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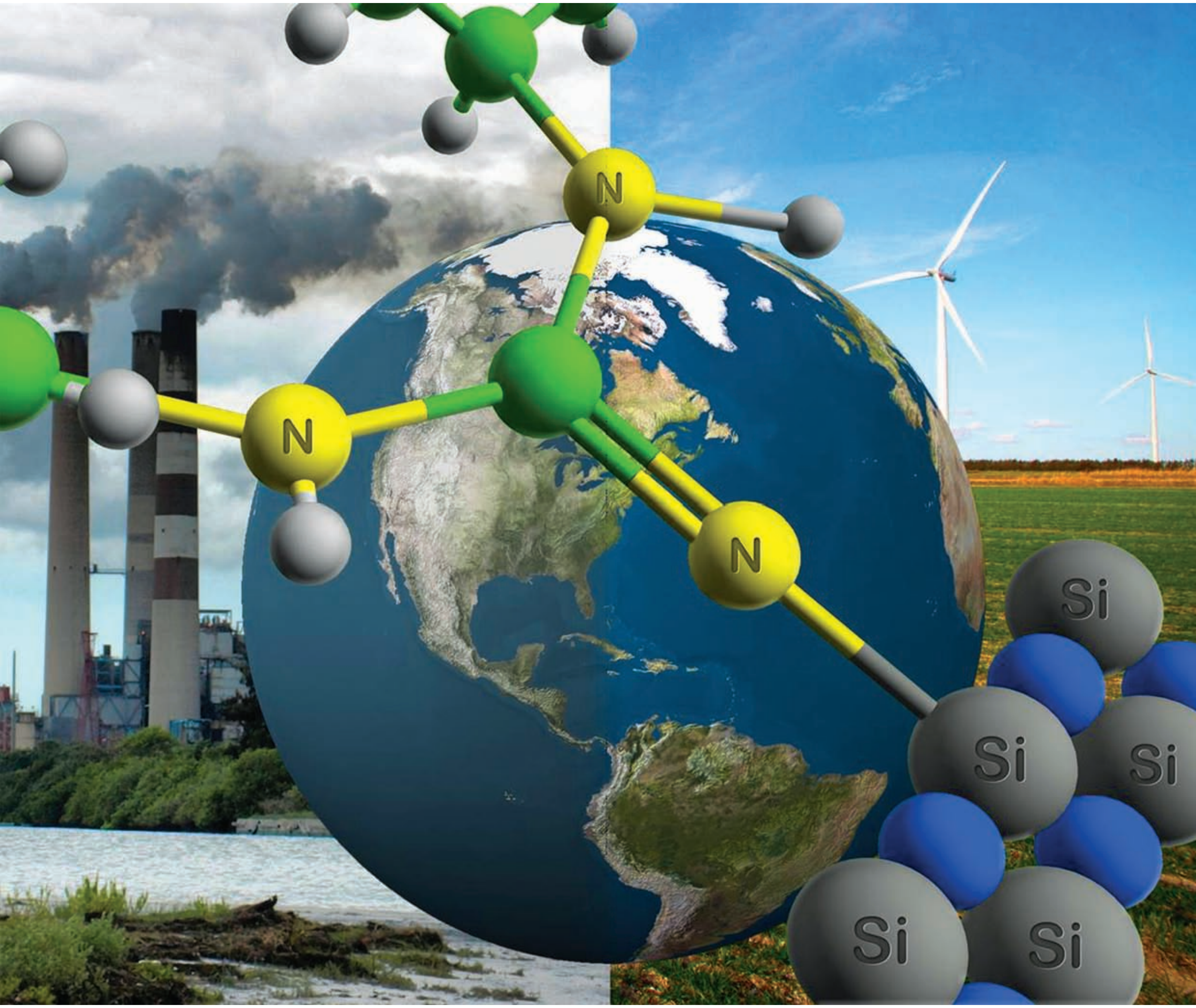
Volume 13 | Number 11 | November 2011 | Pages 2977–3316



ISSN 1463-9262

RSC Publishing

COVER ARTICLE
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Silica-supported guanidine catalyst for continuous flow biodiesel production

1463-9262(2011)13:11;1-8

Green Chemistry

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Cite this: *Green Chem.*, 2011, **13**, 3111

