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Gold Nanoparticles Supported on Imidazole Modified Bentonite: Environmentally Benign Heterogeneous Catalyst for A3 Synthesis of Propargylamines in Water

Mohammad Gholinejad,*[a,b] Reza Bonyasi,[c] Carmen Najera,*[d] Fariba Saadati,[c] Maedeh Bahrami,[a] Neda Dasvarz[a]

Abstract: Gold nanoparticles supported on imidazole modified bentonite, Bent@Im@Au NPs, has been developed for the first time as an effective heterogeneous catalyst for the synthesis of propargylamines under mild reaction conditions in water with using 0.07 mol% of Au. Various techniques such as X-ray diffraction, high resolution transmission electron microscopy, Fourier-transform infrared spectroscopy and element mapping by scanning electron microscopy were used to determine the physicochemical properties of the catalysts. The new gold catalyst was found to be highly active towards achieving the high to excellent yield of the A3 coupling products via the reactions of various electron withdrawing as well as electron donating aldehydes with different amines and alkynes. The catalysts can be easily recovered and reused without a significant loss of activity and the reused catalyst was characterized.

Introduction

Propargylamines are important units in biologically active intermediates in the production of pharmaceuticals and natural products.[1] For example propargylamines moieties have applications in the synthesis of anti-Alzheimer, anti-Parkinson, and anti-depressant drugs.[2] Traditional methods for the synthesis of propargylamines include reaction of stoichiometric amounts of lithium or magnesium acetylides with imines[3] and reaction of only few commercially available propargyl halides with amines.[4] However, these methods require highly dry solvents, inert atmosphere and the use of stoichiometric amounts of organometallic reagents which inhibit the application of these methods in large scale operations.[5]

In recent years, multicomponent reactions (MCRs) receive increasing attention since they provide easy and rapid access to large group of organic compounds with diverse substitution patterns.[6] One of the best examples of MCRs which reduce waste and increase safety, is the catalytic coupling reaction of aldehydes, amines and terminal alkynes (A3 coupling) *via* C—H activation of alkynes for the synthesis of propargylamines.[7] Recently, many transition-metal catalysts such as Ir,[8] Ag,[9] Cu,[7] a Cu–Ru bimetallic system,[9] Fe,[11] Zn,[12] and In [13] have been suggested as new catalysts for the preparation of propargylamines. Because of the well-recognized catalytic properties of gold(I) and (III) in recent years, gold based catalysts are recognized as efficient catalysts in various organic transformations.14 One of the most interesting studied applications of gold catalysts was in A3 coupling reaction via gold activation of the sp C-H bond.15 Along this line, in recent years different various gold catalysts have been introduced for A3 coupling reaction under homogeneous conditions.[16] In spite of the high price of gold and problem of recycling of homogeneous catalysts, less examples of heterogeneous recyclable gold catalysts have been described for A3 coupling reaction.[17,18]

Selection of support and suitable functionalization are important factors for design of efficient heterogeneous catalysts. Different organic and inorganic materials such as polymers, magnetic and silica based compound were used for stabilization of metal nanoparticles. Clay minerals having different properties such as mechanical and thermal stability, high surface area and ion exchange capacity, and economical price are promising supports for the preparation heterogeneous catalysts.[19] Among the different clay minerals, bentonite is a naturally occurring materials which is formed by volcanic ash. Bentonite comprises mainly of crystalline clay minerals belonging to the smectite group, which are hydrous aluminum silicates containing Fe, Mg, Na, and Ca elements.[20] Recently, surface modifications of clay with new ligands have received considerable attention because it allows the formation of new organo-clays with desired properties.[21] Along this line bentonite-supported catalysts have been applied to several types of organic reactions.[22] However to date very limited bentonite-supported gold catalysts have been essayed in organic reactions[23] and there is no report dealing with bentonite-supported gold catalyst applied in A3 coupling reaction.

Herein, we report for the first time a novel gold nanoparticle supported on poly imidazole modified bentonite is an efficient, simple and sustainable catalyst in the three-component coupling reaction of aldehydes, amines and terminal alkynes at low catalyst loading and under mild reaction conditions in water.

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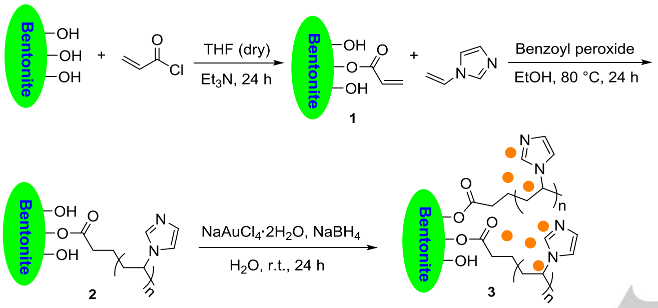
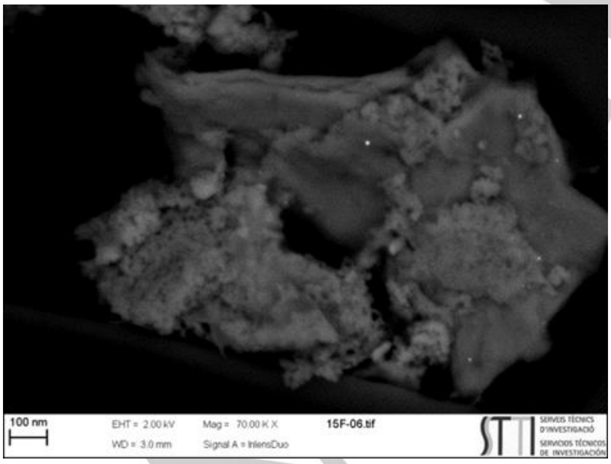
Results and Discussion

For the preparation of bentonite-supported gold nanoparticles (NPs), bentonite was allowed to react with acryloyl chloride in dry THF. The successful attachment of acryloyl was pursued through FTIR spectroscopy showing the carbonyl stretching bond at 1735 cm^{-1} (Figure 1 in supporting information). In the next step, the resulting solid **1** was treated with vinylimidazole in the presence of benzoyl peroxide as initiator. Finally to the bentonite modified polyimidazole **2** was added $NaAuCl_4{\cdot}2H_2O$ and $NaBH_4$ in water. The obtained new gold composite **3** is referred as Bent@Im@Au NPs through the text. Content of nitrogen and gold have been determined by elemental analysis and atomic absorption spectroscopy to be 1.1 and 0.02 mmol/g, respectively.



Scheme 1. Preparation of Bent@Im@Au NPs.

Field emission scanning electron microscopy (FESEM) images of Bent@Im@Au showed presence of gold nanoparticles (bright points) stabilized on sheets of bentonite (Figure 1).



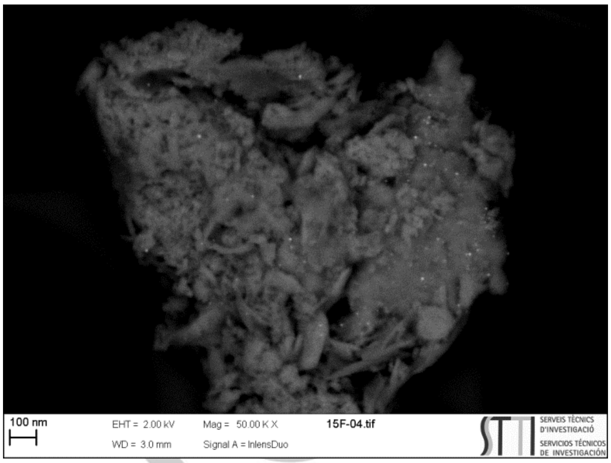


Figure 1. FESEM images of Bent@Im@Au.

