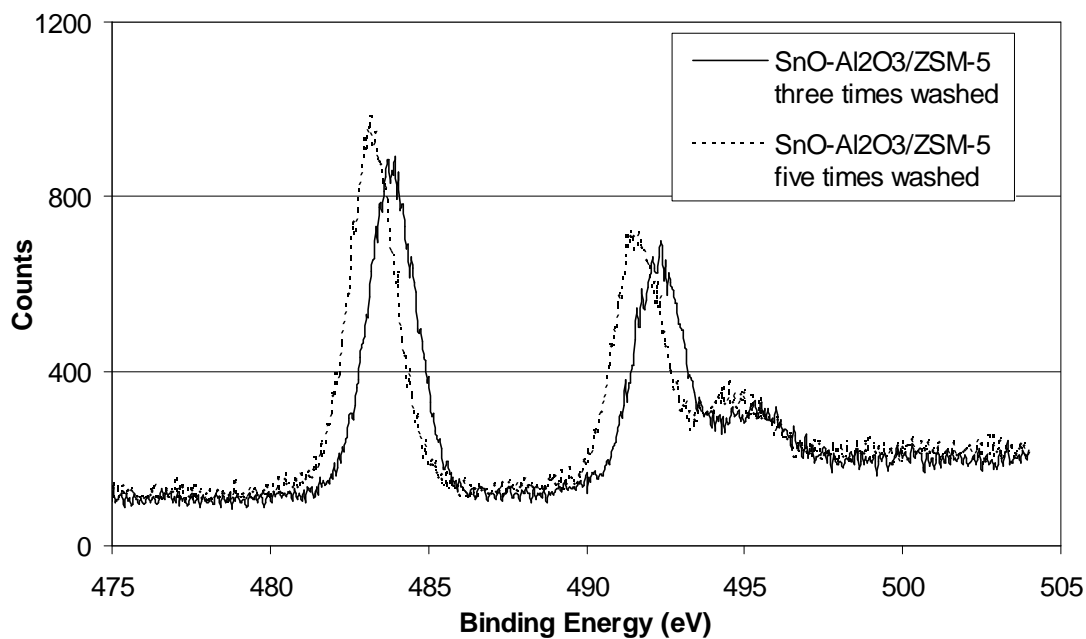

(a)
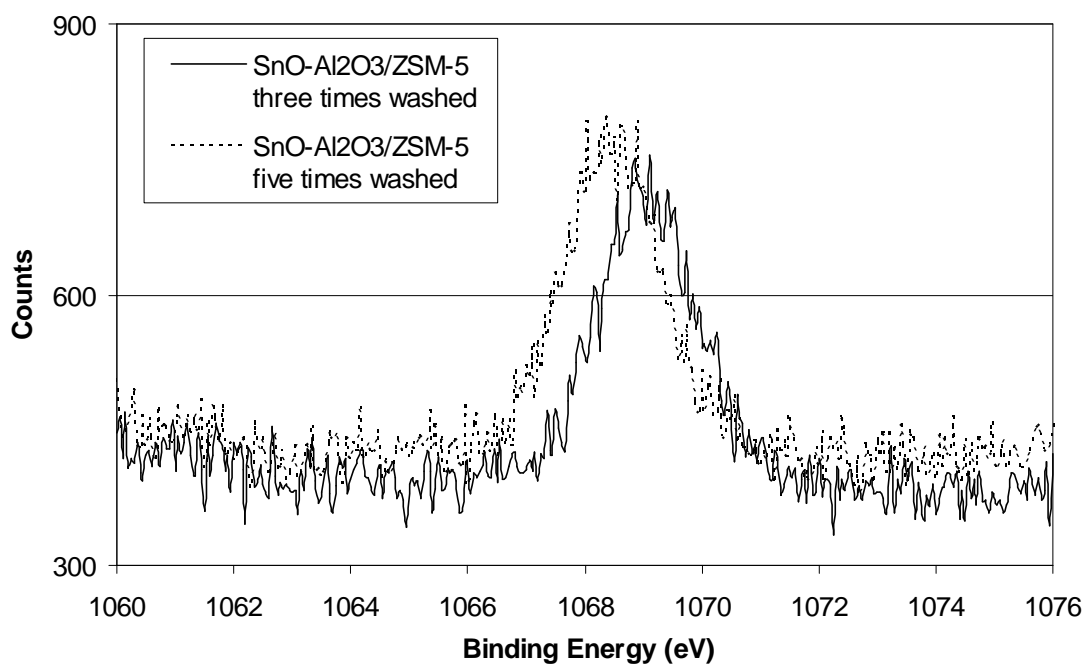
(b)

(c)

(d)

Figure 4. XPS spectra of ZSM-5 supported metal oxides prepared with NaOH: (a) Na (1s) binding energy of the ZnO-Al2O3/ZSM-5, (b) Na (1s) binding energy of SnO-Al2O3/ZSM-5, (c) Zn (2p3/2) binding energy of the ZnO-Al2O3/ZSM-5, (d) Sn (3d5/2) binding energy of SnO-Al2O3/ZSM-5.

