Journal of Materials Chemistry A



View Article Online

View Journal | View Issue

COMMUNICATION



Cite this: J. Mater. Chem. A, 2014, 2, 15726

Received 16th July 2014 Accepted 30th July 2014

DOI: 10.1039/c4ta03641g

www.rsc.org/MaterialsA

Preparation of silver-tungsten nanostructure materials for selective oxidation of toluene to benzaldehyde with hydrogen peroxide[†]

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We have developed a facile one-pot synthetic strategy to prepare Ag/WO₃ nanostructure materials with different morphologies using a cationic surfactant, cetyltrimethylammonium bromide. These materials were employed as catalysts in the direct synthesis of toluene to benzaldehyde using H₂O₂. The morphology of the Ag/WO₃ materials can be varied by changing the synthesis parameters. The size and shape of the Ag/WO₃ nanostructure catalyst has direct influence on the toluene conversion and benzaldehyde selectivity. The effect of different reaction parameters like reaction temperature, H₂O₂ to toluene molar ratio, reaction time, and so forth have been studied in detail. The Ag/WO₃ catalyst with ~7 nm silver nanoparticles on the WO₃ nanorod with a diameter ~60 nm showed the best catalytic activity of 42% toluene conversion with 93% benzaldehyde selectivity. The catalyst did not show any leaching up to four reuses, showing the true heterogeneity of the catalyst.

1. Introduction

Nanoparticles have attracted considerable attention due to their several technological applications especially in catalysis owing to the very high surface to volume ratio and easily available large number of active sites.¹⁻⁴ Enhancement in catalytic efficiency is attributed to the size and shape of the nanomaterials and also the composition of the catalyst material.⁵ Often the addition of a metal significantly enhanced the catalytic efficiency of the nanomaterial to a large extent due to the synergistic effect.⁶ However, it is still a major challenge for the researchers to develop a simple and reliable synthetic method for well defined nanoarchitectures with variable chemical components and controlled size and shape, which strongly affect the properties of nanomaterials. Silver nanoparticles have especially been of interest due to their size dependent properties in various catalytic reactions.^{7,8} Research efforts have been made for the synthesis of silver nanoparticles dispersed on different transitional and non-transitional metal supports such as titania, alumina, silica, *etc.*^{9–13} Despite significant research efforts, controlled synthesis of dispersed silver nanoparticles in the aqueous phase under ambient conditions is one of the most difficult challenges in catalysis. Although 1D nanostructures of WO₃ have been studied extensively,^{14,15} very little has been known about Ag nanoparticles on one-dimensional WO₃ nanostructure supports so far. We report here the preparation of different Ag/WO₃ nanomaterials with different shapes and sizes using a cationic surfactant, CTAB and investigated their catalytic activities for toluene oxidation reaction.

In the realm of oxidation chemistry, the catalytic oxidation reaction involving C-H activation of toluene for selective formation of benzaldehyde, remains a fundamental challenge in chemical research, since it is very difficult to achieve selective transformation under harsh conditions due to the over oxidation of benzaldehyde to benzoic acid.16 Benzaldehyde is one of the most important value-added products in industry, used in the synthesis of a wide range of organic compounds from pharmaceuticals to plastic additives. The challenge lies in controlling the selectivity to the target product benzaldehyde with very good yield in order to meet the market needs. Industrially benzaldehyde is produced through chlorination of the -CH3 group of toluene followed by saponification.17 Apart from the acute environmental problem due to the usage of a significant amount of chlorine, this process is also associated with the production of toxic acidic waste, equipment corrosion, in addition to the costly separation process. In the Rhodia, Dow and Snia-Viscosa processes liquid phase oxidation of toluene is carried out over homogeneous metal salt catalysts using oxygen or peroxides as oxidants in industrial grade, but these processes also involved the indispensable halogen ions and acidic solvents.18-20 Antonietti et al. reported toluene oxidation using B-doped polymeric carbon nitride (graphitic phase) with H_2O_2 as an oxidant¹⁶ and using mesoporous nano-structured carbon

