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Transesterification of triacetin using solid Brønsted bases

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Abstract

This paper reports the results of an investigation into the use of solid Brønsted base catalysts as a potential alternative to homogeneous base catalysts in the transesterification of triacetin with small alcohols carried out under mild reaction conditions. Two catalysts with organic quaternary ammonium functionality (QN^+OH^-), a resin (A26), and a functionalized silica gel (QN^+OH^-/SiO_2), were used for the transesterification of triacetin with methanol (a model reaction), and their performance was studied in detail. Reactions were carried out in a well-mixed isothermal batch reactor at 60 °C. Both solid bases showed appreciable catalytic activity for the transesterification of triacetin conforming to the base strength of the active centers. Although the polymeric organic catalyst showed lower site activity, it was more stable during multiple reaction cycles (i.e., showed less deactivation) than the silica-supported catalyst and exhibited a higher total selectivity for glycerol for a given triacetin conversion. The effect of the support on the Brønsted base catalyzed transesterification is discussed, as is probable routes for silica-supported catalyst deactivation.

Keywords: Transesterification; Triacetin; Solid base catalyst; Brønsted base; Quarternary ammonium hydroxide; Support effect

1. Introduction

Transesterification of triglycerides (TGs) with low-molecular weight alcohols is the central reaction in the synthesis of biodiesel from oils and fats. Commercially, this reaction is carried out using homogeneous base catalysts, which are corrosive and nonreusable but also produce neutralization waste, leading to increased costs and environmental concerns. Replacement of liquid homogeneous catalysts with solid heterogeneous catalysts would greatly solve problems associated with expensive separation protocols involved with the former, yielding a cleaner product and greatly decreasing the cost of synthesis [1].

Great emphasis has been put on the possibility for solid strong bases to replace homogeneous bases such as NaOH. Various basic solids, including alkali ion-exchanged zeolites [2–4], supported alkaline metal ions/oxides/salts [5], alkaline earth oxides [6], aluminum-magnesium mixed oxides derived from clay minerals such as hydrotalcite [7], anion exchange resins [8], and heterogenized alkylguanidines [9], have exhibited some catalytic ability for TG transesterification. However, most of the solid bases reported in the literature are of the Lewis type. The problem for Lewis bases like MgO is that the polar species (i.e., methanol and glycerol) present during biodiesel synthesis can form Mg^{2+} methoxylate and glycerates, which end up leaching from the solid catalyst and acting as homogeneous catalysts in the solution media [1,10]. In recent studies using ETS-10 (Na, K) [4] and alkylguanidines/resin [9], these Lewis bases were found to leach out to the bulk solution even under mild conditions (60 and 70 °C), losing much of their activity after only a few reaction cycles and contaminating the products. Along with leaching, the nucleophilic attack on the carbonyl carbon of esters is also a potential problem for some Lewis bases, such as γ-aminopropylsilica, leading to catalyst deactivation [11].

Here the use of solid Brønsted bases with organic quaternary ammonium functional groups (QN^+OH^-) is reported for TG transesterification. One base was a polymeric resin with QN^+OH^- terminated groups (A26, Rohm & Hass); the other, a QN^+OH^- functionalized silica. The Brønsted base functionality in these materials should result in a reaction initiation step in transesterification of a triglyceride with methanol analogous to that for homogeneous bases. The first step is the formation

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of a methoxide ion, which is able to carry out a nucleophilic attack on the glycerol ester moieties of the glyceride species [1]. The positive counter ions (organic ammonium groups), being bonded directly to the support surface, electronically retain the catalytic anions on the solid surface, preventing base sites from being leached out. For instance, the rehydrated hydrotalcites of Brønsted type have been shown to undergo less deactivation than their Lewis-type counterparts (calcinced hydrotalcites) in fatty ester glycerolysis [12]. Moreover, heterogenized base catalysts with grafted QN^+OH^- groups have been successfully applied in various fine-chemical synthesis reactions, showing high and sustained catalytic activity [13,14] even under mild reaction conditions. Uses of the resin catalyst in organic synthesis have been reviewed in Chinese [15,16].

