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Titania Nanoparticles Stabilized HPA in SBA-15 for the Intermolecular Hydroamination of Activated Olefins

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A liquid phase hydroamination (HA) of α , β -ethylenic compounds with amines was investigated with TiO₂ nanoparticles stabilized 12-tungstophosphoric acid (TPA) in SBA-15. The catalysts were prepared by wet impregnation of TPA/TiO₂ nanoparticles into the SBA-15 and calcined at different temperatures. The characterization results reveal that the textural properties and the acidity of the prepared catalysts can be finely controlled with the simple adjustment of the calcination temperature and the structure of the support, decorated with the TiO₂ and TPA nanoparticles, was intact even after the modification. The prepared catalysts were investigated for HA of ethyl acrylate with different aromatic and aliphatic amines over a wide

range of reaction conditions to optimize the yield and the selectivity of product. It was found that this process is 100% atom efficient and the catalytic performance depended significantly on the loading of TPA over the catalyst and the calcination temperature. Under optimized reaction conditions, the best catalyst, 15 wt %TPA/22.4 wt %TiO₂/SBA-15 calcined at 1123 K, offered the highest conversion of *p*-ethylaniline (70%) with 100% chemo-selectivity to the anti-Markovnikov product, i.e., the mono-addition product. The reaction was heterogeneously catalyzed and no contribution from leached TPA into the reaction was observed.

Introduction

The impact of the global warming and the environmental awareness among the public have made a significant progress on replacing the homogeneous catalysts that are harmful to our environment through generation of hazardous wastes and toxic by-products and used in various petrochemical industrial processes, with sustainable and environmentally friendly catalysts. Moreover, the restrictions imposed by the waste minimization laws and economic considerations drive to the development of a new catalytic technology which should be safe and

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non-hazardous. Modern processes are, in fact, based on solid type heterogeneous catalysts including acid and bases. Nowadays, these catalysts have been widely used in various organic industrial processes because of their advantages, such as easy separation from the product and recyclability.

Heteropoly acids (HPAs) are interesting materials with strong acidity and redox behavior, which make them available as catalysts for various types of organic synthesis, including selective oxidation, and acid-catalyzed organic reactions.^[1-3] However, they have several disadvantages such as low specific surface area, poor thermal stability, and a high solubility in polar solvents which inhibit their use in various liquid phase acid catalyzed organic reactions. These disadvantages can be overcome by various ways including the encapsulation of HPA in porous silica or zeolite matrix and the formation of acidic salt by intercalating the cesium in the Keggin structure.[4-6] It was reported that the thermal stability of these supported catalysts is significantly higher than that of the pure HPA. Therefore, the researchers tried to utilize different supports such as silica, titania, and zirconia to stabilize the HPA and improve the acidic properties.^[7-9] Zirconia modified with tungstophosphoric acid (TPA)^[7-9] and high surface area nanosized HPA supported zirconia encapsulated in mesoporous materials form a high acidic catalytic phase with an excellent catalytic activity in a variety of acid-catalyzed reactions.^[10,11] Although sulfated and tungstated zirconia are highly acidic catalysts, they suffer from poor textural characteristics which restrict their use in acid catalyzed reactions.^[12-14] On the other hand, the mesoporous materials used in these studies have poor water stability, owing to thin walls and a small pore diameter that may easily be blocked by the HPA and sulfated zirconia or tungstated zirconia nanoparticles.

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Mesoporous silica (MS) like SBA-15 has a thick pore walls and a large pore diameter, and possesses a high specific surface area, large pore volume, and a high thermal and hydrothermal stability.^[15] As SBA-15 has interesting structural features, we have previously employed this as a support to prepare nanosized titania supported TPA composite catalysts.^[16] It has been demonstrated that the SBA-15 has been a good support and the acidity of the catalysts can be tuned by the simple adjustment of the calcination temperature and the loading of the TPA in the mesochannels of the SBA-15. These nanocomposites were later tried for various organic transformations including Mannich, hydroamination (HA), and Claisen rearrangement reactions. In the previous report, we described the applicability of these fascinating materials in various organic transformations and presented the preliminary catalytic results. Encouraged by the initial results, we extended our studies to investigate the detailed catalytic activity of these catalysts in relation to the aforementioned organic transformations. In this report, the detailed investigation of the catalysts has been carried out for the HA of activated olefins.