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ta03641g

nitride with O_2 as an oxidant.²¹ Although this catalyst exhibited promising selectivity to benzaldehyde, conversion of toluene is very low. Moreover, the catalyst needs drastic conditions, like high pressure and high temperature. There have been several reports using H_2O_2 ,²² TBHP (ref. 23) and molecular O_2 (ref. 24) as oxidants for oxidation of toluene to benzaldehyde but for most of the cases the yield is very low. Thus, the exploration of a true heterogeneous catalyst with the ease of separability and recyclability is highly demanding for the production of benzaldehyde. H_2O_2 based oxidation is of great advantage to the environment and industry because it generates H_2O as the byproduct, it has the high content of active oxygen species (47 wt%). Moreover, H_2O_2 is cheaper and safer to use than other peroxides and peracids.

Here, we report a facile strategy to prepare Ag/WO₃ materials with different morphologies and found that the Ag/WO₃ material with \sim 7 nm Ag nanoparticles dispersed on WO₃ nanorods with diameter \sim 60 nm is a highly stable and recyclable catalyst for selective conversion of toluene into benzaldehyde. A toluene conversion of 42% with 93% benzaldehyde selectivity can be achieved over this catalyst at atmospheric pressure at 90 °C temperature using environmental benign oxidant H₂O₂.

2. Experimental section

2.1 Materials

 H_2WO_4 , AgNO₃, cetyltrimethylammonium bromide, hydrazine, HPLC grade (~99.9%) toluene, and acetonitrile were purchased from Sigma-Aldrich Co. Hydrogen peroxide (50 wt% in water) was purchased from Merck KGaA, Darmstadt, Germany. All the chemicals were used without further purification.

2.2 Synthesis of silver-tungsten nanostructure materials

All chemicals were purchased from Sigma-Aldrich chemicals and were used without further purification. Ag/WO₃ catalysts (AgW-N) was prepared using AgNO₃, H₂WO₄, CTAB and hydrazine monohydrate (NH₂NH₂, H₂O) (80% solution), maintaining a molar ratio of Ag : CTAB : H_2O : $NH_2NH_2 = 1 : 1 : 300 : 2$. An aqueous solution of 0.84 g CTAB was added to vigorously stirred 5.4 g H₂WO₄ solution at temperature 50 °C followed by dropwise addition of 0.39 g AgNO₃ solution. The pH was then adjusted to \sim 9, by adding NH₄OH solution. The solution was stirred for another 10 minutes and 0.28 g hydrazine solution was added slowly. The total solution was stirred for 7 h continuously maintaining the temperature at 50 °C. After that, the soobtained product was washed with ethanol and dried in an 80 °C oven for 6 h, followed by calcination at 500 °C for 4 h in nitrogen. Aloevera like Ag/WO3 structure (AgW-A) was obtained by maintaining the molar ratio of Ag : $CTAB : H_2O : NH_2NH_2 =$ 1:5:300:2 and keeping the rest of the parameters unaltered. The hexagonal Ag/WO₃ structure (AgW-H) was obtained by maintaining the molar ratio of $Ag: CTAB: H_2O: NH_2NH_2 =$ 1:1:300:2 varying only the stirring time to 48 h keeping the rest of the parameters unchanged.