In this work, triacetin (the acetic acid triester of glycerol) was used as a model compound for TGs to provide fundamental insight into TG transesterification catalyzed by catalysts with Brønsted base functionality. Triacetin, having the same chemical functionality of any triglyceride molecule, shares the same reactivity principles of triglycerides. But triacetin differs from common TGs in terms of size. Therefore, this study should be considered an initial exploration of TG transesterification by solid Brønsted bases. Further studies are needed to address issues relating to substrate size, polarity, alcohol miscibility, and other factors.

2. Experimental

Anhydrous methanol (Aldrich, 99.9 wt%) and triacetin (Fisher Scientific, 99 wt%) were used without further purification. A diacetin mixture (25 wt% triacetin, 45 wt% diacetin, 26 wt% monoacetin, and 4 wt% glycerol; Fisher Scientific) was used for GC calibration. A26 in the hydroxide form and 3-(trimethylammonium)-propyl-functionalized silica gel chloride form (QN^+Cl^-/SiO_2) were purchased from Aldrich. The as-received A26 contained large amounts of water owing to the high hydroscopic character of the OH^- function. Before the reaction, the catalyst was thoroughly washed with methanol and then dried to constant weight at room temperature under vacuum. The activation of QN^+Cl^-/SiO_2 to QN^+OH^-/SiO_2 was carried out following the methodology of Rodriguez et al. [13]. The solid was recovered by filtration and then extensively washed with methanol at room temperature to completely remove NMe_4OH residues physisorbed onto the porous silica matrix. Although the proton transfer between methanol and OH^- occurring in methanol has been shown to have a low equilibrium constant ($K < 1$) [17,18], the extensive washing with methanol is still expected to push the reaction to the right given the large excess of methanol used and the limited concentration of OH^- groups on the catalyst. In addition, multiple methanol washing steps removes the byproduct water each time. However, because an actual exchange of OH^- by MeO^- groups was not experimentally verified, in what follows we will keep referring to these materials as OH^- functionalized. After overnight vacuum drying, the catalyst samples were stored in a desiccator until use. The physicochemical properties of the catalyst samples were characterized by elemental analysis (Galbraith Laboratories, Knoxville, TN) and isothermal N_2 adsorption (using a Micromeritics ASAP 2002). The results are summarized in Table 1.

Table 1
Physicochemical properties of the fresh catalysts

Parameters	A26	QN^+OH^-/SiO_2
Support	Styrene–divinylbenzene	Silica gel
Crosslink (% DVB)	11%	–
Functional group	$\text{–ph–CH}_2\text{N(CH}_3)_3^+$	$\text{–pr–N(CH}_3)_3^+$
Surface area	21.9 m^2/g	244 m^2/g
Pore size	59 nm	5.1 nm
Pore volume	0.33 cm^3/g	0.32 cm^3/g
Site density[a]	2.94 mmol/g	0.61 mmol/g
	0.13 $mmol/m^2$	2.52×10^{-3} $mmol/m^2$

[a] Based on nitrogen elemental analysis of the fresh catalyst after washing and drying.

Reaction experiments were carried out in a well-stirred isothermal batch reactor at 60 °C under nitrogen atmosphere. The presence of mass transfer limitations on reaction at these conditions was experimentally ruled out as reported previously [19]. Before the reaction, methanol and triacetin were mixed in a 6:1 molar ratio (total reaction volume, 30 ml) and heated. The compounds were completely miscible under the conditions used here. Once at the desired temperature, the transesterification reaction was started by charging the catalyst. In one separate experiment, the resin catalyst A26 was presoaked in MeOH before initiating the reaction by adding triacetin. Within experimental error, the reaction profiles obtained for the two different startups of A26-catalyzed transesterification were very close, indicating little effect on reaction kinetics from swelling of the polymer-based catalyst by methanol. Reaction progress was monitored by withdrawing 30-µl aliquots at specified time intervals. A Hewlett–Packard 6890 gas chromatograph equipped with a DB-1 column (0.32 mm × 30 m × 0.53 µm) and a split/splitless inlet was used for sample analysis with ethanol as an internal standard.