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PAPER

Silica-supported guanidine catalyst for continuous flow biodiesel production

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Received 20th June 2011, Accepted 20th July 2011
DOI: 10.1039/c1gc15727b

The new silylant agent 3-(*N*,*N′*-dicyclohexylguanidine)-propyltrimethoxysilane (GPMS) was prepared straightforwardly in high yield by the simple reaction between 3-aminopropyltrimethoxysilane and dicyclohexylcarbodiimide. This new organosilane containing the basic dicyclohexylguanidine group covalently attached on silica gel is an efficient heterogeneous catalyst for the production of biodiesel. Conversions up to 98% were obtained for soybean oil methanolysis at 353 K for 3 h. This catalytic system was transposed to a semi-pilot scale in a continuous flow reactor and gave 44% conversion. The calculated activation energy of the methanolysis in this continuous system indicated that the reaction is probably under mass transfer limitations.

Introduction

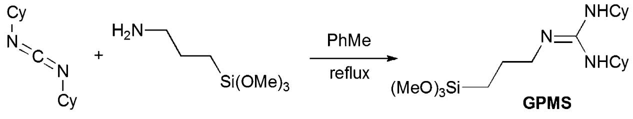
Biodiesel has become an attractive substitute to mineral diesel due to its environmental benefits, in particular for those derived from vegetable oils.[1–4] Biodiesel is mainly synthesized by the transesterification process, catalyzed by acids or bases or under alcoholic supercritical conditions with high efficiency, yielding 40–90% more energy than that used in its production.[5] Industrially, biodiesel is usually produced by homogeneous catalysis in the presence of basic species, since these are much more catalytically active and less corrosive than the acid. However, technological problems such as corrosion, emulsification and separation of glycerine and water and energy consumption are usually associated with these methodologies.[7]

One of the possible solutions is the immobilization of the catalyst on a solid support that will render the processes recyclable with the minimum use of solvents (including water) and energy.[6] It is also apparent that industrial processes resulting from improvement of the catalyst efficiency will be intimately associated with reaction engineering such as continuous flow processes. Indeed, there some interesting examples of optimized conditions for production of biodiesel using heterogeneous catalysts,[6–19] or immobilized acids and bases in ionic liquids.[12,20–22] However, it appears that supported guanidines either in chloromethyl polystyrene[23] or on mesoporous silica[24] are the most promising solid catalysts for the methanolysis of vegetable oils. Indeed, guanidines are strong bases and their basicities are in the range of common inorganic bases such as alkali hydroxides and carbonates.[25] However, there is no direct and simple method for the efficient immobilization of these organic basic catalysts in solid supports.

We report a simple and efficient approach for the preparation of a new organosilane containing a dicyclohexylguanidine group immobilized on silica gel and its use as heterogeneous catalyst for the production of biodiesel in both batch and semi-continuous reactors.

Results and discussion

The new silylant agent 3-(*N*,*N′*-dicyclohexylguanidine)-propyltrimethoxysilane (GPMS) was prepared straightforward in 94% yield by the reaction between 3-aminopropyltrimethoxysilane and dicyclohexylcarbodiimide (Scheme 1).



Scheme 1 Preparation of GPMS.

The supported catalyst (SiGPMS) was obtained by grafting *via* simple reflux of a toluene suspension GPMS with silica gel for 48 h. The GPMS silane amount immobilized on the catalyst surface is 16 w/w% (0.4 mmol of GPMS silane immobilized per gram of catalyst) could be estimated from CHN elemental analysis.

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The covalent attachment of the guanidine fragment was corroborated by solid-state ^{13}C and ^{29}Si NMR measurements (see Fig. 1 and 2). The ^{29}Si NMR spectrum (Fig. 1) shows peaks at −110 and −101 ppm are characteristic of the siloxane (Q^4) and silanol (Q^3) groups, respectively.[24,26] The set of signals between −75 and −55 ppm are formed by silicon atoms bonded to carbon atoms of organic groups, thus forming predominantly $C–Si(OSi)_3$ and $C–Si(OH)(OSi)_2$ species, characterized in that order as signals T^3 and T^2.[27,28] Therefore the silanization of the support by the guanidine occurs *via* at least two covalent bonds. This was further corroborated by ^{13}C NMR experiment (Fig. 2). It is clearly observed peaks at 25.6 and 33.4 ppm, characteristic of the $–CH_2$ and –CH groups of the ring, respectively. It has also peaks at 45.0 ppm related to the $–OCH_3$ and 52.0 ppm associated with the $–CH_2–N=$ groups.[28]

