International Congress of Science and Technology of Metallurgy and Materials, SAM - CONAMET 2013

Transesterification of vinyl acetate with i-amyl alcohol catalyzed by nanostructured sulfated zirconia

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Abstract

Due to environmental concerns, it is highly desirable to replace liquid HF or H_2SO_4 by more benign solid acid such as sulfated zirconia (SZ). Sulfated zirconia materials have been demonstrated to be a good catalyst for the isomerization of lineal alkanes at relatively low temperatures. Our objective was: (1st) prepare nanostructured materials either by controlled hydrolysis of zirconium alkoxide or by impregnation of tetragonal zirconia with H_2SO_4 1 M or ammonium sulfate, (2nd) carry out the characterization by conventional techniques (X ray diffraction, electron microscopy, N_2 adsorption, FT-IR/Raman spectroscopy, UV diffuse reflectance) and (3rd) evaluate the acidity through the transesterification reaction of vinyl acetate with i-amyl alcohol to give i-amyl acetate and acetaldehyde and using toluene as solvent.

1. Introduction

For reasons of environmental care it is advisable to replace the strong inorganic acids such as HF or H_2SO_4, used in various industrial processes, for solid materials derived from sulfated zirconia (SZ) [Katada et al. (2000)]. The surface of SZ posses both Lewis and Brönsted acid sites, the latter with equivalent or superior strength to that of pure

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H_2SO_4 acid (pKa = -16). The relative amount of these centers is strongly dependent on the method used for the preparation of the catalyst and the calcining temperature in air. Such materials have shown to possess interesting catalytic activities against various reactions requiring the presence of strong acid sites. Thus, SZ can catalyze the isomerization of linear low molecular weight alkanes to branched alkanes even at room temperature [Reddy et al. (2005)]. Moreover, the use of SZ in esterification and acylation reactions of aromatic compounds in liquid phase was shown to be an important application especially to replace conventional Lewis acids. It reduces the formation of undesirable side products and facilitates the separation and purification steps, being and insoluble solid and used in catalytic amounts [Klose et al. (2005), Misra et al. (2004)].

The aim of this work was to study the catalytic activity of SZ against the transesterification reaction, in liquid phase, of vinyl acetate with i-amyl alcohol and correlate the observed catalytic activity with the presence of sulfonic groups (-SO_3H) on the surface of the catalyst.

The transesterification reaction studied was (Equation 1):

$$\text{(1)}$$
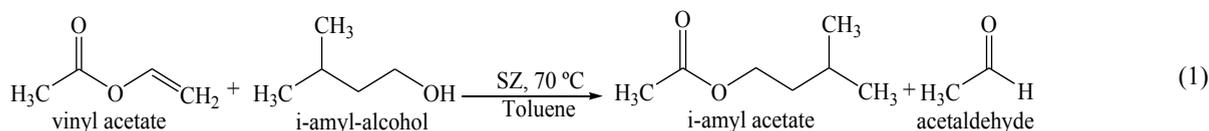
2. Experimental Procedure / Methodology

All reagents and materials used in the preparation of the catalysts were of analytical grade and were used as received from suppliers.

2.1. Catalysts preparation

Sulfated zirconia samples were prepared either by controlled hydrolysis of zirconium n-propoxide (Zr-(n-OC_3H_7)$_4$ 70 % in $CH_3CH_2CH_2OH$, Fluka) in alcoholic medium or by neutralization with ammonium hydroxide of zirconium oxychloride ($ZrOCl_2.8H_2O$ 98 %, Aldrich). Five samples (named A, B, C, CN, CH) were chosen for testing in the transesterification reaction.

Sample A: a given amount of dodecylamine (**DDA**, 98% Aldrich) was added to an aqueous solution of zirconium oxychloride and ammonium sulfate (**AS**, (NH_4)$_2SO_4$ Aldrich) in a way to obtain a final molar ratio DDA:Zr:AS = 1:3:3. This solution was neutralized with 1 M ammonium hydroxide up to pH = 8. The resultant precipitate was filtered, thoroughly washed until no chloride ion was detected with aqueous solution of silver nitrate, and dried in vacuum for 5 h. The white solid was calcined in air at 600 °C to fully remove the organic residues.

