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Comparative hydroamination of aniline and substituted anilines with styrene on different zeolites, triflate based catalysts and their physical mixtures

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ABSTRACT

Catalytic performances of different zeolites (Beta and mordenites), scandium triflate based catalysts, mesoporous UVM-7 encapsulated scandium triflate and physical mixtures prepared under ultrasound irradiation were evaluated in the hydroamination of aniline and substituted anilines with styrene. The performances of these catalysts were controlled by the type of acidity and strength. Thus, the conversion was mainly controlled by the strength of the acid sites and their accessibility, while the selectivity appeared to be controlled by the Lewis/Brønsted type of acidity. Lewis acid catalysts directed the reactions mainly to the formation of the Markovnikov adducts while Brønsted acid catalysts to *anti*-Markovnikov. Zeolites and scandium triflate led to results very close to those reported in the literature. Among different physical mixtures those of scandium triflate with the mesoporous scandium triflate embedded in a UVM-7 structure provided better conversions with a good selectivity in the Markovnikov adduct. These results were attributed to a better dispersion of scandium triflate during the preparation of physical mixtures.

1. Introduction

Amines are very important precursors in the synthesis of fine chemicals such as natural products or pharmaceuticals, but also in the production of bulk chemicals [1–5]. In this respect, hydroamination of double or triple carbon bonds represents an elegant and cheap route since it utilizes cheap and readily available feedstock of olefins and amines and proceeds theoretically with 100% atom efficiency.

Literature reported several catalytic routes for hydroamination reaction [6,7]. Among these, in homogeneous catalysis this reaction may occur via: (i) hydroamination of olefins via oxidative addition of the amine to a transition metal (a late transition metal (Pd, Ru, Rh, Ir) complexed by a phosphine ligand, or early transition metal complexes, such as rare-earth elements) [8–10]; (ii) amination of olefins via an alkaline metal or lanthanide compound (Li, Na, Ln) [11,12]; (iii) a radical mechanism for the alkaline metals-catalyzed hydroamination of α-methylstyrene with aziridine [6]; (iv) hydroamination of alkynes via metal (U, Zr, Ti) imide species, (v) Lewis acid catalyzed hydroamination of olefins and alkynes using metal salts or cationic metal complex catalysts [13–15]. The interaction of the olefin/alkyne with the metal center reduces the electron density in the π-system and allows the nucleophilic attack of the amine nitrogen atom.

The coordination of substrates with Brønsted or Lewis acids may catalyze reactions involving unsaturated systems through the formation of more-electrophilic complexes or charged intermediates. Recent studies in hydroamination of dienes and allenes demonstrated that to achieve this goal under metal-free catalytic conditions the presence of an acid with certain acidity is necessary [16]. The use of Ga, Yb, Pr, In, Bi, Cu, Fe, Sc, Ag, or Zn triflate overcome these problems. Moreover, catalysts based on the late transition metals and salts like triflates have a high tolerance to water and oxygen impurities and are, thus, of high interest for practical applications [17]. Accordingly, the literature reported many examples of intermolecular hydroamination of a high variety of substrates with aliphatic or aromatic amines in the presence of such catalytic species [18–31].

Brønsted HOTf displayed a high activity in the intramolecular hydroamination of *N*-(2-cyclohex-2′-enyl-2,2-diphenylethyl)-*p*-toluene-sulfonamide [32]. In spite of the fact that pure triflic acid showed rather poor efficiency in intermolecular hydroamination [33] mechanistic investigations demonstrated that the coordination of the amine to the copper cationic complex generated a Brønsted acid which was the prominent catalytic species, thus

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questioning whether a true metal-catalyzed process is involved or if the role of the metal is to generate Brønsted acidity [34]. Triflate salts of cationic metal complexes ($[(BINAP)Pd(solvent)_2]^{2+}$) catalyze hydroamination of primary (and secondary) aromatic amines with α,β-unsaturated oxazolidinones [35]. In addition to triflate, bis(trimethylsilyl)amide represents another anion strong enough to activate rare-earth elements for hydroamination reactions using non-activated alkenes [36].

