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Molecular interactions between carbon nanotubes and ammonium ionic liquids and their catalysis properties

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ABSTRACT

A new catalytic method has been developed for the synthesis of aza/thia-Michael addition reactions of amines/thiols, which provide higher product yields. This catalyst is a combination of multi-walled carbon nanotubes (MWCNT) with triethylammonium hydrogen phosphate (TEAP) ionic liquid (IL), commonly referred to as bucky gel. In order to gain insight into the interactions involved between IL and MWCNT, we utilised Raman spectroscopy for our analysis. The interactions between MWCNT with TEAP were clearly evidenced by the increasing intensity ratios and spectral shift in the wavelength for the Raman D and G bands of MWCNT. The morphological studies of the resulting composite materials of TEAP and MWCNT (bucky gel) were carried out using scanning electron microscopy (SEM). The key advantage of using bucky gel as a catalyst is that higher product yield is obtained in reduced reaction time for Michael reactions.

1. Introduction

Ionic liquids (ILs) and carbon nanotubes (CNTs) represent very interesting class materials due to their unique properties and wide range of applications [1–16]. Recently, the interactions between carbon nanotubes and active materials such as inorganic metal oxides render the enhanced catalytic performance [17–20]. However, there has been significant curiosity to explore the properties and interactions of ILs with CNTs [21–27]. These bucky gels are found to be of great usage in chemical, physical and biological applications [26]. Fukushima et al. [21] were the first to report that imidazolium based ILs, such as 1-butyl-3-methylimidazolium tetrafluoroborate can form a gel called "bucky gels" by grinding them with single-walled carbon nanotubes (SWCNTs). Later, Wang et al. [28] studied the dispersion mechanism of SWCNTs in imidazolium-based ILs. In order to boost the applicability of bucky gel in organic reactions, we explored the Michael reactions. The Michael reaction has also been studied for more than one century [29]. It has been used extensively in the synthesis of pharmaceutical intermediates, peptide analogues, antibiotics, and other biologically active molecules and drugs [29–33]. Unfortunately, the reaction is suffering from many limitations, such as the use of expensive reagents, harsh conditions, etc. All these limitations enforced us to explore a new, more efficient catalyst with limited drawbacks. In light of the above considerations, we have explored the combination of IL (triethylammonium dihydrogen phosphate (TEAP)) and MWCNT as a catalyst system for organic reactions commonly known as bucky gel. We also examined the interactions between MWCNT and TEAP using Raman spectroscopy. We were further motivated to carry out morphological studies of the resulting composite materials of TEAP and MWCNT using scanning electron microscopy (SEM). In addition, the synthesis of aza/thia-Michael reaction products was carried out using this bucky gel as a catalyst system.

2. Materials and methods

2.1. Materials

CNTs were obtained from Sigma-Aldrich (USA). All the reagents used were of analytical grade. Melting points were determined using a Thomas Hoover melting point apparatus. ^{1}H (400 MHz) and ^{13}C (75 MHz) nuclear magnetic resonance (NMR) spectra were

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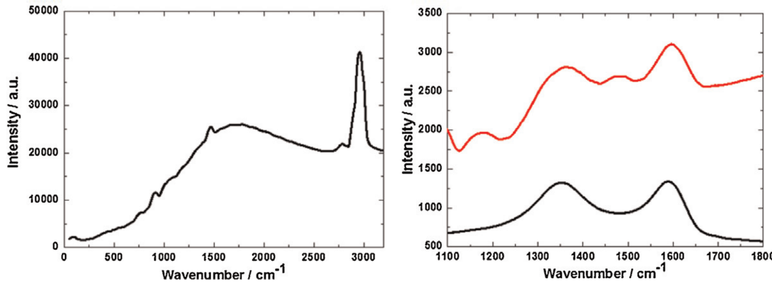


Fig. 1. Raman spectra of (a) TEAP IL, and (b) pure MWCNT (black) and MWCNT–TEAP (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.) Q2