Sample B: a 0.14 M ethanolic solution of AS and water was quickly added to a 0.2 M ethanolic solution of zirconium n-propoxide and DDA. A white precipitate developed immediately after mixing both solutions. After two hours under agitation at room temperature, the precipitate was filtered and dried in vacuum. The surfactant was fully removed by calcination in air at 600 °C.

Sample C: a 0.1 M aqueous solution of zirconium oxychloride was carefully neutralized with 1 M NH_4OH up to reach pH = 8. The white precipitate was filtered, washed several times with ethanol 95 %, and vacuum dried at 60 °C for 5 hours. This is a standard procedure to achieve a tetragonal crystalline structure.

Sample CN: a given amount of sample C was thoroughly milled with an equal amount of AS. The resulting mixture was calcined in air at 200 °C for 20 hours and then at 350 °C for 5 hours.

Sample CH: 1 g of sample C, previously milled, was soaked in 10 mL of 1 M sulfuric acid in a Petri dish. After three days at room temperature, water excess was gently removed in a heating plate. The resulting grayish and very hygroscopic solid was calcined in air at 200 °C for 20 hours and then at 350 °C for 5 hours.

Nafion® NR50 (Sigma Aldrich) was used as a reference solid acid material. The Nafion beads were manually fitted to a size smaller than 0.5 mm.

The reactants and precipitating agents used for preparing SZ samples are summarized in Table1.

Table 1. Precursors and precipitating agents used for SZ sample preparation.

SZ sample name	Precursors of zirconia and reactants	Precipitating agent
A	$ZrOCl_2/H_2O/DDA/AS$	NH_4OH 1M pH = 8
B	$Zr(OPr)_4/EtOH/DDA$	$H_2O/AS/EtOH$
C	$ZrOCl_2/H_2O$	NH_4OH 1M pH = 8
CN	C +AS, 50:50 w/w	(mechanical mixing)*
CH	C +H_2SO_4, 50:50 w/w	(impregnation)*
Nafion®	Beads (size < 0.5 mm)	-

* Samples CN and CH were obtained from sample C, either by mixing with AS or by impregnation with H_2SO_4.

2.2. Physicochemical characterization of SZ samples

Sample characterization was performed by X-ray diffraction (XRD), FTIR and Raman spectroscopy. Textural characterization was done by adsorption of N_2 at -196 ºC, in order to obtain BET surface area, total pore volume and pore size distribution. The results for XRD and textural characterization for materials calcined at 600 ºC are summarized in Table 2.

Table 2. XRD and textural characterization of SZ samples calcined at 600ºC.

SZ sample	XRD[1]	S_{BET} (m^2/g)[2]	V_{pore} (cm^3/g)[3]	r_p (nm)[4]
A	T	46	0.164	7.1
B	T	137	0.198	2.9
C	T	61	0.077	2.5

(1) XRD: T = tetragonal crystal phase.

(2) S_{BET} (m^2/g): specific surface area from BET method.

(3) V_{poros} (cm^3/g) STP: total pore volume at p/p^o = 0.98, according to Gurvitch.

(4) r_p (nm): pore radious from (V_{poros}/S_{BET}).

2.3. Catalytic Activity

Catalytic activity test were performed in a 15 mL flat bottom vial with plastic cap and PTFE/silicone septum. Just prior to the catalytic test, SZ samples were dried in vacuum at 100 ºC. The reaction mixture (RM), containing 0.36 M in *i*-amyl-alcohol (*i*AA) and 0.46 *M* in vinyl acetate (VA), was prepared using toluene as solvent. Each catalytic test was carried out by mixing 10 mL of RM together with 100 mg of dried SZ sample. The reaction temperature was kept at 70 ºC in a shaking bath. Aliquots for GC analysis were taken at regular intervals, chilled and diluted in toluene for quickly quenching the reaction. The concentration of reactants and products was determined by gas chromatography with a Hewlett Packard-5890 equipped with an Inowax column (L = 30 m, DI = 0.32 mm) and a flame ionization detector. Retention times and relative response factors were determined from individual pure components diluted in toluene. To ensure the absence of diffusive phenomena and to determine the effect of the amount of catalyst on the reaction rate, catalytic tests were performed using 35 mg and 100 mg of Nafion respectively. The only side product identified was *i*-amyl ether. The initial reaction rate was calculated from the conversion data obtained at 120 minutes after the reaction started. Table 3 shows the retention times of reactants and products for the transesterification reaction.