Biphasic catalysis methodology may economically improve the hydroamination reactions especially due to the simple and complete separation of the product from the catalyst. A system formed from a polar phase (e.g., 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid) with dissolved Rh(I), Pd(II), Cu or Zn(II) catalytic complexes and a non-polar phase (e.g., heptane) with dissolved substrate exemplified this concept [37–39].

Bi-functional catalysts combining soft Lewis acidic function (activation of the alkene) and strong Brønsted acidic function (acceleration of the rate determining step (r.d.s.)) were reported to provide high catalytic activities in this reaction [40]. Electron rich anilines react more readily and the presence of a Brønsted acid accelerates the reaction. The role of the acidic promoter was explained through protonolysis of the pre-catalyst to give cationic complexes, which seem to be the active species involved in the mechanism [40].

Heterogeneous catalysis provides a more versatile route to carry out the hydroamination reaction and several classes of materials have been reported in literature. Among these are hybrid organic modified TiO_2 nanoparticles [41], heteropolyacid catalysts [42], simple Al-SBA-15 catalysts [43] or heteropolyacid encapsulated SBA-15/TiO_2 nanocomposites [44], copper(II) exchanged Al-SBA-15 [45], zeolites [46], immobilized triflic acid on silica [47] and SILP (supported ionic liquid phase) systems with organometallic complexes like Pd-1,1′-bis(diphenylphosphino)-ferrocene combined with TfOH dissolved in it [48,49]. Catalytic amounts of Brønsted or Lewis acid in ionic liquids were found to provide higher selectivity and yields than those performed in classical organic solvents [50]. The ionic liquid increases the acidity of the media and stabilizes ionic intermediates through the formation of supramolecular aggregates. The simple addition of TfOH to the supported ionic liquid phase was also indicated to promote the intermolecular hydroamination [48]. In contrast to these studies, it was shown that the presence of n-Bu_4PBr has no beneficial effect for the platinum-catalyzed hydroamination of terminal alkynes. Pristine $PtBr_2$ catalyze the hydroamination of terminal alkynes with aniline, and according to its Lewis nature the reaction is fully regioselective affording the branched imine (Markovnikov) [51].

Other ionic catalysts reported in this reaction are double metal cyanides [52] and cation exchanged resins (Amberlyst-15, Nafion) [53]. A cooperative behavior between Lewis and Brønsted acid sites in mesostructured materials was also reported for bifunctional Au nanoparticle-acid catalysts obtained via reduction of Au^{3+} with HS-functionalized periodic mesoporous organosilicas [54].

In the case of zeolites, the initial studies using H-BEA or ZSM-5 zeolites indicated that they are able to protonate the *iso*-butene to the corresponding *tert*-butyl carbenium ion [55,56] that can further react with ammonia or an amine. Ionic-exchange of zeolites (H-BEA) with Rh(I), Cu(I) or Zn(II) led to catalysts with a higher catalytic activity than the corresponding homogeneous $Zn(CF_3SO_3)_2$ catalyst, but smaller than that of the parent BEA-zeolite [17,40,57,58]. However, this rule is not general. For the cyclization of 6-amino-1-hexyne the activity of ion-exchanged zeolites is higher [57].

The activity of ion exchanged heterogeneous catalysts was assigned to residual protons in the material [59]. In fact the reaction was supposed to be initiated by the Lewis acidic metal centers, while the presence of the protons can only enhance the reaction rate [60].

The hydroamination of aromatic amines with activated olefins (methyl acrylate, i.e. an aza-Michael addition) was also examined over Y, MOR or LTA zeolites in both Na- and H-forms showing that amines with an electron-withdrawing functional group gave products in moderate conversions because of their low basicity [61,62]. Methyl acrylate is an α,β-unsaturated carbonyl compound and the addition of a nucleophile occurs via a conjugate addition, where an anti-Markovnikov selectivity is thus expected. The same adduct (e.g., *anti*-Markovnikov) was in majority formed on a montmorillonite clay [63] in a conjugate addition of α,β-unsaturated carbonyl compounds, while using non-activated substrates on the exchanged Brønsted acid sites was accompanied by a change in the selectivity in the favor of Markovnikov regioisomers [64,65].