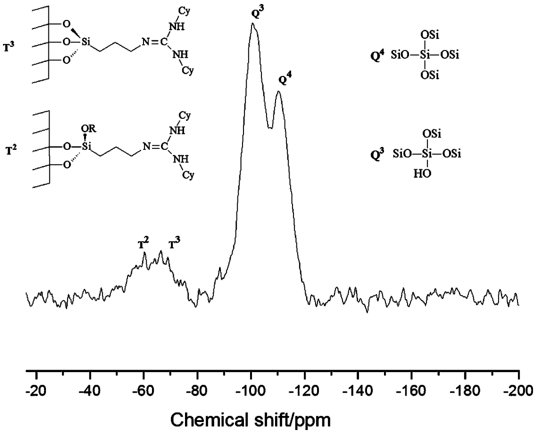

Fig. 1 ^{29}Si CP/MAS NMR spectrum for the SiGPMS catalyst.

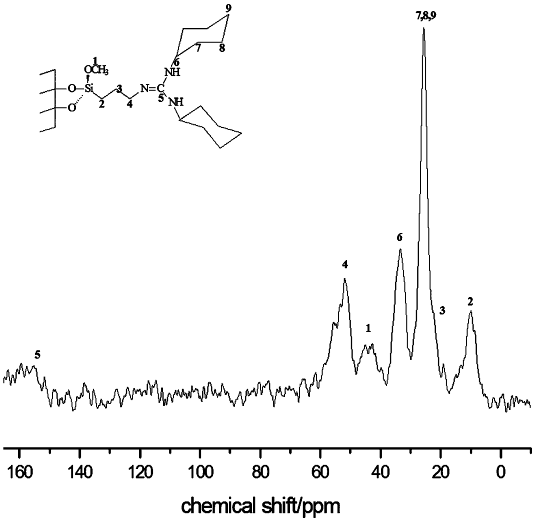

Fig. 2 ^{13}C CP/MAS NMR spectrum for the SiGPMS catalyst.

The GPMS silane immobilization by grafting reaction produces only a slight decreasing in the specific surface and also in the pore volume of porous material (see Table 1), typical of a surface coverage process. The near 1.4 nm decrease on the pore diameter observed for silica support (SiGPMS), after the grafting reaction, is compatible with surface monolayer coverage in which the silane is immobilized in a highly dispersed form. Therefore, considering the flexibility of the GPMS side chain, the thickness of the GPMS group coverage on the silica surface can be estimated as around 1 nm.

Table 1 Textural properties of silica support and the catalyst

Sample	BET surface area/m^2 g^{-1}	BJH pore volume/cm^3 g^{-1}	BJH pore size/Å
SiO_2	340	0.93	97.5
SiGPMS	300	0.71	83.7

The TGA and DTG curves (see Fig. 3) of catalyst show two main weight losses: the first one occurred up to 150 °C due to the water desorption and the second between 240 °C that is probably related to the removal of the GPMS surface derivatives. The high thermal stability of the SiGPMS, is evidence that the GPMS silane was immobilized on catalyst surfaces in a covalent way. The observed GPMS weight loss by thermal analysis of 14% corroborates the value determined by combustion analysis (16%).

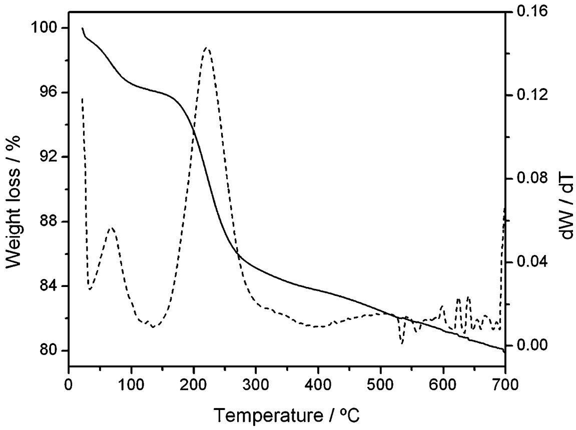

Fig. 3 TGA and DTG curves of SiGPMS catalyst.