3. Results and discussion

Fig. 1 shows typical conversion profiles for triacetin transesterification in the presence of the solid Brønsted bases. As expected, the strong base character of the functionalized quaternary ammonium groups resulted in high catalytic activity. After 240 min, around 60% triacetin conversion was achieved using either base, which is very good considering the low concentration of catalyst used in these experiments (0.88 wt% relative to the total mass of the reaction mixture). On doubling the catalyst loading of A26 (to 1.67 wt%), 90% triacetin conversion was achieved after 240 min (data not shown). The catalytic activity exhibited by the solid Brønsted bases in triglyceride transesterification was still lower than that of the homogeneous base NaOH. For instance, when the same reaction was performed in the presence of only 4×10^{-3} wt% (1.2×10^{-3} g/30 ml) NaOH, 52% triacetin conversion was reached in 2 min. At 15 min, the triacetin conversion was 90%.

Using the N content of A26 and QN^+OH^-/SiO_2 as an estimate of the maximum expected base site density (Ta-

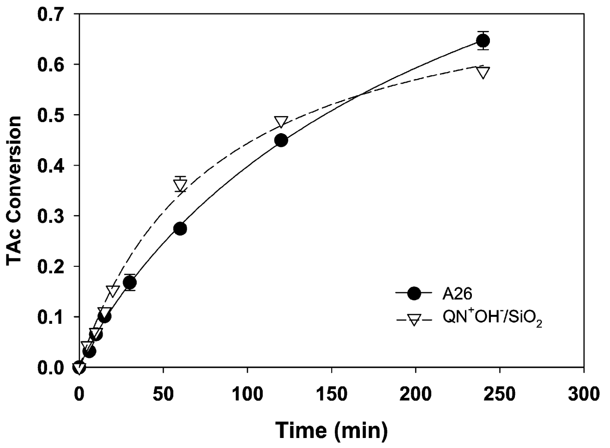

Fig. 1. Triacetin (TAc) conversion during transesterification with methanol using A26 or QN$^+$OH$^-$/SiO$_2$ ($T = 60\,°C$, MeOH/TAc = 6, catalyst loading = 0.25 g/30 ml).

ble 1), a TOF calculation using initial kinetic data (conversion <10%) allows catalytic comparison on a per-site basis. Consequently, TOF values during initial reaction were higher for QN$^+$OH$^-$/SiO$_2$ (56×10^{-3} s^{-1}) than for A26 (11×10^{-3} s^{-1}), pointing to silica as a more efficient support for quaternary ammonium functionalities. Three factors likely cause the discrepancy in apparent site activity between the two catalysts: site accessibility, dispersion, and base site strength.

For the silica catalyst, the location of active sites is restricted to the surface of the support, whereas for the organic resin, some reactive groups are buried inside the nodules and/or gel microspheres, remaining unapproachable for large reactant molecules [20]. The fact that preswelling of A26 with methanol before reaction produced little effect on transesterification kinetics suggests rapid access of methanol throughout the macroreticular resin [21]. But this does not necessarily guarantee that methanol swelling can make available all of the sites buried inside the gel microspheres for the TG reactants. For instance, in comparisons with a silica-supported Nafion (SAC-13) on a per-site basis (TOF), Lopez et al. found that the unsupported Nafion, even when preswollen by methanol, had only 30–40% active sites exposed to the reactant molecules for triacetin transesterification (60 °C) [22].

The higher dispersion of the basic species on SiO$_2$ compared with A26 (2.52×10^{-3} vs 0.13 mmol/m^2) probably accounts in some part for the TOF difference. The macroreticular divinylbenzene polymer with low or medium crosslink level (<25% DVB) is known to have poor ability to disperse organic functional groups homogeneously [20]. Short intervals among immobilized functionalities have been experimentally observed using phosphine displacement on tricarbonylnitrosylcobalt [20]. It is likely that some neighboring sites get too close to carry out reaction simultaneously due to steric constraints. Moreover, the α-positioned benzene ring in A26 with electron-withdrawing properties can increase the positive character of the ammonium ion, thereby increasing the strength of the ionic bond with its counterion and thus decreasing its basic strength. For instance, the quaternary salts of bulkier and more electron-donating alkyl groups, which have greater distances between cations and anions, are known to have higher activity in base-catalyzed organic syntheses [23].