As a short conclusion, the literature indicates a continuous interest for this reaction. All the investigated catalysts exhibit either Brønsted or Lewis acid sites, or both. However, in spite of the sustained effort it is still unclear which kind of acidity is determinant for this reaction and how is it correlated to the selectivity to the Markovnikov or *anti*-Markovnikov products. Based on this state of the art the scope of the present study was to re-visit the hydroamination reaction from the perspective of the influence of the nature of the acid sites to conversion and selectivity. To this purpose zeolites, triflates, and mesoporous silica embedded triflates were comparatively investigated.

2. Experimental

Zeolites with different structures and different chemical compositions were purchased from different companies. H-beta zeolites (PQ25, PQ 30 and PQ 75) were received from PQ-Valfor Company, Mordenite CBV 20A and 30A were purchased from Zeolyst International. $Sc(OTf)_3$ was purchased from Aldrich. Mesoporous UVM-7 encapsulated scandium triflate catalyst with the Si/Sc atomic ratio of 60 (TfSc(60)) was prepared by Atrane route using a methodology reported elsewhere [66,67]. Physical mixtures of these catalysts were prepared following a methodology proposed by Delmon [68]. Accordingly, the concerned samples were dipped in n-pentane and stirred for 10 min and then were submitted to ultrasounds for 10 min. Ultrasonic irradiation was performed at 70 kHz at 298 K. Thereafter, n-pentane was evaporated under reduced pressure in a rotavapor at 298 K. The solid was thereafter dried in air at 353 K overnight. No additional thermal treatment was carried out. The ratios of the components in the different mechanical mixtures are indicated at the appropriate places in the text.

The samples were characterized by a series of techniques such as nitrogen adsorption–desorption isotherms and Py- and NH_3-FT-IR. The NH_3-TPD profiles were done using a Micromeritics Auto-ChemII apparatus. FT-IR measurements were performed at room temperature on a Magna-IR 550 FTIR spectrometer from Nicolet using a MCT-B liquid nitrogen cooled detector, and equipped with a heatable cell (up to 773 K) with NaCl windows connected to a vacuum system and a gas manifold. The FTIR spectra were recorded after desorption of pyridine at RT, 423 K, 523 K, 623 K and 723 K, respectively, at a pressure of 10^{-5} mbar for 15 min. Particle size distribution was determined from DLS measurements using a Mastersize2000 from Malvern Instruments.

The catalytic tests were carried out in a stainless steel autoclave loaded with 50 mg of catalyst, 1 mmol amine (aniline, 4-nitro-aniline, 4-chloro-aniline and 3-aminophenol), 2 mmol styrene under autogenic pressure and temperatures of 363–423 K. A non-polar aprotic solvent, toluene (4 mL), was used. All the reagents were of Aldrich purity. Reactants and products were analyzed by GC–MS using a Trace GC 2000 coupled with DSQ MS from Thermo Electron Corporation. The structure of the resulted products was confirmed by ^1H and ^{13}C NMR spectroscopy using a Bruker AV 400

