Heterogeneous Catalysts for Biodiesel Production

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Abstract

The environmental benefits of biodiesel produced from fully renewable resources could not be underestimated; its production follows the principles of green chemistry and it closes the carbon cycle. Nevertheless, high productions costs preclude replacement of petroleum-based diesel fuel with biodiesel. The introduction of a solid heterogeneous catalyst in biodiesel production contributed to reducing biodiesel price, toward competitiveness with diesel. Lin's group was at the forefront of this endeavor and invented and developed one of the first heterogeneous catalysts for generating biodiesel. Nowadays, current catalysts catalyze transesterification and esterification at low temperatures, are stable, especially in water, and have high selectivities.

xx.1 Introduction

      Biodiesel is a renewable fuel that can be generated from plant oils, rendered animal fats and industrial waste oils.[1] It has evolved into a significant industry in the midwestern United States and in Europe. In the United States biodiesel is prepared primarily from soybean oil. In Europe, biodiesel is generated mostly from rapeseed oil. Biodiesel has a number of advantages over diesel fuel. Although the National Biodiesel Board has listed a number of benefits, the most significant ones are that biodiesel is a renewable fuel that is nontoxic, biodegradable and free of sulfur-containing impurities.[2] Biodiesel also has significant lubricity compared to petrochemical fuels. These qualities make biodiesel especially useful in places such as national parks, harbors and other environmentally sensitive areas. Biodiesel is commonly sold as a mixture with petroleum fuels. For example, B20 is a mixture of twenty percent biodiesel and eighty percent petroleum fuel.

      Biodiesel, also known as Fatty Acid Methyl Esters (FAME), is one of the most promising alternative biofuels and is currently produced by a base-catalyzed transesterification reaction with triglycerides and methanol as illustrated in Scheme 1. Biodiesel is a mixture of compounds because it is produced by transesterification of triglycerides found in soybean oil. Triglycerides contain mixtures of esters of different chain lengths and some chains have alkenes or epoxides. The most common alcohol used in transesterification of soybean oil is methanol, in large part because it is less expensive than other alcohols. For many decades the transesterification reaction was conducted by heating soybean oil, an excess of methanol and a few percent of a homogeneous catalyst such as sodium hydroxide or sodium methoxide for several hours and then neutralizing the catalyst and separating the biodiesel from the glycerol. Although catalysts such as sodium methoxide afford excellent yields of the transesterification product, a methyl ester, the catalyst must be neutralized with an acid when the transesterification reaction is complete. This neutralization produces a salt which often winds up as an impurity in the glycerol, reducing its value. Additionally, the production of biodiesel using homogeneous catalysts has a large water footprint. For every liter of biodiesel produced, almost four liters of water are utilized. Moreover, the free fatty acids present in feedstocks such as rendered animal fats and industrial waste oils would neutralize the basic catalyst. Therefore, a pre-treatment step which converts the

free fatty acids into esters using an acid catalyst is required for feedstocks that contain significant amounts of free fatty acids.
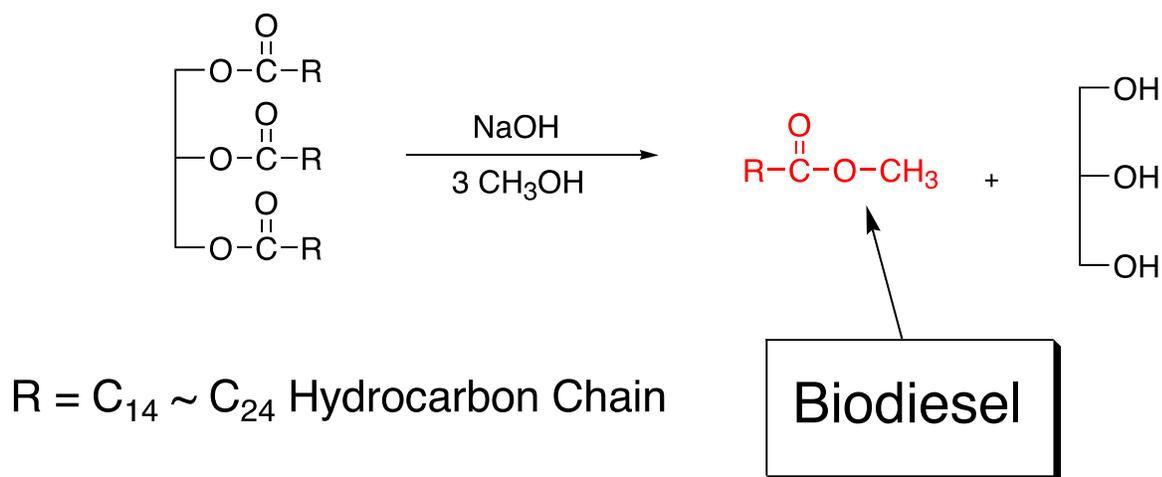
Scheme 1. Base-catalyzed transesterification of tryglicerides to biodiesel