EDX-map analysis of Bent@Im@Au showed the presence of highly uniform and dispersed Au as well as N and C species in the structure (Figure 2 in supporting information). Also, total map image of the Bent@Im@Au showed that the Au nanoparticles are located very uniformly without any agglomeration (Figure 3 in supporting information). In addition, the presence of different elements such as C, N, O, Mg, Ca, Na, Al, Si, and Au was proved in the structure (Figure 4, supporting information). High-Resolution Transmission Electron Microscopy (HRTEM) images from Bent@Im@Au showed small and uniform Au NPs in around 1-2 nm size which are stabilized in the solid surface (Figure. 2).

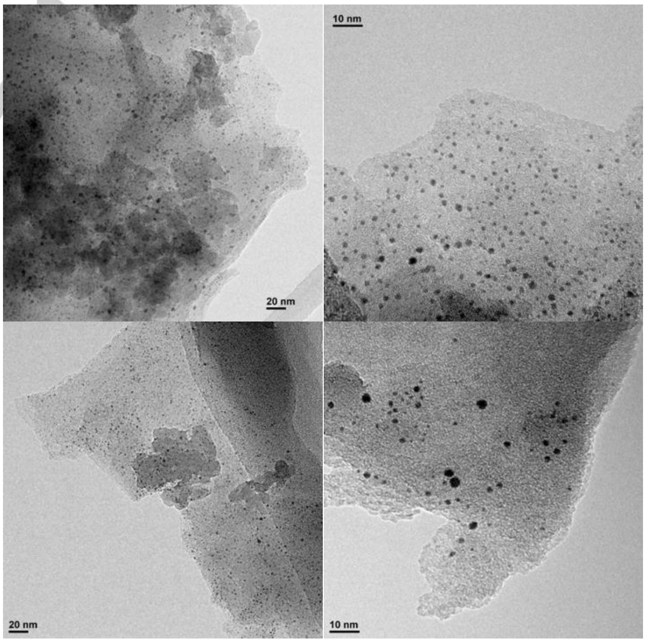


Figure 2. TEM images of Bent@Im@Au in different magnification

X-ray powder diffraction (XRD) of Bent@Im@Au was also studied (Figure 5 in the Supporting Information). However, due to low loading weight of Au on the support and also the overlap of bentonite peaks [22z,24] with Au NPs, this diffractogram did not show any significant peaks for Au NPs. Therefore we studied X-ray photoelectron spectroscopy (XPS) of Bent@Im@Au for Na, Ca, Al, N, Si, and Au elements. XPS spectrum in Na 1s confirms the presence of Na(I) in the structure of bentonite by showing a peak at 1072.5 eV (Figure 3a).[25] XPS study in the Ca 2p region showed a doublet peak centered at 347.1 and 351.1 eV related to the Ca(II) in the solid structure (Figure 3b).[26] The core-level photoelectron spectrum of Al 2p between 72-76 eV was deconvoluted into two main peaks at 74.2 and 74.70 eV, which are related to Al(III) in Al-OH and Al_2O_3 forms (Figure 3c).[27] The binding energy (BE) value of Si 2p in silanol (Si-OH) and silicone oxygen (Si-O) bond appeared at 102.4 and 103.1eV, respectively (Figure 3d).[27a] In order to confirm the presence of the imidazole group, XPS analysis for N1s region was studied indicating the presence of two peaks at 398.9 and 401.05 eV which can be attributed to the C=N and C–N bonds of the imidazole (Figure 3e).[28] Finally the XPS spectrum in the Au 4f region showed two intense doublets at 83.4 and 87.2 eV corresponding to Au(0) and 85.1 and 88.6 eV related to Au(I) species (Figure 3f). These results confirm that during the final catalyst preparation step most of ionic Au was successfully reduced to metallic form.

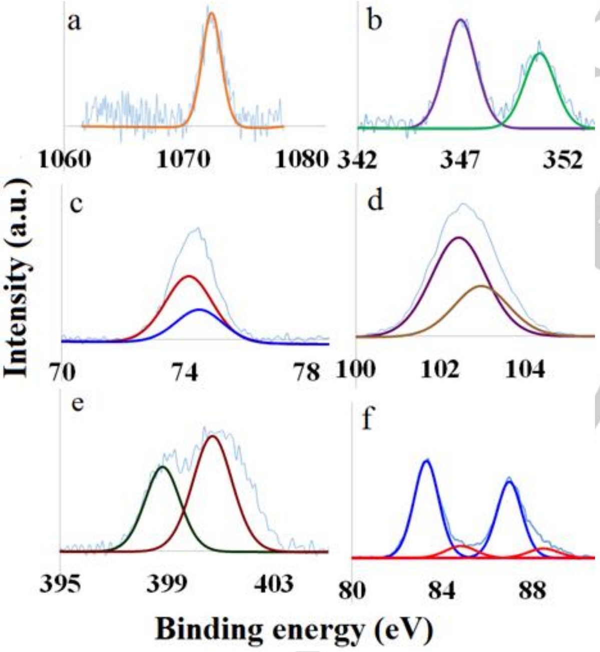
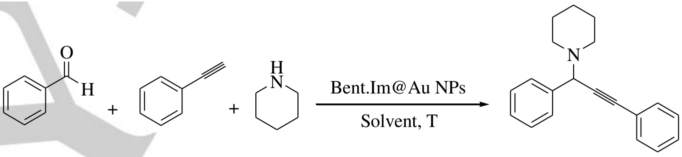


Figure 3. XPS spectrum of Bent@Im@Au NPs (3) in a) Na1s, b) Ca 2p, c) Al2p, d) Si2p, e) N1s and Au 4f regions.

The catalytic activity of Bent@Im@Au NPs was examined in the three-component A3 reaction of amines, aldehydes and alkynes. For this purpose, initially reaction of benzaldehyde, piperidine and phenylacetylene was selected as model reaction to study the effect of different factors such as solvent, reaction temperature and catalyst amount (Table 1). Using 0.07 mol% catalyst loading at 50 °C in different solvents such as CH_3CN, EtOH, THF, DMF, toluene, and H_2O gave high to quantitative yields for the reaction (Table 1, entries 1-6). For further optimization studies we selected water as the best green solvent and performed reaction using 0.07 and 0.05 mol% of catalyst **3**. Under these reaction conditions, 100 and 90% yield were obtained respectively (Table 1, entries 7 and 8). Therefore, we selected 0.07 mol% catalyst as the optimum amount. Also, using 0.07 mol% of catalyst and lowering the reaction time and temperature, gave lower yields for the reaction (Table 1, entries 9 and 10). It should be noted that reaction in the absence of gold using bentonite and imidazole functinalized bentonite (2) failed to proceed (Table 1, entries 11 and 12). Also reactions using bentonite supported Au before addition of $NaBH_4$ and bentonite supported Au reduced with hydrazine gave low yield (Table 1, entries 13 and 14).