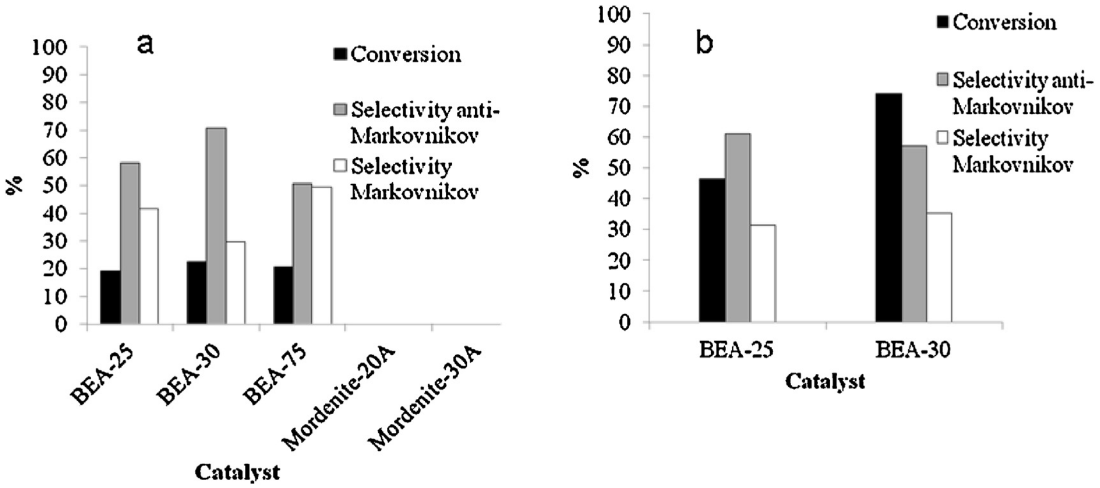


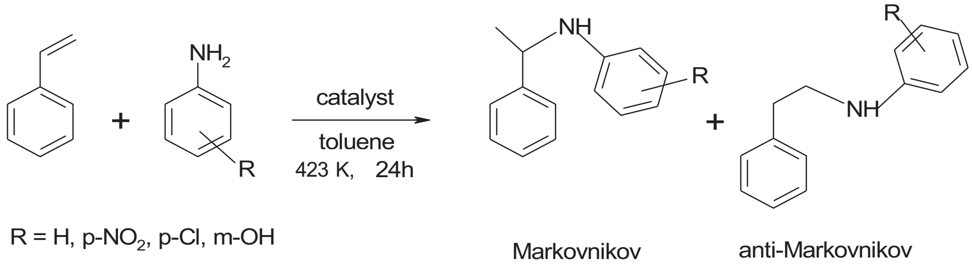
Fig. 1. Conversion and selectivity in the reaction of aniline and styrene on zeolites Beta and mordenite: (a) 363 K, (b) 423 K (1 mmol aniline, 2 mmol styrene, 4 mL toluene, 50 mg catalyst, 24 h).

spectrometer. Thus, the analytic data for Markovikov adduct were GC-MS (*z*/*m*): 197 (M^+, 50), 198 (M^+, +1, 5), 182 (100), 183 (10), 180 (7), 120 (6), 105 (36), 93 (21), 77 (16); **NMR** ^1H NMR ($CDCl_3$; 400 MHz): (1.5 ppm; $J = 6.5$ Hz; 3H; d); (3.9 ppm; $J = 6.5$ Hz; 1H, m); (5.3 ppm; $J = 0$ Hz, 1H, s); (7.19 ppm; $J = 7.05$ Hz; 1H; t); (7.3 ppm; $J = 7.6$ Hz/7.05 Hz; 2H, m); (7.27 ppm; $J = 7.6$ Hz; 2H; d); (6.8 ppm; $J = 7.4$ Hz; 2H, d); (7.27 ppm; $J = 7.38$ Hz/8.2 Hz; 2H; m); (6.8 ppm; $J = 8.2$ Hz; 2H; d); ^{13}C NMR ($CDCl_3$; 400 MHz) δ (ppm) = 27.7; 52.8; 114; 129.8; 116.8; 147.7; 125.9; 128.6; 126.9; 143.8; while for the anti-Markovnikov adduct were GC–MS (*z*/*m*): 197 (M^+, 76), 198 (M^+, +1, 8), 183 (10), 182 (100), 180 (24), 120 (6), 165(27), 105 (4), 91 (5), 77 (4); **NMR** ^1H NMR ($CDCl_3$; 400 MHz): (2.2 ppm; $J = 6.9$ Hz; 2H; t); (3.2 ppm; $J = 6.9$ Hz; 2H; t); (4.4 ppm; $J = 0$ Hz; 1H; s); (6.84 ppm; $J = 7.05$ Hz; 1H; t); (6.9 ppm; $J = 7$ Hz/7.05 Hz; 2H, m); (6.6 ppm; $J = 7$ Hz; 2H; d); (6.82 ppm; $J = 7.4$ Hz; 1H, t); (6.9 ppm; $J = 7.38$ Hz/8.2 Hz; 2H; m); (6.8 ppm; $J = 8.2$ Hz; 2H; d) ^{13}C NMR ($CDCl_3$; 400 MHz δ (ppm) = 36.7; 41.5; 112.8; 127.4; 118.2; 147; 127.6; 128.5; 126.6; 140.