Transmission infrared spectra of the SiGPMS material and pure silica matrix are presented in Fig. 4. Pure silica shows broad bands above 3500 cm^{-1} due to SiO–H stretching and typical silica overtone bands at 1630, 1870 and 1985 cm^{-1}. The main bands observed for SiGPMS catalyst are: band at 1450 cm^{-1}, due to the CH_2 bending of hydrocarbon chain; band at 1340 cm^{-1}, assigned to –N–CH deformation of substituted amine; bands at 2850 and 2930 cm^{-1}, attributed to the symmetric and asymmetric CH_2 stretching, respectively; and a strong band with maximum near to 1630 cm^{-1} that was assigned to –C=N– stretching of the guanidine group. The broad band at 3435 cm^{-1} is due to the NH_2 antisymmetric streching.[29,30] The presence of the guanidine infrared bands in the spectrum, after thermal treatment up to 150 °C in vacuum, is a further evidence that the GPMS silane is immobilized in the silica surface in covalent way, according with the TGA results discussed above.

A basic strength (H_) of $15.0 \leq H\_ \leq 17$ for the SiGPMS catalyst was determined using different acid–base indicators.[31,32] The titration using 2,4-dinitroaniline indicated that SiGPMS a basicity of 0.81 ± 0.02 mmol g^{-1}_{cat}, quite similar that found for the KF loaded on zeolite NaY activated at 673 K.[32]

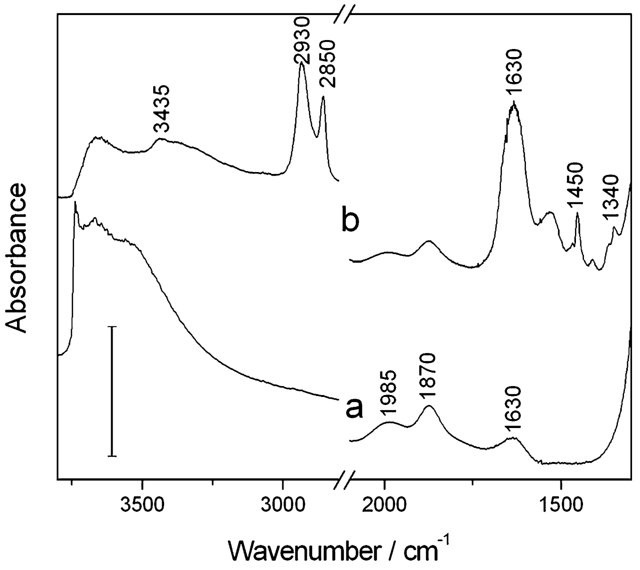

Fig. 4 FTIR spectra of (a) pure silica; (b) SiGPMS catalyst, obtained after heating up to 150 °C in vacuum. The bar value is 1.0.

The SiGPMS catalyst was applied in the transesterification reaction of soybean oil with methanol for 3 h and 50 kgf cm^{-2} nitrogen pressure under various reaction conditions (Table 2). It is clear that the total conversion of soybean oil occurs at a minimum temperature of 353.15 K and reduces down to 62.4% at 333.15 K (entries 5 and 6, Table 2). The reaction is highly influenced by the amount of methanol used from 7.8% at molar ratio of 6 to almost quantitative conversion at molar ratio methanol: soybean oil of 15–20 (entries 8–11, Table 2). The best ratio of SiGMPS : soybean oil at 353.15 K, 50 kgf cm^{-2} argon pressure, molar ratio methanol : soybean of 20 for 3 h to attain conversions above 99% is a minimum of 0.50 g SiGPMS/4.5 g of oil (1.70% m/m GPMS). Finally, for the batch reaction conditions the use of argon pressure is not necessary since almost the same conversion and selectivities are observed at atmospheric pressure (compare entries 13 and 16, Table 2).