When this work began in 1999, the use of heterogeneous catalysts for the generation of biodiesel was not yet employed on an industrial scale. Certain acidic materials such as zeolites and ion exchange resins had been reported to catalyze the transformation.[3] They have the advantage that any free fatty acids present in the feedstock would be esterified. However, the rate of the transesterification using acidic catalysts is much slower than the reaction employing basic catalysts. Certain metal oxides have been used for the transestrification reaction.[4] However, many metal oxides are are somewhat soluble in methanol. Also, free fatty acid impurities would react with the metal oxides. The ideal catalyst for the transesterification reaction would be economical, recyclable, stable to fatty acid impurities, and would eliminate the costly aqueous workup step.

xx.2 Previous work using mesoporous materials

In recent years there have been a number of reports of the use of heterogeneous catalysts to promote the preparation of biodiesel. The reports have been collated in timely reviews by

Basumatary[5] and by Hanna[6]. Melero and coworkers recently utilized mesoporous arenesulfonic acids to convert crude palm oil containing approximately six percent free fatty acids into biodiesel.[7] Chang and coworkers studied mesoporous carbon-silica composites and found these sulfonic acid catalysts to be effective for the production of biodiesel.[8] Zuo and coworkers showed that mesoporous silica functionalized with alkyl sulfonic acids gave good yields of biodiesel with soybean oil contaminated with twenty percent oleic acid.[9] Mar and coworkers synthesized a propyl sulfonic acid-functionalized mesoporous catalyst that could esterify oleic acid and was superior to Amberlyst 15.[10]

Mesoporous materials have received much attention in the past decade because of their ease of formation and their ease of functionalization. This has permitted an extensive study of structure-activity relationships among catalysts. They have larger pore sizes compared to zeolites, allowing larger organic mlecules to enter.

xx.2.1. Structure-activity studies of mesoporous sulfonic acids

Shanks and Mbaraka have studied mesoporous silica with different sulfonic acids at different surface concentrations.[11] Chen and coworkers have studied dual-functionalized mesoporous silica containing both sulfonic acid groups and disulfide groups.[12] Dhainout an coworker prepared macroporous-mesoporous SBA silicas via dual templating. They cite rate enhancements for the transesterification of bulky esters.[13] Chen and coworkers utilized mesoporous sulfonic acids with short channels and high acid capacities. They found that these catalysts were superior to Amberlyst 15 resin.[14] Yadav and Sharma used a mesoporous sulfonic acid catalysttreated with lanthanum chloride to convert fructose into 5-hydroxymethylfurfural in good yield.[15] Karimi and coworkers utilized a phenylene bridged mseoporous silica catalyst to produce biodiesel.[16] They attributed the enhanced yield to the hydrophobic character of the bridged catalyst. Tang and coworkers produced mesoporous silicas having both platinum and sulfonic acid groups. They utilized this catalyst for a novel one-step hydrogenation-esterification of acetic acid and acetaldehyde.[17] Karimi and Mirzael evaluated a number of mesoporous sulfnic acid catalysts and correlated the improved yields of hydroxymethylfurfural with lower surface hydrophobicity.[18]

XX.2.2. Catalysis of organic reactions

Mesoporous silica functionalized with sulfonic acids have been effective in a number of widely-used organic reactions. Bossaert and coworkers have utilized mesoporous sulfonic acids to catalyze the synthesis of monoglycerides.[19] Clark and coworkers have used mesoporous sulfnic acids as substitutes for environmentally hazardous Lewis and Bronsted acids.[20] Macquarrie and coworkers have used perfluorinated sulfonic acids immobilized onto mesoporous silica to catalyze Friedel-Crafts acylation reactions.[21] Shanks and Bootsma have evaluated the hydrolysis of cellobiose using mesoporous silica catalysts.[22] Chen and coworkers studied the synthesis of bisphenol A using dual-functionalized catlysts.[23] Davis and coworkers also synthesized bisphenol A employing a novel thiol/sulfonic acid paired catalyst.[24] Castanheiro and coworkers have evaluated mesoporous silica sulfonic acids for the successful methoxylation of alpha-pinene.[25]