Table 3. Retention times of reactants and products for the transesterification reaction.

Compound	Retention time (minutes)	Compound	Retention time (minutes)
Acetaldehyde	1.280	*i*-amyl acetate	5.016
Vinyl acetate	1.893	*i*-amyl alcohol	6.400
Toluene	3.6 - 4.1	Other	8.026 and 8.203

3. Results and discussion

3.1. Physicochemical characterization

All SZ samples treated at 600 ºC crystallized in the tetragonal form (Table 2). Figure 1 shows the XRD profiles of samples B and C. Sample A (not shown in Figure 1) also shows a tetragonal crystal structure, with diffraction lines at 30, 35 and 50 units of 2 theta. The behavior observed for samples B and C is the expected one for zirconia samples prepared in the presence of a sulfating agent, since sulfate groups help to the development of tetragonal crystalline structure at low temperature. Although both profiles shown in Figure 1 are similar, there are some little differences which can be attributed to differences in the crystal size.

The adsorption isotherms for samples A, B and C are shown in Figure 2. All isotherms are classified as type IVb corresponding to mesoporous materials. Sample A and B, both prepared in presence of DDA an AS, show a similar total pore volume (0.164 /0.198 cm^3/g (STP)), while sample C shows a rather small value (0.077 cm^3/g (STP)). However, sample B has three times more specific surface area than sample A (137 vs. 46 m^2/g) suggesting a different type of porous structure. The pore size distribution plot of sample B has maxima at 32/35 Å for the adsorption/desorption branches respectively, and at 40 Å (desorption branch) for sample A. Sample C, which was prepared simply by neutralizing zirconyl oxychloride with ammonia, shows a broad hysteresis loop and a pore size distribution maximum centered at 62 Å (desorption branch). The α-plots for each of the isotherms show values approaching zero, pointing up the absence of microporosity.
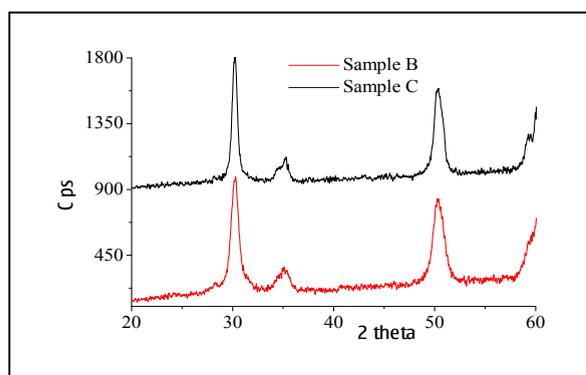
Figure 1. XRD profiles of SZ samples calcined at 600 ºC
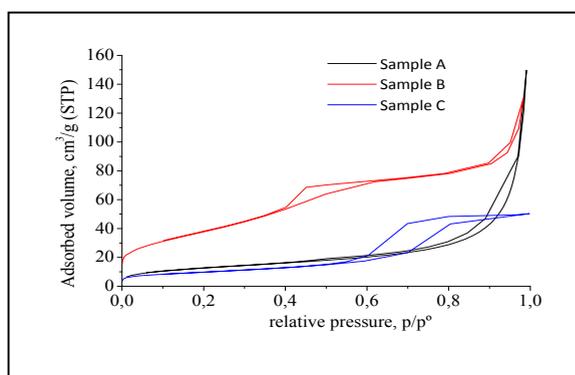
Figure 2. Isotherms from the adsorption/desorption of N_2 at -196 ºC for the materials named A, B and C calcined at 600 ºC.