3.2 Effect of washing agent on catalytic activity of metal oxides loaded ZSM-5

The catalytic activities of ZnO-Al2O3/ZSM-5 and SnO-Al2O3/ZSM-5 catalysts were highly dependent on the number of washing cycles as shown in Figure 5. Unwashed SnO-Al2O3/ZSM-5 catalyst provided a 45% yield of FAME after 9 hrs of reaction. However, the catalytic activity significantly decreased, yielding only 10% FAME after washing twice and 9 hrs of reaction. After three washings, the catalyst was inactive. Similar, unwashed ZnO-Al2O3/ZSM-5 catalyst showed a very high activity (98% yield at 9 hrs). The twice washed catalyst yielded 39.3% FAME after 9 hrs. Increasing the number of washing cycles gradually decreased the yields further.
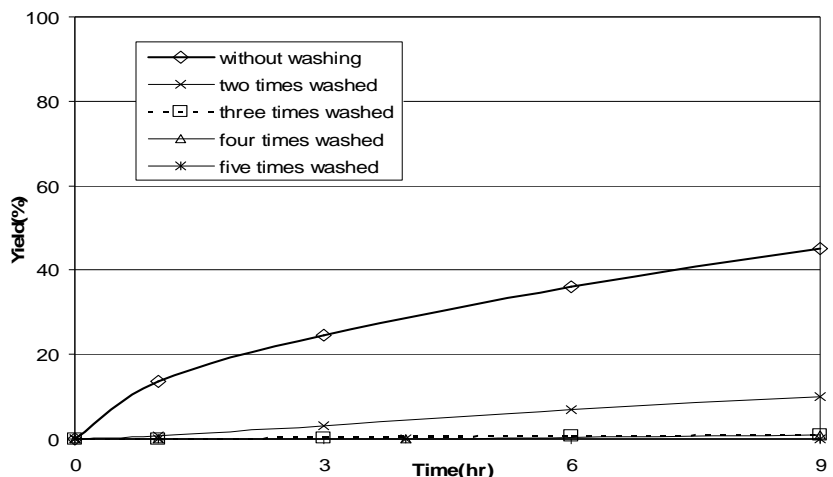
(a)
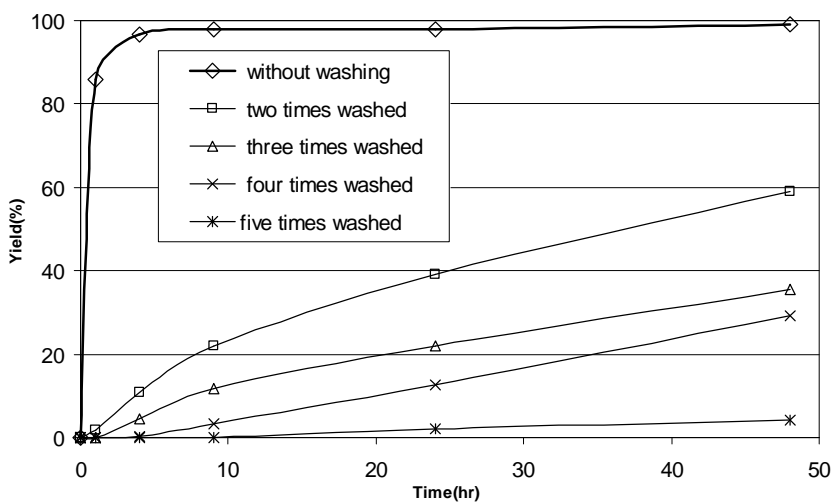
(b)

Figure 5. Washing effects on the catalytic activities of the supported metal oxides prepared with NaOH: (a) SnO-Al2O3/ZSM-5, (b) ZnO-Al2O3/ZSM-5

A number of heterogeneous catalysts for biodiesel production actually contain homogeneous catalytic phases such as sodium methoxide [1], calcium methoxide-like compounds[17], and/or some active species [11, 24] leached out from the heterogeneous catalysts. As a result, these heterogeneous catalysts become deactivated quickly. Similar behavior was observed for the ZnO-Al2O3/ZSM-5 and SnO-Al2O3/ZSM-5 catalysts prepared with sodium hydroxide as a neutralizing agent. In order to isolate the effect of sodium hydroxide from the catalytic activity of the ZSM-5 supported metal oxides catalysts (ZnO-Al2O3/ZSM-5 and SnO-Al2O3/ZSM-5), ethylenediamine instead of sodium hydroxide was used as a neutralizing agent for the metal salts mixture. The resulting catalysts were calcined and washed with de-ionized water. The amounts of the metals (Sn or Zn) loaded increased (6.6% to 10.5%) with increasing calcining temperature as shown in Table 2. No peaks related to SnCl2 and Zn(NO3)2 were detected in the XPS spectra suggesting decomposition of the SnCl2 and Zn(NO3)2 and formation of amorphous metal oxides on the support when calcined at 500 ° C. A trace level (<2%) of sodium was detected because of the sodium balancing ion of the ZSM-5 structure. Interestingly, no measurable catalytic activities were observed from these catalysts (ZnO-Al2O3/ZSM-5 and SnO-Al2O3/ZSM-5) when washed with ethylenediamine. This finding reveals that catalytic activities shown for the catalysts prepared with NaOH (ZnO-Al2O3/ZSM-5 and SnO-Al2O3/ZSM-5) were not due to metal oxides sites on the support, but from sodium hydroxide remaining on the surface or leached out from the catalyst surface. As noted earlier, catalytic activity of the heterogeneous base catalysts in the transesterification of soybean oil show a striking correlation with their corresponding basic strengths [8]. Heterogeneous catalytic activity of a zeolite supported alkali metal (NaX, NaY, NaOx/NaX etc.) has been reported[19]. Suppes et al. separated the reaction mixture that exhibited a nearly 93% methylester yield into the used wet solid catalyst and the liquid product fraction. When fresh soybean oil and methanol as the original reaction mixture were added to each component, a 25% methylester yield was obtained from the mixture containing liquid product while a 90% methylester yield was resulted from the reused catalyst [19]. This result strongly suggests that, although some sodium species dissolve into the liquid phase, they are not responsible for the bulk of the transesterification reaction.