Shi and coworkers studied the transformation of xylose into furfural using mesoporous SBA-15 catalysts.[26] Lopez-Sanz and coworkers used mesoporous sulfonic acids to prepare a library of quinolines.[27] Thiel and coworkers used acid-base bifunctional mesoporous silica nanoparticles to achieve a clever one-pot deacetalization-aldol reaction.[28] Peng and coworkers created acid-base bifunctional mesoporous catalysts by in situ cleavage of a sulfonamide bond. They employed this novel catlyst in several solvent-free Knoevenagel condensation reactons.[29] Agirrezabal-Telleria and coworkers studied the reaction of mesoporous sulfonic acids with xylose as a function of sulfonic acid load and temperature. In their optimized reaction conditions, they obtained a 82% yield of furfural at 170 °C.[30] Hakki and coworkers found that co-condensation of orthosilicates in the presence of titania afforded a superior catalyst for the photocatalytic conversion of aromatic nitro compounds into a variety of quinolines.[31] Jun and coworkers utilized a magnetically recyclable mesoporous catlyst for tandem acid-base reactions.[32] Zhang described a mesoporous acid catalyst for the Mukaiyama aldol reaction in aqueous media.[33]

xx.2.3. Lin group contributions

The Lin group had developed mesoporous silica nanomaterials with well defined geometries. Mesoporous Silica Nanospheres or MSNs, as they were coined by Lin's group in 2001, benefit from a facile synthetic methodology as well as potential for tayloring their structural properties. The MSNs synthesis require condensation of a silica source around a template. The most studied templating reagents are cationic surfactants, which render materials with porosities in the range of 2-5 nm and block co-polymers, generating 5-30 nm porosities. The interior of these materials resemble a honeycomb, with parallel channels running throughout the nanospherical particle.The channels diameter could be further fine-tuned to accommodate a large variety of molecules, from simple organic compounds to macromolecules. These interior structures lead to the idea of converting the pores in nanoreactors, which engaged the group in a large effort toward altering pore functionality with catalytic groups. The functional groups in the channels could be added through either post-synthesis grafting or by *in situ* addtion of an organo-functionalized silane, method also called co-condensation. The difference between the two methods is highlighted in Figures 1 and 2. Figure 1 indicates that post-synthesis grafting could lead to functional groups on the exterior surface of the silica particle. In contrast, co-condensation drives the majority of functional groups inside the pores with some of them with the undesirable possible location inside the pores wall. When applying co-condensation, Lin's group obtained materials functionalized with a variety of functional groups, including thiols, sulfonic acids, amines and ureas.[34]
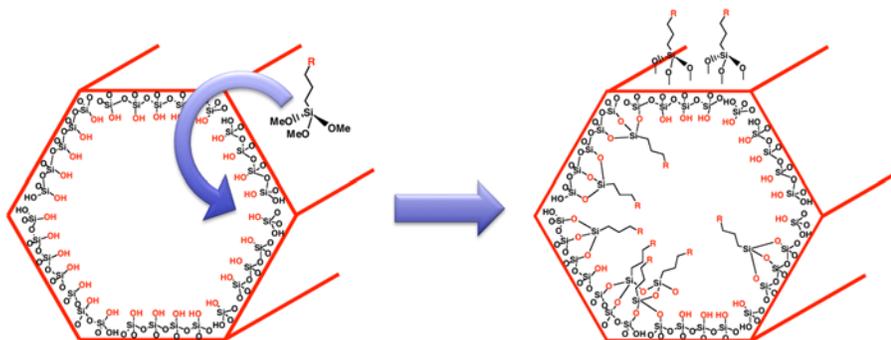

Figure 1. Schematic representation of Post-syntesis grafting of organo-silanes onto silica surface in respect to the silanol groups existent on the pores surface.

In addition, they discovered that by performing the post-synthesis grafting on materials prior removing the surfactant templates, certain functional groups could be selectively grafted to the outside of the nanoparticles. Another intersting finding was that multiple functional groups could be simultaneously added toward forming multi-functional materials.

Novel catalysts could be created by combining grafting and co-condensation to generate selective fuctionalization of MSNs, leading to synergy of catalytic properties.