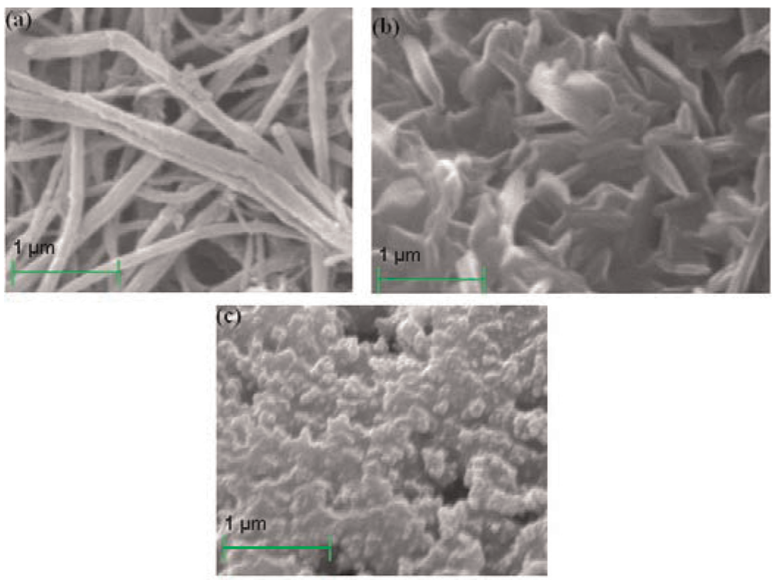
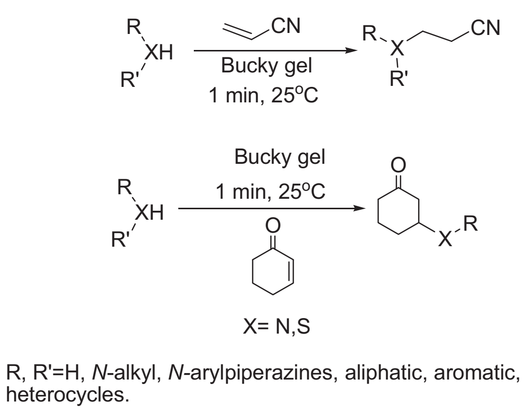


Fig. 2. SEM image of (a) pure MWCNT, (b) TEAP IL and (c) MWCNT–TEAP composite.

recorded on a Jeol 400 NMR spectrometer in $CDCl_3$ (with tetramethylsilane (TMS) for ^{1}H and chloroform-*d* for ^{13}C as internal references).

CNTs could be easily dispersed in the TEAP based room temperature IL by mechanical milling, forming a thermally stable bucky gel as discussed below [21,27,28].



Scheme 1. The conjugate addition of amines and thiols to α,β-unsaturated nitriles and carbonyl compounds using the bucky gel.

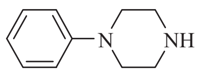
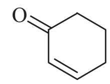
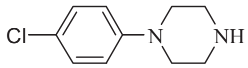
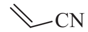
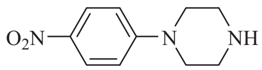
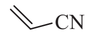
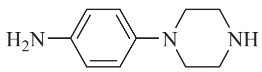
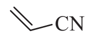
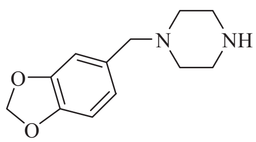
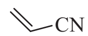
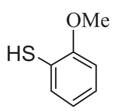
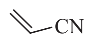
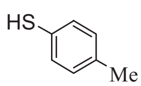
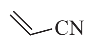
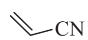
2.2. General procedure for the preparation for aza/thia-Michael reaction

A solution of 1 mmol amine/thiol and 1.2 mmol α,β-unsaturated nitriles or carbonyl compounds was added to bucky gel (0.1 mmol) and the mixture was stirred at 25 °C for 1 min. Likewise, the completion of the reaction was monitored using TLC. The product formed in the one-phase system, was further extracted with ether. In the same way as in the above preparation, the resulting organic phase extract was washed with a saturated solution of $NaHCO_3$, water, and dried over Na_2SO_4. After removal of the solvent, the residue was further purified by recrystallization or silica gel chromatography. The reaction products were then analyzed using ^{1}H and ^{13}C NMR spectroscopy.