Samples	Calcination temperature (°C)	Sn or Zn atomic %	Al atomic %	Si atomic %
SnO-Al$_2$O$_3$/ZSM-5	400	6.6	7.5	84.0
	450	7.1	7.3	84.7
	500	8.0	7.0	83.4
ZnO-Al$_2$O$_3$/ZSM-5	400	8.6	7.0	83.0
	450	8.7	7.0	82.7
	500	10.5	6.3	81.7

Table 2. Effect of calcination temperature on metal contents of the ZSM-5 supported metal oxides prepared with ethylenediamine and determined with SEM-EDS

A similar effect was observed by Lopez et al. They reported that the activity of a ETS-10 (Na, K) catalyst correlated with the amount of alkali species (Na, K) resided on the surface[1]. This was attributed to the enhanced basicity of zeolite X and ETS by ion exchange with higher electropositive metals like Na, K and Cs [19], and associated surface hydroxide groups. When acidic or neutral anions such as chlorine and organic anions are associated with alkali species, a decreased catalytic activity for transesterification was observed.

In our study, the catalytic activity can be attributed to surface hydroxide groups associated with sodium, which have higher basic strengths than the hydroxide associated with metaloxides (ZnO-Al2O3 or SnO-Al2O3). Thus, the leaching of sodium results in significant deactivation of the supported metal oxide catalyst. Additionally, the dissolved sodium concentrations in the glyceride phase, after reaction, are shown in Table 3. The concentration of sodium dissolved from the SnO-Al2O3/ZSM-5 (unwashed) to the oil phase was 39.6 ppm. This concentration decreased to 3.2 ppm when the washed catalyst (one cycle) was used. However, the sodium concentration in the oil phase obtained using the ZnO-Al2O3/ZSM-5 (unwashed) was 6.1 ppm and this concentration decreased to 2.5 ppm when the washed catalyst (one cycle) was used. Thus, sodium is more stable in the ZnO-Al2O3 than in the SnO-Al2O3. Even though the unwashed SnO-Al2O3/ZSM-5 catalyst led to a high level of sodium (39.6 ppm) in the oil phase, the biodiesel yield (45%) was less than the yield (99%) obtained with the unwashed ZnO-Al2O3/ZSM-5 with 6.1 ppm of sodium. Therefore, the catalytic activity is not a direct function of dissolved sodium concentration alone. The concentration and basicity of the surface sodium also plays a significant role.

Samples	Number of wash cycle of the catalysts	Na concentration(ppm) in products
SnO-Al$_2$O$_3$/ZSM-5	0	39.6
	1	3.2
	3	2.1
	5	0.2
ZnO-Al$_2$O$_3$/ZSM-5	0	6.1
	1	2.5
	3	1.0
	5	0.6

Table 3. Effect of catalyst washing cycles on Na concentration in the biodiesel phases measured by inductively coupled plasma spectrometry

4. Conclusions

The effect of sodium on the catalytic activity of the supported mixed metal oxides (SnO-Al2O3 and ZnO-Al2O3) on nano ZSM-5 for the transesterification of soybean oil was investigated. When sodium hydroxide was not involved in the catalyst preparation procedure, the mixed metal oxides catalysts (SnO-Al2O3/ZSM-5 and ZnO-Al2O3/ZSM-5) did not show measurable catalytic activity for the transesterification reaction. Activities of the sodium contaminated catalysts (ZnO-Al2O3/ZSM-5 and SnO-Al2O3/ZSM-5) did not originate from metal oxides sites, but from surface or dissolved hydroxyl groups associated with sodium. This suggests that some of the catalytic activity of the metal oxides, for the transesterification reaction of vegetable oils with methanol reported in the literature, may be attributed to the alkali species involved in their preparation methods. Our findings also explain the rapid deactivation behavior of some of the heterogeneous catalysts reported in transesterification by the leaching of hydroxyl groups associated with sodium from the catalyst during reaction.

Acknowledgements

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