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Introduction 1.

Particles in the nanosize domain have attracted considerable attention not only for their fundamental scientific interest, but also for many technological applications including catalysis due to their very high accessible surface area and easy availability of a large number of active sites.¹⁻⁴ In this nanosize regime, the particles behave differently from their bulk counterparts.¹⁻⁴ The catalytic efficiency of nanostructures is primarily governed by the size and shape of the nanocrystals and the composition of the metals and supports used.⁵ Noble metal nanoparticles such as silver and gold exhibit unique catalytic, electrical and optical properties.⁶⁻¹⁷ Silver nanoparticles (AgNPs) have especially been of interest owing to their interesting size dependent properties in various reactions.¹⁸⁻²¹ Significant research efforts have been made for the synthesis of silver nanoparticles on different transition and non-transition metal supports such as titania, alumina, silica, etc.²²⁻²⁵ The methods associated with the synthesis of supported Ag nanoparticles such as sonochemical methods, microwave irradiation, vapour

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deposition etc. need drastic conditions high temperature, hydrothermal treatment, and use of solvents, which make the whole process not only environmentally unfriendly but also highly energy-intensive. Owing to these factors, considerable research effort has been made to prepare supported Ag nanostructured materials in the solution phase.²⁶⁻²⁹ Despite significant research efforts, the controlled synthesis of dispersed silver nanoparticles in the aqueous phase under ambient conditions is one of the most difficult challenges in catalysis. We report here the preparation of almost uniformly dispersed ~5 nm Ag nanoparticles (AgNPs) supported on WO3 nanorods with diameters between 40 and 60 nm and we found that this catalyst is highly active for selective oxidation of cyclohexene to adipic acid.

Adipic acid (AA) is one of the most important compounds among all aliphatic dicarboxylic acids produced industrially. With the global annual production of over 3.5 million tons, adipic acid is used predominantly as a raw material in the production of a wide range of industrial and commercial products including synthetic fibers, nylon 6,6, polyurethanes, plasticizers, adiponitriles, low temperature synthetic lubricants and so on.^{30,31} Despite its immense importance, no catalyst has been reported to date which can be used industrially with oxidizing agents like molecular oxygen or H2O2. It is still a challenge to develop a clean technological process for the production of adipic acid with the aid of environmentally benign oxidants like molecular oxygen or H2O2. The method deployed by DuPont involves the hydrogenation of benzene to cyclo-

acid over silver supported tungsten oxide nanostructured catalysts*

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Selective oxidation of cyclohexene to adipic

We have developed a new synthesis strategy to prepare ~5 nm metallic silver nanoparticles (AgNPs) supported on tungsten oxide (WO₃) nanorods with diameters between 40 and 60 nm in the presence of a cationic surfactant, cetyltrimethylammonium bromide (CTAB). The catalyst was characterized by XRD, XPS, ICP-AES, FT-IR, Raman spectroscopy, EXAFS, SEM and TEM. The catalyst is very effective in liquid phase oxidation of cyclohexene to adipic acid with hydrogen peroxide as an oxidant. The synergy between the surface AgNPs and WO₃ nanorods plays the most vital role towards this very high catalytic activity. The reusability of the catalyst which is a prerequisite for practical applications was analysed and it was found that the catalyst exhibits no significant changes in its catalytic activity even after five cycles of reuse. A cyclohexene conversion of >99.9% with an adipic acid selectivity of ~94% was achieved over \sim 5 nm AqNPs supported on the WO₃ nanorod catalyst with a very high turnover frequency of \sim 12 h⁻¹.



