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Methanolysis of Soybean Oil Using Tungsten-Containing Heterogeneous Catalysts

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ABSTRACT: The development of alternative methods of biodiesel production still remains a major priority of the biofuel industry. In this work, the catalytic activity of anhydrous and insoluble sodium tungstate (Na_2WO_4) and its heterogenized form in silica (Na_2WO_4/SiO_2) in soybean oil methanolysis was studied. The sol−gel process was conducted by both the acid and basic routes, and it was observed that the obtained solid catalysts Na_2WO_4/SiO_2 presented different characteristics depending on the conditions employed during their synthesis. The solid catalysts afforded high methyl esters yields (above 95%) in one single reaction step, and they were amenable to recovery and recycling for at least four consecutive reaction cycles, during which high catalytic activity was maintained. Recovery and recycling were carried out by simple solid catalyst filtration and washing. In general, all the investigated silica-based solids were catalytically active for soybean oil transesterification; however, there was a decrease in the catalytic yield after each recycling process. The catalytic activity of the heterogenized silica solids was influenced by various physical parameters, such as specific surface area and textural properties. The structure of the solid catalysts and their catalytic behavior was also evaluated by X-ray fluorescence (XRF), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and textural analyses.

1. INTRODUCTION

Biodiesel is a mixture of long chain alkyl esters that is used as a substitute for diesel oil in many countries around the world, either as a neat fuel or as a blend with petrodiesel.[1] In Brazil, the mandatory use of biodiesel blends was established in January 2008, when it was determined that all diesel consumed nation-wide must contain 2% of biodiesel (B2), with the final goal being the achievement of B5 in January 2012.[2] This mandate mobilized several segments of the Brazilian society and, today, the country has become the fourth largest biodiesel producer and third largest biodiesel consumer in the world, with an estimated production capacity of nearly 5 million tons per year. For this reason, the B5 mandate was anticipated to January 2010, and the program is now recognized as a great success.

Currently, most of the biodiesel production processes are based on the transesterification of vegetable oils using alkaline homogeneous catalysts, which are known for their high activity and low cost, making them suitable for large-scale industrial operations.[3] However, this process has some disadvantages, such as the need for numerous separation and purification steps for the reaction products, which forms a large quantity of emulsion wastewater that is difficult to treat and is sometimes hard to dispose of.[4] Aiming to minimize the problems associated with the homogeneous catalysts, several heterogeneous catalytic systems have been proposed.[5,6] These systems are able to reduce the need for washing and purification steps, facilitate catalyst recovery at the end of the reaction, and allow for good practices of catalyst recycling.[7] In fact, this class of catalysts offers economical, ecological, and technical advantages, which are critical parameters for improvement of the efficiency and sustainability of biodiesel manufacture.[8]

In general, the heterogeneous catalysts present high surface concentration of Lewis or Brönsted-Lowry acid or basic sites, and this property has been identified as the key factor for their high performance in biodiesel synthesis.[9,10] This type of compound has a structure based on positive metal ions with Lewis acidity and negative oxygen ions displaying Brönsted-Lowry basicity. According to Zabeti et al.,[5] when these solid catalysts are applied for the methanolysis of vegetable oils, they provide sufficient adsorption sites for methanol, where the O−H bonds are readily broken into methoxide anions and hydrogen cations. The generated methoxide anions thus react with triacylglycerol molecules, to furnish the corresponding methyl esters.[11]

Several classes of heterogeneous catalysts, such as supported enzymes,[12] oxides and oxosalts,[13] impregnated oxides,[14] inorganic complexes,[15] layered double hydroxides,[16,17] metal carboxylates,[17] zeolites,[18] and ion-exchange resins[19] have been reported in the literature as being active for the transesterification (alcoholysis) of vegetable oils.

A series of heterogeneous catalysts based on transition metal oxides has been examined regarding their activity in vegetable oils transesterification. The best catalytic activity and strength were observed for the $CaZrO_3$ and $CaO−CeO_2$ heterogenized catalysts. Both these solids remained highly active up to the fifth and seventh recycling reaction, respectively, and an 80% yield in methyl esters was achieved after 10 h at 60 °C, using a methanol/oil molar ratio of 6:1.[20] The superacid TiO_2/SO_4 has been

synthesized in the presence of different sulfuric acid concentrations as a sulfate source, and its catalytic activity was evaluated in the transesterification of soybean oil. The results indicated that the reaction conversion rose as the concentration of Brönsted/Lewis acid sites increased on the solid catalyst surface, furnishing up to 40% of conversion in just 1 h under solvothermal reaction conditions.[21]

Transition metal oxides and oxosalts have also been investigated as transesterification catalysts due to their elevated Lewis acidity, depending on the metal oxidation state and ion radius size.[22] In this sense, molybdenum- and tungsten-containing solids have been extensively studied in a number of reactions in which the acidity profile plays an important role, such as isomerization,[23] cyclic alkene oxidation,[24] alcohol dehydration,[25] and vegetable oils transesterification.[26]

Likewise, the catalytic activity of tungsten compounds in the transesterification of vegetable oils and in the esterification of fatty acids has also been researched.[27−30] Four different types of solids have been employed for WO_3 heterogenization, and the resulting solids have been utilized as catalysts in transesterification experiments. The solid containing tungsten oxide immobilized in alumina (WO_x/Al_2O_3) gave the best results; i.e., 98 wt % yield was obtained after 2 h of reaction at 110 °C, using 1 wt % catalyst in relation to the mass of vegetable oil and a methanol/oil molar ratio of 10:1.[28] The WO_3 compound impregnated on ZrO_2 was evaluated in the esterification of oleic acid in a packed-bed continuous flow reactor. According to the authors, the acid strength of the WO_3/ZrO_2 catalyst increased with the level of WO_3 impregnation, because this was the major factor determining the acidic properties of the catalyst. In addition, XPS analyses evidenced that the reduced conversion detected during catalyst recycling was accompanied by a decrease in the concentration of available tungsten species (W^{6+} to W^{5+}). This is indication of a close relationship between the tungsten concentration and the level of oleic acid esterification, which depends on the oxidation state and ionic radius of the transition metal.[29]

Recently, sodium molybdate has been described as an efficient heterogeneous catalyst for the methanolysis of soybean oil. However, it was observed that part of the solid catalyst leached out due to its partial solubilization in methanol.[31] Nevertheless, the methanol-soluble moiety of sodium molybdate was not able to act as a homogeneous catalyst. This study was carried out because one of the most important aspects concerning the use of heterogeneous catalysts is the absence of catalytically active soluble (homogeneous) species. Several experiments have also been proposed on different types of solids (e.g., TiO_2 supported on SiO_2 and sulfated zirconia) for elucidation of their actual heterogeneous character.[32,33] It seems that the polarity of some reactants such as methanol and glycerol, as well as a combination of other factors including temperature and pressure, can favor catalyst leaching from the solid support by solubilization.[20,34]

Countless catalysts have been prepared by heterogenization of the active phase in silica using the sol−gel process.[21,35,36] This methodology has raised a lot of interest because it allows for the synthesis of high-purity solids in very mild reaction conditions of temperature and pressure. The sol−gel process consists of the synthesis of silica, which involves kinetically controlled hydrolytic polycondensation around the silicon atom through substitution of alkoxide groups by the nucleophilic attack of water molecules, with elimination of the corresponding alcohol. According to this complex mechanism, the siloxane (Si−O−Si) group is produced as intermediate species, which leads to the

formation of an amorphous silica framework.[37] In addition to this, the sol−gel route can be performed in acid or basic conditions.[38,39] Catalytically active compounds can be heterogenized during the silica formation step, which modifies their textural properties and promotes the generation and optimized exposure of active sites.[40,41]

In this work, the catalytic activity of anhydrous sodium tungstate (Na_2WO_4) in the transesterification of soybean oil was initially investigated. Later, the sol−gel process was used to produce its heterogenized form in silica, which enabled evaluation of the catalytic activity of this compound even when low sodium tungstate concentrations were distributed on the silica surface. This heterogenization process was employed in order to avoid mass losses by solubilization or other physical processes such as shearing, aiming at further improvements in the recovery and recycling performance of the resulting catalyst.