These durable materials were shown to catalyze several common organic reations. In addition to organic functional groups, the Lin group had also reported the incorporation of inorganic materials into the channels. The general structure of the mesoporous nanomaterial catalyst is shown below.
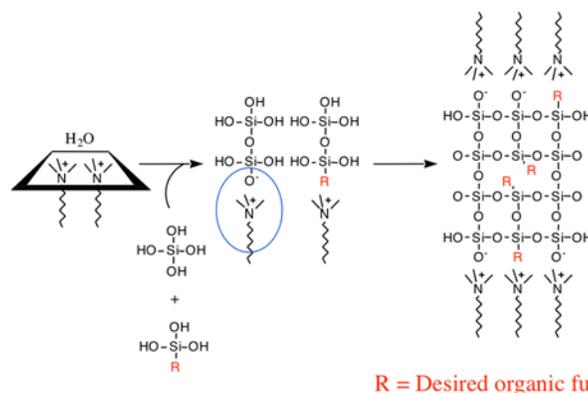
R = Desired organic functionality

Figure 2. Schematic representation of silica functionalization via co-condensation of an organosilane in the presence of a silica source (showed silicic acid)

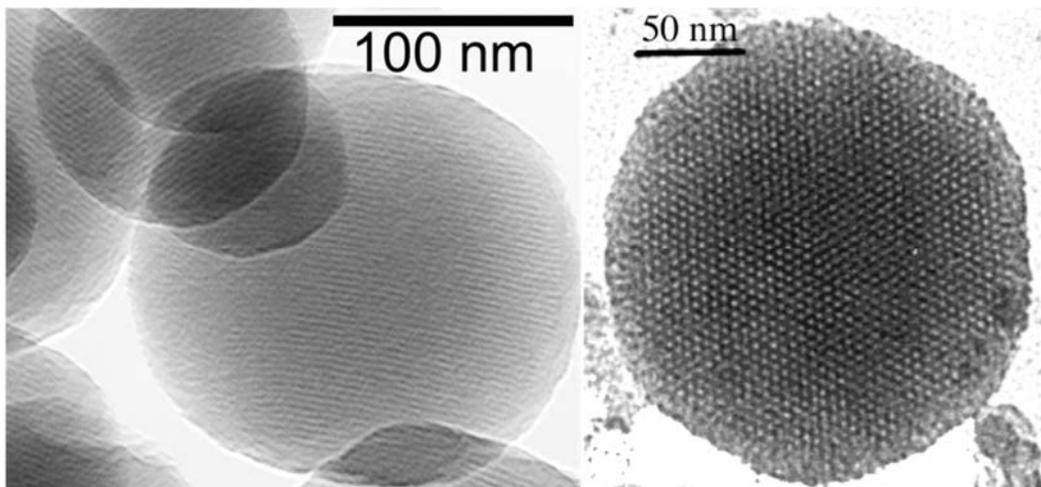structure of the mesoporous nanomaterial catalyst is shown below.

Figure 3. TEM Image of a Mesoporous Silica Nanosphere showing the hexagonal, parallel array of pores

The Lin group used these catalysts for multistep organic reactions.[36] One of the most significant application of the catalysts fabricated in Lin's group was biodiesel preparation, for which the group focused on mesoporous sulfonic acids.[35]

Biodisel fabrication presents a series of challenges, as showed in Scheme zzz.
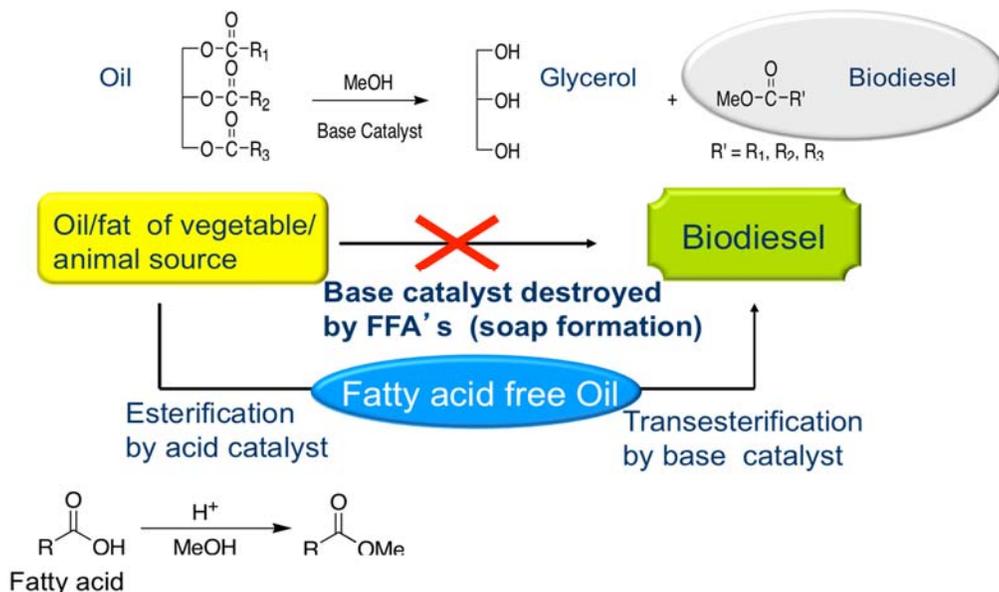