3.2. FTIR- Raman spectroscopy

FT-Raman spectra of SZ samples are shown in Figure 3. The spectra correspond to samples A, B and C without heat treatment. The relative intensity of the signals is different among the three profiles shown. Sample A shows narrow and very intense bands near the 3000 cm^{-1} spectral region due to -CH_3 and -CH_2 groups, and two intense bands at 1439 and 1301 cm^{-1} belong to DDA. Besides, it shows a set of broad bands of low intensity located between 1140 and 900 cm^{-1} attributed to -S=O bonds arising from sulfate groups bounded to zirconia surface. The intensity ratio C-H/S=O shows the relative amount of C-H groups compared to S=O ones; while the number of bands around 1000 cm^{-1}, related to different arrangement of sulfate groups, is a requisite for considering the sample as a highly acidic zirconia. Sample B shows a different behavior with the overall band intensity significantly lower than that observed in sample A. Moreover, the very high intensity of the band located at 976 cm^{-1} along with the little ones at 625, 614 and 450 cm^{-1} indicate the presence of free ammonium sulfate. Sample C shows no significant features in the 3500 -200 cm^{-1} range as it is expected for a sample prepared by slow neutralizing zirconyl oxychloride, without added sulfate.

3.3. FTIR spectroscopy

Figure 4 shows the infrared spectra of samples A and B treated at 200 °C in air. Sample A shows two broad and intense bands around 3400 and 1630 cm^{-1} due to hydrogen bonded -OH groups interacting with water molecules adsorbed on the surface of the solid. There are no absorption bands due to C-H bonds just at the right of 3000 cm^{-1} indicating that DDA was completely removed. The spectrum shows several low intensity bands in the region between 1500 and 900 cm^{-1} which are assigned to different types de S=O bonds. Although sample B also shows two broad bands centered at 3400 and 1630 cm^{-1}, there are new ones at 3236, 2929 and 2858 cm^{-1} indicative of the presence of DDA. The sample B profile between 1200 and 900 cm^{-1} is similar to that shown for sample A although with a much higher intensity. Furthermore, it is observed a medium intensity band located at 1400 cm^{-1} due to remaining free ammonium sulfate in agreement with that shown in the Raman spectra (Figure 3). FTIR spectrum of sample C calcined at 200 °C, not included in Figure 4, only shows absorption bands due to water adsorbed on the surface of the solid.
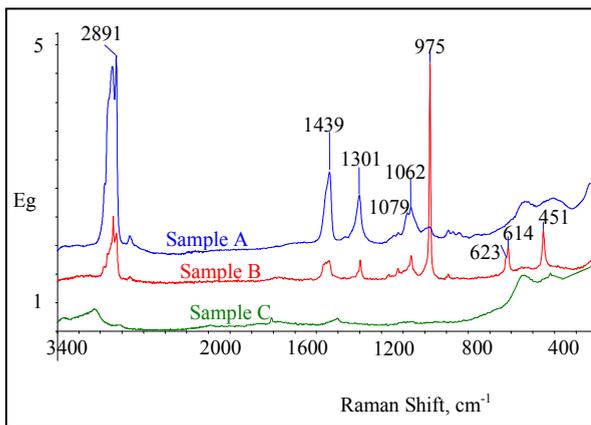
Figure3. FT-Raman spectra of SZ materials as obtained at rT.
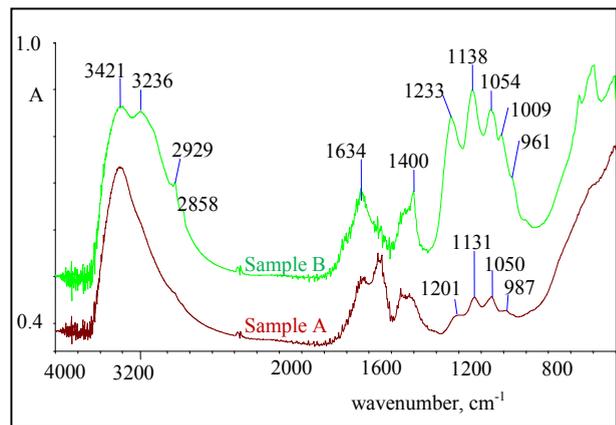
Figure 4. FTIR spectra of SZ materials calcined at 200 °C.