2. EXPERIMENTAL SECTION

2.1. Materials. Commercial refined soybean oil (edible grade) was purchased from the local market. The average molar mass of triacylglycerols (TAGs) present in the soybean oil was considered to be equivalent to that of triolein, which corresponds to 884.70 g mol^{-1}.[42] Tungsten trioxide (MoO_3), sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), and tetraethylortosilicate were acquired from Sigma−Aldrich (St. Louis, MO), Synth (Diadema, Brazil), and Fluka (Steinheim, Germany), respectively. Unless specified otherwise, all other reagents were supplied by Sigma−Aldrich or Acros (Geel, Belgium) in analytical grade and used as received; i.e., without further purification.

2.2. Catalyst Synthesis and Characterization. Na_2WO_4 was synthesized according to Nakagaki et al.[31] To this end, WO_3 (21.6 mmol) was treated for 4 h at 550 °C and immediately dissolved in 10.75 mol L^{-1} NaOH. After that, methanol (50 mL) was added to the mixture, and $Na_2WO_4 \cdot 2H_2O$ was recovered by filtration, washed with methanol and acetone, and dried for 3 h at 120 °C to produce the anhydrous compound. The commercial sample of $Na_2WO_4 \cdot 2H_2O$ was purchased and used as a reference after drying at 120 °C for 3 h.

The synthesized Na_2WO_4 was heterogenized in silica by the sol−gel process using both the acid and basic catalytic routes. Condensation steps were carried out by employing tetraethylortosilicate (TEOS) in the presence of tungsten species. Initially, Na_2WO_4 was dissolved in deionized water and added upon mixing to a TEOS solution in isopropanol. Then, the catalyst (acid or basic) was added, and the resulting solution was kept under stirring for 1 h at 40 °C. Acid catalysis was based on a water/TEOS/alcohol/HCl molar ratio of 16:1:4:50, whereas basic catalysis was performed with a water/TEOS/alcohol/NH$_3$ molar ratio of 50:1:3:40, with TEOS/Na_2WO_4 molar ratio of 13 in both acid and basic routes. Six different types of solids were synthesized by varying the synthesis conditions and the drying time until xerogel formation (see Table 1); among these samples SA3 and SB3 solids were synthesized in the absence of Na_2WO_4 to be used in control experiments.

The Na_2WO_4 catalyst (both purchased and synthesized in lab scale) and WO_3 were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electronic microscopy (SEM), and gas sorption technique. XRD was recorded on a Shimadzu XRD-6000 diffractometer within the 3−60° (2θ) range using Cu Kα radiation (0.15418 nm) at 2°/min. FTIR spectra were collected on a Bio-Rad FTS 35000GX spectrophotometer with KBr discs prepared after mixing (1 wt %) each of the test samples with anhydrous KBr. Analyses were performed in the transmission mode in the 400−4000 cm^{-1} range, with a resolution of 2 cm^{-1} and accumulation of 16 scans. The solids recovered after the recycling experiments were also analyzed by FTIR after washing. ICP-OES analyses were carried out in a

Table 1. Conditions Employed in the Synthesis of Tungsten-Containing Silica Solids Prepared by the Sol-Gel Process

solid	catalyst	thermal treatment (°C)	time
SA1a	HCl	25	26 days
SA1b	HCl	900	3 h
SA2a	HCl	75	2 days
SA2b	HCl	900	3 h
SA3[a]	HCl	75	2 days
SB1	NH₃	25	31 days
SB2a	NH₃	75	2 days
SB2b	NH₃	900	3 h
SB3[a]	NH₃	75	2 days

[a] Silica in the absence of tungsten species. For all tungsten-containing solids the molar ratio TEOS/Na$_2$WO$_4$ of 13 was used.

Thermo Scientific iCAP 6500 equipment with axial visor and yttrium as internal standard. Specific surface areas and pore average diameters were determined by applying the BET[43] and the BJH[44] methods to the corresponding nitrogen adsorption isotherms, which were obtained in a Micrometrics ASAP 2020 physical adsorption analyzer. The samples were previously degassed by treatment at 180−200 °C until the system pressure achieved 10 μmHg. The nitrogen adsorption data were obtained using 0.2 g of the sample. SEM analysis was conducted on either a JEOL 5190 or a JEOL JSM-6360LV microscope, both operating at 15 keV. A small amount of the sample was placed on a sample holder, metalized by gold sputtering, and analyzed in the scan mode.

A sample of the solid catalyst (15 mg) was also submitted to acid digestion with a mixture of 1.0 mL 30 vol% hydrofluoric acid and 1.0 mL 5.0 wt % nitric acid at 80 °C for 1 h and subsequently treated with 8.3 mol L^{-1} aqueous sodium hydroxide until complete dissolution. The solution was filtered through a 0.45-μm membrane and transferred to a 10-mL volumetric flask. Tungsten concentration was obtained by external calibration using the ICP-OES Thermo Scientific iCAP 6500 apparatus.

2.3. Catalytic Experiments. Reactions were accomplished at room pressure (open vessel) and also at the vapor pressure of methanol (closed vessel). Reactions at room pressure were carried out in round-bottom flasks (125 mL) that were attached to a water-cooled condenser and a magnetic stirrer. Soybean oil (10.0 mmol based on triolein), methanol, and the solid catalyst were added to the flasks and stirred vigorously under methanol reflux for the required reaction time. In contrast, reactions performed at the vapor pressure of methanol were conducted inside a 15-mL closed Teflon cup that was fitted into a stainless closed vessel. Soybean oil (1.00 mmol based on triolein), methanol, and the solid catalyst were added to the Teflon cup, and the system was closed and sealed before heating. The closed vessel was mounted on a magnetic stirrer and placed inside a temperature-controlled oven, where it was kept under magnetic stirring at 1250 rpm for the required reaction time.