Scheme 2. Challenges in biodiesel fabrication: presence of free fatty acids

To bypass the potential saponification reaction, a solid acid catalyst is needed to transform free fatty acids, typically present in oil feedstocks in various percentages.

Acid Catalyst. To address the first stage of biodiesel fabrication, the Lin group created periodically ordered, sulfonic acid-functionalized mesoporous silicas with pores sizes ranging from 20 to 60 Å and high acid exchange capacities (1-2 mequiv. of H^+/g of SiO_2). To do this the Lin group utilized a recently developed synthetic method which allows the facile incorporation of various acidic sulfonic groups to the mesoporous structures with the ability to fine-tune the loading of these groups.

As depicted below the sulfonic acids are contained in the channels. The soybean oil and the solvent methanol enter the channel and transesterification occurs in the channel. Free fatty acids also enter the channel and are esterified with methanol.
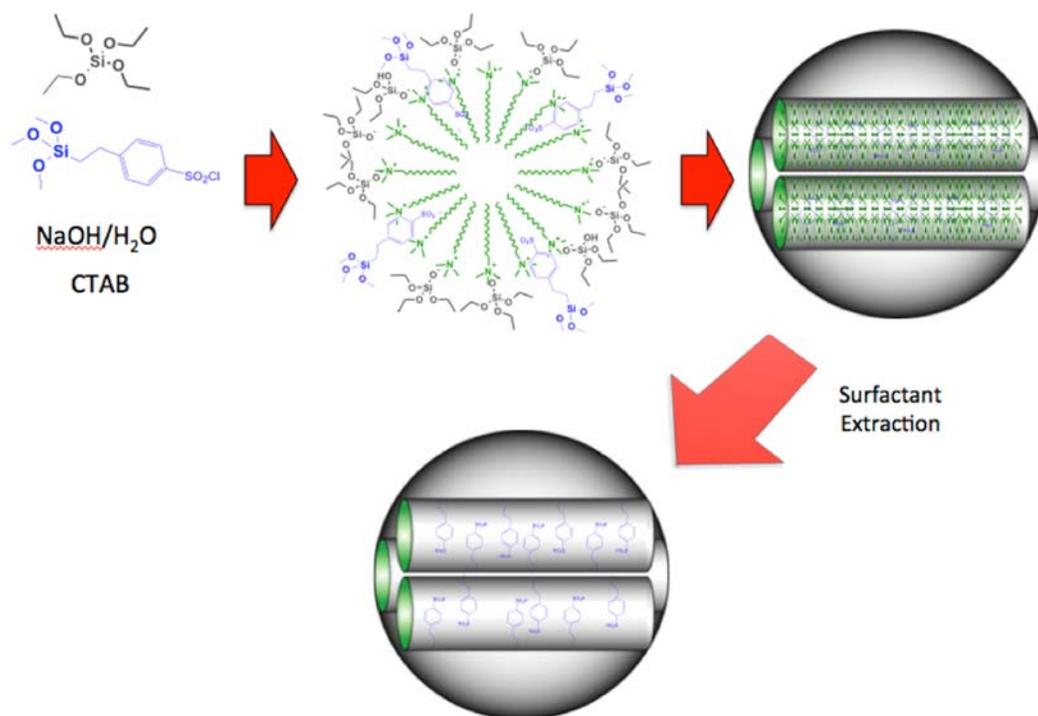
Scheme 3. Synthesis of benzene-sulfonic MSA-1

In addition to the intrinsic catalytic ability and the quantity of acid groups in these catalytic systems, two important factors that can also influence the overall performance of the proposed heterogeneous solid acid catalysts are the sizes of the mesopores and the pore surface properties. These characteristics can have large effects on pore mass transfer of reactant, product, and intermediate species. In particular, functionalization of these derivatized mesoporous silica materials with various surface-bound groups allow modulation of the catalytic systems to enhance substrate selectivity by tuning substrate accessibility and pore hydrophobicity.

