Oxidation of cyclohexene into adipic acid in aqueous dispersions of mesoporous oxides with built-in catalytical sites†

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Reactant incompatibility is a common problem in organic chemistry. This study investigates the use of concentrated aqueous dispersions of mesoporous oxides to overcome incompatibility. Oxidation of cyclohexene into adipic acid using aqueous hydrogen peroxide as oxidant has been performed in a range of ordered and disordered mesoporous materials. The different mesoporous oxides have been characterised with diffraction techniques (XRD and SAXS), electron microscopy (TEM and SEM) and nitrogen adsorption isotherms (BET and BJH methods). The catalyst used in the reaction was either soluble sodium tungstate added to a reaction system based on mesoporous silica, alumina or a silica/alumina mixture; or a catalytic oxide, tungsten oxide or titania, present in the framework of the mesoporous material. Tungsten oxide, either used as the sole oxide material or as a mixed oxide with silica turned out to be very efficient and gave almost quantitative yield of adipic acid. A major advantage with having the catalyst chemically incorporated in the walls of the porous material is that it can be easily reused. The results from recycling experiments show that the catalytic activity is retained.

Introduction

Reagent incompatibility is a common problem in synthetic organic chemistry and different strategies have been developed to solve this problem. The use of a two-phase system with added phase transfer catalyst (PTC) is probably the most common approach and is particularly useful for reactions between lipophilic organic compounds and inorganic salts.[1] Another approach involves the use of self-organizing surfactant media, such as micellar solutions, microemulsions and liquid crystalline systems.[2] High rates of reaction can be obtained between otherwise incompatible reactants in such media.[2,3] The polar reactant is dissolved in the aqueous domain and the apolar reactant in the non-aqueous domain of the systems and the reaction occurs at the interface. However, both the PTC approach and the use of organized surfactant systems as a medium for an organic synthesis are subject to time consuming work-up procedures. The phase transfer catalyst, usually a quaternary ammonium compound or a crown ether, is relatively toxic and needs to be completely removed from the product after the completed reaction.[4] In the organized surfactant system approach, the amphiphile used also needs to be removed from the product and separation of surface active compounds by extraction or distillation is often problematic.

Concentrated dispersions of mesoporous materials present another possibility to overcome the problem of reagent incompatibility. Mesoporous materials are highly ordered materials with pore sizes in the range of 2–50 nm.[5] Most of the mesoporous materials synthesized and studied are oxides such as silica, alumina and titania. These are polar in character and the pores are easily filled with an aqueous solution that may contain the polar reactant of an organic synthesis. The continuous phase of the suspension, *i.e.*, the dispersing medium, may then be the neat apolar reactant or a solution of this reactant in a hydrophobic solvent. The pore openings constitute the interface where the reaction occurs. Thus, similar to the concept of organized surfactant systems, the reaction medium is one with a very large interface between a polar and an apolar domain and the reaction takes place at that interface. The surfactant system has the advantage of giving larger interfaces. The mesoporous materials approach is attractive because the work-up is extremely facile. No auxiliary agent, such as a PTC or a surfactant, needs to be removed. The solid mesoporous material can simply be separated from the solution containing the product by filtration or centrifugation. It has previously been shown that the mesoporous material can be re-used several times.[3a,6]

There is an interest in exploring new and more environmentally benign routes for synthesis of adipic acid. The traditional synthetic route to adipic acid starts with cyclohexanol or with a mixture of cyclohexanol and cyclohexanone. Nitric acid is used as oxidant and cyclohexanol is first oxidized to the ketone, which is subsequently nitrosated to give an intermediate that undergoes C–C bond cleavage.[7] A high valency metal salt is used as catalyst. The process uses technology that dates back to the 1940s and large quantities of NO_2 and particulate matter are emitted.[4,7,8]

Many alternative routes for preparing adipic acid have been proposed.[7,9] High yields have been reported with *tert*-butyl hydroperoxide as oxidant and a titania catalyst.[9e] However, organic peroxides are much inferior to hydrogen peroxide from

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Table 1 Amount of reagents and experimental conditions for preparation of the mesoporous oxide materials