Table 1. Optimization of the reaction conditions for the reaction of benzaldehyde, piperidine and phenylacetylene catalyzed by Bent@Im@Au[a]



Entry	Catalyst (mol%)	Solvent	Yield (%)[b]
1	0.1	CH_3CN	100
2	0.1	EtOH	95
3	0.1	THF	84
4	0.1	DMF	100
5	0.1	Toluene	100
6	0.1	H_2O	100
7	0.07	H_2O	100
8	0.05	H_2O	90
9	0.07	H_2O	61[c]
10	0.07	H_2O	52[d]
11	-	H_2O	0[e]
12	-	H_2O	0[f]
13	0.07	H_2O	19[g]
14	0.07	H_2O	26[h]

[a]Reaction conditions: benzaldehyde (1 mmol), piperidine (1.5 mmol), phenylacetylene (1.5 mmol) and solvent (2 mL) for 1 d.

[b] Isolated crude yields determined by 1H NMR.

[c] Reaction performed during 12 h.

[d] Reaction performed at 25 °C

[e] Reaction using 35 mg bentonite as catalyst

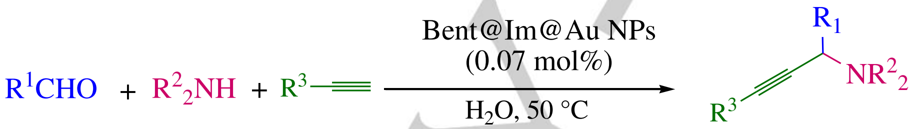
[f] Reaction using 35 mg (3) as catalyst

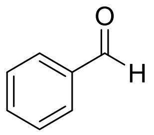
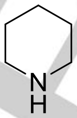
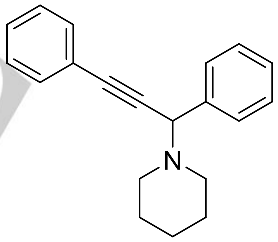
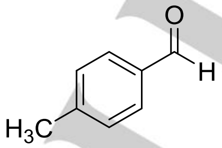
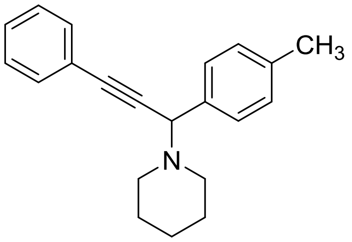
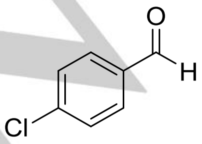
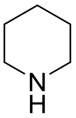
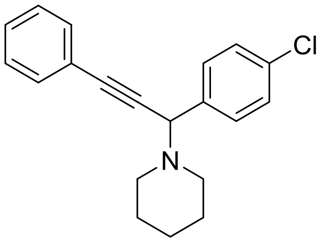
[g] Reaction using bentonite supported Au (0.07 mol%) without reducing agent

[h] Reaction using bentonite supported Au (0.07 mol%) with hydrazine as reducing agent.

Having the optimized reaction conditions in hand, reactions of various aldehydes with secondary amines and alkynes were studied (Table 2). The obtained results indicated that the reactions of different aromatic aldehydes containing electron-donating and -releasing groups such as Cl, Br and Me as well as 1-naphtaldehyde and biphenyl-4-carboxaldehyde with piperidine and phenylacetylene proceed effectively and the corresponding propargylamines were obtained in high to excellent isolated yields (Table 2, entries 1-10). Reaction of 3-thiophenecarbaldehyde as heterocyclic aldehyde took place well without poisoning or deactivation of the catalyst (Table 2, entry 11). Furthermore, reaction of aromatic and aliphatic aldehydes with other secondary amines such as morpholine, pyrrolidine and dimethylamine occurred efficiently affording the corresponding propargylamines in high to excellent yields (Table 2, entries 12-19). It should be noted reaction of pentanal and heptanal as aliphatic aldehydes with morpholine or piperidine and phenylacetylene performed effectively and desired products obtained in 81 and 89% isolated yields respectively (Table 2, entries 20 and 21). Furthermore reaction of 1-octyne as aliphatic alkyne with benzaldehyde and piperidine proceed well and the corresponding product was obtained in 85% isolated yields (Table 2, entry 22).

Table 2. The reactions of different aldehydes, amines and alkynes in the presence of Bent@Im@Au as catalyst.[a]