The synthesis of many important personal care products or pharmaceutical chemicals requires amines as starting compounds. Considerable effort, therefore, has been devoted on the development of efficient protocols for the construction of carbon-nitrogen bonds in the organic molecule, which is of interest owing to the fundamental importance of amines as natural products, pharmacological agents, fine chemicals, and dyes.^[17,18] Compared to the other methods for the synthesis of amines, enamines, and imines,^[12] HA offers one of the most attractive pathways to such molecules. Although the addition of alcohol H-OR bonds to alkenes and alkynes has been known for a long time, additions of amines to alkenes and alkynes are rare. The direct addition of amine to an olefin, leading to a new amine, which is particularly attractive because the desired nitrogen containing products are formed in a single reaction step from inexpensive alkenes without the intrinsic formation of side products.^[13, 14] However, this transformation is weakly exergonic and its reaction entropy is highly negative.^[19] These thermodynamic characteristics make the difficulties for the HA of olefins to catalyze which in fact brings no generally applicable solution for this system.^[17] Significant effort has, therefore, been made to develop metal catalyzed HA processes.^[20,21] Various ion exchanged zeolites and clays^[22-25] and immobilized zinc salts^[26] have been successfully used for the cyclization of 6-aminohex-1-yne and intermolecular HA of phenylacetylene with aniline. Immobilized transition metal complexes were also used in the addition of 4-isopropylaniline to phenylacetylene.^[27] A broad spectrum of the reactions performed on the addition of activated olefins to aliphatic amines are available in the literature.^[28-32] However, the reports on the selective HA of aromatic amines using different solid-acid catalysts are guite limited.^[34-36] HPAs or metal ion exchanged HPAs have also been used as catalysts for the intermolecular HA of olefin.^[37–41] As previously mentioned, the use of HPAs for this reaction without proper support significantly reduces the life of the catalysts and thereby their recyclability.

Consequently, we employed the stable and the most active TiO_2 -supported mesoporous SBA-15 nanocomposites with different loadings of TPA prepared in our lab for the HA of activated olefin, namely ethyl acrylate (EA) with aromatic amines such as *p*-ethylaniline to yield anti-Markovnikov product (linear addition product) (Scheme 1). The effect of the loading of TPA



Scheme 1. Hydroamination (HA) of α , β -ethylenic compounds with amines.

and the calcination temperature affecting the activity of the catalysts on the HA of both aliphatic and aromatic amines has been investigated. The textural parameters and the acidity of the catalyst have been correlated with the performance of the catalysts and reason for the significant changes in the activity of the catalysts at different conditions. Finally, the kinetic results have been interpreted using the initial rate approach model and the results have been discussed in detail.

Results and Discussion

The detailed structural information of the prepared catalysts has been described in our previous report.^[16] However, to get a clear insight into the relation between the textural parameters and the acidity of the catalysts with their performances, some of the results are presented. Low-angle XRD patterns of xT-22.4TO-S-15 with different TPA loadings and calcined at 1123 K reveal that the meso-structure of the materials is intact up to 50 wt% of TPA loading whereas the wide-angle XRD patterns of the samples show that the pure anatase phase of TiO₂ which is critical for the performing organic transformation is changed to rutile phase when the loading of TiO₂ is increased to more than 15 wt% (Figure S1-see the supporting information). In addition, the decomposition of TPA into WO3 crystallites was observed when the loading of TPA was increased above 15 wt%. These results reveal that the sample with a TPA loading of 15 wt% is the best condition that can keep both the structure of the support as well as the active sites of TPA which is crucial for the catalytic studies. It can be seen from Figure S1 that the structure of the samples is affected after the calcination at different temperature. The meso-structure and anatase phase of TiO₂ were intact up to the calcination temperature of 1123 K but collapsed/changed as the temperature was increased above 1123 K.