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hexane, followed by aerial oxidation to obtain KA oil (a mixture of cyclohexanol and cyclohexanone), from where AA is being produced on further treatment of KA oil with HNO₃. The Asahi Kasei process followed the selective hydrogenation path from benzene to cyclohexene, from where AA is being produced. Both these industrial processes are associated with the coproduction of a substantial amount of environmentally unfriendly, unwanted greenhouse gases like N2O.32,33 A titania-based catalyst was found to catalyse cyclohexene to AA effectively, using tertiary butyl hydrogen peroxide (TBHP) as an oxidant.³⁴ But the use of TBHP is cost effective as compared to H₂O₂ and suffers from environmental problems. Thus the improvement of existing catalytic methods by means of environmentally friendly molecular oxygen or H₂O₂ is highly demanding. The hydrogen peroxide-based catalytic conversion has received much attention; it has the high content of active oxygen species (47 wt%) as it generates water as the sole byproduct.³⁵ Moreover, H₂O₂ is cheaper and safer to use than the other peroxides and peracids.36-39 So, direct conversion of cyclohexene to adipic acid using an environmentally benign clean oxidant, such as H2O2, is highly desirable from the industrial point of view. Noyori et al. demonstrated the direct conversion of cyclohexene to AA using a tungsten-based homogeneous catalyst in aqueous H₂O₂ medium in which quaternary ammonium salts were used as phase transfer catalysts.³¹ There have been reports on the production of adipic acid using different acids like H₂WO₄, H₂SO₄ and H₃PO₄ as catalyst precursors in H₂O₂ medium.³⁰ But all the processes suffer either from environmental issues or separation problems. So, the synthesis of AA in aqueous H_2O_2 medium is a topic of potential interest and the exploration of a true heterogeneous catalyst with the ease of separability and recyclability is highly demanding for the production of AA. Herein, we report a cyclohexene conversion of >99.9% with 94% adipic acid selectivity at 90 °C with H₂O₂ as an oxidant over Ag nanoparticles supported on WO₃ nanorods.

2. Experimental

2.1 Materials

 H_2WO_4 , AgNO₃, cetyltrimethylammonium bromide, hydrazine, HPLC grade (~99.9%) cyclohexene, cyclohexene oxide, cyclohexanediol, 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. Double distilled water was used during the preparation of the catalyst.

2.2 Preparation of the Ag/WO₃ nanostructured catalyst

Metallic AgNPs with a size of ~5 nm supported on the WO₃ nanorod catalyst were synthesized using AgNO₃, H_2WO_4 , CTAB and NH₂NH₂ (80% solution) maintaining a molar ratio of Ag : CTAB : H_2O : NH₂NH₂ = 1 : 0.80 : 400 : 2. An aqueous solution of 0.32 g AgNO₃ was added to 5.4 g H₂WO₄ solution at 100 °C under vigorous stirring. The pH was adjusted to ~9 by drop-

wise addition of NH₄OH solution. Then 0.68 g CTAB solution was added dropwise. The mixture was stirred for another 10 minutes and 0.29 g NH₂NH₂ was added. After 24 h of continuous stirring, the product was washed with ethanol and dried in a 110 °C oven for 12 h, followed by thermal heating at 500 °C for 6 h in the presence of helium (10 ml min⁻¹). The anisotropic growth of the tungsten oxide nanorods can be explained by the shape-controlled chemistry of the Ag⁺ ions since we could not observe rod-like morphology in the absence of silver ions. Here, the Ag⁺ ions restrict the growth of tungsten oxide except in one direction by selectively adsorbing onto certain crystal planes of tungsten, leading to preferential growth of tungsten oxide along one direction. Here CTAB acts as a capping agent in controlling the size of silver nanoparticles, and tungsten oxide nanorods and hydrazine served as a reducing agent. The formation of AgNPs supported on the WO₃ nanorod catalyst is shown in the schematic diagram (Scheme S1, ESI[†]).