Triglyceride transesterification can be carried out using both base and acid catalysis. Our group recently investigated various heterogeneous acid catalysts for triacetin transesterification [4]. In comparison, the solid Brønsted bases of the present study demonstrated an obvious edge over the solid acids in catalytic efficiency. For example, even the most active catalyst among those used previously [4], Amberlyst 15 (A15) at a loading of 2 wt%, could reach only 80% triacetin conversion after 480 min with the reaction carried out under otherwise identical reaction conditions. Moreover, if compared on a per-site basis (using N content for the estimation of base sites and S content for that of acid sites), both A26 and QN$^+$OH$^-$/SiO$_2$ catalytically outperformed the sulphonic acid resin A15, with initial TOF values of 11×10^{-3} and 56×10^{-3} s^{-1}, respectively, versus 1.9×10^{-3} s^{-1} for A15 [4]. This is consistent with the lower energy-demanding mechanistic route involved in base-catalyzed transesterification [1]. It should be noted, however, that homogeneous alkali-catalyzed soybean oil transesterification has been estimated to be about 3 orders of magnitude faster than the acid-catalyzed reaction [24]. The smaller activity gap measured for heterogeneous catalysts noted above could be due to an effect of site immobilization and/or the complexity in estimating the number of "active" reaction sites. For instance, the base site density of A26 can vary from 2.94 to 1.6 to 0.33 mmol/g as the methodology used to assess base sites changes from N elemental analysis to aqueous HCl–NaOH back-titration to phenol (in MeOH) adsorption at 60 °C.

A26 drives triglyceride transesterification to completion to a greater extent than QN$^+$OH$^-$/SiO$_2$ does. For instance, for identical amounts of triacetin reacted, a greater methyl ester yield was obtained for A26 (Fig. 2), and this was more obvious as reaction progressed. Fig. 3 shows the observed selectivities of diacetin, monoacetin, and glycerol at ca. 64% triacetin conversion using NaOH as a reference. Similar product distribution profiles were obtained for NaOH and QN$^+$OH$^-$/SiO$_2$, whereby diacetin and monoacetin (intermediate products) were the predominant compounds with concentration levels double that of glycerol (the final product). In contrast, the opposite was observed for A26-catalyzed transesterification, where glycerol was clearly the main product.

Given that the active sites on both catalysts are essentially identical, the significant dissimilarities in selectivity between A26 and QN$^+$OH$^-$/SiO$_2$ seem to be due to the distinct properties of the respective supports. Barrault and co-workers [25,26] and Corma et al. [27] noted that the basic strength of solid bases hardly affects the selectivity of glycerolysis of either methyl stearate or triolein. Indeed, other polymeric matrix-supported catalysts, such as A15 and Nafion, despite operating through different catalytic functions (i.e., acidic sulphonic groups), show triacetin transesterification selectivity rather similar to that obtained with A26 under the same reaction conditions [4]. Moreover, the use of small reagent molecules with relatively little steric constraints helps bring the focus onto the differences in support surface chemistry rather than morphology (product shape selectivity). The cross-linked styrene

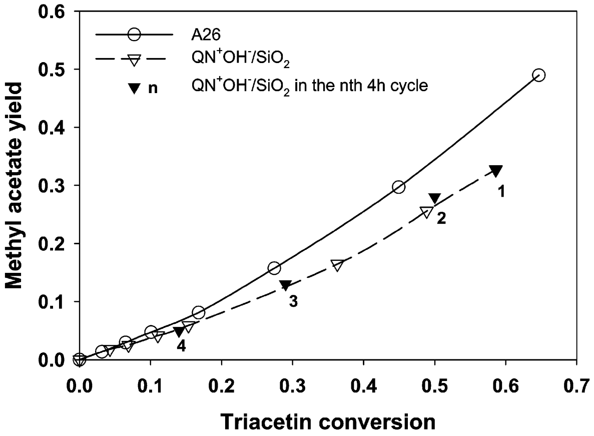

Fig. 2. Methyl acetate (MeAc) yield in A26 or QN$^+$OH$^-$/SiO$_2$ catalyzed triacetin (TAc) transesterification as a function of TAc conversion. (Open symbols and lines denote the behavior of fresh catalyst in the first cycle; the four labeled solid triangles represent the reaction data of QN$^+$OH$^-$/SiO$_2$ at the end of 1–4 consecutive 4 h reaction cycles, respectively.)