2.3 Oxidation of toluene with hydrogen peroxide

The liquid phase oxidation of toluene was carried out in a double neck round bottom flask at 90 °C in an oil bath connected with a spiral condenser (length 60 cm) using 0.10 g catalyst, 10 ml acetonitrile solvent and 1 g of toluene to which 2.2 g H_2O_2 (50% aq. solution) (toluene : H_2O_2 molar ratio = 1 : 3 ratio) was added dropwise over a period of 30 minutes in order to avoid the immediate decomposition of H2O2. The condenser was attached to a water circulating bath (Julabo, FC 600) maintaining a constant temperature of 10 °C. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis. At the end of the reaction, the solid particles (catalyst) were separated by filtration and the products were analysed by Gas Chromatography (GC, Agilent 7890) connected with a HP5 capillary column (30 m length, 0.28 mm id, 0.25 µm film thickness) and flame ionisation detector (FID). The toluene conversion and benzaldehyde formation were calculated using a calibration curve (obtained by manually injecting the authentic standard compounds). The individual yields were calculated and normalized with respect to the GC response factors. The product identification was carried out by injecting the authentic standard samples in GC and GC-MS. The C-balance as well as material balance was carried out for most of the experiments and was found between 98 and 102%. Conversion of toluene was calculated based upon the GC-FID using anisole as external standard results, where toluene conversion = [moles of toluene reacted]/[initial moles of toluene used] \times 100 and selectivity of products calculated by [total moles of product formed]/[total moles of toluene converted] \times 100. For the reusability test, after completion of the reaction, the catalyst was recovered from the reaction mixture by filtration and washed thoroughly with acetone and reused as such for multiple circles.

2.4 Catalyst characterization

A thorough characterization of the catalyst was done using different characterization techniques like XRD, SEM, TEM, XPS, FT-IR, etc. Powder X-ray diffraction patterns were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K_{α} radiation source. Diffraction patterns in the $2-80^{\circ}$ region were recorded at a rate of 0.5 degrees (2θ) per minute. Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (LaB₆) as an X-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. TEM images were collected using a JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon formvar coated Cu grid. X-Ray photoelectron spectra (XPS) were recorded using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer and binding energies (± 0.1 eV) were determined with respect to the position C 1s peak at 284.8 eV. Fourier Transformation Infra-red Spectroscopy (FTIR)

3. Results and discussion

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3.1 Generation of the silver-tungsten nanostructure

It is well known that Ag, W and CTAB exist in the form of Ag^+ , WO_4^{2-} , and CTA⁺ in aqueous alkaline solution (pH > 7)²⁴ and cooperative self assembly between cationic part of the surfactant, CTAB and anionic species can be formed via electrostatic interaction.²⁵ When the CTAB concentration is high (more than the critical micelle concentration), cationic CTAB molecules adsorb onto the surface of the WO42- ions and form spherical micelles.²⁶ The curvature of an ionic micelle can be tuned from spherical to rod-like micelle by adding certain additives.27 Here, in our preparation method, during addition of Ag⁺ ions, the spherical micelles of CTA-WO₄¹⁻ were transformed into rod shaped micelles as a result of attractive electrostatic interaction between the CTA-stabilized negatively charged tungstate ions and positively charged silver ions, where Ag⁺ ions induce symmetry-breaking anisotropic growth on selective adsorption onto particular crystal planes of tungsten. Thus, the decrease in surface energy of the WO₃ seed crystals in one direction results in the formation of the one dimensional rod-like micellar structure and this acts as a nucleating agent for the growth of WO₃ nanorods. Ag⁺ adsorbs at the specific surface on WO_4^{2-} , leading to preferential growth of WO₃ along one direction and we could observe the Ag supported WO₃ nanorod structure (designated as AgW-N). In our case, WO₃ nanoparticles were formed instead of a rod-like morphology in the absence of Ag⁺ ions (Fig. S2b⁺). In the absence of CTAB, agglomerated Ag/WO3 was formed (Fig. S2a⁺). Therefore, the amphiphilic CTAB is not only acting as a ligand for the WO_4^{2-} ions, but also as a capping agent for both the silver and WO₃ and stabilize them against aggregation. When the synthesis was performed with a high concentration of CTAB, with a [CTAB] to [Ag] molar ratio of 5, an aloevera-like structure was formed (designated as AgW-A). Here, hydrazine also plays a crucial role in the synthesis procedure. Generally, hydrazine reduces Ag⁺ through the formation of a complex Ag(N2H4)+.28 So, hydrazine acts not only as a reducing agent but also as a chelating agent. In the absence of hydrazine, we could observe only agglomeration, suggesting that hydrazine also act as a stabilizer (Fig. S2c[†]). Being a reducing agent hydrazine reduces Ag⁺ to Ag onto the surface of WO₄²⁻, thus controls the growth of tungsten and silver nanoparticles and we observed only silver deposition on the WO₃ surface. On prolonging stirring from 7 h to 48 h, the nanorods nucleate and aggregate to grow into the hexagonal structure (designated as AgW-H). This can be attributed to the fact that the diameter of the nanorods being small, their surface energy is comparatively higher, the nanorods assembled together in order to reduce the surface energy, and form the hexagonal structure which is clear from SEM and TEM images discussed later. So, well-defined Ag/WO₃ structures can be prepared by tuning the synthesis parameters.