2.3 Catalyst characterization

A thorough characterization of the catalyst was done using different characterization techniques like XRD, SEM, TEM, EXAFS, XPS, TGA 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° region were recorded at a rate of 0.5 degree (2q) per minute. Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200 F, using a tungsten filament doped with lanthanumhexaboride (LaB_6) as an X-ray source, fitted with an ETD detector in 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 along with SEM for the elemental analysis. The elemental mapping was also performed with the same spectrophotometer. 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 spectroscopy (XPS) spectra were recorded on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer and binding energies $(\pm 0.1 \text{ eV})$ were determined with respect to the position of C 1s peak at 284.8 eV. Raman spectra were measured at 298 K using a laser Raman spectrometer (JASCO, NRS-3100) with the 532 nm line from a diode-pumped solid-state laser for excitation. Measurements of the extended X-ray absorption fine structure (EXAFS) at the Ag-K edge were carried out in transmission mode at room temperature at the NW10A station of the Photon Factory Advanced Ring for pulse X-rays at the Institute of Materials Structure Science, High Energy Accelerator Research Organization in Japan (KEK-IMSS-PF-AR). The electron storage ring was operated at 6.5 GeV. Synchrotron radiation from the storage ring was monochromatized by a Si (311) channel cut crystal at the Ag K-edge. Ionization chambers, which were used as detectors for incident X-rays (I_0) and transmitted X-rays (I), were filled with 50% Ar-N2 mixture gas and 100% Ar gas,

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respectively. The EXAFS raw data were analyzed with the UWXAFS analysis package,40 including the background subtraction program AUTOBK⁴¹ and the curve fitting program FEFFIT.⁴² The amplitude reducing factor S_0^2 for Ag was fixed at 0.95. The backscattering amplitude and phase shift were calculated theoretically using FEFF 8.4 code.43 ATOMS44 was used to obtain the FEFF input code for crystalline materials. Chemical analyses of the metallic constituents were carried out using an inductively coupled plasma atomic emission spectrometer; model: PS 3000 UV (DRE), Leeman Labs, Inc. (USA). Fourier transformation infra-red (FTIR) spectra were recorded on a Thermo Nicolet 8700 (USA) instrument with the operating conditions: resolution: 4 cm^{-1} , scan: 36, operating temperature: 23-25 °C and the frequency range: 4000-400 cm⁻¹. Thermogravimetric analyses (TGA) of the uncalcined catalyst were carried out in a Pyris Diamond, Perkin Elmer Instruments, and technology by SII (Seiko Instruments Inc., USA) instrument-balance by heating 2.15 mg samples at 5 °C min⁻¹ under flowing nitrogen.

2.4 Oxidation of cyclohexene

Liquid phase oxidation of cyclohexene 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 0.15 g catalyst, 10 ml acetonitrile solvent and 1 g cyclohexene to which 4.15 g H_2O_2 (50% aq. solution) 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 5 °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 filtering during the hot conditions and products were analysed using a gas chromatograph (GC, Agilent 7890) connected with an OV-1701 capillary column (30 m length, 0.28 mm id and 0.25 µm film thickness) and a flame ionization detector (FID). Conversion of cyclohexene was calculated based upon the GC-FID results, where cyclohexene conversion = [moles of cyclohexene reacted]/[initial moles of cyclohexene used] × 100 and the selectivity of products was calculated by [total moles of product formed]/[total moles of cyclohexene converted] × 100. During the GC analysis, diethyl malonate was used as an internal standard. The individual yields were calculated and normalized with respect to the GC response factors. The product identification was carried out by injecting authentic standard samples into GC and GCMS. For few cases, we carried out column chromatography to get the isolated yield and ¹H-NMR was performed to identify the product. The C-balance as well as material balance was carried out for most of the experiments and it was found to be between 98 and 102%. 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.