Table 1
The Michael reaction in entry 1, Table 2 in the presence of bucky gel.

Entry	Catalyst	Temperature (°C)	Time for complete conversion	Yield (%)
1	No catalyst	25	24 hr	No product
2	MWCNT	25	24 hr	No product
4	TEAP	25	1 min	80
5	TEAP	25	24 hr	89
6	MWCNT–TEAP	25	1 min	98

Table 2
Michael reaction of products catalyzed by MWCNT–TEAP at room temperature as per Scheme 1. Q3

Entry	Amine/thiols		Michael acceptor time (min)	Yield (%)[a]
1			1	98
2			1	95
3			1	96
4			1	94
5			1	93
6			1	97
7			1	96
8	*n*-HS-$(CH_2)_7CH_3$		1	99

[a] Yields determined by GC analysis.

3. Results and discussion

Our present investigation has revealed a new catalyst system (bucky gel) for the synthesis of Michael reaction products. We have utilized the Raman spectroscopy to ascertain the interactions between TEAP and CNTs during the formation of bucky gel. Raman spectroscopy (Renishaw Raman spectroscopy, of 514 nm) proves to be a powerful tool for the structural characterization of CNTs. The Raman spectra of TEAP IL is as displayed in Fig. 1a and its comparison with that of MWCNT (black curve) and MWCNT–TEAP composite (red curve) is well exhibited in Fig. 1b. The curvature and the graphene like sheet character in the MWCNTs is better exemplified by the characteristic D and G bands of MWCNTs as depicted by all the curves. The Raman spectra clearly depicts that the D band shifts from 1357 to 1362 cm^{-1} and likewise the G band shifts from 1585 to 1597 cm^{-1} in case of MWCNT–TEAP composite. The significant shifts in the characteristic D and G bands in Raman spectra of MWCNT may be assigned due to the modifications in the surface characteristics of the MWCNT with the addition of TEAP. The 12 cm^{-1} shift in the G-band of MWCNT–TEAP composite is most likely due to the interaction of MWCNT with TEAP, which correlates very well with the studies done in the past [34].

To quantify the morphologies of the resulting MWCNT–TEAP composites, we used scanning electron microscopy (SEM) of Zeiss EVO 40 Company for further analysis. On comparing the SEM images of pure MWCNT morphology, TEAP and MWCNT–TEAP composite, was found to be quite distinct from each other (Fig. 2). Fig. 2c clearly illustrates that MWCNT is buried inside the TEAP. And, the SEM images strongly suggest that MWCNT–TEAP gel composites produce more flat film morphology with a smoother surface. We find these results to be in good agreement with the reported results [25,27].

In order to investigate the applicability of bucky gel in organic reactions, we have further explored Michael reactions. Further, to gain more insight into the effectiveness of this environment friendly catalyst (bucky gel) for C—N and C—S bond formation reactions, herein we report the conjugate addition of amines and thiols to α,β-unsaturated nitriles and carbonyl compounds using the bucky gel catalyst (Scheme 1). The standardized results are as represented in Table 1, which clearly indicate that the yield of the desired product increases with the addition of MWCNT–TEAP catalyst under solvent free conditions. However, it is hard to predict the actual mechanism for the increase in yield in the presence of MWCNT–TEAP, while this might be due to high surface to volume ratio [35] that helps the MWCNT–TEAP to increase the yield in short intervals of time. In the presence of TEAP after 24 h, yield increases up to the 89%, while in the presence of MWCNT–TEAP the yield increases up to 98% in 1 min. Similar results were obtained by Zhang and coworkers [20] depicting that CeO_2 nanoparticles can convert the NO up to 50%, while the pure