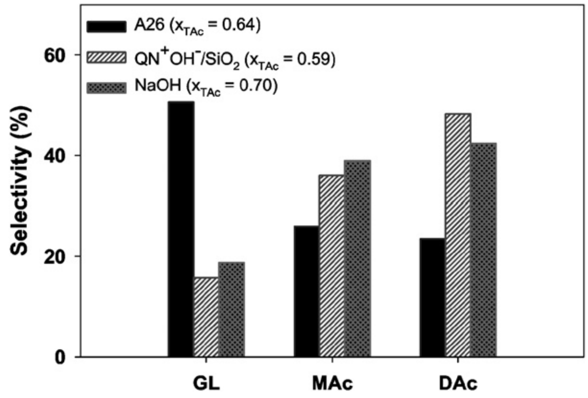

Fig. 3. Selectivity to diacetin, monoacetin and glycerol of NaOH, A26, and QN$^+$OH$^-$/SiO$_2$ at triacetin conversion (x_{TAc}) of 64 ± 5.5% ($T = 60\,^\circ\text{C}$).

Table 2
Cycling experiments (4 h reaction) for triacetin transesterification (TAc) on A26 and on QN$^+$OH$^-$/SiO$_2$

			1st	2nd	3rd	4th
A26	TAc conversion		0.65	0.67	0.58	0.61
	MeAc yield[a]		0.49	0.52	0.43	0.44
	Selectivity[c] (%)	GL[b]	50.6	53.8	47.5	48.4
		MA[b]	25.9	25.8	25.6	27.4
		DA[b]	23.4	20.5	26.9	24.2
QN$^+$OH$^-$/SiO$_2$	TAc conversion		0.58	0.50	0.29	0.14
	MeAc yield[a]		0.33	0.28	0.13	0.05
	Selectivity[c] (%)	GL[b]	15.7	15.0	4.5	0
		MA[b]	36.0	33.6	24.9	12.1
		DA[b]	48.2	51.4	70.6	87.9

[a] Methyl acetate (MeAc) yield $= C_{\text{MeAc}}/(3 \times C_{\text{TAc},0})$.

[b] GL, MA, and DA denote glycerol, monoacetin and diacetin, respectively.

[c] Glycerol selectivity, GL% $= C_{\text{GL}}/(C_{\text{GL}} + C_{\text{MA}} + C_{\text{DA}}) \times 100\%$. Monoacetin selectivity, MA% $= C_{\text{MA}}/(C_{\text{GL}} + C_{\text{MA}} + C_{\text{DA}}) \times 100\%$. Diacetin selectivity, DA% $= C_{\text{DA}}/(C_{\text{GL}} + C_{\text{MA}} + C_{\text{DA}}) \times 100\%$.

divinylbenzene copolymer is hydrophobic in nature, favoring the adsorption of lipophilic species. Thus, the interaction of the nonpolar matrix with the polar hydroxyl group in the glycerol backbone must be thermodynamically less favorable. Consequently, the ester branch(es) of tri/di/monoglycerides should have a greater tendency to be exposed to methoxide anions within the vicinity of the active sites. In addition, glycerol is known to be a rather polar species that can form a strong solvation sphere around the ionic active center [28]. As triacetin transesterification progresses and glycerol production continues, the stepwise replacement of methoxy moieties by glycerate species at the reaction sites favors the reverse glycerolysis reaction. Thus, the high glycerol selectivity of A26 further suggests that glycerate formation was hindered in this case, probably due to the lower tendency of the polar glycerol molecule to remain around active sites. In line with the above explanation, we found that the presence of a hydrophobic solvent, hexane, can make triglyceride transesterification using A26 more selective to glycerol even at a lower MeOH/TG ratio (data not shown). In contrast, the silanol groups on the silica matrix constitute a rather hydrophilic microenvironment around highly isolated active sites, affecting product selectivity in a manner exactly opposite to that of the polymeric resin. For NaOH, the mobile OH$^-$/MeO$^-$ species were favorably solvated by methanol molecules, also establishing a hydrophilic sphere around the catalytic sites.