In both situations described above, methanol/soybean oil molar ratios of 54:1 and 30:1 were evaluated at catalyst concentrations varying from 5.0 to 10.0 wt % (relative to the vegetable oil mass) and residence times of 3, 5, and 24 h at the selected reaction conditions. Both purchased and synthesized solids Na$_2$WO$_4$ were evaluated. After cooling to room temperature, the reaction mixture was centrifuged, and the solid catalyst was recovered for characterization and reuse. The methanol used in excess was removed by evaporation under low pressure, and both alkyl esters and glycerin phases were recovered after phase separation. The alkyl esters phase was analyzed by high-performance liquid chromatography (HPLC) which were considered as methyl linoleate, methyl linolenate, methyl oleate, methyl palmitate, and methyl stearate and by nuclear magnetic resonance of hydrogen (^{1}H NMR), without any further treatment.
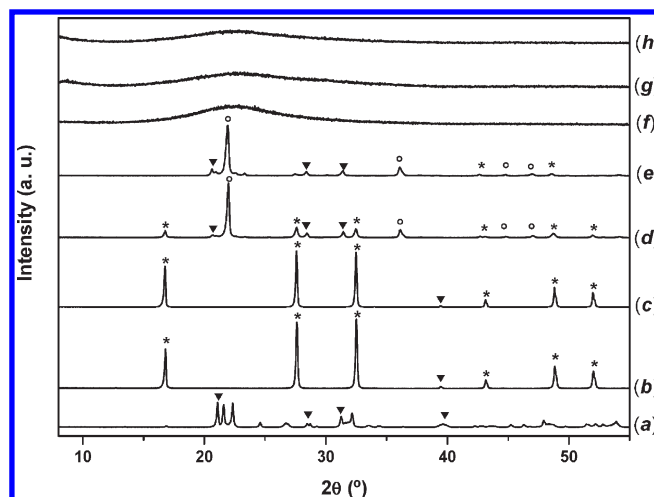

Figure 1. XRD analyses of solids: (a) WO$_3$, (b) synthesized Na$_2$WO$_4$, (c) commercially available Na$_2$WO$_4$, (d) SA1b, (e) SB2b, (f) SA1a, (g) SA2a, and (h) SB2a. Equivalent peaks in different diffractograms are indicated by symbols.

2.4. Alkyl Esters Characterization. Alkyl esters derived from tungsten-based heterogeneous catalysts were analyzed by reverse-phase chromatography (HPLC-RP), and the leaching of metal species from the catalyst surface was monitored by ICP-OES. HPLC was carried out in a LC10AD Shimadzu workstation, equipped with an SIL-10A autosampler and an RID-10A differential refractive index detector. Data collection and analyses were performed with the CLASS LC-10 software. The sample injection volume was kept at 20 mL, and quantification was accomplished by external calibration. A Waters Spherisorb column (250 mm, 4.6 mm, 5 mm) was set at 35 °C and eluted with 9:1 (v/v) acetonitrile/acetone at 0.9 mL/min. The calibration curves were measured from standard solutions of the appropriate alkyl esters. The reaction yield was calculated as previously reported by Kucek et al.[45]

Both the recycling capacity and possible homogeneous contribution of the solid catalyst were assessed in separate experiments.

2.5. Recycling Experiment. From a typical reaction procedure, the solid catalyst was recovered by decantation, filtered, and washed three times with 1:3 (v/v) methanol/hexane mixture. After that, the solids were dried at 120 °C for 3 h and reused for soybean oil methanolysis in the same reaction conditions employed before. This experimental procedure was repeated twice, to evaluate the recyclability of the solid catalysts.

2.6. Evaluation of the Conversion Rate Based on Homogeneous Catalysis. Experiments were performed to investigate whether the amount of Na$_2$WO$_4$ dissolved in methanol, under the reaction conditions used in this study, could have contributed as homogeneous catalyst to the final catalytic activity. For this purpose, methanol (25 mL) and the solid catalyst (0.50 g) were mixed in the absence of soybean oil for 1 h under the same conditions applied for a regular catalytic conversion. After that, the suspension was filtered, and the methanol was recovered and mixed with enough soybean oil to achieve the same proportion used before in the catalytic conversion. The reaction was kept for 5 h under methanol reflux, and the reaction products were analyzed as described before.

3. RESULTS AND DISCUSSION

3.1. Characterization of Synthesized Solids. The XRD analyses are depicted in Figure 1. All the synthesized solids were characterized using WO$_3$ and thermally treated Na$_2$WO$_4$·2H$_2$O (120 °C, 3 h) as reference standards. The WO$_3$ XRD pattern
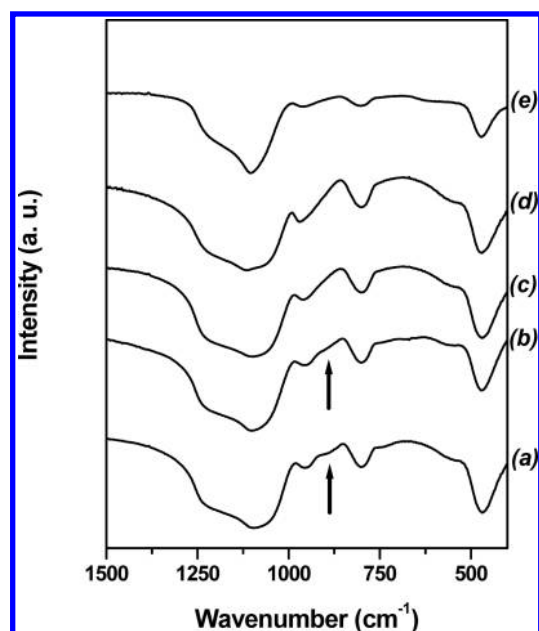
Figure 2. FTIR spectra of the synthesized solids presented in Table 1 in the range of 400−1500 cm^{-1}: (a) SA1a, (b) SA2, (c) SA3, (d) SB1, (e) SB2b. The position of the W−O vibration mode is indicated in the FTIR profile.

(see Figure 1a) evidenced a typical monoclinic phase structure.[46,47] Figure 1b and 1c show the XRD patterns of the synthesized and purchased Na_2WO_4 after the thermal treatment, respectively. Both solids displayed the same diffraction peak profile at 2θ = 16.80°, 27.62°, 32.50°, 39.42°, 43.16°, 48.84°, 52.06°, 57.02°, and 59.90°, corresponding to the 111, 220, 311, 400, 331, 422, 511, and 440 diffraction planes, respectively. On the basis of the reference standard, the cell parameter was 0.9133 nm, typically attributed to anhydrous sodium tungstate in a cubic crystalline system.[48,49] The similarity between the two XRD patterns confirmed that the synthesized solid is very similar, if not identical, to the commercially available sample. The use of Na_2WO_4 synthesized from the WO_3 is warranted due to sustainability of process, given that numerous technologies for recovery of tungsten from industrial wastes have been developed, taking as feedstock scrap alloy containing this metal.[50,51]

The tungsten compounds heterogenized in silica by the sol−gel process exhibited an amorphous XRD pattern before thermal treatment, as demonstrated by the halo between 20 and 30° of 2θ resulting from the dispersion in the angles and bond distances in the basic structural units (silicates). It destroys the periodicity and produces a noncrystalline material, in which tungsten species are not observed because of their high dispersion degree and low concentration (see Figure 1f−1h). After thermal treatment at 900 °C, tungsten species formed crystalline phases that are clearly observed (see Figure 1d and 1e), moreover, the crystobalite phase of the silica in tetragonal arrangement was observed.[52] Other diffraction peaks can be ascribed to the crystalline Na_2WO_4 and WO_3 phases which are indicated by appropriate symbols in Figure 1a−1c.

The solids synthesized in the absence of Na_2WO_4 (SA3 and SB3) are not crystalline, even after being submitted to thermal treatment (data not shown).