3.2 Properties of the silver-tungsten nanostructure material

XRD patterns of the three samples are shown in Fig. 1. All the three samples exhibit the characteristic peaks at 2θ values of 38.1°, 44.3°, 64.4° and 77.4°, and are indexed to the diffractions of the (111), (200), (220) and (311) crystal planes of metallic Ag (JCPDS no. 04-0783), respectively. The peaks at 2θ values of 23.2° , 23.5° , 24.3° , 33.2° and 34.2° correspond to the monoclinic WO₃ (JCPDS no. 43-1035). SEM images of the AgW-N sample exhibit a nearly uniform rod-like morphology (Fig. 4a and b) and the HRTEM images show a high dispersion of \sim 7 nm Ag nanoparticles on the WO₃ nanorod support with diameter ~ 60 nm (Fig. 4d). The particle size distribution of silver nanoparticles is shown in the inset (Fig. 4d). The lattice fringes in the HRTEM image with d-spacings of 0.23 nm and 0.38 nm correspond to the (111) and (020) crystal face of Ag and WO_3 , respectively, and can also be seen in Fig. 4e. The energy dispersive X-ray analysis also confirms the presence of Ag, W and O species in the sample and no impurities could be observed in the spectra (Fig. 4c). The mean diameter of AgNPs remained \sim 7 nm after the reaction confirms the stability of the small metallic AgNPs on WO3 nanorods, presumably resulting from the strong metal support interaction, which also helps to resist the sintering of AgNPs (Fig. S3[†]). Fig. 5a shows that the aloevera like microstructure (AgW-A) is composed of one dimensional nanorods extended outward from the centre. The average diameter of individual nanorod as confirmed from the TEM image is approximately ~ 400 nm (Fig. 5b). The lattice fringes in the HRTEM image with d-spacings of 0.20 nm and 0.43 nm, correspond to the (200) and (111) crystal face of Ag and WO₃, respectively, and can also be seen in Fig. 5c. The hexagonal morphology (AgW-H) is also composed of nanorods which could be observed from the corresponding SEM and TEM images (Fig. 5e and f). The lattice fringes in the HRTEM image with *d*-spacings of 0.15 nm and 0.23 nm correspond to the (220) and (111) crystal face of Ag and d spacings of 0.36 nm and 0.38 nm correspond to the (200) and (020) crystal plane of WO_3 , respectively, can also be observed (Fig. 5g). The samples prepared by the conventional impregnation method show irregular and larger particles (Fig. S2d†). The association of the



Fig. 1 XRD patterns of (a) Ag(0), (b) Ag(ı) oxide, (c) W(vı) oxide, (d) AgW-N, (e) AgW-A and (f) AgW-H.

surfactant cetyltrimethylammonium bromide (CTAB) with the Ag/WO₃ moiety was confirmed by the FT-IR analysis of the AgW-N catalyst as shown in Fig. 3. The as-synthesized sample showed the presence of the organic moiety in the catalyst strongly suggests the embedment of surfactant CTAB with the catalyst. The peak at 1426 cm⁻¹ corresponds to the symmetric stretching vibration of the CH₃-N⁺ moiety of CTAB. The frequency between 1626 and 3023 cm^{-1} may be due to the CH₂ symmetric antisymmetric vibration region.29 However, after thermal heating, the absence of the organic moiety reflects the complete removal of CTAB during calcination. The morphology of the AgW-N catalyst is not affected by the removal of the surfactant during calcination, and thus showed the excellent stability of the AgW-N nanostructure catalyst. The XPS spectra of Ag and W are presented (Fig. 2 and S1, Table S1[†]). The 3d orbital of silver clearly resolved into Ag 3d_{5/2} and Ag 3d_{3/2} contributions centred upon 368.5 eV and 374.5 eV, respectively, which is in good agreement with the binding energies of metallic silver Ag (0).³⁰ The W 4f 5/2 and 4f 7/2 spectra attributed to the binding energies 38.1 eV and 36.0 eV, respectively, suggesting that the tungsten in the tungsten oxide nanostructure exists as W⁶⁺.18 The absence of binding energy peak at 34.8 eV confirms that there is no substoitiometric WO_{3-x} present in the sample.³¹ So,