Thus, to adress the above toward increasing selectivity of the transesterification reactions, various functional groups have been employed in addition to the sulfonic acid groups. The materials design involved making the pore surface hydrophobic. The reasoning behind this step was matching the channel hydrophobicity with the long alkyl chains in the tryglicerides, and thus, promoting their fast diffusion into the channels; this drove to increase reaction kinetics.

In preliminary investigations, the Lin group tested the catalytic activity of the aforementioned mesoporous solid acid catalyst in comparison with two commercially available
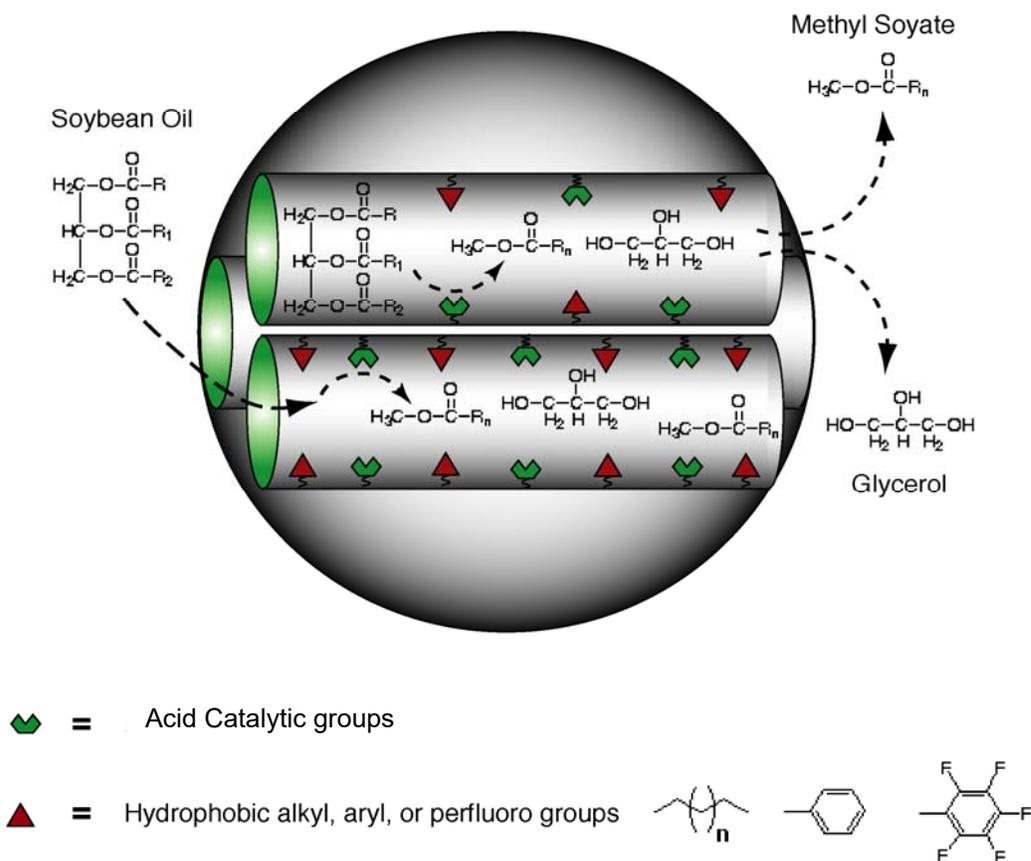

Figure 4. Schematic representation of the proposed catalytic system for the synthesis of methyl soyate and glycerol formation.

homogeneous catalysts (sulfuric acid, H_2SO_4, and p-toluene sulfonic acid, p-TSA) and an SBA-type mesoporous silica catalyst with a propylsulfonic acid functionality (SBA-15-SO_3H-P123) also developed in the Lin group group. Compared with its homogeneous counterpart, p-TSA, it showed similar reaction kinetics, indicating a fast mass-transfer process for the reactants and the products to diffuse in and out of the large pores.