Table 2 Methanolysis of soybean by SiGPMS (cat.) for 3 h, 50 kgf cm^{-2} nitrogen pressure and under various reaction conditions[a]

Entry	*T*/K	MeOH/oil	Cat. (%)	T	D	M	B	C
1	473	30	3.4	0.1	1.3	0.9	97.7	99.9
2	423	30	3.4	0.2	1.7	1.2	96.9	99.8
3	393	30	3.4	0.7	2.3	3.2	93.8	99.3
4	373	30	3.4	1.4	2.5	1.2	94.9	98.6
5	353	30	3.4	0.1	0.9	3.5	95.5	99.9
6	333	30	3.4	37.6	5.6	1.2	55.6	62.4
7	323	30	3.4	42.3	6.8	3.2	47.7	57.7
8	353	20	3.4	1.2	4.9	1.5	92.4	98.8
9	353	15	3.4	56.3	3.5	2.7	37.5	43.7
10	353	10	3.4	70.2	2.7	1.9	25.2	29.8
11	353	6	3.4	92.2	1.4	1.1	5.3	7.8
12	353	20	2.5	1.9	1.3	1.2	95.6	98.1
13	353	20	1.7	0.8	1.9	1.6	95.7	99.2
14	353	20	1.4	5.7	1.3	1.4	91.6	94.3
15	353	20	0.8	23.7	3.4	1.2	71.7	76.3
16[b]	353	20	1.7	0.9	1.9	2.3	94.9	99.1

[a] M – monoglycerides. D – diglycerides. T – triglycerides. B – biodiesel (methyl esters). C – total conversion. [b] At atmospheric pressure.

Table 3 Methanolysis of soybean by SiGPMS in semi-pilot scale flow reactor at various temperatures[a]

Entry	*T*/K	MeOH/oil	T	D	M	B	C
1	357	20	88.7	1.4	0.3	9.8	11.3
2	367	20	82.7	1.3	2.0	14.0	17.3
3	373	20	79.8	1.9	1.4	16.9	20.2
4	378	20	76.7	1.1	1.9	20.3	23.8
5	389	20	68.2	1.7	1.5	28.6	31.8
6	394	20	61.7	2.8	1.2	34.3	38.3
7	399	20	56.4	1.0	0.7	41.9	43.6
8	357	30	81.3	1.0	0.4	17.3	18.7
9	367	30	78.6	0.3	0.4	21.0	21.4
10	373	30	76.7	0.6	0.7	22.0	23.3
11	378	30	75.3	1.9	0.4	22.3	24.7
12	389	30	70.4	1.7	1.8	26.1	29.6
13	399	30	67.0	1.2	1.1	30.7	33.0
14	409	30	63.2	1.5	0.3	35.0	36.8

[a] M – monoglycerides. D – diglycerides. T – triglycerides. B – biodiesel (methyl esters). C – total conversion.

The yields and selectivities on biodiesel obtained using the new SiGPMS catalyst are the same or even slightly superior to those obtained by guanidine-based catalyst either under homogeneous or heterogeneous conditions.[23,24,33] Moreover, the SiGPMS catalyst could be re-used at least 7 times without lost in its catalytic activity or selectivity and most important it can be used in a continuous flow processes (Fig. 5). In preliminary studies a reactor with a total volume of 10.0 mL was loaded with 6.0 g of the catalyst. The pressure was maintained at 50 kgf cm^{-2} and fractions were collected throughout the day, for each experiment, after stabilization of reaction temperature and the results are summarized in Table 3.

The highest conversion was obtained on the reaction performed at 399 K temperature and low flow of the reactants methanol (1.47 g h^{-1}) and soybean oil (2.0 g h^{-1}).