Fig. 2 Ag 3d core level spectra of the AgW-N catalyst.



Fig. 3 FT-IR spectra of the Ag/WO $_3$ catalyst (a) before calcination and (b) after calcination.

it can be stated that silver is in metallic state on the support WO_3 (Fig. S1[†]).

3.3 Synthesis of benzaldehyde from reaction with toluene and hydrogen peroxide using silver-tungsten nanostructure materials

We have investigated the catalytic activity of different Ag/WO₃ with different morphologies towards the direct toluene oxidation reaction at atmospheric pressure using H₂O₂ as an oxidant. As shown in Table 1, the catalytic activities of the different Ag/ WO₃ catalysts follow the order: AgW-N > AgW-A > AgW-H. For the AgW-N catalyst where Ag (111) and WO₃ (020) planes are exposed are found to be more catalytically active and give toluene conversion of 42% with 93% benzaldehyde selectivity at atmospheric pressure at 90 °C temperature. The AgW-A catalyst enclosed by Ag (200) and WO_3 (111) planes gives toluene conversion of 29% with 79% benzaldehyde selectivity, whereas for the AgW-H catalyst, Ag (220) and Ag (111) planes and WO₃ (200) and (020) planes are exposed, gives toluene conversion of 15% with 72% benzaldehyde selectivity (Table 1, entry 7, 10, 11). From these experiments we conclude that different crystal planes have direct influence on the toluene activity. In the case of the AgW-H catalyst, the nanorods assembled together, which would account for the absence of dispersed small silver nanoparticles and the catalyst shows low activity. The specific rodlike morphology of WO₃ facilitates the higher dispersion of silver nanoparticles on the support which might be responsible for higher activity of the AgW-N catalyst. However, the comparatively lower activity of the AgW-A catalyst might be attributed to the larger particle size as well as the slight aggregation of the silver nanoparticles on the surface of WO₃, resulting in the decrease of number of active sites on the surface of the catalyst available for reaction. We believe that the small AgW-N nanocatalyst acts as more efficient catalysts because they have a larger surface area than bigger nanoparticles of the same mass. So, the nanosize effect plays a vital role in the higher activity of the AgW-N nanostructure catalyst. But in the case of the AgW-H catalyst, the nanorods assembled together, which would account for the absence of dispersed small silver nanoparticles and the catalyst shows low activity. No toluene conversion was detected in the blank experiment without any catalyst (Table 1, entry 17). The Ag/WO3 catalyst synthesized by the conventional impregnation method showed no activity due to the larger particle size (Table 1, entry 5). We measured the BET surface area of the AgW-N nanostructure catalyst which gives the value $\sim 50 \text{ m}^2 \text{ g}^{-1}$, where the surface area of the conventional Ag/WO₃ catalyst is only $\sim 5 \text{ m}^2 \text{ g}^{-1}$. So the surface area of our catalyst is almost 10 times higher than that of the conventional catalyst. We have carried out the toluene oxidation reaction taking individual components such as AgNPs or WO₃NPs alone in order to exploit the individual role of each corresponding metal nanoparticle (Table 1). Commercial tungsten oxide and silver powder did not give any reaction (Table 1, entry 1, 2). When tungsten oxide or silver nanoparticles were employed as catalysts they exhibited very little conversion of toluene (Table 1, entries 3 and 4). Ag nanoparticles supported



Fig. 4 (a) Low resolution SEM image and (b) high resolution SEM image of AgW-N catalyst, (c) SEM-EDX, (d) TEM of AgW-N catalyst, (e) lattice fringes and (f) SAED pattern.