Material	Precursor		Template		Days	Calcination		
From chloride precursor	Type	Amount/g	Type	Amount/g	40 °C[b]	Ramping/h	Time/h[d]	Temp/°C
SiO_2–A	$SiCl_4$	17.0	P123	10.0	2	1	4	400
Al_2O_3	$AlCl_3$	13.3	P123	10.0	5	1	4	400
TiO_2	$TiCl_4$	18.9	P123	10.0	7	1	4	400
WO_3	WCl_6	39.8	P123	10.0	5	1	4	400
WO_3/SiO_2-1	$WCl_6/SiCl_4$	10.0/12.7	P123	10.0	3	1	4	400
WO_3/SiO_2-2	$WCl_6/SiCl_4$	4.0/15.3	P123	10.0	3	1	4	400
WO_3/SiO_2-3	$WCl_6/SiCl_4$	2.0/16.1	P123	10.0	3	1	4	400
WO_3/SiO_2-4	$WCl_6/SiCl_4$	1.0/16.6	P123	10.0	3	1	4	400
WO_3/SiO_2-5	$WCl_6/SiCl_4$	0.4/16.8	P123	10.0	3	1	4	400
From alkoxide precursor	Type	Amount/g	Type	Amount/g	80 °C[c]	Ramping/h	Time/h	Temp/°C
SiO_2–B	$Si(OEt)_4$	17.0	P105	8.0	1	2	15	500
WO_4/SiO_2	$Si(OEt)_4/Na_2WO_4$	17.0/0.26[a]	P123	8.0	1	1	6	500
Al_2O_3/SiO_2	$Si(OEt)_4/Al(OiPr)_3$	12.8/4.25	CTAB	32.7		4	16	520

[a] After calcination the material contains 9.86 mg tungsten per g mesoporous material as determined by ICP-AES. [b] Time allowed for gelation. [c] Time allowed for aging under condenser. [d] Total time of calcination (ramping and heating included).

an environmental point of view. Hydrogen peroxide is a very attractive oxidant since it is a relatively cheap reagent and water is the only by-product. Hydrogen peroxide also has a fair atom efficiency with 47% active oxygen.[10] Hydrogen peroxide is capable of oxidizing cyclohexene to adipic acid but a metal oxide catalyst, such as titania or tungstate, is needed to attain proper reactivity.[9a,11]

Hydrogen peroxide is employed as an aqueous solution and cyclohexene is immiscible with water. This is a typical case where reactant incompatibility is an issue. In this work the use of a concentrated dispersion of mesoporous materials is explored as reaction medium for oxidation of cyclohexene to adipic acid using hydrogen peroxide as oxidant. The pores of the mesoporous material are filled with the aqueous hydrogen peroxide and the particles are suspended in cyclohexene. The catalytic effect is obtained by adding sodium tungstate to the reaction system based on mesoporous SiO_2, Al_2O_3 or SiO_2/Al_2O_3 or by using a framework of either WO_3- or TiO_2-containing mesoporous oxide or of a mixed WO_3/SiO_2 material.

Experimental

Reagents and materials

Sodium tungstate (Aldrich, 99%), cyclohexene (Sigma-Aldrich, 99% Reagent plus), hydrogen peroxide (Aldrich, 30% in H_2O), sulfuric acid (Aldrich 95–98% A.C.S.), hydrochloric acid (Aldrich, 37%), Pluronic P105 (BASF), Pluronic P123 (BASF), ethanol (Kemetyl, 99.5%), tetraethyl orthosilicate (Aldrich, 98%), aluminium chloride (Aldrich 98.0%), titanium chloride (Aldrich, 99%), tungsten(VI) chloride (Aldrich, 99.9%), silicon(IV) chloride (99.0% Aldrich), aluminium isopropoxide (Aldrich, 98%), hexadecyltrimethylammonium bromide (CTAB, Sigma, 98%), sodium hydroxide (Aldrich, 97% A.C.S.), chloroform-d (ARMAR Chemicals, 99.8 atom% D), and dimethylsulfoxide-d_6 (ARMAR Chemicals, 99.8 atom% D).

Preparation of mesoporous materials

Two routes were used for the synthesis of the mesoporous materials, one starting from a metal chloride precursor and one using a metal oxide as precursor. Choice and amounts of reagents, as well as synthesis details, are collected in Table 1.

Oxide material from chloride precursor

Hexagonal mesoporous silica, alumina, titania, tungsten oxide and mixed tungsten oxide/silica. The material was synthesised according to a method described by Yang *et al.* using an EO–PO–EO triblock copolymer as template.[12] The template was dissolved in ethanol (100.0 g) under stirring at room temperature. After 30 min the chloride precursor was added stepwise and the stirring continued for 30 min. The solution was transferred to an open petri dish and was gelled by standing for an appropriate time in the oven. The thin film obtained was directly calcined.

