Alkylguanidine-Catalyzed Heterogeneous Transesterification of Soybean Oil

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ABSTRACT: Transesterification of soybean oil with methanol has been carried out in the presence of heterogenized alkylguanidines as catalysts. The alkylguanidines were anchored to modified polystyrene or siliceous MCM-41, encapsulated in the supercages of zeolite Y, or entrapped in SiO_2 sol-gel matrices. The catalytic activity of these catalysts was compared with that of their homogeneous counterparts, showing that the yields of methyl esters obtained in the homogeneous phase can be obtained with the guanidines anchored to the supports after longer reaction times. The catalysts prepared by immobilization of alkylguanidines in microporous systems showed diffusion restrictions for the vegetable oil as well as the low stability of the inorganic framework.

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KEY WORDS: Alkylguanidines, heterogeneous catalysis, MCM-41, sol-gel matrices, soybean oil, transesterification, zeolite Y.

For a long time, transesterification of vegetable oils with short-chain alcohols (e.g., methanol and ethanol) has been the method of choice for preparing fatty acid esters which, together with related alcohols, represent important oleochemical intermediates for further syntheses (1,2). Furthermore, these esters can be employed directly in diesel engines as an alternative fuel, without modification (3,4). The transesterification process can be accomplished by using several compounds as catalysts (2). Recently, we found that alkylguanidines (strong organic bases) in the homogeneous phase are very efficient catalysts for the methanolysis (5) and glycerolysis (6) of triglycerides. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) is the most active alkylguanidine, furnishing high yields of methyl esters or monoglycerides with short reaction times. However, when heterogenized on different substituted polystyrenes (PS), TBD showed slightly lower catalytic activity than its homogeneous analog, reaching the same high yields only after prolonged reaction times (7). In order to find more efficient heterogeneous catalysts to carry out the methanolysis of vegetable oils, we decided to investigate the behavior of 1,2,3-tricyclohexylguanidine (TCG, a trisubstituted alkylguanidine) encapsulated in zeolite Y (8), as well as TCG and TBD anchored onto the surface of MCM-41, as catalysts for this process. TBD has already shown good catalytic activity in Michael additions (9) and in the transesterification of ethyl propionate with *n*-butanol (10). The results obtained with these new catalytic systems were compared to those observed with TCG and TBD in the homogeneous phase, as well as supported on modified polystyrenes.

EXPERIMENTAL PROCEDURES

Guanidines. TBD > 98% (Fluka, Buchs, Switzerland) was used as purchased. TCG was synthesized according to our previously described method (5) from 2.0 g (9.7 meq) of 1,3-dicyclohexylcarbodiimide and 2.0 g (20.2 meq) of cyclohexylamine in 20 mL of *tert*-butanol. The mixture was stirred under a nitrogen atmosphere at 100°C for 19 h. The solvent was evaporated and the product recrystallized from *tert*-butanol. This produced a yield of 3.1 g (75%) with a melting point of 94–95°C. It was calculated that the crystallized product would consist of 74.7% C, 11.5% H, and 13.8% N. The actual percentages were: 74.1% C, 11.4% H, and 13.9% N. *p*-(6-bromohexyl)Polystyrene (PS-$(CH_2)_6Br$) was prepared according to the method described by Tundo (11) with a yield of 35% and 1.35 meq Br/g of polymer. TBD was heterogenized with PS-$(CH_2)_6Br$ using the procedure described by Tomoi *et al.* (12). Elemental analysis furnished 3.1% of nitrogen, which corresponds to a capacity of 0.74 meq TBD/g. TCG was anchored to PS-$(CH_2)_6Br$ by reacting a suspension of 1.0 g (1.35 meq Br) of the polymer in 100 mL of dry dimethylformamide, with 0.9 g (3 meq) of TCG, in the presence of 0.08 g (0.5 meq) of KI. The mixture was vigorously stirred in an argon atmosphere at 70°C for 60 h. The polymer was recovered by filtering and washed with methanol (3 × 50 mL) and tetrahydrofuran (3 × 50 mL). It was then suspended in 100 mL of 1,4-dioxane and reacted with 50 mL of a 20% methanolic NaOH solution at 25°C for 2 h. The TCG-containing polymer was washed with water until the washings were neutral and bromide-free and dried at 70°C under reduced pressure to constant weight. C/H/N analysis revealed 3.7% nitrogen, which corresponds to a capacity of 0.9 meq TCG/g. TCG was anchored to MCM-41 (a mesoporous ordered silica with channel diameters of 20–100Å, prepared in the presence