The effects of TPA and TiO_2 loading on SBA-15, and the calcination temperature on the textural parameters of the catalysts have been shown Figure 1 and Figure 2, respectively. It is evident from the data that the specific pore volume and the spe-



Figure 1. Variation of physico-chemical properties such as (\mathbf{V}) surface area, (**A**) pore volume, (**•**) pore diameter and (**•**) total acidity with a variation of TPA loading (*x*) in *x*T-22.4TO-S-15 catalyst calcined at 1123 K. For 1 *x* = 15.



Figure 2. Variation of physico-chemical properties such as (\mathbf{v}) surface area, (**A**) pore volume, (**o**) pore diameter and (**n**) total acidity of 1 calcined at different calcination temperatures.

cific surface area of the modified samples are much lower than those of the parent SBA-15, and decrease with increasing TPA or TiO₂ loadings, which is mainly due to the coverage of the surface of the support with the well-dispersed TPA or TiO₂ nanoparticles. It can be seen from Figure 2 that the increasing the calcination temperature from 923 to 1273 K, the specific surface area and pore volume of the support decrease from 462 to 202 m²g⁻¹ and from 0.61 to 0.31 cm³g⁻¹, respectively.

The total acidity in terms of the amounts of NH_3 in mmol g⁻¹ for the catalysts with different loadings of TPA and different calcination temperatures is also presented in Figure 1 and Figure 2, respectively. It is evident from the data in Figure 1 that the total acidity of the catalyst increases with increase in TPA loading from 5 to 15 wt% and then decreases with further increase in TPA loading. On the other hand, total acidity increases with increasing the calcination temperature from 923 to 1123 K and reaches to a maximum value of 0.38 mmol g^{-1} .

However, the value of the acidity decreases drastically when the calcination temperature was increased above 1123 K, which is mainly due to the decomposition of TPA into WO₃ crystallites. All the samples were also characterized by using different characterization techniques such as ³¹P MAS NMR, HRTEM, FT-IR of adsorbed pyridine, UV/vis. Analysis of the spectroscopy, XPS, and FT-Raman and their conclusions were discussed in detail in our previous report.^[16] As the sample containing 15 wt%TPA, 22.4 wt%TiO₂ on SBA-15 calcined at 1123 K (1-1123) showed the optimum surface area, with a monolayer coverage of TPA and small TiO₂ nanoparticles on the surface and a high total acidity (Figure 1), it was chosen for the HA of activated olefins with a series of aliphatic and aromatic amines (Scheme 1).

The catalytic activity of 1-1123 for the addition of aliphatic amines with EA at room temperature has been investigated and the results are presented in Table 1. All the reactions were exclusively regioselective and only the product of anti-Markovnikov addition to amine to CC double bonds is formed. The electron rich carbonyl group of EA combines with the electron deficient centers in the 1-1123 (mainly Brønsted acidic), which makes β -carbon electron deficient and attacks the electron rich center in the amine. This is followed by 1,3-proton shift in step III with the release of anti-Markovnikov product in step IV to regenerate the catalyst (Scheme S1).^[42] In the absence of any solvent, the catalyst gave excellent conversion for all the aliphatic amines to the selective product at the amine/acrylate molar ratio of 1. The reaction of *n*-propylamine and *n*-butylamine with EA gave a conversion of \approx 99% with a selectivity of 90% and 87% for mono-substituted product with 10% and 13% for di-substituted product, respectively. Bulkier molecules like dicyclohexylamine also gave higher yield (85%) with 100% selectivity for mono-addition product, which indicates that the bulky amines can easily pass through the mesopores of 1-1123. The catalyst offered 86.83% conversion and a yield of 96% for the mono-addition product and 4% for the di-addition product when a long chain primary amine, n-octylamine was used.