The activation energy for the methanolysis in this system was estimated by the modified Arrhenius equation $\ln(\%\text{conversion}) = -E_a/RT^{-1} + \ln A$ (Fig. 6). The activation energy (37 kJ mol^{-1}) for the reaction performed with a 20 : 1 (methanol : oil) molar ratio is in the range of those obtained for the transesterification of vegetable oils with basic catalysts (33–84 kJ mol^{-1}) and it is limited by mass transfer and catalyst activity.[3,34,35] However, at 30 : 1 (MeOH : oil) ratio the calculated activation energy (16 kJ mol^{-1}) is typical of heterogeneous catalytic processes that is under mass transfer limitations.[35]

Conclusions

In summary we have reported a straightforward method for the preparation a guanidine containing a silylant agent by the simple condensation of 3-aminopropyltrimethoxysilane and dicyclohexylcarbodiimide. This reagent allows the covalent attachment of the basic dicyclohexylguanidine catalyst on silica gel that was demonstrated to be one of the most efficient and recyclable catalytic systems for the methanolysis of soybean under relatively mild reaction conditions. Moreover this solid catalyst allows the development of a continuous flow processes for the production of biodiesel. Calculations of activation energy for the reaction in this system indicated mechanism limited by mass transfer and catalyst activity.

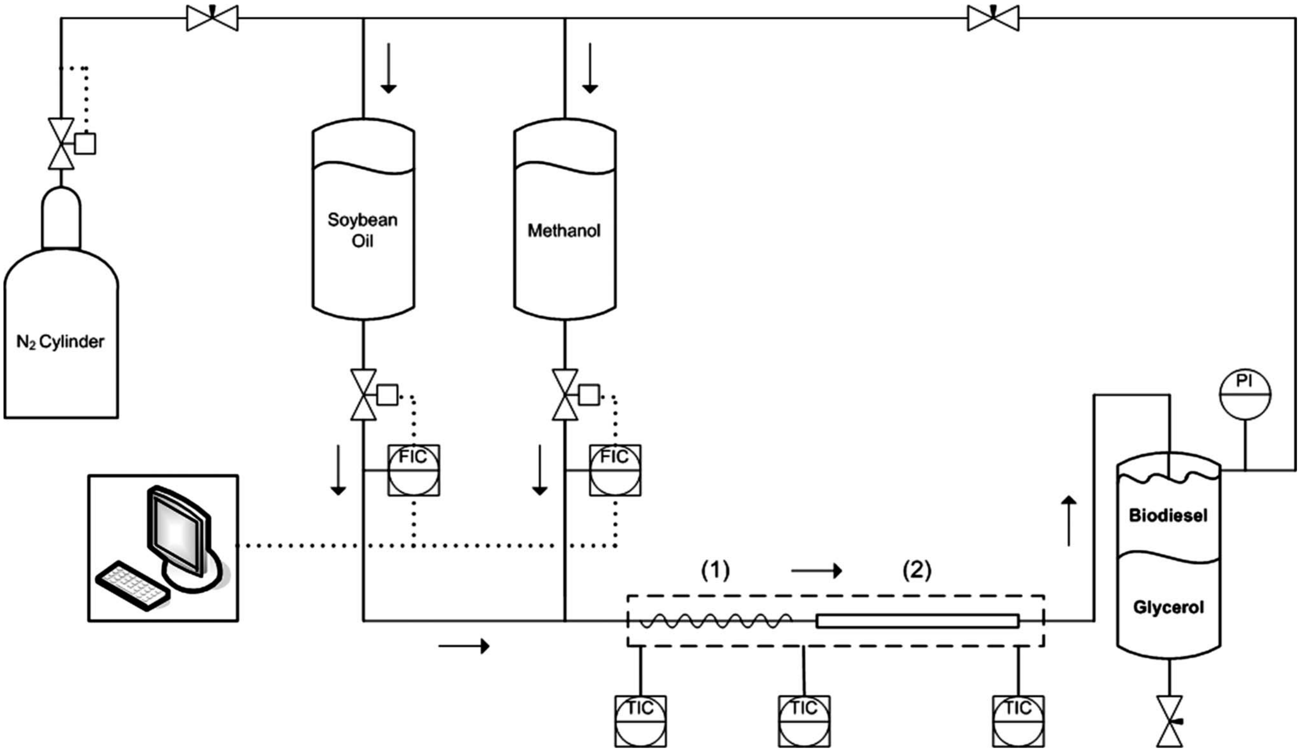

Fig. 5 Reaction system in semi-pilot scale flow for synthesis of biodiesel. (→) Direction of flow; (1) Serpentine and (2) differential isothermal reactor with a capacity of 10 mL. FIC: flow indicator and controller; TIC: temperature indicator and controller. TI: temperature indicator; PI: pressure indicator.