3. Results and discussions

Fig. 1 shows results in the hydroamination of styrene with aniline on the investigated catalysts (Scheme 1). Zeolites with different structure (Beta and mordenite) and Si/Al ratios (25–75) showed different behavior. Mordenites, characterized by a bi-dimensional channel system with straight 12-membered ring channels with crossed 8-membered ring channels showed no activity in this reaction, while on BEA zeolite the *anti*-Markovnikov isomer was the main reaction product. These results however agree with data reported previously on zeolites and clays where the *anti*-Markovnikov adducts were the main product as a conjugate addition [61,62,69]. At 363 K, the change of the Si/Al ratio in the range 25–75 did not generate a major change in the conversion (Fig. 1a). However, the selectivity in the *anti*-Markovnikov isomer reached a maximum (70%) for a Si/Al ratio of 30, while the increase of the Si/Al ratio to 75 led to an almost equal selectivity in Markovnikov and *anti*-Markovnikov adducts that is again in agreement with previous findings showing that less acidic zeolites generate higher yields in the *anti*-Markovnikov isomer.

The increase of the temperature to 423 K led to an increase of the conversion (almost double compared to that at 363 K). However, a decrease in the selectivity to the *anti*-Markovnikov isomer was determined for the zeolite with a Si/Al ratio of 30, especially because at this temperature a certain percent of polystyrene (less than 10%) was detected on all zeolites. Actually, the performances of the BEA zeolites were very close in terms of the conversion. Mordenites showed no activity, irrespective of the Si/Al ratio. In a previous work of Müller and Lercher [40] it was reported that the products face strong constraints to diffuse out of the pores and that the larger, but one-dimensional, pores of Mordenite led to low activity. Zeolite BEA presents two interconnecting channel systems forming a smaller space than the faujasite supercage. Consequently, the reactants and the desired products can diffuse into and out of the pores, and the reaction rate is higher, but also the selectivity. In addition, although both kinds of materials possess Lewis and Brønsted acid sites, BEA zeolites are characterized by a stronger acidity (with preponderantly Brønsted acid sites) while mordenites possess softer acidity (with preponderantly Lewis acid sites) (see FTIR and TPD results and Table 1). For BEA zeolites these characteristics correlate to the selectivity in the hydroamination. In a way they also well correlate to the differences in the particle size (34.3 μm (BEA-25), 31.2 μm (BEA-30), 28.7 μm (BEA-75). Müller



Scheme 1. Hydroamination of styrene with substituted anilines.

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Table 1
Textural and chemical characteristics of beta zeolites and mordenites.

Catalyst	Surface area[a] (m^2/g)	Pore volume[a] (mL/g)	Pore size[a] (nm)	Density of acidic sites[b] (mmol/g)	B acid sites[c]	L acid sites[c]
BEA-75	534	0.18	<1.0	0.02	0.2	0.05
BEA-30	480	0.18	<1.0	0.16	0.8	0.5
BEA-25	465	0.19	<1.0	0.18	0.9	0.7
Mordenite-20A	362	0.16	<1.0	0.29	0.4	1.6
Mordenite-30A	438	0.18	<1.0	0.48	0.6	2.6

[a] Textural properties measured with N_2 at 77 K.
[b] Calculated from TPD measurements.
[c] The relative population of Lewis (L) acid sites and Brønsted (B) acid sites calculated from the ratio of the integrated area of IR adsorption peak to the sample weight.

and Lercher [40] also claimed that the rates of reaction decreased with the particle size. Differences between our results and those reported by Müller and Lercher can be related to the fact we used BEA with different particle sizes and acidity than reported in that study.