No.	Aliphatic	Conv. ^[b]	Selectivity [%] ^[c]		MA product	TOF	RC, <i>k</i> ,
	Amines	[%]	MA	DA		$[s^{-1}]$	[×10 ⁻⁴ s ⁻
1.	morpholine	95.00	100	0	ethyl-3-morpholinopropanoate	0.80	8.32
2.	piperidine	87.01	100	0	ethyl-3-(piperidin-1-yl) propanoate	0.75	5.67
3.	dicyclohexylamine	85.00	100	0	ethyl-3-(dicyclohexylamino) propanoate	0.48	5.27
4.	dipropylamine	93.35	100	0	ethyl-3-(dipropylamino) propanoate	0.74	7.53
5.	cyclohexylamine	91.68	100	0	ethyl-3-(cyclohexylamino) propanoate	0.73	6.91
6.	<i>n</i> -octylamine	86.83	96	4 ^[d]	ethyl-3-(octylamino) propanoate	0.60	5.63
7.	benzylamine	93.37	99.7	0.3 ^[e]	ethyl-3-(benzylamino) propanoate	0.72	7.54
8.	propylamine	98.8	90.0	10 ^[f]	ethyl-3-(propylamino) propanoate	0.98	12.29
9.	butylamine	98.9	87.0	13 ^[g]	ethyl-3-(butylamino) propanoate	0.91	12.53

time = 1 h; [b] Conversion determined by GC analysis with respect to amine; [c] The anti-Markovnikov product selectivity was determined by GC analysis. MA: monoaddition; DA: di-addition; [d] diethyl 3,3'-(octylazanediyl) dipropanoate; [e] diethyl 3,3'-(benzylazanediyl) dipropanoate; [f] diethyl 3,3'-(bropylazanediyl) dipropanoate; [g] diethyl 3,3'-(butylazanediyl) dipropanoate.

No.	Aromatic Amines	Conv. ^[b] [%]	Select. ^[c] [%]	MA product	TOF [s ⁻¹ ×10 ⁻¹]	RC, $k_{\rm a}$ [×10 ⁻⁵ s ⁻¹]
1.	<i>p</i> -anisidine	68	100	ethyl-3-(4-methoxyphenylamino) propanoate	0.40	5.28
2.	<i>p</i> -ethylaniline	63.3	100	ethyl-3-(4-ethylphenylamino) propanoate	0.38	4.64
3.	2,4-xylidene	55.8	100	ethyl-3-(2,4-dimethylphenylamino) propanoate	0.33	3.78
4.	N-methylaniline	48.6	100	ethyl-3-(methyl(phenyl)amino) propanoate	0.31	3.08
5.	aniline	57.5	100	ethyl-3-(phenylamino) propanoate	0.39	3.96
6.	o-nitroaniline	nil	nil	nil	nil	nil
7.	<i>p</i> -ethylaniline ^[d]	2	100	ethyl-3-(4-ethylphenylamino) propanoate	-	-

tion anti-Markovnikov product selectivity was determined by GC analysis. [d] No Catalyst.

To gain more insight into the scope and limitation of our method, we carried out the reaction with a series of aromatic amines using 1-1123. It was found that the catalyst was not active at room temperature when aromatic amines were used as the reactants. However, the aromatic amines reacted with EA to yield mono-addition product in good conversion and selectivity as the reaction temperature is increased. When the reaction was tried without the catalyst, only 2% of mono-addition product was obtained, revealing the active role of the catalyst in this particular reaction. In addition, the influence of electronic effects of the substituents in the 2 and 4-position of amine on the yield and selectivity of the reaction has been investigated using 1-1123 and the results are given in Table 2. It is found that the substitution on the aromatic amine significantly influences the outcome of the catalytic reaction. The aniline derivatives having electron-donating groups at the ortho- and para- positions reacted smoothly with EA to give corresponding HA products (Table 2). It is interesting to note that the *p*-anisidine having a strongly electron donating group gave higher yield than 2,4-xylidene (Table 2, Entry 1, 3). This is mainly due to the fact that the methoxy group of *p*-anisidine is strongly electron donating and the 2-methyl groups of 2,4xylidene cause some steric hindrance. The role of the electron withdrawing groups in the amines on the activity of the catalyst was also investigated. As expected, the reaction of amines with electron withdrawing substituents like nitro group did not undergo HA reaction (Table-2, Entry 6). The feasibility of secondary amines to undergo this addition was demonstrated using N-methylaniline and EA (Table 2, Entry 4). These results reveal that the reactivity of amine depends on their basicity. It should be noted that aliphatic amines are more basic than aromatic amines and amines with electron donating substituents are more basic than amines with electron withdrawing substituents. As it strongly influences the adsorption on the surface of the catalysts with acid functional groups, the difference in the activity of the catalyst was expected. From these results, it can be concluded that the activity of the catalyst increases with the basicity of the amines for the HA reactions of α , β -ethylenic compounds with amines using this particular catalyst, 1-1123.