Entry	R^1CHO	$R^2{}_2NH$	Product	Isolated yield [b]
1				92
2				90
3				93

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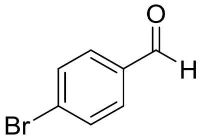
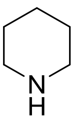
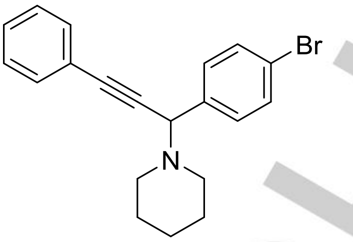
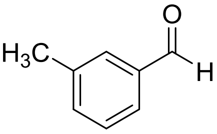
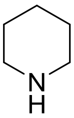
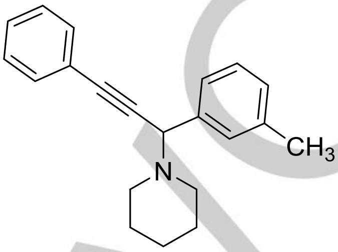
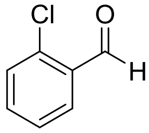
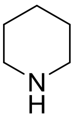
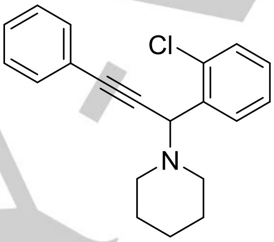
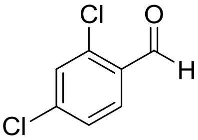
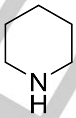
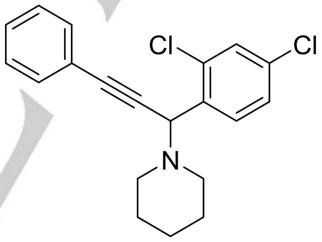
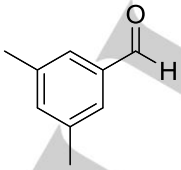
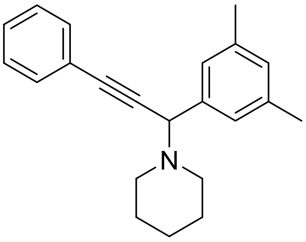
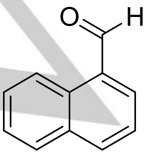
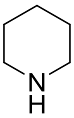
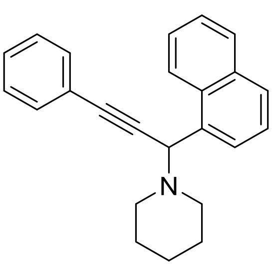
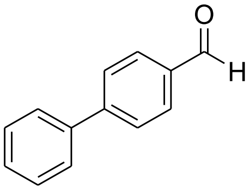
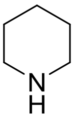
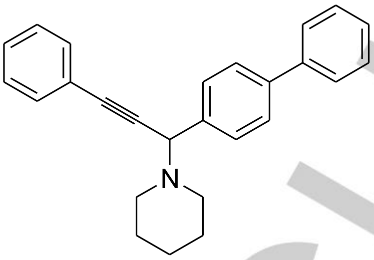
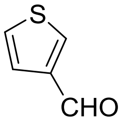
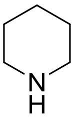
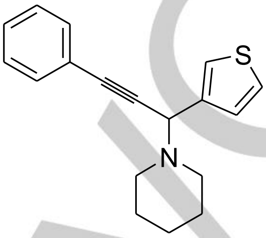
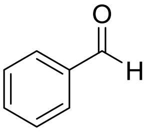
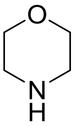
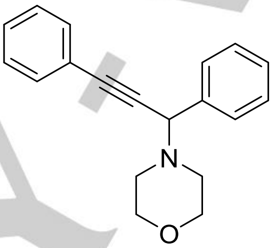
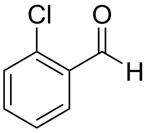
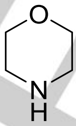
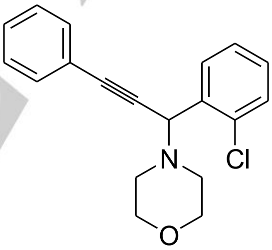
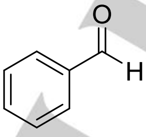
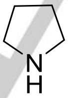
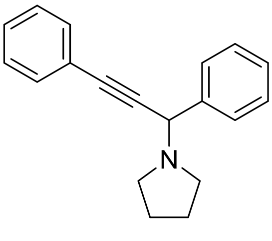
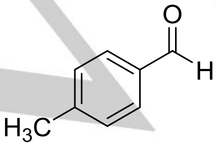
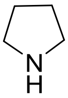
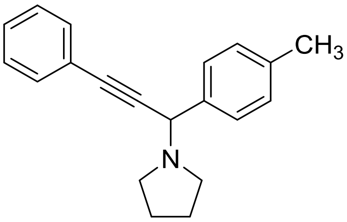
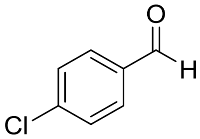
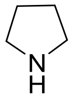
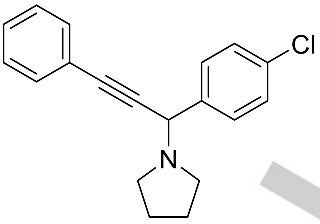
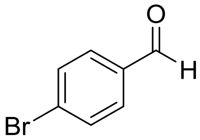
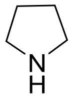
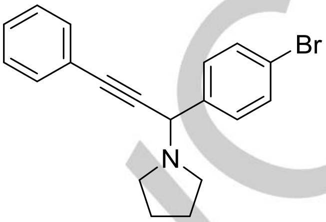
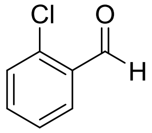
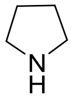
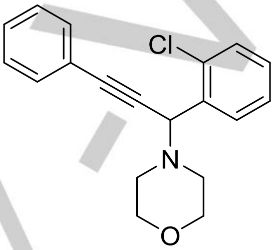
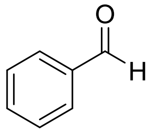
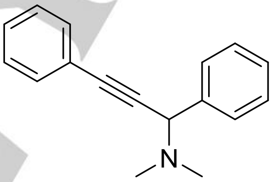
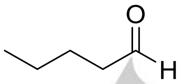
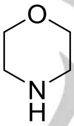
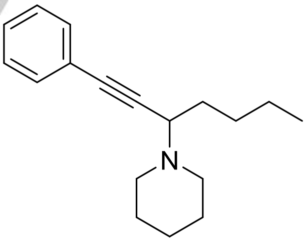
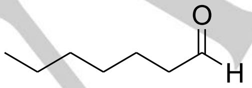
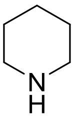
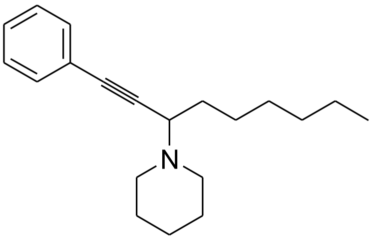
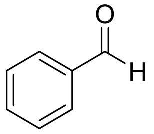
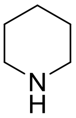
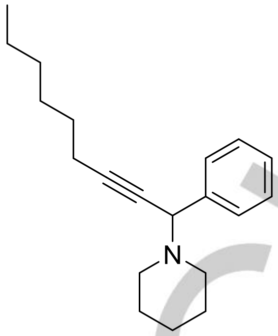
4				84
5				90
6				89
7				84[c]
8				85
9				81[d]

10				90
11				82
12				88
13				84[c]
14				90
15				88[c]

16				87
17				82[c]
18				83[c]
19		$HN(CH_3)_2$		94
20				81
21				89

22				85

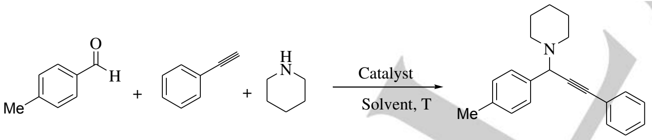
[a] Reaction conditions: aldehyde (1 mmol), amine (1.5 mmol), alkyne (1.5 mmol), H_2O (2 mL), catalyst (35 mg, containing 0.07 mol% Au), and during 1 d.

[b] Isolated yields after column chromatography.

[c] Reaction timeIs 30 h

Comparison catalytic activity of Bent@Im@Au catalyst with othersupported gold catalyst in A3 coupling reaction of 4-methylbenzaldehyde, piperidine and phenylacetylene as a common substrate (Table 3), showed overall efficiency of the presented catalyst (Bent@Im@Au). Also, It should be noted that in compared to our previous reports regarding A3 coupling reaction,[7b,17i,18f-g] novel Bent@Im@Au catalysed reactions under mild and greener reaction conditions (50 °C in water). Briefly, the advantages of the catalyst are described below. 1) Bentonite was modified for the first time with poly imidazole with very simple methode; 2) Poly imidazole modified bentonite was used for the stabilization of gold NPs; 3) The new material was used for the first time as the catalyst in A3 coupling reaction; 4) In comapred to other previous Au catalysts and our reported Au or Cu catalysts, reactions proceed efficiently under mild reaction conditions in water.

Table 3. Comparison catalytic activity of Bent@Im@Au with other reported Au catalysts in A3 coupling reaction



Catalyst	T(°C)/t(h)	Solvent	Au mol%	Yield
$Au_{38}(SC_2H_4Ph)_{24}$[16l]	80/5	Solvent-free	0.01	84
Au@PMO-IL[17i]	60/11	$CHCl_3$	0.2	88
NAP-Mg-Au(0)[17f]	100/24	Toluene	0.04	81
MNP@PILAu[18a]	60/18	H_2O	1	95
Au NPs[17n]	75/12	CH_3CN	10	83
$Au_{25}(PET)_{18}$[18d]	80/24	Toluene	0.1	89
Au@HS-MCM[18e]	80/24	H_2O	2	75
IRMOF-3-LA-Au[18h]	80/7	1,4-dioxane	1.7	54
Au@MIL-101[18j]	120/4	1,4-dioxane	-	5.7[a]
NP@Au/NNN-pincer[18k]	85/8	H_2O	0.07	83
Fe_3O_4@Au[18l]	100/24	Toluene	10	63
Bent@Im@Au	50/24	H_2O	0.07	90

[a] 60 mg catalyst containing 4.96 wt% gold

Since the recovering and reusing of heterogeneous catalysts are very important aspects for sustainable chemistry and economical stand points, we studied recycling of the catalyst in the model reaction of benzaldehyde, piperidine and phenylacetylene under optimized reaction conditions. For this purpose, in each run after 24 h, catalyst was separated by centrifugation and after washing with ethyl acetate and drying was used in another reaction batch. Results showed this catalyst **3** was recyclable for 7 runs with small decrease in activity (Figure 4).