From the FTIR results it was possible to detect the characteristic broad bands of silica: at 3460 cm^{-1} attributed to the hydroxyl

(νOH) vibration mode at the silica surface (not shown), at 1630 cm^{-1} corresponds to adsorbed water molecules,[53] at 1080, 960, 800, and 470 cm^{-1} ascribed to Si−O−Si antisymmetric stretching, Si−OH vibrations, Si−O−Si symmetric stretching, and Si−O−Si angular deformations, respectively (Figure 2). FTIR spectroscopy was almost unable to detect the presence of [$WO_4{}^{2-}$] because these species were present at very low concentrations, not to mention that their corresponding absorption bands at 790 and 940 cm^{-1} were probably superimposed with other bands of the inorganic structure.[54,55] Even so, small shoulders can be observed at these same wavenumbers in the FTIR spectra of the SA1a and SA2a solids, and these can be collectively assigned to the stretching modes of W−O in [WO_4]$^{2-}$ anions (Figure 2).

SEM analyses (Figure 3) contributed to the elucidation of the morphological characteristics of the solid catalysts. According to the recorded micrographs, the acid-catalyzed sol−gel process followed by slow drying for 26 days at room temperature afforded solids (SA1a) with particle sizes greater than 2 μm, indicating that the longstanding drying time may have caused the particle growth, possibly increasing the tungsten content in the solid structure (see Figure 3a). In contrast, the solids obtained by basic catalysis and fast drying for 2 days at 75 °C (SB2a) gave rise to rather small particle sizes, thereby confirming the important role of the drying conditions in determining the morphological features of the synthesized solids (see Figure 3b). The effect of temperature on the structure of the synthesized solids can be seen in Figure 3c, which shows an increase in particle sizes greater than 2 μm even after short treatment times (up to 3 h) at 900 °C (solid SB2b).

Table 2 lists the data from XRF and textural analysis for the synthesized solids. The results reveal that the amount of immobilized tungsten depends on the catalyst (acid or basic) that was employed in the synthesis. Compared to the basic route, the acid route favored tungsten immobilization in the silica, with the solids SA2a and SA1a presenting tungsten contents around 5 and 10 wt %, respectively. On the other hand, the solids synthesized by the basic route (SB1 and SB2a) contained much less tungsten, around 0.4 wt %. The achievement of higher tungsten incorporation under acid conditions is apparently linked to the type of intermediates generated during TEOS hydrolysis. According to Kubota and Alfaya,[56] TEOS hydrolysis under acid conditions involves protonation of the alkoxide group. Therefore, the electronic density of the silicon atom is withdrawn, making it more susceptible to the nucleophilic attack of a water molecule, thereby producing a positively charged pentacoordinated intermediate.[56−58] So the [WO_4]$^{2-}$ anions may have interfered in the hydrolysis mechanism, destabilizing the positive intermediate and being included in the framework as a Si−O−W−O−Si structure. Alternatively, [WO_4]$^{2-}$ anions may have been entrapped in the silica network without being included in the framework structure (physical adsorption). Under basic conditions, the mechanism apparently involves the nucleophilic attack of the silicon atom by the hydroxide anion to form a negatively charged pentacoordinated intermediate, followed by removal of an alkoxide anion. This negatively charged intermediate does not exert any attraction on the tungstate anion, thus complicating its heterogenization in the silica framework.

Another possible explanation for the high tungsten incorporation in acid-catalyzed sol−gel processes may be that the physical properties of each solid (SA1a and SA2a) are strongly dependent on the parameters used in the sol−gel process. Under acid conditions, condensation preferably involves the silanol groups
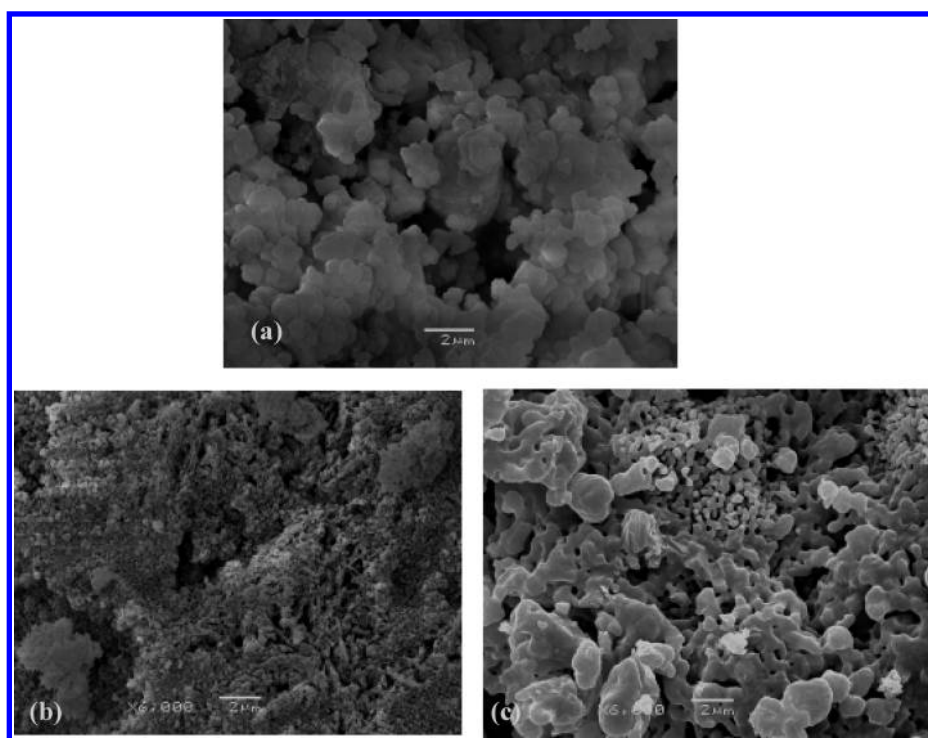
Figure 3. SEM images of the solids obtained by the heterogenization of sodium tungstate using the sol−gel process: (a) SA1a, (b) SB2a, and (c) SB2b.

Table 2. Tungsten Content and Textural Analysis of the Synthesized Solids

| solid	W (wt%)	specific surface area (m^2/g)	average pore diameter (nm)	pore volume (cm^3/g)
SA1a	10.51 ± 0.19	5	44.9	0.05
SA1b	ND^{a,b}	ND^c	ND^c	ND^c
SA2a	5.63 ± 0.85	15	27.4	0.1
SA2b	ND^b	ND^c	ND^c	ND^c
SA3	control^d	370	2.20	0.2
SB1	0.47 ± 0.03	92	29.0	0.7
SB2a	0.30 ± 0.04	93	28.3	0.7
SB2b	ND^b	ND^c	ND^c	ND^c
SB3	control^d	400	5.10	0.5

^{a} ND = not determined. ^{b} It is expected that present similar contents of W (wt%) as the precursor solids SA1a, SA2a and SB2a, respectively. ^{c} Meaningless results. ^{d} Silica prepared by the sol−gel process in the absence of tungsten species using HCl (SA3) or NH$_3$ (SB3).

located at the end of monomers or polymer chains. This leads to the formation of gels composed of linear interlaced polymer chains, which furnishes dense materials after drying. Under basic conditions, though, condensation preferably occurs between highly branched oligomers, culminating in the formation of particulate gels. After drying, these gels furnish materials with high porosity.[57,58] In this sense, formation of the silica structure under acid conditions probably facilitated incorporation of the tungsten species. Differences in tungsten incorporation were also investigated for two solids synthesized in acid medium. The SA1 solid, dried slowly, had greater tungsten content compared with the SA2a solid, which was dried more quickly at 75 °C. Hence, the thermal treatment plays a crucial role in tungsten incorporation.