Experimental

Materials

The 3-aminopropyltrimethoxysilane (APMS) (Alfa Aesar) and *N*,*N′*-dicyclohexylcarbodiimide (DCC) (Acros) were used without purification. Toluene (Vetec) was used after distillation. Silica gel (Merck) with a particle size of 0.2–0.5 mm was used as support for the catalyst. Commercial soybean oil and methanol (Vetec) were used in the transesterification reactions without further purifications.

Nuclear magnetic resonance (^1H and ^{13}C NMR) spectra of GPMS silane were obtained in Varian spectrometer 300 MHz using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as internal standard.

Elemental analysis of the organic groups immobilized on the support surface was carried on a CHN Perkin Elmer M CHNS/O Analyzer, model 2400.

Solid-state ^{13}C and ^{29}Si NMR measurements for the SiGPMS catalyst were performed on a Bruker 300/P spectrometer using cross polarization and Magic angle spinning (CP/MAS). The ^{13}C experiments were obtained using acquisition time of 0.18 ms while ^{29}Si measurements were made utilizing acquisition time of 0.082 ms. Frequencies of 75.5 and 59.6 MHz for carbon and silicon, respectively, were used.

The thermogravimetric analysis of the samples was performed under nitrogen flow on a TA Instrument system model TGA Q5000, with a heating rate of 20 °C min^{-1}, from room temperature up to 700 °C.

The N_2 isotherms of the catalyst and pure silica, previously degassed 160 °C under vacuum, for 3 h, were obtained using a Tristar 3020 Micromeritics equipment. The specific surface areas were determined by the BET multipoint method and the average pore size was obtained by BJH method.

For infrared analysis, self-supporting disks of the samples were heated in up to 150 °C for 2 h, under vacuum. The equipment used was a Shimadzu FTIR, Prestigie 21. The spectra were obtained at room temperature with a resolution of 4 cm^{-1}, with 150 cumulative scans.

The basic strength (H_) and basicity, or basic sites density (mmol $g^{-1}{}_{cat}$), were determined according to the methods based on the colour change of Hammet indicators and titration with benzoic acid, respectively.[31,32] The H_ indicators used in this study (their pK_a values are given in parentheses) were: indigo carmine (12.2), 2,4-dinitroaniline (15.0), 4-chloro-2-nitroaniline (17.2) and 4-nitroaniline (18.4).

Synthesis of 3-(*N*,*N′*-dicyclohexylguanidine)propyltrimethoxy silane

Dicyclohexylcarbodiimide (DCC) (10.70 g. 51.9 mmol) and 3-aminopropyltrimethoxysilane (APMS) (9.30 g. 51.9 mmol) were mixed in dry toluene (50 mL) and kept at 100 °C under stirring for 24 h. The toluene was removed under reduced pressure yielding an amber oil (18.8 g. 94% yield) sufficiently pure for further work. ^1H NMR (300 MHz. $CDCl_3$) δ: 7.23 (singlet. 2H. NH); 3.50 (singlet. 9H. OCH_3); 3.20–3.09 (multiplet. 2H. NCH ring); 2.93 (triplet. 2H. $J = 7.2$ Hz. NCH_2); 1.92–1.76 (multiplet.