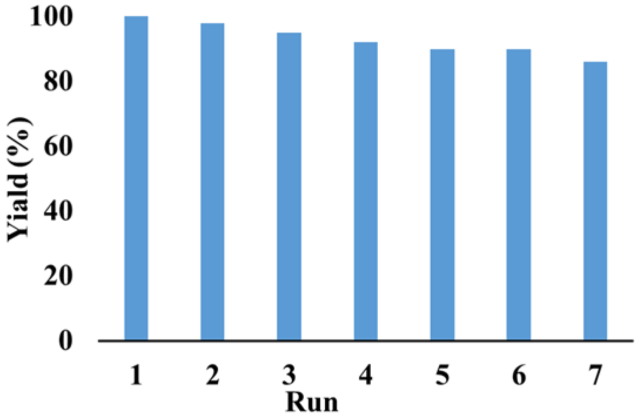


Figure 4 Recycling of the catalyst for the reaction of benzaldehyde, piperidine and phenylacetylene.

FESEM mages of the reused catalyst after 7 runs showed very similar pattern to fresh catalyst (Figure 5). However, TEM images of reused catalyst after 7 runs showed presence of mostly uniform nanoparticles and sligtly aggrigate form. (Figure 6).

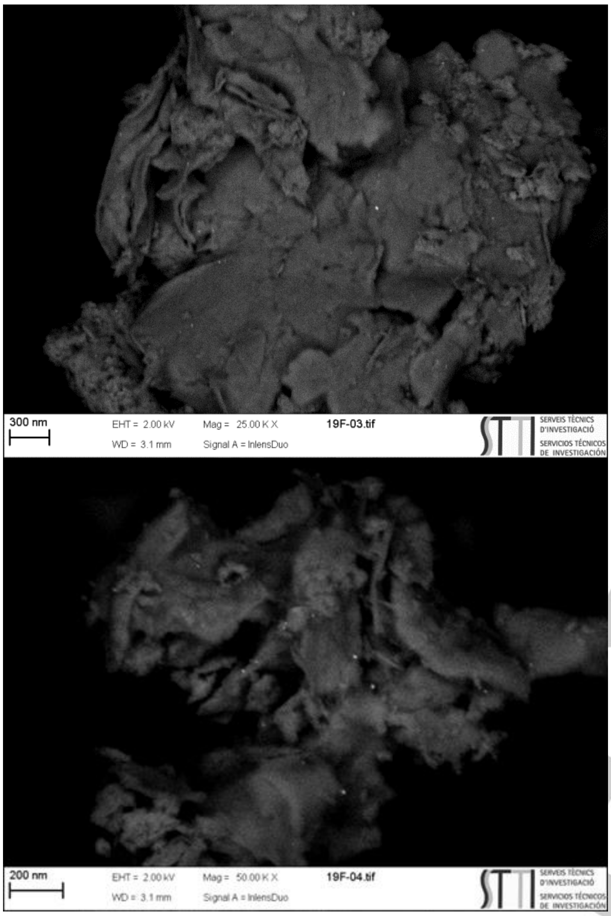


Figure 5 FESEM images of reused catalyst after 7 runs.

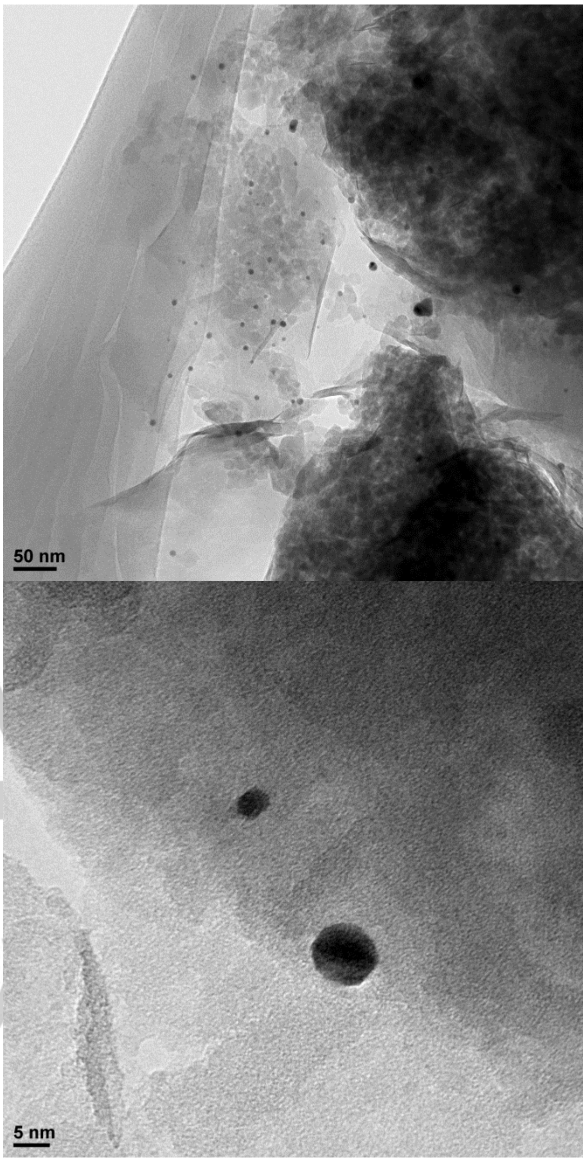


Figure 6 TEM images of reused catalyst after 7 runs.

In addition, XPS analysis of the reused catalyst showed stability and the presence of imidazole group in the structure. On the other hand, the XPS spectrum in the Au 4f region indicates the presence of Au(0) as a sole species in the reused catalyst structure, it means that during the A3 reaction all of the ionic Au species were reduced to Au(0) (Figure 7). Atomic absorption spectroscopy of the reused catalyst after seven runs showed the amount of leaching of Au was 2.7%.

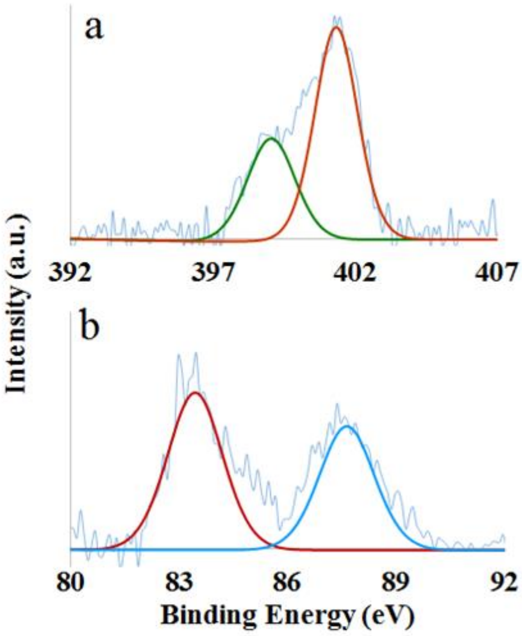


Figure 7 XPS analysis of reused catalyst after 7 runs a) N1S and b) Au 4f regions.

Conclusions

The new bentonite supported Au catalyst, Bent@Im@Au, prepared by a very simple method and characterized by different techniques. The catalyst showed good activity in synthesis of propargylamines via A3 coupling reaction in water at 50 °C. Both aromatic and aliphatic aldehydes and alkynes were reacted effectively with different amines. Using centrifuge separation, catalyst was recovered and reused for seven consecutive runs with small decrease of activity.