According to the textural analyses (see Table 2), the physical characteristics of the synthesized solids were strongly influenced by the tungsten content but slightly influenced by the synthetic route (acid or basic) that was used in the sol−gel heterogenization process. The solids can be classified as mesoporous materials, with pore sizes lying between 2 and 50 nm.[59] However, the pore sizes of both the SA1b and SB2b solids did not fall within the same range, probably due to the presence of micropores (pore size smaller than 2 nm) that were generated after thermal treatment at 900 °C in the structure.[60] The specific surface area and the average pore size of the synthesized solids are summarized in Table 2. In addition, the pore size distribution of both the SB1 and SA1a solids (Figure 4) revealed that the conditions utilized during the synthesis of SB1 gave rise to a more homogeneous pore size distribution, predominantly mesoporous, in contrast with the SA1a solid, which led to a more heterogeneous pore size distribution.

Compared with pure silica (SA3), Na$_2$WO$_4$ heterogenization by the sol−gel process under acid conditions (SA1a and SA2a) resulted in solids with lower specific surface area and greater average pore diameter, suggesting that small pores may have been occluded by adsorption of tungsten-containing isopolyanions onto the matrix surface. Indeed, tungsten has been found to form polymeric compounds called isopolytungstates in aqueous solution at low pH values, as exemplified by the equation described below:[61,62]

$$q\text{WO}_4{}^{2-} + p\text{H}^+ \leftrightarrow [\text{H}_x\text{W}_q\text{O}_y]^{n-} + (4q - y)\text{H}_2\text{O} \quad x = p - 8q + 2y^2$$
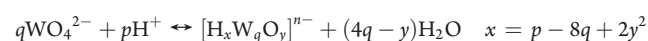
As isopolyanions may take days or weeks to form under acid conditions,[61] the observed increase in pore diameter, more evident in the SA1a solids compared with the SA2a solids, may have been a consequence of the occlusion of small pores of the silica matrix by the adsorption of isopolyanions, which are much
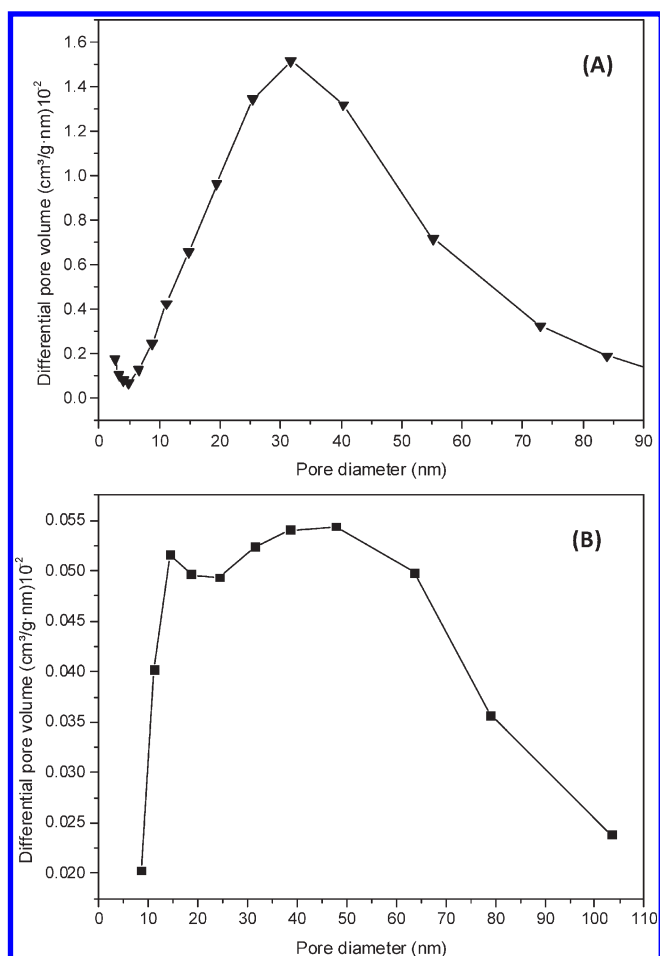
Figure 4. Pore size distribution of the solids synthesized by the sol—gel process: SB1 (A) and SA1a (B).

larger than tungstate anions. In fact, SA2a has a pore diameter similar to that achieved for the SB1 and SB2a solids, which were synthesized under conditions that are not suitable for the formation of such isopolyanions. Therefore, in the latter case tungstate anions would be the only species adsorbed onto the silica matrix, explaining why both SB1 and SB2a solids have specific surface areas and pore diameters greater than those observed in the SA1a and SA2a solids, which were synthesized under acid conditions, as mentioned above.

Table 2 also shows that SA3 and SB3 solids had very similar textural properties. These results suggest that, for solids obtained in the absence of Na_2WO_4, the type of catalysis used in the sol—gel synthesis does not affect the properties of the resulting solid. However, in the presence of Na_2WO_4, the use of a basic catalyst produces solids with very distinct structural features.

3.2. Catalytic Activity of Tungsten-Containing Solids in the Methanolysis of Soybean Oil. Na_2WO_4 samples, as well as the solids comprising Na_2WO_4 heterogenized in silica, were investigated as heterogeneous catalysts for the methanolysis of refined soybean oil. In general, the reaction yields were influenced by several factors, such as the oil/methanol molar ratio, the catalyst concentration, and the time and temperature used for conversion. The purchased Na_2WO_4 solid presented catalytic results (not shown) similar to synthesized Na_2WO_4 solid. Table 3 presents the results obtained by HPLC and ^{1}H NMR; it is known

that yield of the transesterification reactions measured by ^{1}H NMR has an average variation of about 5% in relation to the HPLC technique.[31]

The catalytic activity of Na_2WO_4 was evaluated under various experimental conditions, and product yields up to 99.6 wt % were achieved when the reaction parameters were optimized (see Table 3, reactions 1—4). Compared with other heterogeneous tungsten-based catalysts, some advantages of the Na_2WO_4 catalysts employed here are related to the easy preparation of Na_2WO_4. Indeed, most of the solids based on tungsten reported in the literature demand several preparation steps, some of which involve thermal treatment at high temperatures.[28,63−65] Another advantage is that the catalysts obtained in this work present high reactivity and recycling capacity. This was demonstrated by the recycling experiments involving at least four sequential reaction cycles with marginal loss in reaction yields, which always remained around 95 wt %. With respect to the alcohol/soybean oil molar ratio, the proportion used herein (54:1) can be considered high compared with those described in the literature. For instance, the tungsten-containing alumina (WO_x/Al_2O_3) gave yields around 98% with methanol/soybean oil molar ratios of 10:1.[28] Anyway, the alcohol reagent used in excess can always be recovered and reused in the next reaction cycle.

Another important benefit of using Na_2WO_4 as a heterogeneous catalyst for methanolysis is that mild temperatures are required for optimal performance (just 80 °C). Heterogeneous catalysts usually operate at much higher reaction temperatures. Such is the case of tungsten and molybdenum species immobilized in zirconia, which require 200 °C for optimal performance and, even so, the yields are always lower than 70 wt %.[10,64,66]

These results highlight the potential of Na_2WO_4 as an efficient heterogeneous catalyst for alcoholysis. However, Na_2WO_4 mass losses around 10 wt % have been verified after each reaction cycle in the recycling experiments, which has prompted the present investigation of its heterogenization in silica by means of the sol—gel process.