Oxide material from alkoxide precursor

Hexagonal mesoporous silica. The material was prepared essentially following the procedure of Witula *et al.*[13] The template triblock copolymer was dissolved under stirring at 35 °C in an aqueous solution containing 2 M HCl (240 g) and distilled water (60 g). The precursor was added after 1 h and the stirring was continued for 20 h at 35 °C. The mixture was subsequently aged for an appropriate time. The solid product obtained was vacuum filtered, washed with water and dried in air at room temperature over night and then calcined.

Hexagonal oxotungstate/mesoporous silica. The material was prepared by a procedure adopted from Cheng *et al.*[9a] The template triblock copolymer was dissolved under stirring at 35 °C in an aqueous solution containing 2 M HCl (240 g) and distilled water (60 g). After 15 min a mixture containing sodium tungstate (0.26 g) and hydrogen peroxide solution (1.1 g, 30% in water) was added. After 1 h the alkoxide precursor was added and the stirring continued for 24 h at 35 °C. The mixture was subsequently aged and the solid product vacuum filtered, washed with water and air dried at room temperature for 2 h. The calcined product was immersed in aqueous 1 M ammonium acetate solution for 6 h at 80 °C and then vacuum filtered, washed with water and dried in air at room temperature over night.

Hexagonal mesoporous alumina/silica. The material was prepared essentially following the procedure described by Wang *et al.*[14]

Aluminium isopropoxide was added to a water solution (90 g) containing sodium hydroxide (7.8 g) under stirring at room temperature. More water was added (910 g) and the solution was stirred for 30 min. The template triblock copolymer was added and the temperature fixed to 25 °C. When the template had completely dissolved the alkoxide precursor was added and the resulting gel was stirred for 2 h. Hydrochloric acid (37 wt%) was added dropwise until the pH had decreased to 12. After 4 h at pH 12 the pH was lowered to 11 and stirring continued for another 12 h. The solid was vacuum filtered, washed with water and calcined.

Procedure for oxidation in a slurry of mesoporous material

Mesoporous material (400 mg), cyclohexene (200 mg, 2.6 mmol), hydrogen peroxide solution (1.5 g, 11.8 mmol), sulfuric acid (10 mg, 0.010 mmol), and optionally tungstic acid (15 mg, 0.045 mmol; used when silica, alumina, or alumina/silica was used as mesoporous material) was added in that order into a round bottom flask fitted with a magnetic stirrer (600 rpm). The slurry was heated to 80 °C (which is just below the boiling point of cyclohexene which is 83 °C) in an oil bath under a condenser. The consumption of the starting material, cyclohexene was monitored by terminating the reaction after 0.5, 2.0, 4.0, and 6.0 h. To each of the terminated reaction flasks an eightfold volume of deuterated solvent was added. Aliquots were then taken and analysed for cyclohexene with ^{1}H-NMR. The yield of adipic acid was obtained by scaling up the reaction 3.75–7.5 times and allowing the reaction to continue for 24 h. Then the reaction was terminated, the slurry vacuum filtered and the mesoporous material washed with ethanol. The eluate was placed in a round bottomed flask (250–500 ml) and rotary evaporated. The resulting solid in the round bottomed flask was collected, dissolved in deuterated solvent and analysed for adipic acid with ^{1}H-NMR. To determine the ratio of cyclohexene, cyclohexanediol intermediate, other (in Table 3) and adipic acid from the 24 h reaction a sample for ^{1}H-NMR analysis was directly taken after terminating the 24 h reaction.

Procedure for recycling experiments

Vacuum filtered, washed mesoporous material collected from the 24 h reaction experiment was air dried at room temperature. It was then transferred to a reaction flask and used for a new 24 h reaction under the same experimental conditions. The mesoporous material was stored at room temperature in air atmosphere between the experiments.

Results and discussion

Characterization of mesoporous catalysts

A range of different types of hexagonal mesoporous materials were prepared. Either Pluronic P123, Pluronic P105 or CTAB was used as template. The two Pluronics are triblock copolymers based on a central polyoxypropylene (PO) block surrounded by polyoxyethylene (EO) blocks. P123 has the composition EO_{20}–PO_{70}–EO_{20} and P105, which is more hydrophilic, is EO_{37}–PO_{58}–EO_{37}. CTAB is a cationic surfactant of much lower molecular weight. The first mesoporous materials, whose structures were published in the beginning of the 1990s were made with CTAB and related cationic surfactants as templates but the use of an EO–PO–EO copolymer as structure-directing agent to organize the metal oxide network is well established today.[15]

Table 2 Characteristics of the mesoporous oxide materials obtained by the BET and BJH methods