The influence of TPA loading (5 to 70 wt%) on the conversion and selectivity was studied at a reaction temperature of 383 K, the reaction time of 2 h and pethylaniline to EA ratio of 1. It was observed that the conversion of amines was highly dependent on the loading of TPA on the catalyst. The conversion was increased from 35.49 to 47.53% with increasing the TPA loading from 5 to 15 wt%. However, the activity of the catalyst was significantly decreased (32.3%) with the further increase

of TPA loading to 70 wt.%. Among the catalysts with different TPA loading studied, 1-1123 registered the highest conversion for *p*-ethylaniline (47.53%) for the reaction time of 2 h (Figure 3 A). These results indicate that the structural features of the catalysts play a significant role in controlling the activity of the catalysts. It was previously discussed that the Keggin structure of the TPA was collapsed when the TPA loading in the samples is higher than 15 wt%. Therefore, it may be concluded that the higher catalytic activity of 1-1123 is mainly due to the



Figure 3. Influence of A) TPA loading (catalysts calcined at 1123 K) and B) calcination temperature (1) on the HA of EA with *p*-ethylaniline (\bullet) Conversion in (%) and (\mathbf{v}) TOF. Reaction conditions: *p*-ethylaniline/EA ratio = 1, temperature = 383 K, 10 wt % catalyst, Toluene = 2 mL and time = 2 h. Anti-Markovnikov mono-addition product selectivity (100%) was determined by GC analysis.

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retention of the Keggin structure of TPA which offers a high acidity. High acidity is important parameter for obtaining better performance on the HA of EA with *p*-ethylaniline. On the other hand, the partial decomposition of TPA is responsible for the lower activity of the catalyst loaded with the higher amount of TPA wherein the acidity of the catalyst is lower as compared to that of the samples loaded with 15 wt% of TPA.^[16]

The influence of calcination temperature on the catalytic activity for HA of EA with *p*-ethylaniline over **1** calcined at different temperatures (923–1273 K) was investigated and the results are shown in Figure 3B. The **1**-923 gave a conversion of only 13.24%, which is increased to 47.53% for **1**-1123 (Figure 3B). This clearly shows the relationship between the catalytic activity of **1** and the calcination temperature. The conversion of *p*-ethylaniline decreases to as low as 15% when the calcination temperature of the catalyst was increased to 1273 K. It was found that the calcination temperature 1123 K was found to be the best which is mainly due to the availability of the highest Brønsted acidity together with the perfect monolayer coverage of TPA on the surface of the catalytic support (15 wt%).^[16]

In order to optimize the yield of the catalyst with a maximum conversion and selectivity for mono-addition product in the HA of EA with p-ethylaniline, the reaction parameters have been varied (Scheme 2). The best catalyst, **1**-1123, was chosen



Scheme 2. HA of ethyl acrylate with *p*-ethylaniline on titania stabilized over HPA supported SBA-15.