Fig. 2 shows results in the hydroamination of styrene with aniline on $Sc(OTf)_3$ and mesoporous UVM-7 silica embedded scandium triflate (TfSc(60)), and on physical mixtures of $Sc(OTf)_3$ with Beta zeolites or TfSc(60), and of TfSc(60) with Beta 30 zeolite. On pure $Sc(OTf)_3$ the conversion was moderate that is in a good agreement with the previous reports [28]. TfSc(60) showed a very close behavior to $Sc(OTf)_3$. In both cases, the dominant product was the Markovnikov adduct, accordingly to the Lewis acid character of these catalysts. Indeed, in the case of TfSc(60) NH_3-DRIFT spectra indicated the presence of Lewis acid sites as inferred from the band located at 1627 cm^{-1} (Fig. 3). A band with a smaller intensity located at 1490 cm^{-1} was also detected and assigned to Brønsted acid sites. Nevertheless, the relative intensity of Lewis/Brønsted band ratios indicated a very high excess of the Lewis acid sites (higher than 10). Increasing the NH_3-desorption temperature from room temperature to 423 K, the band located at 1490 cm^{-1} completely disappear that means that on the surface remained almost only Lewis acid sites.

Interestingly, although $Sc(OTf)_3$ is supposed to be a purely Lewis acid and TfSc(60) was demonstrated as a predominantly Lewis acid type catalyst, the *anti*-Markovnikov adduct was formed as well on both catalysts. No polystyrene formation was evidenced.

The 50:50 mixture of the $Sc(OTf)_3$ with zeolites led to both a decrease of the conversion and a change in the isomer distribution. Using these mixtures the selectivity was quite different comparing to the individual catalysts. While on the mixture BEA-25–$Sc(OTf)_3$ the two adducts were equally resulted, for the mixture BEA-30–$Sc(OTf)_3$ the dominant product was the *anti*-Markovnikov adduct. Previous results reported that the Lewis acidic metal sites are initiating the reaction while the presence of the protons enhances the reaction rate [60]. Extending these results it was expected that the intimate physical mixture of the two catalysts will increase both the conversion and the selectivity in one of adducts. Actually such an effect was not determined and they demonstrated that if this approach is correct it could become effective only in the case the two active sites (Lewis and Brønsted) are in an intimate atomic proximity. We should also note that our results were verified using five successive 50:50 mixtures.

Beside this, the decrease in conversion comparing the two individual catalysts may suggest two parallel reactions on individual catalysts that are modified by each other. A similar behavior was determined for the physical mixture of Beta zeolite with TfSc(60).

Interestingly, a synergistic effect was determined for a 50:50 physical mixture of mesoporous TfSc(60) embedded scandium triflate and scandium triflate. On this system, the conversion was almost 70% and the selectivity in the Markovnikov adduct was over 70%. The reaction occurred with no polymerization of styrene.

Based on this result, different TfSc(60)–$Sc(OTf)_3$ physical mixtures were investigated. Data presented in Fig. 4 demonstrate that, indeed, a 50:50 ratio provided the best results. While the conversion showed the maximum for this mixture, the selectivity suffered a slight depletion for TfSc(60)–$Sc(OTf)_3$ ratio higher than 50:50. This slight decrease may account to the fact that the OH of silica UVM-7 is not completely inert in this reaction. The weak Brønsted acidity of these species may be responsible for the very slight increase of the selectivity in the *anti*-Markovnikov adduct. However, the pure siliceous UVM-7 was completely inert in this reaction.