Fig. 5 (a)–(d) represent the SEM image, TEM image, lattice fringes and SAED pattern of AgW-A catalyst, (e)–(h) represent the SEM image, TEM image, lattice fringes and SAED pattern of AgW-H catalyst.

on commercial WO₃ also showed negligible activity (Table 1, entry 6). But when Ag nanoparticles supported on the WO₃ nanorod (AgW-N) catalyst was employed, significant enhancement in the catalytic activity was observed, so, WO₃ nanorods are directly influencing the activity Ag nanoparticles for the toluene to benzaldehyde oxidation reaction. The open structure of the WO₃ nanorods allows easy access of the reactants. Based on the above results we strongly believe that the synergistic effect between Ag nanoparticles and WO3 nanorods directly influence the oxidation reaction, demonstrating a clear synergistic effect between the Ag nanoparticles and the WO₃ nanorod support. The AgW-N nanostructured catalyst possesses very high specific surface area which enables the easy accumulation of oxidant and reactant molecules, as a result higher activity could be expected. The AgW-N catalyst exhibits very high selectivity (93%) towards benzaldehyde with a toluene conversion of 42% at 90 °C and at atmospheric pressure. Increasing the temperature to 110 °C, the benzaldehyde yield was decreased due to the decomposition of H2O2 and also the formation of overoxidised product benzoic acid. Although the

self-decomposition temperature of H₂O₂ is around 73 °C, we believe that due to the presence of tungsten species in the catalytic system, the self decomposition of H₂O₂ was restricted at 90 °C. We observed that at room temperature, the catalyst does not show any activity, but with increasing temperature, the toluene conversion increases significantly (Fig. 6). With increasing temperature, the selectivity of benzaldehyde decreased due to the formation of benzoic acid. The molar ratio of toluene : H_2O_2 was used in three fold excess (Fig. 7). In fact when toluene : H_2O_2 was adjusted to 1 : 1, the conversion of toluene was very low (15%) with benzaldehyde selectivity \sim 43% and benzyl alcohol selectivity \sim 57%. When the toluene : H₂O₂ mole ratio was increased to 1:3, the toluene conversion increases to 42% with 93% benzaldehyde selectivity, further increase in the mole ratio to 1:5, although the toluene conversion increases to 48%, the selectivity to benzaldehyde decreases to 86%. The selectivity drops down due to the formation of the overoxidized product benzoic acid. Upon further increase in the toluene : H_2O_2 molar ratio to 1 : 10, the conversion did not increase rapidly (from 47% to 51%), since

Table 1	Activities of d	ifferent catalyst	s over toluene	oxidation	reaction ^a
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				S_{P}^{d} (%)					
Entry	Catalyst	Ag loading ^{b} (wt%)	C_{T}^{c} (%)	$\varPhi_{\rm CHO}$	$\varPhi_{ m CH_2OH}$	$\varPhi_{\rm COOH}$	$Y_{\rm B}^{\ e}$ (%)	$\mathrm{TOF}^{f}\left(\mathbf{h}^{-1} ight)$	E_0^g (%)
1	Ag ^{com}	_	_	_	_	_	_	_	_
2	WO ₃ ^{com}	_	_	_	_	_	_	_	_
3	Ag ^{NPs}	_	2	45	55		0.9	_	_
4	WO ₃ ^{NPs}	_	5	78	22		3.9	_	_
5	AgW ^{imp}	4.6	7	66	30	4	4.6	0.75	1.5
6	AgNPs-WO ₃ ^{com}	4.5	8	63	30	7	5.0	0.82	1.7
7	AgW-N	4.6	42	93	6	1	39.0	6.25	13.0
8	AgW-N	7.3	55	87	4	9	47.8	7.70	16
9	AgW-N	11.2	64	82	2	16	52.5	5.50	17.5
10	AgW-A	4.5	29	79	13	8	23	3.75	7.6
11	AgW-H	4.5	15	72	12	11	10.8	1.75	3.6
12^h	AgW-N	4.5	42	92	6	2	38.6	6.25	12.9
13	AgW-N + NBS	4.6	48	95	5	—	45.6	7.3	15.2
14	AgW-N + phenol	4.6	3	35	65	—	1.05	0.16	—
15	AgW-N + acetic acid	4.6	43	6	36 (58)	—	2.6	0.41	—
16^{i}	AgW-N	4.6	81	95	—	5	77	12.2	25.6
17	No catalyst	—	—	—	—	_	_	_	_