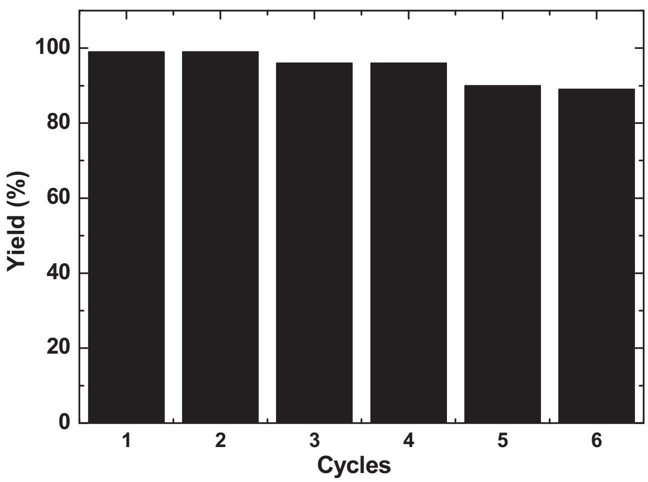


Fig. 3. Catalytic cycles *versus* yield for Michael reaction.

CNT had very low conversion rate. Whereas, in the presence of CeO_2 supported CNT the conversion of NO was found to be very high. Additionally, another group showed that the activity of the C—C bond coupling reaction in the presence of palladium nanoparticle supported CNT was very high as compared to the palladium supported activated carbon [36]. Therefore, we catalyzed the rest of the Michael addition of various substituted piperazines, aliphatic, aromatic amines, imidazoles, and thiols with α,β-unsaturated nitriles or carbonyl compounds in the presence of MWCNT–TEAP catalyst system. The results of the above reactions are schematically summarized in Table 2. We also observed the recyclability of bucky gel that shows that it will retain its yield up to six cycles in high yield, as shown in Fig. 3.

In conclusion, the interaction between MWCNT and TEAP results in a new catalyst system which is well documented as an accomplished catalyst for the synthesis of Michael reactions under solvent-free conditions. The use of this catalyst provides several advantages; (i) MWCNT–TEAP is a cost effective and environmentally benign reagent, (ii) green synthesis (avoiding hazardous and toxic organic solvents for work-up), (iii) applicability to a wide range of substituted aldehydes and (iv) mild temperature reaction condition. So, basically the type of MWCNT governs the catalytic efficiency of bucky gel. Hence, the MWCNT–TEAP catalyst provides a better product yield, simple reaction conditions, shorter reaction times, easy work-up and recyclability making it a green, easy and superior method for the synthesis.