Material From chloride precursor	Specific surface area/$m^2 g^{-1}$ [a]	Pore size/nm [b]	Pore size/nm [c]	Pore volume/$cm^3 g^{-1}$ [b]	Pore volume/$cm^3 g^{-1}$ [c]
SiO_2–A	781	3.32	3.28	0.46	0.58
Al_2O_3	372	13.6	11.6	1.22	1.24
TiO_2	108	9.12	8.21	0.30	0.30
WO_3	31	11.5	10.1	0.10	0.10
WO_3/SiO_2-1	333	4.46	3.98	0.26	0.30
WO_3/SiO_2-2	530	3.09	3.06	0.27	0.36
WO_3/SiO_2-3	490	3.03	2.89	0.27	0.22
WO_3/SiO_2-4	784	2.86	2.77	0.34	0.31
WO_3/SiO_2-5	818	3.25	3.20	0.45	0.52
From alkoxide precursor					
SiO_2–B	885	5.56	4.82	0.75	0.93
Al_2O_3/SiO_2	167	7.03	6.71	0.20	0.22
WO_4/SiO_2	401	7.26	6.45	0.77	0.77

[a] Calculated from nitrogen sorption using the BET method. [b] Calculated from the adsorption branch of the nitrogen sorption isotherm using the BJH method. [c] Calculated from the desorption branch of the nitrogen sorption isotherm using the BJH method.

Table 3 Yields of adipic acid and of the intermediate diol 2 in reaction systems based on different precursors

Material			Products (%)		
From chloride precursor	Cyclohexene conversion (%)	TON[a]	Adipic acid	Diol	Other
SiO_2–A and Na_2WO_4 [20]	100	17	44	41	15
Al_2O_3 and Na_2WO_4 [21]	100	0	0	90	10
TiO_2 [21]	100	>1	5	56	39
WO_3 [21]	100	>1	95	5	—
WO_3/SiO_2-1	100	3	94	6	—
WO_3/SiO_2-2	100	8	95	5	—
WO_3/SiO_2-3	100	15	93	7	—
WO_3/SiO_2-4	100	7	22	12	66
WO_3/SiO_2-5	100	20	24	3	73
From alkoxide precursor					
SiO_2–B [1]	57	—	0	48	9
SiO_2–B and Na_2WO_4 [1]	100	20	55	2	43
Al_2O_3/SiO_2 and Na_2WO_4 [22]	100	8	17	65	18
WO_4/SiO_2 [10]	100	>1	1	43	46

Reaction time: 24 h; temperature: 80 °C; molar ratio H_2O_2/cyclohexene = 4.5; mesoporous material: 1.5–3.0g; mol of active site/reaction system: SiO_2–A, SiO_2–B and Al_2O_3: 0.19 mmol Na_2WO_4; WO_4/SiO_2 0.09 mmol Na_2WO_4; TiO_2: 37.5 mmol; WO_3: 8.6 mmol; WO_3/SiO_2-1: 2.22 mmol; WO_3/SiO_2-2: 0.89 mmol; WO_3/SiO_2-3: 0.44 mmol; WO_3/SiO_2-4: 0.22 mmol; WO_3/SiO_2-5: 0.09 mmol (for the WO_3/SiO_2-1–5 active site loading are calculated from the preparation step and the added amount of the specific material). [a] TON (turnover number) = moles of adipic acid produced per mol of tungsten or titanium after a 24 h reaction

In this work, two different types of inorganic precursors have been used, metal chlorides and metal alkoxides. Calcination was employed as a template removal method. The mesoporous materials were characterized by TEM, SEM, SAXS, XRD, and XPS and by determination of the specific surface area as well as of pore diameter and volume from nitrogen adsorption-desorption isotherms.

Typical TEM images of long range ordered and disordered mesoporous materials are given in Fig. 1. The TEM images indicate that WO_3 groups are incorporated into the oxotungsten silica (WO_4/SiO_2) material and in the tungsten silica mixtures (WO_3/SiO_2-1–5). Inversion of the polarized light (dark field image) onto the WO_4/SiO_2 material discloses no metals. However, WO_3/SiO_2-4 displays reflections characteristic of metal oxide crystals. Dark field TEM imaging has previously been used to confirm the presence of metal oxide crystals in amorphous matrices.[12]

The bright field and dark field TEM analyses indicate that the oxotungsten is primarily located inside the pore channels of the WO_4/SiO_2 mesoporous material. Fig. 1 also includes a SEM image of one of the WO_3/SiO_2 materials, showing a porous network.