The obtained Na_2WO_4 solids heterogenized in silica were evaluated in the same conditions employed for the study of the catalytic activity of Na_2WO_4, but their catalytic performance was not satisfactory (data not shown). For this reason, the heterogenized solids were then evaluated under solvothermal conditions using a stainless steel reactor.

Results from Table 3 (reactions 5—8 and 10—12) demonstrate that all the silica heterogenized solids prepared by us displayed pronounced catalytic activity in soybean oil methanolysis. The best yields were achieved with the SA1a and SB1 solids (reactions 5 and 10, respectively), with values always above 90 wt %. Interestingly, these solids were the only ones that had been slowly dried at room temperature (25 °C). On the other hand, differences in tungsten content (see Table 2) did not affect the catalytic activity significantly. Hence, solids with tungsten content lower than 0.5 wt % (SB1, SB2a, and SB2b), all of them derived from heterogenization under basic conditions, gave conversions similar to those obtained under acid conditions (SA1a, SA1b, SA2a, and SA2b). So it seems that the small tungsten content, which must be directly associated with the concentration of active sites, was offset by the favorable textural properties, including the more homogeneous pore size distribution (Figure 4). It is known that the specific surface area has a crucial role in catalysis using heterogeneous materials, primarily due to the simplification of the mass transfer and diffusion phenomena.[21,59,60] So solids with higher specific surface area

Table 3. Ester Yields Obtained in Different Experimental Conditions Using Na$_2$WO$_4$ or the Corresponding Heterogenized Solids

run	catalyst	molar ratio methanol/oil	catalyst (wt%)[a]	time (h)	temperature (°C)	yield (%)[b]	TOF[b] (s^{-1}) × 10^{-3}
1	Na$_2$WO$_4$	30:1	5	5	80	37.7	0.132
2	Na$_2$WO$_4$	54:1	5	5	65	41.2	0.144
3	Na$_2$WO$_4$	54:1	5	3	80	32.2	0.112
4	Na$_2$WO$_4$	54:1	5	5	80	99.6	0.355
5	SA1a	54:1	10	24	120	91.0	0.208
6	SA1b	54:1	10	24	120	88.4	0.205
7	SA2a	54:1	10	24	120	87.2	0.363
8	SA2b	54:1	10	24	120	74.0	0.314
9	SA3	54:1	10	24	120	9.1	NA
10	SB1	54:1	10	24	120	91.6	4.75
11	SB2a	54:1	10	24	120	75.8	6.03
12	SB2b	54:1	10	24	120	75.7	5.95
13	SB3	54:1	10	24	120	8.9	NA

[a] Catalyst amount in relation to the vegetable oil weight. [b] Results derived from experiments 1−4 were obtained by HPLC and those from experiments 5−13 were obtained by ^{1}H NMR. NA = not applicable. [b] TOF = (soybean oil converted/mol of tungsten per gram of solid). The value of apparent activation energy found to the solid SB1 was 2.8 kJ mol^{-1}, indicating that this solid catalyst does not demonstrate an apparent dependence between activation energy and temperature under the experimental catalytic conditions used in this work.
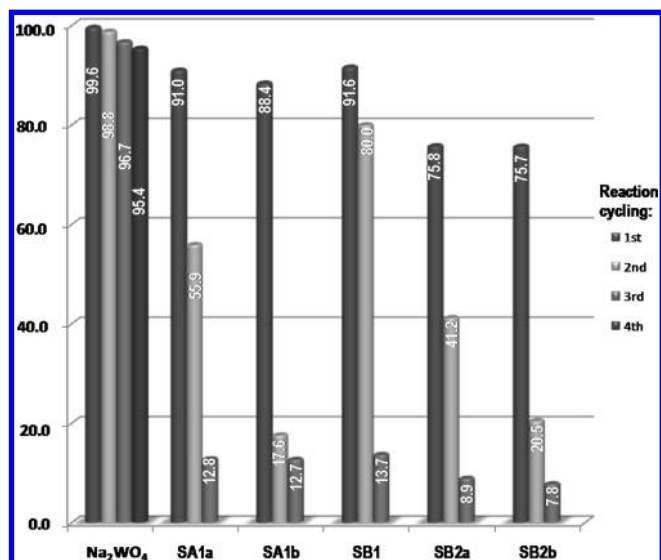
Figure 5. Recycling experiments of the solid catalysts in soybean oil methanolysis.

and structural homogeneity performed better as catalysts (see Table 2).

The catalytic activity of pure silica solids (SA3 and SB3), prepared by the sol−gel process in the absence of sodium tungstate, was also assessed in control experiments. These solids contributed little to soybean oil methanolysis (see Table 3, reactions 9 and 13). In other words, the catalytic activity of the heterogenized silica solids was directly related to the presence of tungsten species acting as Lewis acid sites in their structure, which are related to the high ratio load/radius of metal and the stabilization of pairs of electrons coming from species π-donors, as the case of carboxyl and carbonyl groups present in the triacylglycerol and fatty acids molecules or an alcohol molecule acting as a nucleophilic group.[11] In the same way, the catalytic activity of the Na$_2$WO$_4$ can be attributed to the high concentration of tungstate ions containing species considered Lewis acids.

Table 4. Recycling of the SA1a and SB1 Solids and Determination of Tungsten Leaching from the Solid Catalyst by ICP-OES Analysis

reaction	solid	W (%)	W leaching (%)	yield (%)
1	SA1a[a]	10.49 ± 0.38	-	91.0
2	SA1a[b]	6.88 ± 1.26	34.4	55.9
3	SA1a[c]	6.63 ± 0.17	3.60	12.8
4	SB1[a]	0.26 ± 0.06	-	91.6
5	SB1[b]	0.18 ± 0.007	43.1	80.0
6	SB1[c]	0.12 ± 0.03	29.2	13.7

[a] First consecutive reaction cycle. [b] Second consecutive reaction cycle. [c] Third consecutive reaction cycle.

3.3. Recycling Studies. All the solids used as heterogeneous catalysts in the reactions described in Table 3 were recovered, washed, and investigated in new reaction cycles under the same previously employed experimental conditions. In general, the results obtained with the Na$_2$WO$_4$ catalyst were quite satisfactory (see Figure 5). The catalytic activity of this insoluble salt was comparable to that of Na$_2$MoO$_4$,[31] since it was possible to carry out at least four consecutive reaction cycles without any significant decrease in the reaction yield. This indicates the large recycling capacity of this catalyst, as demonstrated by the fact that the yields varied marginally between 99.6 and 95.4 wt % from the first to the fourth reaction step.

For the heterogenized silica solids, on the other hand, there was progressive reduction in the reaction yields upon recycling, and these values reached levels similar to those obtained with the control reactions (Table 3, reactions 9 and 13). These results suggest that the tungsten species were either inactivated or leached out from the silica surface, which diminished the amount of readily available catalytic sites. The smallest decreases between the first and second reaction cycles were achieved for the SA1a and SB1 solid catalysts, which presented yield drops of 56 and 80%, respectively, in the second reaction cycle. The SB1 solid gave rise to high yields even at low tungsten content, whereas the SB2a solid afforded only 41 wt % in the second reaction cycle, as shown in Figure 5.