^{*a*} Reaction conditions: solvent (MeCN) = 10 ml, substrate (toluene) = 1 g, catalyst = 0.1 g, benzene : H_2O_2 (molar ratio) = 1 : 3, reaction temperature = 90 °C; time = 16 h. ^{*b*} Loading of Ag determined by ICP-AES. ^{*c*} C_T = conversion of toluene FID-GC using anisole as the external standard. ^{*d*} S_P = selectivity to product(s). ^{*e*} Y_B = yield of benzaldehyde (Φ_{CHO}) = $C_T \times S_P/100$. ^{*f*} TOF = turn over frequency = [moles of benzaldehyde formed/one mole of Ag in the catalyst]/reaction time (h). ^{*g*} $E_o = H_2O_2$ efficiency = [moles of benzaldehyde formed/total moles of H_2O_2 added] × 100. ^{*h*} Catalyst after 4 reuses. ^{*i*} Benzyl alcohol (Φ_{CH_2OH}) as the substrate (time = 8 h). ^{*j*} com: commercial; imp: impregnation method; NPs: nanoparticles; parenthesis: 58% benzyl acetate.



Fig. 6 Effect of temperature on toluene oxidation. [A] Conversion of toluene; [II] selectivity to benzaldehyde; [II] selectivity to benzolc acid. Reaction conditions: toluene = 1 g; catalyst = 0.1 g; toluene : H_2O_2 molar ratio = 1 : 3; time = 16 h.



Fig. 7 Effect of toluene : H_2O_2 molar ratio on toluene oxidation. [A] Conversion of toluene; [I] selectivity to benzaldehyde; [I] selectivity to benzyl alcohol; [V] selectivity to benzoic acid. Reaction conditions: toluene = 1 g; weight of catalyst = 0.1 g; time = 16 h; temperature = 90 °C.

water produced in the medium due to the decomposition of hydrogen peroxide which hinders the reactant molecules to come in close contact with the catalyst. To check the insight into the reaction pathway we did some experiments. When we added *N*-bromosuccinimide (NBS) during the reaction, we found that it promotes the reaction and gave toluene conversion of 48% with 95% benzaldehyde selectivity (Table 1, entry 13). But when we added phenol during the reaction, we found that it almost inhibited the reaction (Table 1, entry 14). These results indicate that this is a radical auto-oxidation reaction, where NBS acts as the initiator of the radical reaction by supplying bromine radical and phenol acts as a radical scavenger. In a different reaction, after 8 hours, we added acetic acid to the reaction

mixture under the optimum reaction conditions and after 16 hours (of optimum reaction time), we found very little formation of benzaldehyde with co-formation of benzyl acetate as the major product (Table 1, entry 15). So we believe that benzyl alcohol is the intermediate species. To confirm this, benzyl alcohol was subjected to an oxidation process with H_2O_2 and found that it gives benzaldehyde within 8 hours (Table 1, entry 16). This result is consistent with the earlier reports.¹⁸ The reaction kinetics shows that the reaction is free of diffusion limitation (the detail kinetic calculation provided in the ESI†). The reaction follows pseudo first order reaction kinetics. We