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*To whom correspondence should be addressed at Instituto de Química, Universidade Estadual de Campinas, P.O. Box 6154, 13083-970 Campinas, SP, Brazil. E-mail: ulf@iqm.unicamp.br of surfactants as template agents) by a procedure described in the literature (13) and adapted from Jacobs *et al.* (9). The C/H/N analysis furnished 2.4% nitrogen, which corresponds to a capacity of 0.56 meq TCG/g of MCM-41. C/H/N analysis showed a nitrogen content of 1.47%, which corresponds to a capacity of 0.35 meq TBD/g of MCM-41. TCG was encapsulated in zeolite Y according to our previously described procedure (8). TBD anchored to MCM-41 was kindly provided by Dr. P.A. Jacobs (Katholieke Universiteit Leuven, Leuven, Belgium). The C/H/N analysis showed a nitrogen content of 1.8%, which corresponds to a capacity of 0.43 meq TCG/g of zeolite Y. TCG was entrapped in a SiO_2 sol-gel matrix after reaction of a mixture containing 5 mL (85.3 meq) of ethanol, 5 mL (277.7 meq, pH 8) of deionized water, 2.5 mL (11.2 meq) of tetraethyl orthosilicate, and 0.1 g (0.33 meq) of TCG. The mixture was stirred at 25°C for 30 min, left to stand in a 50-mL beaker for 12 h until gelation was completed, washed with hot dichloromethane (50 mL), and dried at 40°C under reduced pressure to a constant weight. C/H/N analysis showed a nitrogen content of 1.0%, which corresponds to a capacity of 0.23 meq TCG/g of SiO_2 sol-gel matrix.

The experimental procedure for the transesterification reactions was performed as previously described (5,7) without any changes. The reaction mixture was analyzed for methyl esters as described in an earlier paper (14).

RESULTS AND DISCUSSION

The graphical representations of the alkylguanidines grafted onto the different supports and encapsulated in zeolite Y are shown in Figure 1. TCG and TBD were covalently anchored to polystyrene and onto the surface of MCM-41 after reaction with the "spacer-arms" introduced to the supports, which kept the bases distal from the polystyrene and the hydrophilic surface of MCM-41. On the other hand, TCG immobilized in the microporous materials was not anchored to the surface of the support, but encapsulated within the supercages of the zeolite Y (13 Å diameter) or entrapped within the porous system of