Monitoring of tungsten leaching from the silica after the catalytic use was only evaluated for the solids that gave the best catalytic performance (SA1a and SB1 in Table 3). In general, for the heterogenized silica solids the yields decreased linearly upon reduction of the tungsten content in the solids, and this decrease remained constant during the entire recycling process (see Table 4).

For the SA1a solid, the reaction yield decreased from 91.0 (first reaction) to 55.9 wt % (second reaction), while its tungsten content decreased from 10.5 to 6.9 wt %, respectively. These results reveal that the drop in reaction yield is accompanied by the leaching of approximately 30% of the solid tungsten content. However, although after the second reaction the leaching did not exceed 4%, the reaction yield still declined to 12.8%. The same behavior was noted for the SB1 solid; i.e., the reaction yields diminished with decreasing tungsten content. Nevertheless, the latter solid gave the highest activity in the second reaction cycle: the yield went down from 91.6 (first reaction) to 80.0 wt % (second reaction) even when the tungsten content had decreased 43%. In the third reaction cycle, the yield dropped sharply from 80.0 to 13.7 wt %, in parallel with a 33.0% reduction in the tungsten content of the solid.

Considering the data from the methanolysis experiments, as well as the leaching and surface area results, it can be hypothesized that the catalysis probably occurs on the surface of the solids. This assumption is made on the basis of the following observations: (a) in general, the textural properties were more important than the tungsten content, since solids with low tungsten levels and high surface area furnished the best results; (b) tungsten leaching was detected during recycling of the heterogenized catalysts, together with significantly decreased conversion. This is because, in this case, tungstate anions are bound to the silica surface through electrostatic interactions or by hydrogen bonding, which have relatively weak bonding strength and culminate in tungsten leaching from the silica surface during the reaction course, particularly under more drastic reaction conditions; (c) even though the SA1a solid has high tungsten content, there was significant reduction in the conversion results during the recycling experiments (reaction 3, Table 4). In the latter case, the remaining tungsten may have formed $W-O-Si-O-W-Si$ species, which probably are not able to exert any catalytic activity on soybean oil methanolysis.

By ICP-OES analysis of both glycerin and ester layers, it was possible to demonstrate that approximately 34% of the total leached tungsten was incorporated into the glycerin phase. Due to the fact that glycerin is a polar solvent, this result indicates that the washing procedure may have been responsible for removing most of the leached tungsten species (about 54%). The amount of tungsten in the chemical composition of methyl esters samples was insignificant. All the samples displayed tungsten contents falling below the detection limit of the method ($1 \mu g/mL$), thus confirming that tungsten species leached out almost exclusively to the glycerin phase.

3.4. Homogeneous Catalysis Investigation. Finally, the heterogeneous character of the insoluble Na_2WO_4 catalyst was evaluated by measuring the catalytic activity of its methanol-soluble moiety (see Table 3, reactions 1−4). Initially, the solubility of Na_2WO_4 under methanol reflux was shown to be 27 $\mu g/mL$. This fraction was subsequently used for the methanolysis of soybean oil with the reaction yield being monitored by ^1H NMR spectroscopy. The results revealed that the methanol-soluble fraction of Na_2WO_4 was catalytically inactive, demonstrating the actual heterogeneous

character of the Na_2WO_4 solid catalyst under the conditions employed in this study. On the basis of these findings, the tungsten species that leached out from the heterogenized silica solids are not expected to act as homogeneous catalyst in soybean oil methanolysis.

4. CONCLUSION

Sodium tungstate (Na_2WO_4) was shown to exhibit excellent catalytic performance in soybean oil methanolysis. Additional advantages of this system included high catalytic activity even under mild reaction conditions and insolubility that was large enough to characterize it as having real heterogeneous behavior as well as high recycling capacity. No significant decrease in reaction yields was observed after four consecutive reaction cycles, and these values always remained above 95 wt % methyl esters. Furthermore, it was possible to heterogenize Na_2WO_4 in silica, in order to avoid mass losses during recovery and recycling. Heterogenization was carried out using the sol−gel process under acid and basic conditions. The solids prepared by these methods displayed satisfactory catalytic performance in soybean oil methanolysis. However, leaching of tungsten species from the silica matrix was verified during reutilization of the solid catalysts, which was followed by a decrease in the reaction yields. Tungstate heterogenization was facilitated when the sol−gel process was carried out under acid conditions. Nevertheless, the use of a basic catalyst provided a solid with higher surface area, which exerted considerable influence on the catalytic performance of the resulting solids.

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■ REFERENCES

(1) Demirbas, A. *Energy Convers. Manage.* **2009**, *50*, 14–34.
(2) Pousa, G. P. A. G.; Santos, A. L. F.; Suarez, P. A. Z. *Energy Policy* **2007**, *35*, 5393–5398.
(3) Leung, D. Y. C.; Wu, X.; Leung, M. K. H. *Appl. Energy* **2010**, *87*, 1083–1095.
(4) Vicente, G.; Martínez, M.; Aracil, J. *Bioresour. Technol.* **2004**, *92*, 297–305.
(5) Zabeti, M.; Daud, W. M. A. W.; Aroua, M. K. *Fuel Process. Technol.* **2009**, *90*, 770–777.
(6) Cantrell, D. G.; Gillie, L. J.; Lee, A. F.; Wilson, K. *Appl. Catal., A* **2005**, *287*, 183–190.
(7) Narasimharao, K.; Lee, A.; Wilson, K. *J. Biobased Mater. Bioenergy* **2007**, *1*, 19–30.
(8) Kiss, F. E.; Jovanović, M.; Bošković, G. C. *Fuel Process. Technol.* **2010**, *91*, 1316–1320.
(9) Di Serio, M.; Cozzolino, M.; Tesser, R.; Patrono, P.; Pinzari, F.; Bonelli, B.; Santacesaria, E. *Appl. Catal., A* **2007**, *320*, 1–7.

(10) Jacobson, K.; Gopinath, R.; Meher, L. C.; Dalai, A. K. *Appl. Catal., B* **2008**, *85*, 86–91.

(11) Rothenberg, G. *Catalysis - Concepts and Green Applications*; Wiley-VCH: Weinheim, 2008; pp 132−133.

(12) Hernández-Martín, E.; Otero, C. *Bioresour. Technol.* **2008**, *99*, 277–286.

(13) Jitputti, J.; Kitiyanan, B.; Rangsunvigit, P.; Bunyakiat, K.; Attanatho, L.; Jenvanitpanjakul, P. *Chem. Eng. J.* **2006**, *116*, 61–66.

(14) Arzamendi, G.; Campo, I.; Arguiñarena, E.; Sánchez, M.; Montes, M.; Gandía, L. M. *Chem. Eng. J.* **2007**, *134*, 123–130.

(15) Abreu, F. R.; Lima, D. G.; Hamú, E. H.; Wolf, C.; Suarez, P. A. Z. *J. Mol. Catal. A: Chem.* **2004**, *209*, 29–33.

(16) Liu, Y.; Lotero, E.; Goodwin, J. G., Jr.; Mo, X. *Appl. Catal., A* **2007**, *331*, 138–148.

(17) Cordeiro, C. S.; Arizaga, G. G. C.; Ramos, L. P.; Wypych, F. *Catal. Commun.* **2008**, *9*, 2140–2143.