for these studies. Initially, the effect of temperature on the activity of the catalyst in the HA at the temperature range of 363–403 K was investigated and the results are displayed in Figure 4A. It was found that the increase of the reaction temperature has a profound effect on the conversion and selectivity for mono-addition product. The conversion was increased with increasing the reaction temperature from 363 to 403 K for the reaction time of 2 h. The catalyst offered only 27.4% conversion of *p*-ethylaniline at 363 K, which further increased to 68.9% when the reaction temperature was increased to 403 K. However, the selectivity of the mono-addition product was decreased slightly at a high reaction temperature (403 K) as a function of time. Interestingly, at a high reaction tempera-



Figure 4. Influence of reaction parameters on the HA of EA with *p*-ethylaniline: A) Influence of reaction temperature (reaction conditions: *p*-ethylaniline/EA molar ratio = 1, catalyst = 1-1123 (10 wt% of total reaction mixture), Time = 2 h. B) Influence of reactant molar ratio (reaction conditions: temperature = 383 K, catalyst = 1-1123 (10 wt% of total reaction mixture), Time = 2 h. C) Influence of catalyst wt% (Reaction conditions: *p*-ethylaniline to EA molar ratio = 1, Temperature = 383 K, Time = 2 h with (•) conversion in (%) and (•) TOF. Anti-Markovnikov mono-addition product selectivity (100%) was determined by GC analysis.

ture, the trace amount of di-addition product is formed which indicates that harsh condition is required for the formation of the Markovnikov adduct.

The influence of *p*-ethylaniline to EA molar ratio (2–0.25) for HA of EA with *p*-ethylaniline was studied over **1**-1123 at a reaction temperature of 383 K and a reaction time of 2 h but keeping the total weight of the reaction mixture constant (Figure 4B). At a molar ratio of 1, the conversion was 33.38% with 100% selectivity for mono-addition product i.e. ethyl-3-(4-ethylphenyl amino) propanoate. When the *p*-ethylaniline to EA molar ratio decreased from 1 to 0.25, the conversion is found to increase from 33.38 to 67.15%. The increase of the conversion may be attributed to the availability of more amount of EA which may enhance its adsorption over the surface of the highly active sites of the catalysts. As a result, the conversion of *p*-ethylaniline is increased as the ratio increases. It was also expected that the availability of excess amount of EA actually leads to the addition of another molecule of EA for the di-addition product. However, only trace amount of di-addition product (0.3%) is formed even at the *p*-ethylaniline to EA of 0.25. This indicates that the mesoporosity of the catalyst plays an important role and the reaction indeed takes place inside the mesopores which favors the formation of the mono-addition product with almost 100% selectivity and 100% atom efficient process.

The weight of the catalyst was tuned to investigate its influence on the conversion and product selectivity in the HA of EA with *p*-ethylaniline at a reaction temperature of 383 K, *p*-ethylaniline to EA molar ratio of 1 and the reaction time of 2 h and the results are shown in Figure 4C. The weight of the 1-1123 was varied from 2.5-10 wt% of the total reaction mixture. The activity of the catalyst was significantly increases as the weight of the catalyst is increased. The conversion of *p*-ethylaniline increases from 13.5 to 47.53% with increasing the weight percentage of the catalyst from 2.5 to 10. This could be due to the increase of more number of active sites for the reactant molecule when higher amount of catalyst was supplied, and thereby the conversion increases significantly. It should be also noted that the selectivity of the mono-addition product was almost 100% and was not at all affected upon increasing the weight of the catalyst in the reaction mixture.

The influence of time on stream on conversion and selectivity of products for the HA reaction over 1-1123 for the time period of 1 to 8 h at a *p*-ethylaniline to EA molar ratio 1 and reaction temperature of 383 K was investigated and the results are given in Figure-5. With the increasing the reaction time, the conversion of *p*-ethylaniline also increases to a maximum of 69.35% with a clean selectivity for mono-addition product under the selected reaction conditions. These results clearly indicate that the catalyst is quite stable and its activity is retained. The availability and the stability of the active sites on the surface of the SBA-15 support are responsible for the sustainability and the higher activity of the catalyst. In addition, the coke was not formed on the surface of the catalyst even after the reaction time of 8 h.