Although highly active in the initial period, QN$^+$OH$^-$/SiO$_2$ began to suffer significant activity decay after 50% triacetin conversion. At this point, QN$^+$OH$^-$/SiO$_2$ was outperformed by A26 (reaction time of 4 h) (Fig. 1), suggesting that the active sites on A26 were more stable. Catalyst reusability was examined by carrying out subsequent reaction cycles. The used catalyst was separated from the reaction mixture after 4 h and used again with fresh reactants in a second reaction cycle under the same reaction conditions as before. The same procedure was repeated twice more, for a total of four reaction cycles. Results for all consecutive reaction cycles are given in Table 2. As can be seen, A26 was able to largely maintain its overall catalytic activity and selectivity for all reaction cycles. The small variation in reaction activity observed in the series of reaction cycles was probably due to experimental error or to hydrocarbon accumulation on the catalyst surface in the absence of any washing treatment between cycles. In contrast to our observations, deactivation of anionic resins used for biodiesel synthesis was reported by Shibasaki-Kitakawa et al. [8] to be due to neutralization of active sites by fatty acid molecules formed during reaction. Fatty acids formed via the reaction of active catalytic sites consisting of OH$^-$ groups with ester species in the reaction media (glycerides and the biodiesel product). Indirectly, the results of these authors support our earlier hypothesis that methanol washing is able to exchange most OH$^-$ groups in the resin by MeO$^-$ groups that cannot give rise to the formation of carboxylic acid, thereby precluding catalyst deactivation by this route.

The silica-supported catalyst underwent continuous activity loss with consecutive reaction cycles, however. The triacetin conversion at 4 h quickly dropped from 58 to 14% after 3 cycles. The glycerol selectivity exhibited a sharp decrease as well. This latter observation, however, was due to the decreased total triacetin conversion. For instance, when the methyl ac-

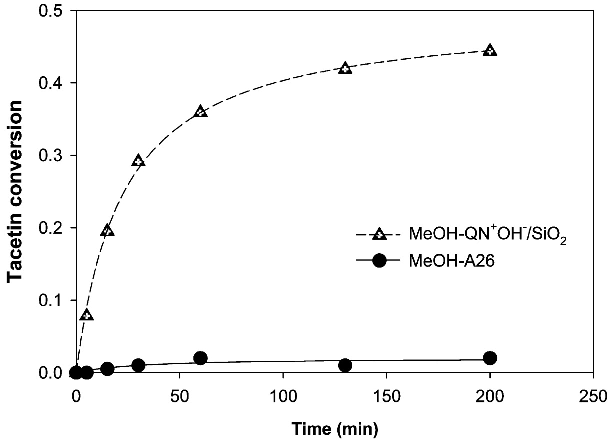

Fig. 4. Transesterification of triacetin using methanol that had been exposed to A26 or QN^+OH^-/SiO_2 at 60 °C overnight.

etate yields were compared at the same level of conversion, no change was found for the used catalysts (Fig. 2). The nitrogen elemental analysis for the fresh and the used QN^+OH^-/SiO_2 catalyst after 4 cycles showed a decreased N content from 0.86 to 0.26 wt%, indicating a permanent loss of base sites accompanying the strong deactivation.

To further confirm the presence and absence of site leaching for functionalized silica and polymeric resin, respectively, catalyst samples were soaked in methanol at 60 °C for 4 h, after which the methanol was recovered by filtration and used for triacetin transesterification in the absence of the solid catalyst. As shown in Fig. 4, appreciable transesterification activity was found when using the methanol from the QN^+OH^-/SiO_2 soak, but only negligible activity when using the methanol from the A26 soak. This result provides further evidence of the different chemical stabilities of the two Brønsted solid bases and also indicates that the sites of the silica-supported catalyst were leached out in the form of basic species.

Site leaching for the QN^+OH^-/SiO_2 catalyst probably occurs through bond cleavage of the methylene moiety alpha to the ammonium center. In this way, active site leaching can occur in the form of a tertiary amine. To identify the leached species, fresh catalyst samples of QN^+OH^-/SiO_2 were placed in contact with deuterated methanol (CD_3OD) at 60 °C overnight. After catalyst separation, the residual methanol was analyzed by ^1H NMR (JEOL ECX 300, 300.5 MHz). In the resulting spectrum, the proton peak at 2.14 ppm corresponding to trimethylamine [29] indicates the degradation of the quarternary ammonium sites via the cleavage of the $CH_2–N^+(CH_3)$ bond. In contrast, this characteristic peak is absent from the ^1H NMR spectrum of the residual methanol separated from A26, coinciding with the high chemical stability of the functionalized polymer.