Experimental Section

General

All chemicals were purchased from Sigma-Aldrich, Acros, and Merck companies and were used without further purification. All ^1H and ^{13}C NMR were recorded on a Bruker 400 and 250 MHz spectrometer at 400 MHz and 62.5 MHz, respectively. Chemical shifts were given as δ values with reference to tetramethylsilane (TMS) as the internal standard. FT-IR spectra were recorded on a Bruker Vector 22. Transmission electron microscopy (TEM) was performed by JEOL JEM-2010 instrument. Scanning electron microscopy (SEM) was performed by Hitachi S3000N. Energy dispersive X-ray analysis (EDX) results were obtained using Carl Zeiss Sigma instrument. The content of gold in the catalyst was determined using Varian atomic absorption spectrometry. X-Ray diffraction was performed using Bruker D8-Advance.

Preparation of polyimidazole functionalized bentonite (2)

In a 25 mL flask, bentonite (1 g) was sonicated in THF (15 mL) for 10 min. Then, acryloyl chloride (10 mmol, 0.8 mL) and Et_3N (15 mmol, 2.1 mL) were added at 0 °C under argon atmosphere. Then the mixture was stirred for 24 h at room temperature and was subjected to centrifugation. The obtained isolated solid was washed with distilled water (2×15 mL) and ethanol (2×15 mL) and then dried in an oven at 70 °C giving product 1. For introducing the imidazole group, product 1 (1 g) was dissolved in EtOH (20 mL) and the mixture was deoxygenated by bubbling argon for 5 min. Then, *N*-vinilimidazole (10 mmol, 0.9 mL) and benzoyl peroxide (8 mg) were added and the mixture was stirred at 80 °C for 24 h. The resulting suspension was centrifuged and the resulting solid (2) was washed with water (15 mL) and ethyl acetate (3×15 mL) and dried at 60 ºC.

Preparation of Bent@Im@Au NPs (3)

$NaAuCl_4\cdot 2H_2O$ (0.03 mmol, 12 mg) was dissolved in H_2O (1 mL) and bentonite (800 mg), which was previously sonicated in H_2O (10 mL), was added. Then, an aqueous solution of $NaBH_4$ (0.3 mmol, 11 mg in 1 mL water) was added slowly and the mixture was stirred for 24 h at room temperature under argon atmosphere. The resulting solid was separated with centrifugation, and washed with water (3×10 mL) and ethyl acetate (3×10 mL) and finally dried at 60 °C. Atomic absorption spectroscopy analysis indicated that the Au content 0.55 wt (0.02 mmol/g).

General procedure for the synthesis of propargylamines

To a 5 mL flask, the catalyst (35 mg, containing 0.07 mol% Au), aldehyde (1 mmol), amine (1.5 mmol), phenylacetylene (1.5 mmol) and H_2O (2 mL) were added and the mixture was stirred at 50 °C for 24 h. After the complication of reaction, the crude products were extracted using ethyl acetate (4×5 mL). Further purification was performed by column chromatography on silica gel using hexane and ethyl acetate as eluent. All products were characterized by ^1H NMR and ^{13}C NMR.

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Keywords: Bentonite • Gold• A3 coupling • Water • Heterogeneous

[1] A. P. Kozikowski, *J. Med. Chem.* **2000**, 43, 2064–2071; b) A. Kochman, J. Skolimowski, L. Gêbicka, D. Metodiewa, *Pol. J. Pharmacol.* **2003**, 55, 389–400; c) B. Jiang, M. Xu, *Angew. Chem. Int. Ed.* **2004**, 43, 2543–2546; d) J. J. Fleming, J. D. Bois, *J. Am. Chem. Soc.* **2006**, 128, 3926–3927; e) K. Lauder, A. Toscani, N. Scalacci, D. Castagnolo, *Chem. Rev.* **2017**, 117, 14091–14200.

[2] a) M. Naoi, W. Maruyama, M. Shamoto-Nagai, H. Yi, Y. Akao, M. Tanaka, *Mol. Neurobiol.* **2005**, 31, 81–93; b) J. J. Chen, D. M. Swope, K.

Dashtipour, *Clin.Ther.* **2007**, 29, 1825–1849; c) M. Baranyi, P. F. Porceddu, F. Gölöncsér, S. Kulcsár, L. Otrokocsi, Á. Kittel, A. Pinna, L. Frau, P. B. Huleatt, M. L. Khoo, C. L. L. Chai, P. Dunkel, P. Mátyus, M. Morelli, B. Sperlágh, *Mol. Neurodegener.* **2016**, 11, 6–26.

[3] a) R. Bloch, *Chem. Rev.* **1998**, 98, 1407–1438; b) V. V. Kouznetsov, L. Y. V. Mendez, *Synthesis*. **2008**, 491–506; c) G. Blay, A. Monleon, J. Pedro, *Curr. Org. Chem.* **2009**, 13, 1498–1539.

[4] I. E. Kopka, Z. A. Fataftah, M. W. Rathke, *J. Org. Chem.* **1980**, 45, 4616–4622.

[5] a) B. J. Wakefield, *Academic Press*, London, **1988**, p 32; M. Umeno, A. Suzuki, *Handbook of Grignard Reagent*, (Eds.: G. S. Silvermanand, P. E. Rakita), Dekker, New York, Vol. 64, p 645; b) R. Bloch, *Chem. Rev.* **1998**, 98, 1407–1438; c) V. V. Kouznetsov, L. Y. V. Mendez, *Synthesis* **2008**, 2008, 491–506.

[6] a) A. Dömling, W. Wang, K. Wang, *Chem. Rev.* **2012**, 112, 3083–3135; b) M. Haji, *Beilstein J. Org. Chem.* **2016**, 12, 1269–1301; c) J. P. Wan, L. Gana, Y. Liu, *Org. Biomol. Chem.* **2017**, 15, 9031-9043.

[7] a) H. Naeimi, M. Moradian, *Appl. Catal., A*. **2013**, 467, 400–406; b) M. Gholinejad, B. Karimi, A. Aminianfar, and M. Khorasani, *ChemPlusChem* **2015**, 80, 1573–1579; c) M. Varyani, P. K. Khatri, S. L. Jain, *Catal. Commun.* **2016**, 77, 113–117; d) J. Rosales, J. M. Garcia, E. Ávila, T. González, D. S. Coll, E. O. Mavárez, *Inorg. Chim. Acta.* **2017**, 467, 155–162; e) J. R. Cammarata, R. Rivera, F. Fuentes, Y. Otero, E. O. Mavárez, A. Arce, J. M. Garcia, *Tetrahedron Lett.* **2017**, 58, 4078–4081; f) V. S. Kashid, M. S. Balakrishna, *Catal. Commun.* **2018**, 103, 78–82.

[8] S. Sakaguchi, T. Kubo, Y. Ishii, *Angew. Chem. Int. Ed.* **2001**, 113, 2602–2604.

[9] a) S. J. Borah, D. K. Das, *Catal. Lett.* **2016**, 146, 656–665; b) N. Salam, S. K. Kundu, R. A. Molla, P. Mondal, A. Bhaumik, S. M. Islam, *RSC Adv.* **2014**, *4*, 47593.

[10] E. Ryaná Bonfield, *Org. Biomol. Chem.* **2007**, 5, 435–437.