Acid-Base Catalyst. In paralel with fatty acids transformation, transesterification reactions converts tryglcerides in oil feedstocks in biodiesel. To avoid introduction of a second base

catalyst, acid and base groups were introduced simultaneously and site-separated on the different surfaces of mesoporous silica nanoparticle through co-condensation to functionalize the internal surface and post-synthesis grafting to functionalize the external surface. As a result of this ideal site-isolation, reaction cascades requiring two or more catalysts, which are incompatible in one solution system, could be done by this new internal and external surface-bifunctionalized particle.

Furthermore, following the same strategy used for sulfonic acid catalysts, the unoccupied pore surface of the superbase and the acid-derivatized mesoporous silicas were functionalized with propyl, phenyl, or pentafluorophenyl groups via postsynthesis grafting procedures using propyl, phenyl, and pentafluorophenyl trialkoxysilanes, respectively, to yield a series of multi-functionalized mesoporous silica supported "microreactors" for the transesterification and esterification of various FFA-containing oil feedstocks. These mixed-functionality materials allowed control the surface reactivity of these materials. There were three organosulfonic acid functional groups used in the study. The catalytic activities of the functionalized mesoporous silicas were compared with several commercial catalysts, including homogeneous catalysts (sulfuric acid and p-toluenesulfonic acid, p-TSA) and heterogeneous catalysts such as Nafion®).

The success of acid catalyst in esterification of The Lin group also conducted a preliminary transesterification of purified soybean oil to methyl ester using a functionalized mesoporous solid catalyst. The resulting nanomaterials were inexpensive to produce, were reproducible, and could be reactivated simply by heating. A 100% conversion of the soybean oil to methyl ester was accomplished in 20 minutes at 25 °C with a 5-fold excess of methanol. The above studies suggested that a mesoporous sulfonic acid with superbase and hydrophobic-groups functionality could be employed for transformation of crude oil feedstocks in biodiesel from soybean oil efficiently. Based on these preliminary results, there is an opportunity to design a series of new solid catalysts with (1) higher amounts of catalytic groups, and (2) more reactive catalytic functionalities for both the proposed esterification and transesterification of various feedstocks.

xx.3 Industrial Partnership

We sought an industrial partner to explore the large-scale applications of the Lin cataysts. West Central Cooperative is a full-service, farmer-owned cooperative located in west-central Iowa, less than an hour's drive from Iowa State University. The corporate headquarters at Ralston, Iowa acts as the hub for the company's trade territory that spans ten counties and extends 55 miles in each direction. West Central's operating divisions include grain, agronomy, feed, soy processing, and administration. West Central Soy is the manufacturing division of West Central Cooperative. West Central Soy products are processed in a $30 million manufacturing complex in Ralston, Iowa. More than six million bushels of soybeans are processed annually at this facility. The product line of West Central Soy includes: biodiesel, graffiti remover, penetrant and lubricant, methyl esters, diesel fuel additive, asphalt release concentrate, fifth wheel grease, and soy-based lubricants.

West Central's $6 million biodiesel plant is adjacent to its Soy Center. The biodiesel plant processes 8 million pounds of the co-op's soybean oil into methyl esters each year. West Central's current methyl ester process involves heating the soybean oil and introducing alcohol and a catalyst. The resulting reaction separates glycerin from the soybean oil. The catalyst is then removed from the methyl ester through water washing and neutralization process. The end products are biodiesel, glycerin, and fatty acid. The excess water and catalyst is left with the glycerin byproduct, which is sold at an 80% purity level to companies that further process it into hundreds of industrial products.

In 2000, methyl ester production practices at the West Central Cooperative biodiesel plant include the use of a non-recyclable catalyst (sodium methoxide, 1%).   During processing, the catalyst concentrates in the glycerin phase and must be neutralized with aqueous hydrochloric acid. This adds downstream shipping weight in the form of water, methanol, and sodium chloride (transportation energy costs) and energy required to distill the glycerin. They also need to dispose of the non-recyclable catalyst in landfills (at the rate of ten pounds per 1,000 pounds of methyl ester produced).

They perceive several environmental benefits of a heterogeneous catalyst:

- less energy expended to produce the (currently) non-renewable catalyst;

- less transportation (and its associated emissions) to move the (currently) non-renewable catalyst from its point of production to the end user;
- less potential of contamination from a spill of (currently) non-renewable catalyst during transport, handling, and storage;
- minimal water usage due to the elimination of the wash step;
- lower disposal costs associated with the removed catalyst residue since it will be recyclable and regeneratable.