(18) Leclercq, E.; Finiels, A.; Moreau, C. *J. Am. Oil Chem. Soc.* **2001**, *78*, 1161–1165.

(19) López, D. E.; Goodwin, J. G., Jr.; Bruce, D. A. *J. Catal.* **2007**, *245*, 381–391.

(20) Kawashima, A.; Matsubara, K.; Honda, K. *Bioresour. Technol.* **2008**, *99*, 3439–3443.

(21) Almeida, R. M.; Noda, L. K.; Gonçalves, N. S.; Meneghetti, S. M. P.; Meneghetti, M. R. *Appl. Catal., A* **2008**, *347*, 100–105.

(22) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3534–3539.

(23) Hattori, H.; Asada, N.; Tanabe, K. *Bull. Jpn. Chem. Soc.* **1978**, *51*, 1704–1707.

(24) Xia, X.; Jin, R.; He, Y.; Deng, J.; Li, H. *Appl. Surf. Sci.* **2000**, *165*, 255–259.

(25) Davis, B. H. *J. Catal.* **1978**, *55*, 158–165.

(26) Furuta, S.; Matsuhashi, H.; Arata, K. *Catal. Commun.* **2004**, *5*, 721–723.

(27) Komintarachat, C.; Chuepeng, S. *Ind. Eng. Chem. Rev.* **2009**, *48*, 9350–9353.

(28) Park, Y.; Lee, D.; Kim, D.; Lee, J.; Lee, K. *Catal. Today* **2008**, *131*, 238–243.

(29) López, D.; Suwannakarn, K.; Goodwin, J. G., Jr; Bruce, D. A. *Ind. Eng. Chem. Res.* **2008**, *47*, 2221–2230.

(30) Jothiramalingam, R.; Wang, M. K. *Ind. Eng. Chem. Res.* **2009**, *48*, 6162–6172.

(31) Nakagaki, S.; Bail, A.; Nunes, F. S.; dos Santos, V. C.; de Souza, V. H. R.; Vrubel, H.; Ramos, L. P. *Appl. Catal., A* **2008**, *351*, 267–274.

(32) Di Serio, M.; Tesser, R.; Casale, L.; D'Angelo, A.; Trifuoggi, M.; Santacesaria, E. *Top. Catal.* **2010**, *53*, 811–819.

(33) Fu, B.; Gao, L.; Niu, L.; Wei, R.; Xiao, G. *Energy Fuels* **2009**, *23*, 569–572.

(34) Granados, M. L.; Alonso, D. M.; Sábada, I.; Mariscal, R.; Ocón, P. *Appl. Catal., B* **2009**, *89*, 265–272.

(35) Castro, K. A. D. F.; Halma, M.; Machado, G. S.; Ricci, G. P.; Ucoski, G. M.; Ciuffi, K. J.; Nakagaki, S. *J. Braz. Chem. Soc.* **2010**, *21*, 1329–1340.

(36) Papacídero, A. T.; Rocha, L. A.; Caetano, B. L.; Molina, E.; Sacco, H. C.; Nassar, E. J.; Martinelli, Y.; Mello, C.; Nakagaki, S.; Ciuffi, K. J. *Colloids Surf., A* **2006**, *275*, 27–35.

(37) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62–69.

(38) Brinker, C. J.; Scherer, G. W. *Sol-gel Science: The Physics and Chemistry of Sol-gel Processing*; Academic Press: San Diego, CA, 1990; pp 47−50.

(39) Schneider, M.; Duff, T. M.; Wildberger, M.; Baiker, A. *J. Catal.* **1994**, *147*, 500–514.

(40) Francisco, M. S. P.; Landers, R.; Gushikem, Y. *J. Solid State Chem.* **2004**, *177*, 2432–2439.

(41) López, T.; Bosch, P.; Tzompantzi, F.; Gómez, R.; Navarrete, J.; López-Salinas, E.; Llanos, M. E. *Appl. Catal., A* **2000**, *197*, 107–117.

(42) Byrdwell, W. C.; Neff, W. E. *J. Chromatogr., A* **1999**, *852*, 417–432.

(43) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.

(44) Barrett, E. P.; Joyner., L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373–380.

(45) Kucek, K. T.; César-Oliveira, M. A. F.; Wilhelm, H. M.; Ramos, L. P. *J. Am. Oil Chem. Soc.* **2007**, *84*, 385–392.

(46) Laruelle, S.; Figlarz, M. *J. Solid State Chem.* **1994**, *111*, 172–177.

(47) Cazzanellia, E.; Vinegonib, C.; Mariottob, G.; Kuzminc, A.; Puransc, J. *Solid State Ionics* **1999**, *123*, 67–74.

(48) JCPDS. International Centre for Diffraction Data, 70-1040,1974.

(49) Okada, K.; Morikawa, H.; Marumo, F.; Iwai, S. *Acta Crystallogr.* **1974**, *B30*, 1872–1873.

(50) Vadasdi, K.; Olfih, R.; Szilassy, I.; Jeszenszky, A.; A'rvay, P.; Chikfin, T. *Int. J. Refract. Met. Hard Mater.* **1994**, *12*, 357–368.

(51) Luo, L.; Kejun, L.; Shibayama, A.; Yen, W.; Fujita, T.; Shindo, O.; Katai, A. *Hydrometallurgy* **2004**, *72*, 1–8.

(52) JCPDS. *International Centre for Diffraction Data, 42-1425,* 1988.

(53) Fidalgo, A.; Ilharco, L. M. *J. Non-Cryst. Sol.* **2004**, *347*, 128–137.

(54) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; John Wiley: New York, 1970; pp 98.

(55) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part A: Theory and Applications in Inorganic Chemistry*; John Wiley & Sons: New York, 1997; pp 199.

(56) Alfaya, A. S.; Kubota, L. T. *Quim. Nova* **2002**, *25*, 835–841.

(57) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed.* **1996**, *35*, 1420–1436.

(58) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33–72.

(59) Leofanti, G.; Padovan, M.; Tozzola, G.; Venturelli, B. *Catal. Today* **1998**, *41*, 207–219.

(60) Lenza, R.F. S.; Vasconcelos, L. W. *Quim. Nova* **2002**, *25*, 893–896.

(61) Greenwood, N. M.; Earnshaw, A. *Chemistry of the Elements*; Butterworth Heinemann: Oxford, 1997; pp 1010−1014.

(62) Borzenko, M. I.; Botukhova, G. N.; Tsirlina, G. A.; Petrii, O. A. *Electrochim. Acta* **2008**, *53*, 3854–3861.

(63) Teng, G.; Gao, L.; Xiao, G.; Liu, H. *Energy Fuels* **2009**, *23*, 4630–4634.

(64) Sunita, G.; Devassy, B. M.; Vinu, A.; Sawant, D. P.; Balasubramanian, V. V.; Halligudi, S. B. *Catal. Commun.* **2008**, *9*, 696–702.

(65) Narasimha Rao, K.; Sridhar, A.; Lee, A. F.; Tavener, S. J.; Young, N. A.; Wilson, K. *Green Chem.* **2006**, *8*, 790–797.

(66) Suwannakarn, K.; Lotero, E.; Ngaosuwan, K.; Goodwin, J. G., Jr. *Ind. Eng. Chem. Rev.* **2009**, *48*, 2810–2818.