Leaching of quarternary ammonium ions could have occurred due to a nucleophilic attack of hydroxy and/or methoxy ions on the alpha carbon (Fig. 5a), resembling the Hofmann thermal degradation of quaternary ammonium groups. However, it can be imagined that this reaction scheme should have been more important for A26, which has a more labile methylene due to the adjacent benzene ring [30]. But evidently, this does not occur to any great extent for A26 under our reaction conditions. Thus, a likely deactivation mechanism for the deactivation behavior of QN^+OH^-/SiO_2 may be associated with the silica support. For instance, nitroxide groups immobilized on a silica surface have been found to have much higher mobility (i.e., rotational motion) than those covalently attached to a polystyrene matrix [18]. The surface-solvent-substrate hydrogen-bonding interaction has been suggested to be an important factor influencing the rotational freedom of the silica-bound nitroxide function [18]. Likewise, it is reasonable to assume that the quarternary ammonium species grafted on silica are less rigid than those grafted on a polystyrene–divinylbenzene matrix. Moreover, charge transfer can be expected to be more favorable on a silica surface in which a methanol solvation sphere may be more easily developed around ionic sites than on a polymeric matrix, such as in A26. In this sense, the leaching route depicted in Fig. 5a may be more favorable on functionalized silica in which less steric hindrance is present. Alternatively, considering the weak acidity of surface silanol groups on silica, the other plausible route for active site leaching could occur through the nucleophilic attack of $Si–O^-$ groups (formed in the vicinity of active sites) on the methylene group alpha-bonded to the ammonium ion moiety (Fig. 5b). To date, the exact nature of the resulting deactivated sites has not been determined.

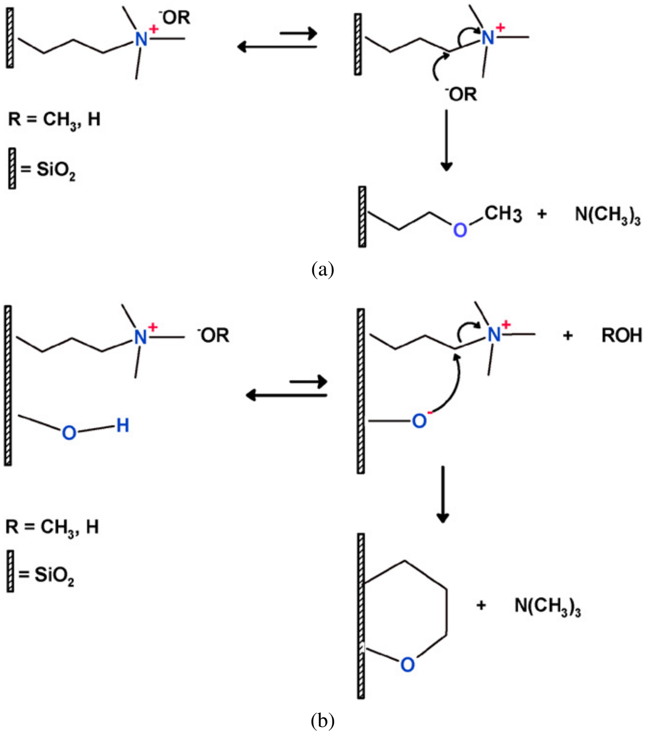

Fig. 5. Schematic representation of possible active site leaching mechanisms for QN^+OH^-/SiO_2.

4. Conclusion

The transesterification of triacetin with methanol was successfully carried out under mild reaction conditions using solid catalysts with Brønsted base functionality of organic ammonium quaternary ions bonded to either silica or a polymeric support. The support played an important role in catalyst selectivity and deactivation behavior. Despite a greater site activity, the basic groups grafted to silica were less selective to glycerol for a given triacetin conversion and more prone to deactivation. In contrast, the polymeric resin catalyst exhibited outstanding features, such as a great capacity to drive the series reaction of glycerides to completion and to sustain high activity through multiple reaction cycles without signs of significant deactivation. This catalyst appears to be an interesting alternative to strong soluble inorganic bases for triglyceride transesterication. Deactivation of the QN^+OH^-/SiO_2 catalyst was due to site leaching caused by cleavage of the $CH_2–N^+(CH_3)$ bond. Such deactivation routes may be precluded by raising the steric hindrance for the nucleophilic attack using bulkier tetraalkylammonium (e.g., tetrabutylammonium) groups as the active site and/or silanol group derivation of the silica surface.

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