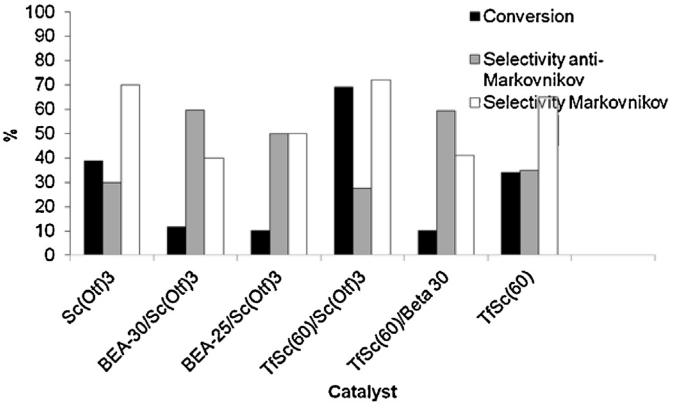

Fig. 2. Conversion and selectivity in the reaction of aniline and styrene on $Sc(OTf)_3$, TfSc(60), and 50:50 physical mixtures of these and with zeolites (1 mmol aniline, 2 mmol styrene, 4 mL toluene, 50 mg catalyst, 423 K, 24 h).

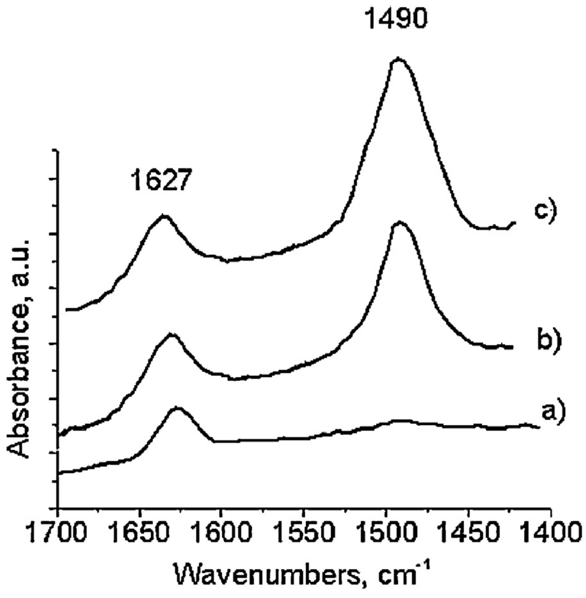

Fig. 3. NH_3-FT-IR for (a) TfSc(60), (b) BEA-30, (c) physical mixture of TfSc(60) and BEA-30 (NH_3-desorption at 423 K).

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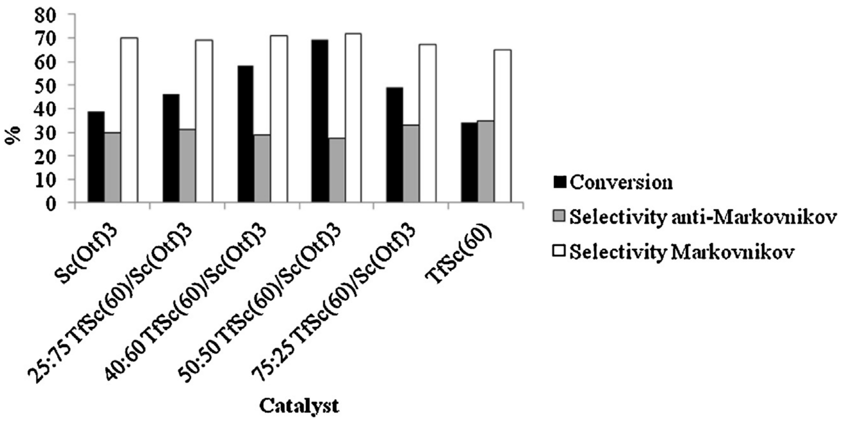

Fig. 4. Conversion and selectivity in the reaction of aniline and styrene on Sc(OTf)$_3$, TfSc(60), and different physical mixtures of these (1 mmol aniline, 2 mmol styrene, 4 mL toluene, 50 mg catalyst, 423 K, 24 h).

Table 2
Conversion and selectivity in the hydroamination of 4-nitro-aniline, 4-chloro-aniline and 3-aminophenol with styrene on the investigated physical mixtures.