3. Results and discussion

3.1 Catalyst characterization

Fig. 1 shows the XRD pattern of the prepared Ag/WO₃ catalyst. The powder XRD pattern of the catalyst showed the peaks at 2θ values of 23.2°, 23.5°, 24.3°, 33.2° and 34.2° (20), which correspond to the monoclinic WO3 (JCPDS no. 43-1035, space group: P21/n). In addition, four diffraction peaks at 2θ values of 38.1, 44.3, 64.4 and 77.4° corresponding to the metallic Ag crystal faces of (111), (200), (220) and (311) respectively were observed, which coincide well with the literature values (JCPDS no. 04-0783). The metallic Ag does not change its phase after the reaction as confirmed by XRD (Fig. 1e). The amount of silver present in the Ag/WO₃ nanostructured catalyst was estimated by ICP-AES. SEM images showed that the samples prepared by our own surfactant-assisted procedure exhibit a nearly uniform rod-like structure with diameter around 40-60 nm (Fig. 2a, 2b). The high resolution SEM image (Fig. 2b) showed the presence of very small silver particles on WO₃ nanorods. EDS showed only the presence of silver, oxygen and tungsten and no impurities could be observed in the spectra (Fig. 2c). The samples prepared by the conventional impregnation method show irregular and larger particles (Fig. 2d). High resolution transmission electron microscopy (HRTEM) revealed a one-dimensional rod-like morphology of tungsten oxide (Fig. 3a) with an average width of ~50 nm deposited by uniformly dispersed silver particles with average size nearly ~5 nm. The spacing of the lattice fringes was found to be about 0.26 nm and 0.22 nm, possibly due to the (022) plane of WO_3 and the (111) plane of metallic Ag, respectively (Fig. 3b). The silver particle size distribution histogram is shown in Fig. 3d. To check the possible morphological changes of the catalysts during reaction, TEM measurements have been performed on the Ag/WO3 nanostructured catalyst after 5 cycles of reuse. The mean diameter of AgNPs remained ~5 nm after the reaction, which confirms the stability of the



Fig. 1 XRD patterns of (a) metallic Ag(0), (b) Ag(I) oxide, (c) W(VI) oxide, (d) fresh Ag/WO_3, and (e) spent Ag/WO_3.



Fig. 2 SEM image of the Ag/WO₃ nanostructured catalyst: (a) low magnification, (b) high magnification, (c) SEM-EDAX spectra and (d) Ag/WO₃ catalyst prepared by the impregnation method.

ultra small metallic AgNPs on WO₃ nanorods, presumably resulting from the strong metal support interaction which also helps to resist the sintering of AgNPs (Fig. 3c and Fig. S9†).

To gain deeper insight into the surface constitution and properties of the catalyst, Ag 3d, W 4f and O 1s binding energies were measured by X-ray photoelectron spectroscopy (Fig. 4, Fig. S1, S2, ESI[†]). The 3d orbital of silver clearly resolved into Ag $3d_{5/2}$ and Ag $3d_{3/2}$ contributions centred at 368.4 eV and 374.4 eV respectively, which are in good agreement with the binding energies of metallic silver Ag(0).⁴⁵ The absence of negative shift of the Ag 3d_{5/2} binding energy for silver oxides with respect to metallic silver (368.4 eV) clearly supports that no silver oxide was present on the surface of the catalyst. The W $4f_{5/2}$ and $4f_{7/2}$ spectra are attributed to the binding energies 38.1 eV and 36.0 eV respectively suggesting that the tungsten in the tungsten oxide sample exists as W^{+6} .⁴⁶ The O_{1s} spectra of the sample show a peak occurring at 530.8 eV, which corresponds to W=O bonding modes. Ag-K edge extended X-ray absorption fine structure (EXAFS) analysis of the Ag/WO₃ nanostructured catalyst revealed that no significant changes occurred in the oxidation state of the silver species of the fresh and the spent Ag/WO3 nanostructured catalyst during the cyclohexene oxidation reaction. Table 1 shows the structural parameters of the catalyst by curve-fitting of the Ag K-edge EXAFS data. It was observed that an Ag-Ag

contribution at 0.2873 nm with a coordination number (C.N.) of 7.7 and the absence of Ag-O contribution indicate the formation of metallic silver in the fresh catalyst. For the spent catalyst, an Ag-Ag bond at 0.2872 nm with a C.N. of 7.6 was observed. No Ag-O coordination shell was observed after the reaction. The observation indicated that the oxidation state of metallic silver remained unchanged after the reaction. Raman spectra of the Ag/WO3 nanostructured catalyst are characterized by well resolved sharp bands as shown in Fig. 5. The highly intense band at 807 cm⁻¹ in the Raman spectrum corresponds to the symmetric stretching vibration and the intense band at 718 cm⁻¹ corresponds to the asymmetric stretching vibration of the O-W-O bond.47 The medium intense band at 272 cm⁻¹ and weak bands at 245 and 328 cm⁻¹ are due to the bending vibrations of the O-W-O bond. After the reaction, the Raman spectrum of the spent catalyst remained unchanged, reflecting the structural stability of the catalyst under the reaction conditions.