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References

[1] S. Iijima, Nature 354 (1991) 56–58.
[2] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, Science 297 (2002) 787–792.
[3] P. Attri, P. Venkatesu, A. Kumar, Physical Chemistry Chemical Physics 13 (2011) 2788–2796.
[4] P. Attri, P. Venkatesu, T. Hofman, The Journal of Physical Chemistry B 115 (2011) 10086–10097.
[5] C. Chen, J. Zhang, F. Peng, D. Su, Materials Research Bulletin 48 (2013) 3218–3222.
[6] R. Atchudan, J. Joo, A. Pandurangan, Materials Research Bulletin 48 (2013) 2205–2212.
[7] S.S. Bhoware, M.S. Maubane, A. Shaikjee, I. Beas, A. Ziegler, N.J. Coville, Materials Research Bulletin 48 (2013) 2347–2350.
[8] C. Liu, H. Chen, K. Dai, A. Xue, H. Chen, Q. Huang, Materials Research Bulletin 48 (2013) 1499–1505.
[9] J. Luo, H.-J. Niu, H.-L. Wen, W.-J. Wu, P. Zhao, C. Wang, X.-D. Bai, W. Wang, Materials Research Bulletin 48 (2013) 988–994.
[10] X. Fu, H. Yang, K. He, Y. Zhang, J. Wu, Materials Research Bulletin 48 (2013) 487–494.
[11] D. Xue, K. Li, J. Liu, C. Sun, K. Chen, Materials Research Bulletin 47 (2012) 2838–2842.
[12] X. Li, Z. Xu, Materials Research Bulletin 47 (2012) 4383–4391.
[13] S.H. Kim, T.K. Lee, J.H. Jung, J.N. Park, J.B. Kim, S.H. Hur, Materials Research Bulletin 47 (2012) 2760–2764.
[14] S. Saipanya, T. Sarakonsri, P. Wongtap, Materials Research Bulletin 47 (2012) 2765–2766.
[15] S. Santangelo, M. Lanza, E. Piperopoulos, S. Galvagno, C. Milone, Materials Research Bulletin 47 (2012) 595–601.
[16] F.-J. Zhang, W.-C. Oh, K. Zhang, Materials Research Bulletin 47 (2012) 619–624.
[17] D. Zhang, L. Zhang, L. Shi, C. Fang, H. Li, R. Gao, L. Huang, J. Zhang, Nanoscale 5 (2013) 1127–1136.
[18] C. Fang, D. Zhang, S. Cai, L. Zhang, L. Huang, H. Li, P. Maitarad, L. Shi, R. Gao, J. Zhang, Nanoscale 5 (2013) 9199–9207.
[19] D. Zhang, L. Zhang, C. Fang, R. Gao, Y. Qian, L. Shi, J. Zhang, RSC Advances 3 (2013) 8811–8819.
[20] C. Fang, D. Zhang, L. Shi, R. Gao, H. Li, L. Ye, J. Zhang, Catalysis Science & Technology 3 (2013) 803–811.
[21] T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii, T. Aida, Science 300 (2003) 2072–2207.
[22] T. Fukushima, T. Aida, Chemistry – A European Journal 13 (2007) 5048–5058.
[23] M. Mohammadi, M. Foroutan, Physical Chemistry Chemical Physics 15 (2013) 2482–2494.
[24] Y. Chen, L. Bai, C. Zhou, J.-M. Lee, Y. Yang, Chemical Communications 47 (2011) 6452–6454.
[25] S.H. Hong, T.T. Tung, L.K.H. Trang, T.Y. Kim, K.S. Suh, Colloid and Polymer Science 288 (2010) 1013–1018.
[26] M.L. Polo-Luque, B.M. Simonet, M. Valcárcel, TrAC Trends in Analytical Chemistry 47 (2013) 99–110.
[27] M. Tunckol, J. Durand, P. Serp, Carbon 50 (2012) 4303–4334.
[28] J.Y. Wang, H.B. Chu, Y. Li, ACS Nano. 2 (2008) 2540–2546.
[29] Y.E. Ahmad, E. Laurent, P. Maillet, A. Talab, J.F. Teste, R. Dohkan, G. Tran, V. Ollivier, Journal of Medicinal Chemistry 40 (1997) 952–960.
[30] N. Azizi, M.R. Saidi, Tetrahedron 60 (2004) 383–387.
[31] A.K. Verma, P. Attri, V. Chopra, R.K. Tiwari, R. Chandra, Monatshefte fur Chemie 139 (2008) 1041–1047.
[32] M.R. Saidi, Y. Pourshojaei, F. Aryanasab, Synthetic Communications 39 (2009) 1109–1119.
[33] V.R. Choudhary, D.K. Dumbre, S.K. Patil, RSC Advances 2 (2012) 7061–7065.
[34] L. Zhao, Y. Li, Z. Liu, H. Shimizu, Chemistry of Materials 22 (2010) 5949–5956.
[35] X.R. Ye, Y. Lin, C.M. Wai, Chemical Communications (2003) 642–643.
[36] A. Corma, H. Garcia, A. Leyva, Journal of Molecular Catalysis A: Chemical 230 (2005) 97–105.

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