FTIR spectra of materials A, B, CH and CN calcined at 350 °C are shown in Figure 5. All of them show a broad and intense band centered at 3415 cm^{-1} assigned to terminal H-O-Zr groups interacting through hydrogen bond. Samples CN and CH also show peaks at 3230 and 3170 cm^{-1} attributed to the stretching of H-O bonds in Zr-OSO$_2$-OH groups.

The shift to lower frequencies (3415 to 3170 cm^{-1}) is related to the weakening of the O-H bond and consequently to the increased acidity [Morterra et al. (2002), Luzgin et al. (2004)]. From these results it is expected that CN and/or CH materials have a higher acidity than materials A and B calcined at 350 °C.

Kustov and coworkers (1996) proposed that the broad and intense band appearing at 3200 cm^{-1} is related to the presence of Brönsted acid sites formed from sulfate ions bounded to zirconia surface. On the other hand, Buzzoni et al. (1996) suggested that the band centered at 3100 cm^{-1} (full width at half maximun = 500 cm^{-1}) in the FTIR spectrum of **Nafion**® corresponds to SO$_3$-H groups bounded to the polymer backbond.

The medium to weak intensity bands observed between 1600 and1650 cm^{-1} range are related with the previous ones in the region above 3000 cm^{-1}. They are assigned to the bending mode (δ) of H-O-H interacting with other water molecules (1636 cm^{-1} band in sample CN, Figure 5) and to water molecules bound to Lewis acid centers (1650 cm^{-1} band in sample CH, Figure 5).

Between 1500 to 900 cm^{-1} there are several bands due to vibrational stretching (ν) modes of S=O groups, linked to the zirconia surface, with different configurations. Only samples CN and CH show two bands at 1412 and 1430 cm^{-1} which are associated to the signals at 3230/3170 cm^{-1}, due to -SO$_3$H groups previously discussed. Samples A and B do not show these bands.
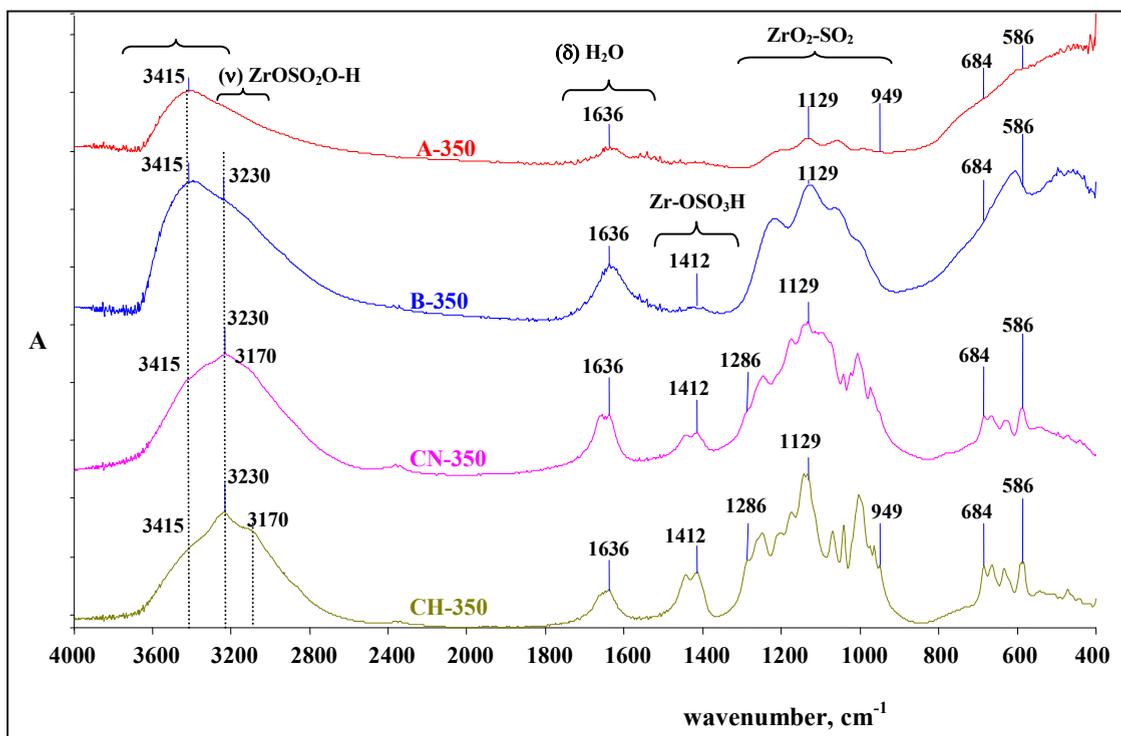
Figure 5. FTIR spectra of materials A, B, CN and CH calcined at 350 ºC used as catalysts in the transesterification reaction.