The study of heterogeneity of the catalyst in the reaction media is important because of the solubility of TPA in EA (polar media). In order to study the heterogeneity of the catalyst in the reaction mixture, the reaction was carried out for 30 min under selected reaction conditions using fresh 1-1123. The reaction was stopped and catalyst was separated by filtration and then the filtrate was stirred for another 4 h under same reaction conditions. It was found that there was no further increase in the conversion of *p*-ethylaniline in the absence of the catalyst, which indicated the absence of leaching of TPA into the reaction medium (Figure S2). In addition, the leaching of TPA (dissolution of P or W) into the hot filtrate was tested by inductively coupled plasma-optical emission spectroscopy (ICP-OES), which did not show any trace of P or W in the reaction mixture. For reusing the catalyst, the catalyst used in the

first cycle of the reaction was separated by filtration, washed three times with 1, 2-dichloromethane, dried in an oven at 373 K for 24 h and activated at 773 K for 4 h in an air. The activated catalyst was used for HA of EA with *p*-ethylaniline under selected reaction conditions. Same procedure is repeated for second cycle and the data on the conversion of aniline are presented in Table S1. From the result, it is concluded that there is no appreciable loss in the catalyst cativity and product selectivities in the two cycles and catalyst could be reused.

Conclusions

The liquid phase HA of EA with *p*-ethylaniline was carried out with a series of nanosized titania supported 12-tungstophosphoric acid (TPA) in SBA-15 composite prepared by vacuum impregnation of TPA/TiO₂ nanoparticles inside the mesoporous channels of support. It was found that the catalytic activity is mainly related with the textural parameters and the acidity of the catalyst which solely depend on the TPA coverage on the surface of the catalyst and the calcination temperature. The effects of various reaction parameters affecting the activity of the catalyst in the HA of EA with amines were investigated. Under the optimized reaction conditions, the most active catalyst 1-1123, gave a maximum conversion of 70% over a period of 8 h with a high regio- and chemo-selectivity to anti-Markovnikov product, i.e. mono-addition product. The catalyst also showed higher activities for HA of EA with aliphatic and aromatic amines with electron withdrawing substituents, and secondary amine. Among the catalysts studied, 1-1123 was found to be highly active, recyclable and heterogeneously catalyzed for intermolecular HA of activated olefins with amines under optimized reaction conditions. This process was found to be 100% atom efficient and gave only single mono-addition product. As the prepared catalysts have excellent textural parameters and a high acidity, these materials can be used for various other acid catalyzed organic transformation and open the door for the synthesis of various fine chemicals under mild reaction conditions.

Experimental Section

Tetraethylorthosilicate (TEOS), triblock copolymer of ethylene oxide (EO) and propylene oxide (PO), $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) ($M_{avg} = 5800$), titanium chloride (TiCl₄) were purchased from Aldrich and 12-tungstophosphoric acid (TPA) was obtained from Merck. *p*-Ethylaniline was also procured from Aldrich. EA, acrylonitrile and acrylic acid were purchased from Loba Chemicals, Mumbai. All the amines and toluene were purchased from S. D. Fine chem. Ltd., Mumbai. Toluene used in the reaction was distilled over sodium wire before use.

Catalyst preparation: Synthesis of mesoporous silica SBA-15: SBA-15 was synthesized with the following gel composition: 0.041 TEOS: 0.24 HCI: $6.67 H_2 O.^{[43]}$ In a beaker, 4 g of P123 was dispersed in 30 g of water and stirred for 4 h. Then, 120 g of 2 m HCl solution was added and stirred for 2 h. To this homogeneous solution, 8.54 g of TEOS was added under stirring. The resulting gel was aged at 313 K for 24 h and finally heated to 373 K for 48 h. Then,

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the solid was filtered, washed with distilled water and dried in an oven at 373 K in air for 5 h followed by calcination at 813 K to remove the triblock-copolymer.