Substrate	Physical mixture TfSc(60)–Sc(OTf)$_3$	C (%)	TON	Selectivity (%)	
				Markovnikov	*anti*-Markovnicov
4-Nitro-aniline	0:100	88	9.0	100	–
4-Nitro-aniline	25:75	92	12.0	100	–
4-Nitro-aniline	40:60	95	15.0	100	–
4-Nitro-aniline	50:50	100	18.0	100	–
4-Nitro-aniline	75:25	91	29.0	100	–
4-Nitro-aniline	100:0	86	98.0	100	–
4-Chloro-aniline	0:100	92	9.0	72	28
4-Chloro-aniline	25:75	94	12.0	72	28
4-Chloro-aniline	40:60	96	15.0	73	27
4-Chloro-aniline	50:50	100	18.0	75	25
4-Chloro-aniline	75:25	91	29.0	70	30
4-Chloro-aniline	100:0	86	98.0	68	32
3-Aminophenol	0:100	92	9.0	50	50
3-Aminophenol	25:75	94	12.0	51	49
3-Aminophenol	40:60	95	15.0	54	46
3-Aminophenol	50:50	99	18.0	56	44
3-Aminophenol	75:25	91	29.0	50	50
3-Aminophenol	100:0	85	97.0	46	54

Reaction conditions: 1 mmol amine, 2 mmol styrene, 4 mL toluene, 50 mg catalyst, 423 K, 24 h.

Ultrasound has an effect a better dispersion of the added molecular scandium triflate in the reaction mixture. It is also known that under ultrasounds irradiation using powders the energy is enough high to cause their fragmentation [70]. On the other hand, in the case of very fine powders, the particles are accelerated to high velocity by cavitational collapse and may collide to cause surface abrasion. In this way the interaction of ScTf$_3$ with TfSc(60) as a physical mixture is enhanced. As an effect, TfSc(60) allows a better dispersion of the added Sc(OTf)$_3$ and thus an increase of the conversion. Some chemical interaction of Sc(OTf)$_3$ with TfSc(60) could not be neglected. However, such an effect is limited by the ratio of the two components. We should notice again that the reactions were carried out in batch conditions, namely, where the catalysts are dispersed in the liquid phase.

Table 2 compiles the values of the conversion, TON and selectivity in the hydroamination of 4-nitro-aniline, 4-chloro-aniline and 3-aminophenol with styrene on the same physical mixtures. For all the substrates the variation of the conversion followed the same order as for aniline. However, the use of these substituted anilines led to considerable higher values of the conversion. The selectivity in the hydroamination of these substrates was found to depend on the nature of the substituent. Using 4-nitro-aniline as substrate the selectivity was total in the Markovnikov adduct, while for 4-chloro-aniline and 3-aminophenol the *anti*-Markovnikov adduct resulted as well. The selectivity in the *anti*-Markovnikov adduct had the same evolution with the TfSc(60)–Sc(OTf)$_3$ ratio as for aniline and, therefore, is supposed to based on the same explanation. It is also worth to mention that the pK_b of substituted anilines parallels the selectivity of the reaction (aniline: 9.4, 3-aminophenol: 9.8, 4-chloro-aniline: 10.0 and 4-nitro-aniline: 13.0) [71]. From our measurements it appears the role of the anion into hydroamination reaction is that to control the Lewis acidity of Sc. In the presence of triflate, scandium is more naked due to the strong electrondrawn effect of the anion [72].

4. Conclusions

Hydroamination of aniline and substituted anilines with styrene occurred on both zeolites and triflate based catalysts with performances controlled by the type of acidity and strength. The conversion in these reactions was controlled by the strength of the acid sites and their accessibility. The selectivity was controlled by the type of acidity and Brønsted and Lewis acidity have to be taken into account to allow the formation of the *anti*-Markovnikov or Markovnikov adducts. While the use of zeolites and scandium triflate led to results very close to those reported in the literature, physical mixtures of scandium triflate with a mesoporous scandium triflate embedded in a UVM-7 structure provided better conversions with a good selectivity in the Markovnikov adduct.

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These results were attributed to a better dispersion of scandium triflate during the preparation of physical mixtures.

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