[11] R. K. Sharma, S. Sharma, G. Gaba, *RSC Adv.* **2014**, 4, 49198–49211.

[12] M. Periasamy, P. O. Reddy, A. Edukondalu, M. Dalai, L. M. Alakonda, B. Udaykumar, *Eur. J. Org. Chem.* **2014**, 2014, 6067–6076.

[13] M. Rahman, A. K. Bagdi, A. Majee, A. Hajra, *Tetrahedron Lett.* **2011**, 52, 4437–4439.

[14] a) R. Dorel, A. M. Echavarren, *Chem. Rev.* **2015**, 115, 9028–9072; b) K. Sugimoto, Y. Matsuya, *Tetrahedron Lett.* **2017**, 58, 4420-4426; c) F. Gao, Y. Zhou, H. Liu, *Curr. Org. Chem.* **2017**, 21, 1530–1566.

[15] C. Wei, C. J. Li, *J. Am. Chem. Soc.* **2003**, 125, 9584–9585.

[16] a) V. K. Lo, Y. Y. Liu, M. K. Wong, C. M. Che, *Org. Lett.* **2006**, 8, 1529–1532; b) J. S. Yadav, B. V. S. Reddy, N. N. Yadav, M. K. Gupta, B. Sridhar, *J. Org. Chem.* **2008**, 73, 6857–6859; c) V. K. Y. Lo, K. K. Y. Kung, M. K. Wong, C. M. Che, *J. Organomet. Chem.* **2009**, 694, 583–591; d) B. T. Elie, C. Levine, I. Ubarretxena-Belandia, A. Varela-Ramírez, R. J. Aguilera, R. Ovalle, M. Contel, *Eur. J. Inorg. Chem.* **2009**, 2009, 3421–3430; (e) Q. Zhang, M. Cheng, X. Hu, B. G. Li, J. X. Ji, *J. Am. Chem. Soc.* **2010**, 132, 7256–7257; f) Y. Suzuki, S. Naoe, S. Oishi, N. Fujii, H. Ohno, *Org. Lett.* **2012**, 14, 326–329; g) J. Li, L. Liu, D. Ding, J. Sun, Y. Ji, J. Dong, *Org. Lett.* **2013**, 15, 2884–2887; h) B. J. Borah, S. J. Borah, D. K. Dutta, *J. Nanosci. Nanotechnol.* **2013**, 13, 5080-5087; i) V. Srinivas, M. Koketsu, *Tetrahedron* **2013**, 69, 8025–8033; j) G. A. Price, A. K. Brisdon, K. R. Flower, R. G. Pritchard, P. Quayle, *Tetrahedron Lett.* **2014**, 55, 151–154; k) J. Li, H. Wang, J. Sun, Y. Yang, L. Liu, *Org. Biomol. Chem.* **2014**, 12, 2523–2527; l) Q. Li, A. Das, S. Wang, Y. Chen, R. Jin, *Chem. Commun.* **2016**, 52, 14298–14301; m) E. Belmonte-Sánchez, M. J. Iglesias, H. el Hajjouji, L. Roces, S. García-Granda, P. Villuendas, F. López Ortiz, *Organometllic* **2017**, 36, 1962–1973.

[17] a) M. L. Kantam, B. V. Prakash, C. R. V. Reddy, B. Sreedhar, *Synlett* **2005**, 2005, 2329–2332; b) M. Kidwai, V. Bansal, A. Kumar, S. Mozumdar, *Green Chem.* **2007**, 9, 742–745; c) X. Zhang, A. Corma, *Angew. Chem. Int. Ed.* **2008**, 120, 4430-4433; d) K. K. R. Datta, B. V. Reddy, K. Ariga, A. Vinu, *Angew.Chem. Int. Ed.* **2010**, 49, 5961–5965; e) L. Abahmane, J. M. Köhler, G. A. Groß, *Chem. Eur. J.* **2011**, 17, 3005–3010; f) K. Layek, R. Chakravarti, M. L. Kantam, H. M. and A. Vinu, *Green Chem.*, 2011, **13**, 2878; g) G. Villaverde, A. Corma, M. Iglesias, F. Sánchez, *ACS Catal.* **2012**, 2, 399–406; h) L. F. Bobadilla, T. Blasco, J. A. Odriozola, *Phys. Chem. Chem. Phys.* **2013**, 15, 16927–16934; i) B. Karimi, M. Gholinejad, M. Khorasani, *Chem. Commun.* **2012**, 48, 8961-8963; j) L. Lili, Z. Xin, R. Shumin, Y. Ying, D. Xiaoping, G. Jinsen, H. Jing, *RSC Adv.* **2014**, 4, 13093–13107; k) S. K. Movahed, N. F. Lehi, M. Dabiri, *RSC Adv.* **2014**, 4, 42155–42158; l) B. J. Borah, S. J. Borah, D. K. Dutta, K. Saikia, *Catal. Sci. Technol.* **2014**, 4, 4001-4009; m) A. Berrichi, R. Bachir, M. Benabdallah, N. Choukchou-Braham, *Tetrahedron Lett.* **2015**, 56, 1302–1306; n) M. Nasrollahzadeh, S. M. Sajadi, *RSC Adv.* **2015**, 5, 46240–46246; o) S. Shabbir, Y. Lee, H. Rhee, *J. Catal.* **2015**, 322, 104–108;

[18] a); Moghaddam, F. M.; Ayati, S. E.; Hosseini, S. H.; Pourjavadi, A. *RSC Adv.* **2015**, *5*, 34502 b) L. Liu, X. Tai, N. Zhang, Q. Meng, C. Xin, *React. Kinet. Mech. Catal.* **2016**, 119, 335–348; c) L. Liu, X. Tai, G. Yu, H. Guo, Q. Meng, *Chem. Res. Chin. Univ.* **2016**, 32, 443–450; d) Y. Adachi, H. Kawasaki, T. Nagata, Y. Obora, *Chem. Lett.* **2016**, 45, 1457–1459; e) A. Feiz, A. Bazgir, *Catal. Commun.* **2016**, 73, 88–92; f) M. Gholinejad, F. Saadati, S. Shaybanizadeh, *RSC Adv.* **2016**, 6, 4983–4991; g) M. Gholinejad, F. Hamed, C. Najera, *Synlett* **2016**, 27, 1193-1201; h) L. Liu, X. Tai, X. Zhou, C. Xin, Y. Yan, *Sci. Rep.* **2017**, 7, 12709–12718; i) X. B. Zhao, W. Ha, K. Jiang, J. Chen, J. L. Yang, Y. P. Shi, *Green Chem.* **2017**, 19, 1399–1406; j) L. Liu, X. Tai, X. Zhou, *Materials* **2017**, 10, 99–112; k) N. Zohreh, S. H. Hosseini, M. Jahani, M. S. Xaba, R. Meijboom, *J. Catal.* **2017**, 356, 255-268.; l) A. M. Munshi, M. Shi, S. P. Thomas, M. Saunders, M. A. Spackman, K. S. Iyer, and N. M. Smith, Dalton Trans., 2017,46, 5133-5137

[19] G. Nagendrappa, *Appl Clay Sci.* **2011**, 53, 106–138.

[20] a) J. W. Hosterman, S. H. Patterson, Bentonite and Fuller's earth resources of the United States, *Washington D.C.* USA **1992**; b) M. Moosavi, *Iran. J. Public Health* **2017**, 46, 1176–1183; c) D. D. Eisenhour, R. K. Brown, *Elements* **2009**, 5, 83-88.