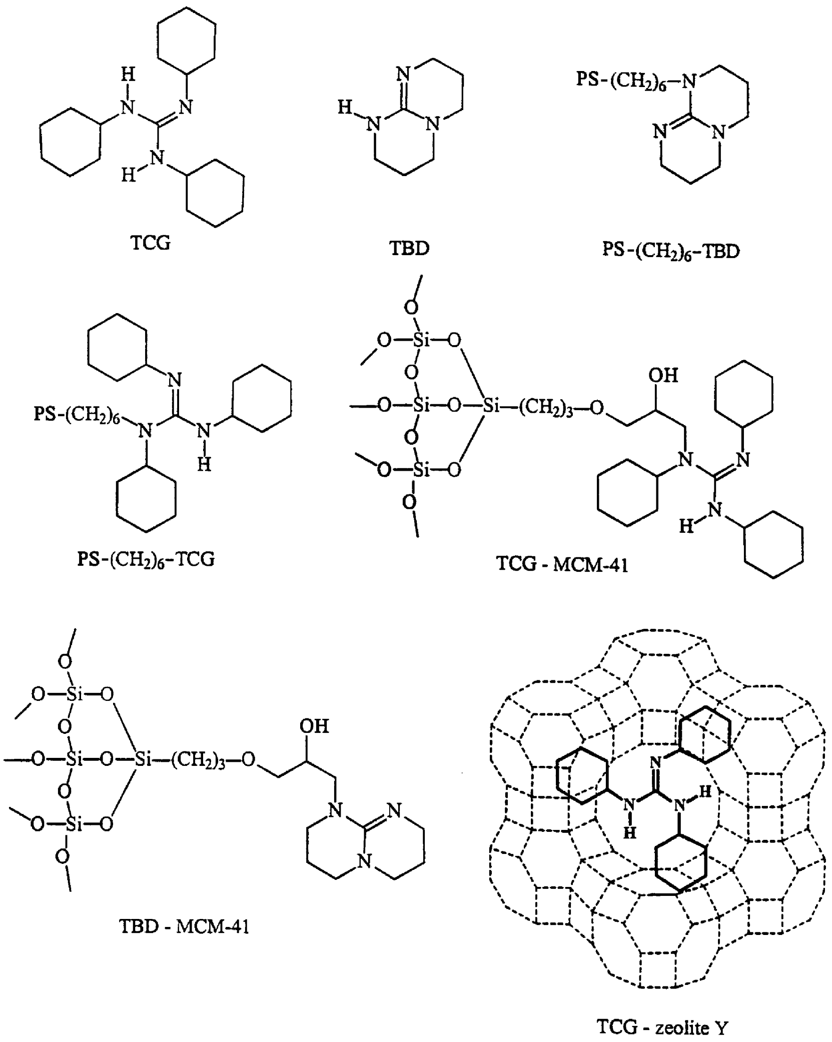

FIG. 1. Graphical representation of immobilized guanidines. TBD,1,5,7-triazabicyclo [4.4.0]dec-5-ene; TCG, tricyclohexylguanidine; PS, polystyrene; MCM, a mesoporous ordered silica with channel diameters of 20–100 Å, prepared in the presence of surfactants as template agents.

TABLE 1
Conversion of Soybean Oil as a Function of Time, Catalytic System, and Catalyst Concentration[a]

	Yields in methyl esters (%)				
Catalyst (mol%)	1 h	2 h	3 h	4 h	5 h
TBD (1)	90	92	93	94	95
TBD (2)	91	95	97	97	97
TBD (5)	> 99	—	—	—	—
TCG (1)	64	71	76	76	—
TCG (2)	91	93	93	95	96
TCG (5)	97	>99	—	—	—
PS-$(CH_2)_6$TBD (5)	65	74	79	85	88
PS-$(CH_2)_6$TCG (5)	60	72	77	81	86
{TBD}-MCM-41 (5)	29	51	65	72	92
{TCG}-MCM-41 (5)	18	46	51	61	63
{TCG}-Zeolite-Y (10)	—	—	—	—	14
{TCG}-SiO_2 gel (10)	75	78	83	83	—

[a]Conditions: 4.00 g (13.7 mmol) of soybean oil and 3.0 g (93.8 mmol) of methanol at 70°C. TBD, 1,5,7-triazabicyclo[4.4.0]dec-5-ene; TCG, tricyclohexylguanidine; PS, polystyrene; MCM-41, a mesoporous ordered silica with channel diameters of 20–100 Å, prepared in the presence of surfactants as template agents.

the sol-gel matrices. The dimensions of TCG (8.7 × 11.0 A), determined by the semiempirical program Spartan 4.0 (Wavefunction, Irvine, CA), prevent its exit from the microporous systems of these materials.