Mesoporous silica embedded TiO₂ supported TPA: The mesoporous silica SBA-15 (2 g) was first wet-impregnated along with an aqueous solution of titanium tetrachloride (TiCl₄) under vacuum condition using a turbo pump. An aqueous solution of the TiCl₄ solution was prepared in an ice-water bath under air-tight condition. Different amount of this solution was kept in contact with the mesoporous silica SBA-15 for 6 h under vacuum. An excess aqueous solution of TiCl₄ (22.4 wt%) was introduced and kept in contact for 6 h under vacuum. After the volatiles were pumped out, the solid was dried at 373 K in air. Similar procedure was followed for the wetimpregnation of TPA (10, 15, 30, 50, 70, and 90 wt%) over an optimized 22.4 wt of TiO₂ loaded on SBA-15. 15 wt %TPA over SBA-15 samples loaded with different amount of TiO₂ were also prepared. All the catalysts were dried at 373 K and further calcined at 1123 K. The nanocomposites were calcined at different calcination temperatures. The samples were named as xT-22.4TO-S-15-z, where xT, TO, S-15, and z denote the wt% of TPA, the wt% of TiO_2 , SBA-15, and the calcination temperature, respectively.

Characterization methods: Inductively coupled plasma-optical emission spectroscopy (ICP-OES) and EDAX were used to determine the Ti, W, and P contents in the samples. XRD patterns were determined with a Bruker instrument equipped with a general area detector diffraction system (GADDS) using $Cu_{K\alpha}$ radiation at a step size of 0.018, the generator operating at 40 kV and 40 mA. The wide angle X-ray diffraction patterns were detected using Rigaku Model D/MAXIII VC, Japan, $\lambda = 1.5418$ Å with Cu_{Ka} radiation. The specific surface area, pore volume and pore size distribution of samples were calculated from the nitrogen adsorption isotherms measured using an Omnisorb 100CX (Coulter, USA). The total amount of acidity of the catalysts was obtained using temperature programmed desorption (TPD) of NH₃ on Micromeritics AutoChem 2910. The experiments were conducted initially by dehydrating 0.1 g of the catalyst sample at 773 K in dry air for 1 h and purging with helium for 0.5 h. The temperature was decreased to 398 K under the flow of helium and then 0.5 mL pulses of NH₃ were supplied to the samples until no more uptake of NH₃ was observed. Then, the NH₃ was desorbed in helium flow by increasing the temperature to 813 K with a heating rate of 10°C min⁻¹ and measured using TCD detector. Thermo-gravimetric measurements (TG-DTG) were performed on a Setaram TG-DTA 92 apparatus from room temperature to 1273 K in flowing dry air (\approx 50 mLmin⁻¹). For each experiment, 25-30 mg of the sample was used with a heating rate of 10 Kmin⁻¹.

Hydroamination: The liquid phase HA of activated olefins with amines was carried out in a 50 mL two necked flask equipped with a nitrogen inlet for maintaining an inert atmosphere and an additional port with a septum for withdrawal of the product. The temperature of the reaction vessel was maintained using an oil bath. The reaction was carried out under selected reaction conditions, that is, the reaction temperature of 383 K with *p*-ethylaniline to EA molar ratio of 1 and with 10 wt% of the catalyst (total reaction mixture). The catalysts were activated at 773 K in air for 4 h with a flow rate of 50 mLmin⁻¹ and cooled to room temperature prior to their use in the reaction mixture was magnetically stirred and heated to the required temperature under atmospheric pressure. Samples were analyzed using a gas chromatograph (HP-6890) equipped with an FID detector and a capillary column (30 m) with

cross-linked 5% diphenyl-95% dimethylpolysiloxane. The products were also identified by GC-MS (HP-5973) equipped with an identical column and a mass detector. Conversion of the various reactions conducted using the catalysts was calculated based on amines. The reaction mixture was cooled to room temperature after the completion of the reaction and filtered to remove the catalyst whereas the solvent was removed by distillation. The product was separated by column chromatography using neutral alumina as the stationary phase and petroleum ether/ethyl acetate (95:5) as the eluent and characterized.

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