3.4. Catalytic activity

Figure 6 and Table 4 summarize the catalytic activity results of SZ samples used as catalysts for the transesterification reaction. Materials CN and CH show initial reaction rates comparable with that observed for **Nafion**®, a very acidic material; while sample A shows an initial reaction rate two order of magnitude lower than CN or CH ones. In spite of the larger surface area of sample B (Table 2), it shows no activity as catalyst in the reaction studied. The reason for this behavior must be attributed both to differences in the Brönsted acidity as a consequence of a specific configuration of sulfate groups attached to the zirconia surface and to their relative amount. Taking into account that the transesterification reaction is catalyzed by extremely acid Brönsted acid sites, it is expected that the catalytic behavior must be related to the presence of $-SO_3H$ groups that develops absorption bands in the 3200 - 3100 cm^{-1} and 1630-1412 cm^{-1} spectral regions, as it is seen in Figure 5 for samples CN an CH. Conversely, samples A and B develop bands mainly in the 1200 to 900 cm^{-1} region, related to the presence of Lewis acid centers.

Table 4. Catalytic activity and selectivity of SZ samples used in the transesterification reaction.

Material	M (mg)	r_i (mol/h.g)	Selectivity
Nafion®	100	1.72×10^{-5}	>95%
Nafion®	35	1.68×10^{-5}	>95%
C	100	(*)	
CN	103	2.37×10^{-5}	>95%
CH	106	1.17×10^{-5}	>95%
A	100	3.25×10^{-7}	>95%
B	100	(*)	

r_i (mol/h.g): initial reaction rate (moles/(hour grams of SZ catalyst)); (*) no reaction was observed.
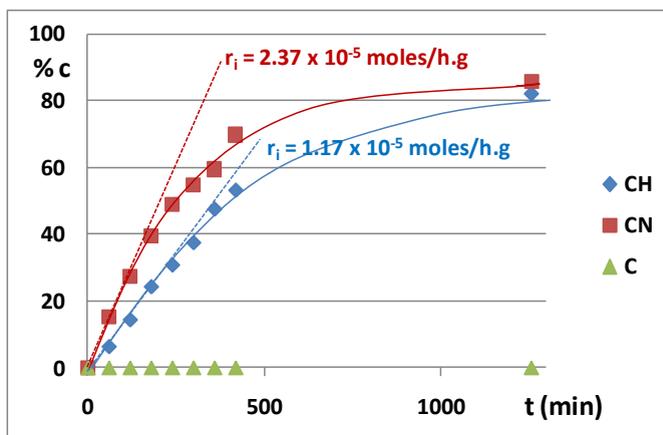
Figure 6. Catalytic activity (% conversion vs reaction time) shown by SZ materials.
r_i: calculated initial reaction rate of CH, CN and C materials used as catalysts in the transesterification reaction.

4. Conclusion

The transesterification reaction of vinyl acetate with i-amyl alcohol is catalyzed by materials containing -SO$_3$H groups bounded to the zirconia structure. The presence of these groups can be easily detected by FTIR spectroscopy. Therefore, this reaction is a useful tool for the assessment of Brönsted acidity in SZ materials.

The catalytic activity of SZ materials prepared either by impregnation with sulfuric acid or by mixing with ammonium sulfate is comparable to that observed for **Nafion**®, a material known as superacid (pKa = 16).

These SZ materials could be used as catalyst in many other reactions of industrial interest, especially those requiring Brönsted acid sites.

Acknowledgement

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