Table 1 summarizes the results of the methanolysis of soybean oil with the different catalysts (Fig. 2). In the homogeneous phase, TBD and TCG furnish very high conversions of soybean oil even at low molar concentrations (1 or 2 mol%). When the catalyst content is increased to 5 mol%, the reactions are essentially complete after only 1 h of reaction time. When supported on modified PS, TBD and TCG show similar activity which is, however, lower than that found for the homogeneous systems. As observed earlier (7), the hydrophobicity of the polymer chain, and the reduction of the symmetry of the alkylguanidinium cations, are responsible for the loss of activity. The guanidines anchored onto the surface of MCM-41 are less active than their PS-anchored counterparts at the beginning of the reaction. The results obtained after 1 h for the reactions catalyzed by TCG and TBD anchored to MCM-41 suggest a slow diffusion of the bulky triglycerides through the channels of the support to the active sites. However, at longer reaction times, the yields of methyl esters are similar to those obtained with guanidines anchored to modified PS. The low yield obtained after 5 h in the reaction catalyzed by the larger TCG anchored to MCM-41 is probably due to the lower symmetry of the guanidinium cation formed in the activation step (7). Recycling of the catalysts after filtration and washing with methanol leads to a loss of the catalytic activity in a second run, which is explained by a parallel loss of the guanidines of approximately 15% from the support during the first run, as shown by the microanalysis of the recycled catalysts. The leaching of the bases from the support may be due to a nucleophilic substitution of the linked guanidines by the methoxide ions formed in the reaction.

TCG encapsulated in the supercages of zeolite Y is much less active than the polymer–anchored guanidines, probably due to the poor triglyceride diffusion through the microporous system of the zeolite Y (8). As a consequence, the reaction rate is lowered and the conversion of the vegetable oil (14%) is not satisfactory, even using a higher concentration of the catalyst (10 mol%) and a longer reaction time (5 h). Microanalysis of the recycled catalyst shows no leaching of TCG during the reactions and X-ray diffraction shows that the crystalline structure of the zeolite Y remains intact after transesterification.

TCG entrapped in a SiO_2 sol-gel matrix appears to be the most active of the heterogeneous catalysts. However, when it is subjected to reflux with methanol for 5 h under transesteri-

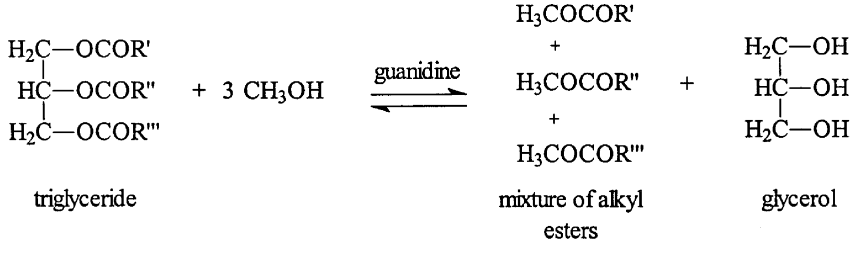

FIG. 2. Transesterification of vegetable oils.

fication reaction conditions, filtered, and soybean oil is added to the filtrate, an 80% yield of methyl esters is obtained after 5 h of reaction time. This demonstrates that TCG is leaching from the SiO_2 matrix during the reaction, and the result shown in Table 1 may not be due to heterogeneous catalysis. Furthermore, microanalysis data show a loss of TCG from the catalyst up to 78%, suggesting that the amorphous structure of the support is partially dissolved under transesterification conditions, which liberates TCG to the homogeneous phase.

We demonstrated that alkylguanidines anchored to modified PS or siliceous MCM-41 are nearly as active as their homogeneous counterparts in the methanolysis of soybean oil. These catalysts can be easily recycled, but the bases do leach out slowly during the reactions, reducing their activities. On the other hand, the catalysts prepared by the immobilization of guanidines in microporous supports are not effective catalysts for this process, as the lack of diffusion of the triglycerides through the channels of the zeolite Y reduces the conversion of the oil while the amorphous structure of the SiO_2 sol-gel matrix collapses under the reaction conditions, resulting in a homogeneously catalyzed reaction. The development of a truly heterogeneous guanidine catalyst for the transesterification of vegetable oils is still a promising goal, as one could obtain the fatty acid esters in an environmentally friendly process without the formation of any hazardous byproducts.

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