[21] a) H. Firouzabadi, N. Iranpoor, A. Ghaderi, M. Gholinejad, S. Rahimi, S. Jokar, *RSC Adv.* **2014**, 4, 27674–27682; b) B. Narayanamoorthy, S. Balaji, *Appl. Clay Sci.* **2015**, 104, 66–73; c) Q. F. Li, Z. Liu, L. Jin, P. Yang, Z. Wang, *RSC Adv.* **2017**, 7, 44614–44618; d) Q. F. Li, L. Jin, L. Li, W. Ma, Z. Wang, J. Hao, *J. Mater. Chem. C* **2017**, 5, 4670–4676.

[22]a) H. Zhang, X. Peng, ^{Yuan}, L. *Asian J. Chem.* **2012**, 24, 3927–3928; b) W. Wang, H. Liu, G. Ding, P. Zhang, T. Wu, T. Jiang, B. Han, *ChemCatChem.* **2012**, 4, 1836–1843; c) N. Hamzah, N. M. Nordin, A. H. A. Nadzri, Y. A. Nik, M. B. Kassim, M. A. Yarmo, *Appl. Catal., A, General* **2012**, 419–420, 133–141; d) A. M. Sevim, R. Hojiyev, A. Gul, M. S. Celik, *Monatsh. Chem.* **2012**, 143, 385–400; e) W. Wang, H. Liu, T. Wu, P. Zhang, G. Ding, S. Liang, T. Jiang, B. Han, *J. Mol. Catal. A: Chem.* **2012**, 355, 174–179; f) G. T. Wei, C. Y. Fan, L.Y. Zhang, R. C. Ye, T. Y. Wei, Z. F. Tong, *Catal. Commun.* **2012**, 17, 184–188; g) R. J. Kalbasi, A. R. Massah, B. Daneshvarnejad, *Appl. Clay Sci.* **2012**, 55, 1–9; h) O. B. Ayodele, B. H. Hameed, *JIEC* **2013**, 19, 966-974; i) J. Z. Jin, N. B. Sun, *Asian J. Chem.* **2013**, 25, 4441-4443; j) K. Muzakky, Wijaya, I. Prayogo, *Int. J. Appl. Chem.* **2013**, 9, 243-252; k) G. Ding, W. Wang, T. Jiang, B. Han, *Green Chem.* **2013**, 15, 3396-3403; l) C. C. Yan, M. Li. Kai, Z. Yong. Hua, *Toxicol. Environ. Chem.* **2013**, 95, 747–756; m) J. G. Qu, N. N. Li, B. J. Liu, J. X. He, *Mater. Sci. Semicond. Process.* **2013**, 16, 99–105; (n) R. Zhang, G. Guo, Y. Gao, L. Wang, N. Zhang, J. Cai, *Mater. Lett.* **2013**, 113, 146–148; o) H. Faghihian, M. H. Mohammadi, *Appl. Surf. Sci.* **2013**, 264, 492– 499; p) A. Juan, L. Meleroa, F. Bautista, J. Iglesias, G. Moralesa, R. Sánchez-Vazquez, *Appl. Catal. B*, **2014**, 145, 197–204; q) G. E. Sataeva, N. M.

Daurenbek, M. K. Myrzakhmet, *J. Eng. Phys. Thermophys.* **2014**, 87, 686–690; r) A. M. Al-Sabagh, F. Z. Yehia, G. h. Eshaq, A. E. El Metwally, *Ind. Eng. Chem. Res.* **2015**, 54, 12474–12481; s) N. Belaidi, S. Bedrane, A. Choukchou-Braham, R. Bachir, *Appl. Clay Sci.* **2015**, 107, 14–20; t) Y. Gao, Y. Wang, H. Zhang, *Appl. Catal., B.* **2015**, 178, 29–36; u) R. Liu, X. Xia, X. Niu, G. Zhang, Y. Lu, R. Jiang, S. He, *Appl. Clay Sci.* **2015**, 105–106, 71–77; v) X. Lu, F. Gub, Q. Liu, J. Gao, Y. Liu, H. Li, L. Jia, G. Xu, Z. Zhong, F. Su, *Fuel Process. Technol.* **2015**, 135, 34–46; w) L. Rozic, B. Grbic, S. Petrovic, N. Radic, L. Damjanovic, Z. Vukovi, *Mater. Chem. Phys.* **2015**, 167, 42-48; x) Y. Jiang, X. Li, Z. Qin, H. Ji, *Chin. J. Chem. Eng.* **2016**, 24, 1195–1200; y) H. Gaffour, M. Mokhtari, *Res. Chem. Intermed.* **2016**, 42, 6025–6038; z) L. Yuan, *Pol. J. Environ. Stud.* **2017**, 26, 2355-2361; aa) V. M. Abbasov, H. C. Ibrahimov, G. S. Mukhtarova, M. I. Rustamov, E. Abdullayev, *Energy Fuels* **2017**, 31, 5840−5843; bb) Y. Jiang, T. Huang, Y. Xu, X. Li, Z. Qin, H. Ji, *Chem. Eng. Technol.* **2018**, 41, 175–181.

[23] a) M. Shahabinejad, G. Ghasemi, M. V. Martínez-Huerta, M. Ghiaci, *J. Mol. Catal. A: Chem.* **2015**, 406, 118–126; b) R. J. Maya, J. John, R. L. Varma, *Chem. Commun.* **2016**, 52, 10625–10628; c) P. K. Rastogi, D. K. Yadav, S. Pandey, V. Ganesan, P. K. Sonkar, R. J. Gupta, *Chem. Sci.* **2016**, 128, 349–356; d) R. J. Maya, S. Poulose, J. John, R. Luxmi Varma, *Adv. Synth. Catal.* **2017**, 359, 1177–1184.

[24] L. Zhirong, M. A. Uddin, S. Zhanxue, *Spectrochim. Acta A.* **2011**, 79, 1013–1016.

[25] Y. Zhang, L. Chen, J. J. Zhao, H. B. Chen, M. X. He, Y. P. Ni, J. Q. Zhai, X. L. Wang, Y. Z. Wang, *Polym. Chem.* **2014**, 5, 1982–1991.

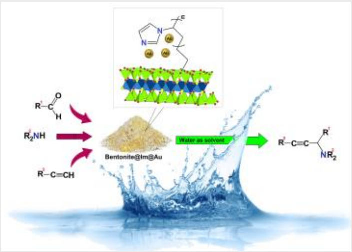
[26] Q. Liu, J. Li, Z. Zhou, J. Xie, J. Y. Lee, *Sci Rep.* **2016**, 6, 19593-19603.

[27] a) Y. Zhang, X. He, J. Ouyang, H. Yang, *Sci. Rep.* **2013**, 3, 2948-2954; b) V. Dalmoro, J. H. Z. dos Santos, I. M. Baibich, I. S. Butler, E. Armelin, C. Alemán, D. S. Azambuja, *Prog. Org. Coat.* **2015**, 80, 49–58.

[28] a) E. Mazzotta, S. Rella, A. Turco, C. Malitesta, *RSC Adv.* **2015**, 5, 83164–83186; b) Y. Zhang, Z. Xie, Z. Wang, X. Feng, Y. Wang, A. Wu, *Dalton Trans.* **2016**, 45, 12653–12660.

Layout 2:

FULL PAPER



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