Utilizing a heterogeneous solid acid catalyst for the synthesis of biodiesel could also circumvent the separation of catalyst problem and at the same time eliminate the free fatty acids (FFA) in the crude FFA-containing feedstocks. To prevent ionic base-induced saponification during the transesterification reaction, the West Central process uses NaOMe. Therefore, a highly efficient solid acid catalyst can serve not only as a "pretreatment catalyst" to remove FFA's from the triglycerides, but also as a catalyst for the conversion of the oil to biodiesel.

Synthesis of over 700 grams of the acid-functionalized mesoporous solid catalyst was completed using a pilot-scale test stand configured at the West Central facilities. Analysis by the Lin lab confirmed success in both reactivity and structural integrity of the synthesized materials. These catalysts also perform as expected with respect to recyclability during multiple bench-scale conversion reactions. See Figure 3 as a representation of the catalyst produced to date.

The economic modeling used to gauge viability of these catalyst materials was modified with data from the pilot-scale synthesis activities. Knowing the usage rates and costs of the raw materials used in the synthesis, the economic model could be refined with more realistic inputs. The results of this ongoing feasibility test still show promise in use of these catalysts as an economically viable alternative to today's homogeneous catalyst technology.

Fig. 5 Acid-functionalized mesoporous solid catalyst, synthesized at West Central

Upon completion of the acid catalyst synthesis reactions, the pilot-scale test stand was re-configured to utilize the catalyst in larger scale conversion reactions (1 gallon/hour). Much of the same resources from previous tests were able to be reused in the new configuration, with the exception of the 1-gallon reaction vessel that was incorporated into the flow scheme.

Current Process
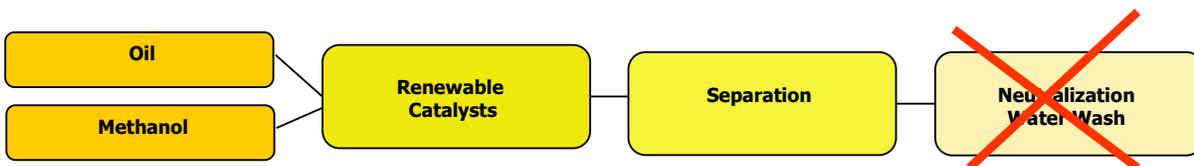
Uses Non renewable Catalyst   Catalyst left in glycerin co-product   Catalyst requires water washing
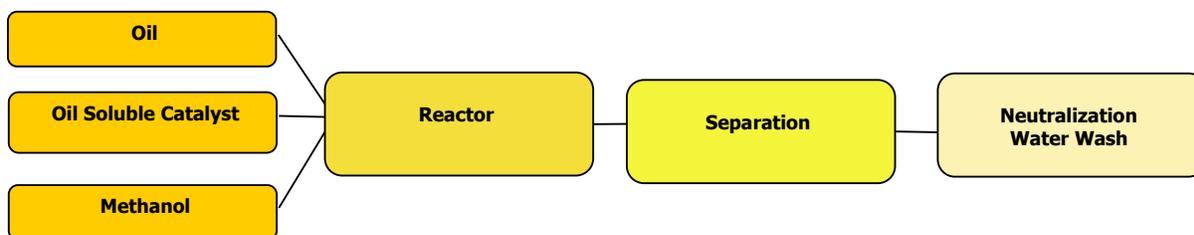
New Catalysts Process

Renewable catalysts   Eliminates catalyst from glycerin co-product   Eliminates water washing

xx.4. Conclusions

Multifunctional mesoporous silica nanosphere catalysts have been synthesized by Lin's group through simultaneous derivatization with acid-containing aryl radicals and superbase on the surface of mesoporous silica. The derivatization was designed to reach a complete separation of the acid and base groups, which enables the catalyst to perform this otherwise antagonistic acid-base function. The benefit of such catalyst is the capability of converting both free fatty acids and tryglicerides in one pot reaction with high yield and excellent separation which allows biodiesel fabrication in one step. This implies a tremendous processing-costs reduction due to eliminating expensive intermediate steps. Compared with other solid acid and solif base catalysts, the MSN catalyst materials show stable and highly efficient catalytic performance in biodiesel production with conversions reaching 100%. The catalysts are highly efficient, environmentally friendly, inexpensive, and easy to prepare.

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