



# 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.

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## 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  $\alpha$ -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  $\pi$ -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 ( $[(\text{BINAP})\text{Pd}(\text{solvent})_2]^{2+}$ ) catalyze hydroamination of primary (and secondary) aromatic amines with  $\alpha,\beta$ -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  $\text{TiO}_2$  nanoparticles [41], heteropolyacid catalysts [42], simple Al-SBA-15 catalysts [43] or heteropolyacid encapsulated SBA-15/ $\text{TiO}_2$  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  $n\text{-Bu}_4\text{PBr}$  has no beneficial effect for the platinum-catalyzed hydroamination of terminal alkynes. Pristine  $\text{PtBr}_2$  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  $\text{Au}^{3+}$  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  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  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  $\alpha,\beta$ -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  $\alpha,\beta$ -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.  $\text{Sc}(\text{OTf})_3$  was purchased from Aldrich. Mesoporous UVM-7 encapsulated scandium triflate catalyst with the Si/Sc atomic ratio of 60 ( $\text{TfSc}(60)$ ) 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  $\text{NH}_3$ -FT-IR. The  $\text{NH}_3$ -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-nitroaniline, 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  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy using a Bruker AV 400

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