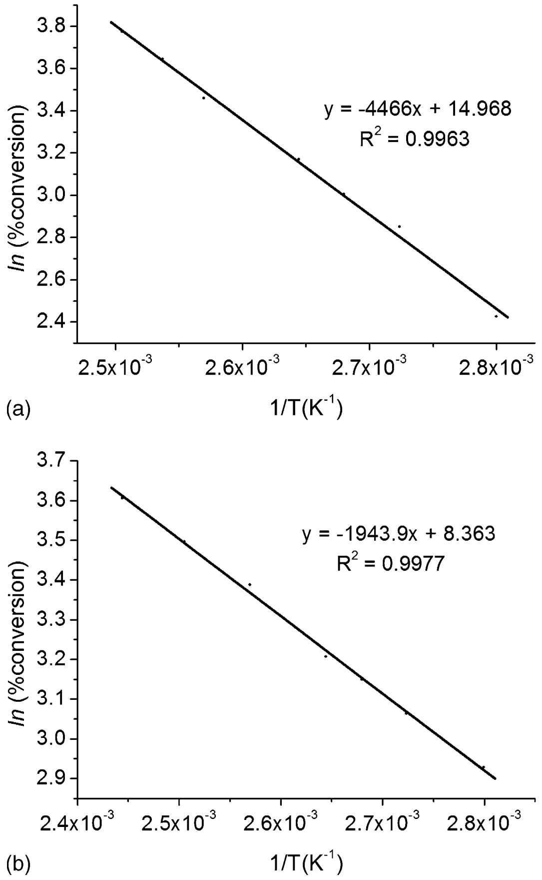

Fig. 6 Curves according to the Arrhenius equation for the transesterification of soybean oil in the continuous flow system with molar ratio methanol : soybean oil equal to (a) 20 : 1 and (b) 30 : 1.

4H. CH_2); 1.74–1.44 (multiplet. 8H. CH_2); 1.36–1.00 (multiplet. 10H. CH_2); 0.65–0.55 (multiplet. 2H. $SiCH_2$). ^{13}C NMR (75 MHz. $CDCl_3$) δ: 153.5 (NNC=N); 77.2 (OCH_3); 55.0 and 49.8 (NCH_2 and NCH ring); 33.8 ($NCH_2\boldsymbol{C}H_2$); 25.0. 24.7 and 24.3 (CH_2 ring); 5.2 ($SiCH_2$).

Catalytic reactions

The transesterification reaction in batch system was carried out in a stainless steel reactor (15 mL) with mechanical stirring and controlled temperature. The reactor was loaded with reagents and catalyst, was pressurized with N_2 at room temperature and, subsequently, it was placed in bath with silicone oil at the desired temperature. After the reaction, the catalyst was separate and the resultant product was placed in separation funnel. The upper phase (alkyl ester) was analyzed by using a high performance liquid chromatography (HPLC) (Shimadzu, LC-20A) equipped with an evaporative light scattering detection (ELSD) and Shim-Pack (C-18, 250 mm, 4.6 mm i.d.) column, using a method published elsewhere.[36]

The identification of peaks was done by comparison of retention's times of samples and standard compounds (triglyceride, diglyceride, monoglyceride and fatty acid methyl esters). The percentage of conversion was then determined by integration of the peaks, assuming that the sum total of the areas corresponding to 100% of the initial amount of soybean oil. The soybean conversion and selectivities associated error were estimated in 12% using methyl esters standards from the correction of the peak areas using oleic acid as internal standard. Thus, the conversion was obtained by the equation: conversion yield = $[(A_M + A_D + A_B)/A_{Total}] \times 100$, where A_M, A_D and A_B are the areas corresponding to the monoglycerides, diglycerides and methyl esters of fatty acids, respectively, and A_{Total} is the sum total of the areas, which include products obtained as well as non-transesterified triglycerides.

In the continuous flow reactor the methanol and soybean oil feed was controlled with flow controllers, previously calibrated in order to adjust the flow of reagents to the reactor internal volume (10 mL). Once the reactants, methanol and vegetable oil, are immiscible at room temperature and pressure, they were heated through a small diameter coil (3.2 mm i.d.) at reaction temperature, with simultaneous pressure adjustment with the aid of a back pressure valve, allowing homogenization of the sample. After this step, the reaction mixture was sent through a differential isothermal reactor containing the catalyst. The mixture emerged from the reactor was treated and analyzed as same as outlined above for the batch experiments.

Knowing that residence time and percentage of conversion are small in the differential reactor, so far from equilibrium conditions, it is possible to determine the kinetic constant as a function of temperature. Therefore, at different reaction temperatures tested, it was observed that an increase in the percentage of conversion also corresponds to an increase in the value of the rate constant, keeping valid the approximation: % of conversion ~ k. Thus, the activation energy for the transesterification of soybean oil with methanol in continuous flow system was estimated from the modified Arrhenius equation: $\ln(\%\text{conversion}) = -E_a/RT^{-1} + \ln A$.

Acknowledgements

Thanks are due to CNPq (575469/2008-0), INCTCatal., FAPERGS and CAPES for partial financial support.

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