In order to check the association of the surfactant cetyltrimethyl ammonium bromide (CTAB) with the Ag-WO₃ moiety, the IR spectra of the Ag/WO₃ catalyst were taken before and after thermal heating. The as-synthesized sample showed that the presence of the organic moiety in the catalyst strongly suggests the association of the surfactant CTAB with the catalyst. The peak at 1402 cm⁻¹ corresponds to the symmetric



Fig. 3 TEM images of (a) fresh catalyst, (b) lattice fringes, (c) spent catalyst after 5 cycles of reuse and (d) particle size distribution of silver nanoparticles.



Fig. 4 Ag 3d_{3/2} spectrum of the Ag/WO₃ catalyst.

stretching vibration of the CH_3-N^+ moiety. The frequencies between 1600 and 3000 cm⁻¹ may be due to the CH_2 symmetric and antisymmetric vibration regions.⁴⁸ However, after thermal heating, the absence of the organic moiety reflects the complete removal of CTAB during calcination (Fig. S4, ESI†). The TGA spectrum showed a decomposition peak at ~400 °C, well consistent with the decomposition temperature of the surfactant cetyltrimethyl ammonium bromide (CTAB) (Fig. S5, ESI†). A total 14% mass loss suggests that surfactant molecules are strongly bound with the WO_4^{-} and Ag^+ crystals for the assynthesized sample. The morphology of the Ag/WO₃ catalyst is not affected by the removal of the surfactant during thermal heating, thus showing the excellent stability of the Ag/WO₃ nanostructured catalyst at higher temperature which is attributed to the strong metal–support interaction between AgNPs and WO₃ nanorods.

3.2 Activities of the catalysts

Table 2 shows the activities of the different Ag/WO₃ catalysts in the selective oxidation of cyclohexene in the liquid phase using H_2O_2 as an oxidant. The Ag/WO₃ nanostructured catalyst showed >99.9% cyclohexene conversion with ~94% adipic acid (AA) selectivity (Table 2, entry 6). The catalyst does not show

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Table 1 EXAFS curve-fitting parameters at Ag–K-edge Fourier-filtered k^3 -weighted EXAFS functions

Catalyst	Shell	CN	$R(1 \times 10^{-1} \text{ nm})$	$DW \left(1 \times 10^{-3} \text{ nm}^2\right)$	$\Delta K (1 \times 10 \text{ nm}^{-1})$	$\Delta r \left(1 \times 10^{-1} \text{ nm}\right)$	S_0^{2}	$\Delta E_0 (\text{eV})$	$R_{\rm f}$ (%)
Fresh catalyst Spent catalyst	Ag-Ag Ag-Ag	7.7 ± 0.6 7.6 ± 0.6	$\begin{array}{c} 2.873 \pm 0.031 \\ 2.872 \pm 0.032 \end{array}$	9.4 ± 0.4 8.6 ± 0.4	3-14 3-16	1.0-3.0 1.5-3.0	0.95 0.95	$\begin{array}{c} 1.8\pm0.6\\ 2.1\pm0.7\end{array}$	1.04 1.06



Fig. 5 Raman spectra of the Ag/WO $_3$ catalyst: (a) fresh catalyst and (b) spent catalyst.

any activity at room temperature but with increasing temperature both the conversion of cyclohexene as well as the selectivity of adipic acid increased. At 90 °C, we found that the formation of AA was maximum. At higher temperature (120 °C), the yield of adipic acid decreases (Fig. S6, ESI[†]). Most probably at higher temperature the decomposition of H_2O_2 is taking place. The effect of reaction time on cyclohexene conversion and adipic acid selectivity is shown in Fig. 7. It is well observed that with increasing time, initially the formation of cyclohexane oxide (till 6 h) and cyclohexane diol (till 12 h) increases, but after 12 h the formation of AA increases very rapidly. In order to find out the reaction intermediates, we took aliquots of the sample at regular intervals and analysed them by GC. We observed that after 12 h of reaction, the conversion of cyclohexene rose to almost 90%, but the selectivity towards AA was low, ~40%. This is due to the fact that most probably the formation of AA follows the consecutive reaction pathway and proceeds through the intermediates cyclohexene oxide and cyclohexene diol. We performed parallel reactions with cyclohexene oxide and cyclohexane diol as the respective reactants under the same reaction conditions and found that 100% conversion of both cyclohexene oxide and cyclohexane diol was achieved (Table 2, entries 9, 10). So, cyclohexene to AA formation took place via cyclohexene oxide and cyclohexane diol intermediates. The amounts of catalyst weight and Ag loading were found to be very important, since lower Ag loading and lower catalyst weight decrease the reaction rate without affecting the adipic acid selectivity significantly. Although the self-decomposition temperature of H₂O₂ is around 73 °C, we can say that in the presence of tungsten species in the catalytic system, the self-decomposition of H₂O₂ is restricted.⁴⁹ It has to be noted that the Ag/WO₃ catalyst pre-