can rationally assume that since tungsten oxide is weakly acidic in nature; the weakly basic toluene can be easily adsorbed onto the acidic WO₃ through electrostatic interactions. Once toluene is converted into benzaldehyde, a weak acidic molecule, it desorbed immediately from the acidic site, thus preventing further formation of overoxidized product benzoic acid. The amount of silver loading has an influential effect and with higher Ag loading although the conversion of toluene increases significantly, but at the same time the selectivity to benzaldehyde decreases due to the formation of benzoic acid (Fig. 8). We found that the Ag/WO₃ nanostructure catalyst with 4.6 wt% silver loading exhibits much higher benzaldehyde selectivity compared to the higher loading Ag catalyst. The catalyst with 7.3 wt% Ag loading showed a toluene conversion of 55% with 87% benzaldehyde selectivity. The effect of run time on toluene conversion and benzaldehyde selectivity is shown in Fig. 9. It was observed that the toluene conversion increases with increasing reaction time but the selectivity of benzaldehyde decreases after 16 hours due to the formation of overoxidized product benzoic acid.

The optimum reaction conditions of toluene oxidation were applied on various substituted toluenes (Table S2†). The reaction was remarkably selective for the aromatic aldehyde products regardless of the presence of electron donor or acceptor groups in the phenyl ring. The significantly enhanced activity of our AgW-N nanostructure catalyst was mainly due to the presence of uniformly dispersed very small silver nanoparticles supported on WO₃ nanorods, and the synergistic interaction between the ~7 nm AgNPs and WO₃ nanorods (~60 nm).

3.4 Reusability test

The reusability of the AgW-N catalyst was studied without further regeneration. The activity of the recovered catalyst after four consecutive runs did not lead to any significant decline in its catalytic activity in terms of conversion and selectivity (Table S4†). After the completion of reaction, the solid catalyst was removed from the reaction mixture by filtration under hot conditions and the reaction was allowed to proceed with the



Fig. 8 Effect of silver loading on toluene oxidation. [**A**] Conversion of toluene; [**I**] selectivity to benzaldehyde; [**o**] selectivity to benzol alcohol; [**v**] selectivity to benzoic acid. Reaction conditions: toluene = 1 g; toluene : H_2O_2 molar ratio = 1 : 3; temperature = 90 °C; time = 16 h.



Fig. 9 Effect of time on toluene oxidation. [A] Conversion of toluene; [I] selectivity to benzaldehyde; [I] selectivity to benzyl alcohol; [V] selectivity to benzoic acid. Reaction conditions: toluene = 1 g; weight of catalyst = 0.1 g; toluene : H_2O_2 molar ratio = 1 : 3; temperature = 90 °C.

filtrate under the same conditions. The reaction was completely stopped after the removal of the catalyst. Another important finding is that the oxidation pathway does not involve homogeneous catalysis by dissolving tungsten or silver species. TEM images do not show any changes compared to the initial morphology (Fig. S2†). We also observed that the amount of Ag and W present in the spent catalyst after 4 reuses is the same as that of the fresh catalyst as estimated by ICP-AES confirming the true heterogeneity of the catalyst.

4. Conclusions

In summary, we have demonstrated a simple preparation method for the one pot synthesis of the Ag/WO₃ nanostructured material with different morphologies like aloevera (AgW-A), nanorod (AgW-N) and hexagonal (AgW-H). The AgW-N catalyst (\sim 7 nm AgNPs supported on WO₃ nanorod with diameter 60 nm) serves as a highly selective heterogeneous catalyst for the one step oxidation of saturated primary C–H bonds of toluene to desired benzaldehyde with selectivity 93% with benign H₂O₂ as the oxidant at atmospheric pressure. Optimizing the synthesis parameters has the scope to design new Ag/W nanostructures with unique catalytic properties. Furthermore, this material shows true heterogeneity without changing its catalytic activity even after 4 reuses. This catalyst was not only capable of catalyzing the oxidation of toluene, showing high catalytic conversion and selectivity, but also avoids the use of chlorine as well as acidic solvents.

Acknowledgements

S.G. thanks UGC, S.S.A. thanks CSIR, India for the fellowship. R.B thanks CSIR, New Delhi for the financial support in the form of 12 FYP Project (CSC-0125). Director, CSIR-IIP, is acknowledged for his support and encouragement. The authors thank the Analytical Section Division at CSIR-IIP for their help.

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