pared by the conventional impregnation method exhibited much lesser activity due to the larger particle size and excessive leaching of the metals (as shown in a comparative study in Fig. 6, Table 2, and entry 5). From this observation, it can be concluded that the preparation method determines both the size and morphology of the Ag/WO3 nanostructured catalyst. WO₃ nanorods with diameter \sim 50 nm act as an excellent platform for higher dispersion of very small AgNPs (~5 nm). Being very small in size, these ~5 nm AgNPs possess very high specific surface area which corresponds to higher dispersion of silver and leads to a higher reaction rate due to the availability of more exposed surface active sites, where the catalytic reaction takes place. Moreover, the superior accessibility of the AgNPs' surfaces for oxidants and substrates leads to higher catalytic activity than that of the impregnated one. The poor catalytic activity of the impregnated Ag/WO₃ catalyst may be attributed to their irregular shape and larger size of Ag and WO₃ particles, which limit the accessibility of the catalyst towards the reacting substrates. We also noticed that the impregnated catalyst showed leaching of Ag particles during the cyclohexene oxidation reaction. It is very clear from the experiment that the nanosize effect has a vital role in the high activity and selectivity of the Ag/WO3 nanostructured catalyst. The blank experiment (Table 2, entry 8, without any catalyst) gave no conversion. Commercial silver or tungsten oxide alone also does not show any activity (Table 2, entries 1, 2). Even bare silver and tungsten oxide prepared by our surfactantassisted method also exhibit very poor yields (Table 2, entries 3, 4). We believe that AgNPs and WO₃ nanorods both act synergistically to enhance the catalytic activity of the Ag/WO3 nanostructured catalyst towards the cyclohexene to adipic acid reaction. This synergistic effect is absent for the conventional catalyst, so they are inactive for reaction. The catalyst showed its activity in the acetonitrile solvent. Most probably in the presence of a catalyst, the acetonitrile solvent forms perhydroxyl anions (OOH, nucleophile) with hydrogen peroxide which attacks the C-N group of acetonitrile to generate peroxycarboxyimidic acid, which is a very good oxygen donor species.⁵⁰ This explains the necessity of the solvent in the reaction.

3.3 Reusability of the catalyst

To check whether the catalyst is truly heterogeneous or not, the catalytic oxidation of cyclohexene was carried out with the reused catalyst under the same reaction conditions. The activity of the recovered catalyst after 5 consecutive runs did not lead to any significant decline in its catalytic activity in terms of conversion and selectivity (Table 2, entry 7 and Fig. S7, ESI[†]). After completion of the reaction, the solid cata-

		Substrate	Cyclohexene conversion $C_{T}^{b}(\%)$	Selectivity $S_{\rm P}^{c}$ (%)				Turnover
Entry	Catalyst			AA	Diol	Others	Yield $Y_{\rm A}^{d}$ (%)	TOF (h^{-1})
1	Ag ^{com}	\bigcirc	1.2	2	3	95	0.02	_
2	WO ^{com}	\bigcirc	4.7	3.5	5.2	91.3	0.16	_
3	Ag ^{us}	\bigcirc	3.4	3.3	4	92.7	0.01	_
4	WO ₃ ^{us}	\bigcirc	12	10	8	82	1.2	_
5	Ag/WO ₃ ^{imp}	\bigcirc	15	12	6	84	1.5	0.23
6	Ag/WO ₃ nanostructured catalyst ^{e}	\bigcirc	>99.9	94	6	_	94	12.0
7	Ag/WO ₃ nanostructured catalyst ^f		>99.9	91	9	_	91	11.6
8	No catalyst	\bigcirc	_	_	_	_	_	_
9	Ag/WO ₃ nanostructured catalyst ^g		>99.9	95	5	_	95	ND
10	Ag/WO ₃ nanostructured catalyst ^{h}	ОН	>99.9	>99	_	_	99	ND

 Table 2
 Activities of the different Ag/WO₃ catalysts^a

^{*a*} Reaction conditions: solvent (acetonitrile) = 10 ml, substrate (cyclohexene) = 1 g, weight of the catalyst = 0.15 g, silver loading = 3.8 wt%, reaction temperature = 90 °C; time = 18 h; cyclohexene : H_2O_2 mole ratio = 1 : 5. ^{*b*} C_T : conversion of cyclohexene based upon the FID-GC results = [moles of cyclohexene reacted/initial moles of cyclohexene used] × 100. ^{*c*} S_P : selectivity of the product calculated by total moles of the product formed/total moles of cyclohexene converted. ^{*d*} Y_A (Yield of adipic acid) = conversion × selectivity/100. ^{*e*} ~5 nm Ag nanoparticles supported on WO₃ nanorods. ^{*f*} Catalyst after 5 cycles of reuse. ^{*g*} Time = 12 h. ^{*h*} Time = 8 h; com = commercial; us = bare Ag and WO₃ prepared by our method; imp = impregnation method.



Fig. 6 Comparison of the activities of the Ag/WO_3 nanostructured catalyst and the impregnated catalyst.

lyst was removed from the reaction mixture by filtration during the hot conditions and the reaction was allowed to proceed with the filtrate under the same conditions. The reaction was completely stopped after the removal of the catalyst. The leaching test was performed for Ag and W by ICP-AES analysis using the filtrate and it was found that no Ag or W ions were present in the filtrate. We also observed that the amount of Ag and W present in the spent catalyst after 5 cycles of reuse is the same as that of the fresh catalyst as estimated by ICP-AES. XPS analysis also confirmed that the Ag concentration for the fresh and the spent catalyst on the surface are the same (Table S1⁺). TEM images of the spent catalyst showed an almost similar particle size to that of the fresh catalyst (Fig. S9[†]). So the catalyst is truly heterogeneous in nature. The Raman spectrum of the reused catalyst is almost the same as that of the fresh catalyst, which further suggests the structural stability of the nanostructured catalyst under the reaction conditions, which is a prerequisite for practical applications.





Fig. 7 Effect of time on cyclohexene oxidation. **[II]** Conversion of cyclohexene; **[II]** selectivity to adipic acid; **[III]** selectivity to cyclohexene oxide; **[III]** selectivity to cyclohexane diol. Reaction conditions: solvent = acetonitrile; cyclohexene = 1 g; weight of catalyst = 0.15 g; cyclohexene : H_2O_2 mole ratio = 1:5; temperature = 90 °C.

4. Conclusions

We have described a facile method for the synthesis of ~5 nm AgNPs supported on WO₃ nanorods with diameter around 50 nm for the direct conversion of cyclohexene to adipic acid with hydrogen peroxide as an oxidant. The catalyst shows a cyclohexene conversion of >99.9% with 94% adipic acid selectivity after 18 h. The catalyst was characterized by XRD, XPS, ICP-AES, FT-IR, Raman spectroscopy, EXAFS, SEM and TEM. The activity of the catalyst depends on Ag loading and the size of the Ag nanoparticles. The enhanced activity of ~5 nm AgNPs on WO₃ nanorods is likely caused by their very small size and the synergy between the well-dispersed AgNPs and WO₃ nanorods (40–60 nm) in the supported Ag/WO₃ nanostructured catalyst. The catalyst did not show any leaching after 5 cycles of reuse, confirming the true heterogeneity of the catalyst.

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