This interpretation is supported by the light scattering properties of the materials, the WO_4/SiO_2 sample being colorless in contrast to the WO_3/SiO_2-1–5 materials, which are blue-green in color. The color of the materials increases with the loading of WO_3. The ICP-AES analysis of the WO_4/SiO_2 material, see supplementary data section (ESI†), shows that much of the loaded Na_2WO_4 is lost and not present in the final product. Most likely, loosely attached WO_4 groups in the WO_4/SiO_2 material were removed during the 6 h treatment of the calcined product with an ammonium acetate solution at 80 °C. Thus, the results indicate that the WO_3/SiO_2-1–5 materials, but not WO_4/SiO_2, have crystalline WO_3-groups in the framework.

The XRD analysis, see Fig. 2, confirms presence of crystalline WO_3 in the WO_3, as well as in the WO_3/SiO_2-1–2, materials. Previous XRD analyses of related materials have revealed compositions between WO_2 and WO_3, such as $W_{20}O_{58}$ and $W_{18}0_{49}$, with the oxides that contain mainly WO_3 being blue and those that are dominated by WO_2 being brown or purple.[16]

The tungsten-containing oxides of this work were blue-green. The diffraction pattern and curve fitting resemble monoclinic WO_3 groups with space group $P2_1/n$ (14).[17] The XRD diffractograms of WO_3/SiO_2-3–5 resemble that of amorphous SiO_2 and peaks indicative of monoclinic WO_3 are seen in the WO_3/SiO_2-3–4 materials. The XRD diffractogram shows no crystalline structures of SiO_2 in the SiO_2–A or WO_3/SiO_2-1–5 materials. The broad peaks in the diffractograms are due to small particle sizes or low crystallinity of the samples.[13] Unfortunately, the WO_x groups in the WO_4/SiO_2 and WO_3/SiO_2-3–5 are too few compared to the amount of SiO_2 to be detected. Hence the XRD data together with the TEM analysis indicate that the WO_3 groups are situated in the framework and covalently bonded into an amorphous silica matrix in the WO_3/SiO_2-1–5 materials. Even though the crystalline WO_3 groups cannot be detected in the WO_3/SiO_2-3–5 materials by the XRD technique, they can be seen in the TEM, see Fig. 1.

The XPS analysis, Fig. 3, does not give evidence for a specific oxidation state occurring in the WO_3/SiO_2-1–5 materials. According to the literature W(II) should appear at 32 eV, W(IV) at 33.4 eV, W(V) at 34.6 eV, and W(VI) at 35.4 eV.[18] The two large peaks are below these values and there are virtually no peaks in the 30–35 eV region. We have no explanation to why the W peaks appear at such low binding energy.

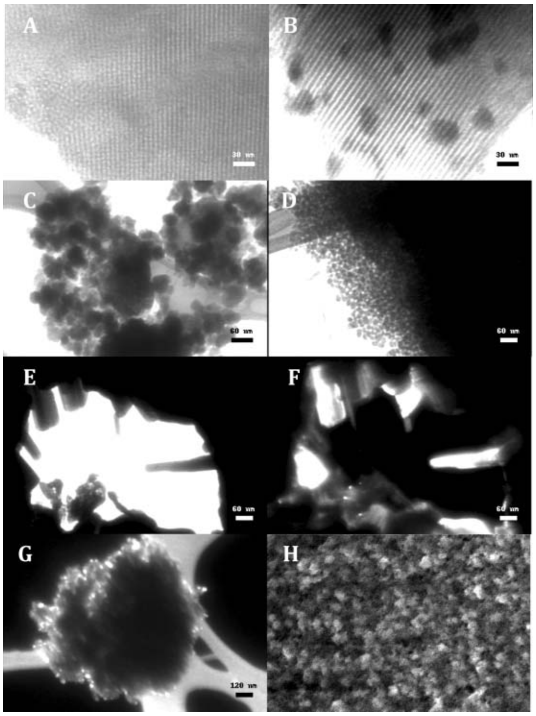


Fig. 1 Microscopy images of mesoporous oxides. (A) and (B) show the long range order of SiO_2–B and WO_4/SiO_2, respectively. The dark spots in (B) are probably sodium tungstate particles incorporated into the silica structure. Such black spots are only visible in this material. (C) and (D) are micrographs of WO_3/SiO_2-1 and SiO_2–A, respectively, which both lack long range order. (E) and (F) show bright and dark field micrographs, respectively, of the WO_3 material. As can be seen, the WO_3 groups are visible in the dark field mode, which is a sign of crystallinity. (G) is a dark field mode micrograph of WO_3/SiO_2-4, representative of the WO_3/SiO_2-1–5 group. Crystalline WO_3 groups can be seen in the outer regions of the particle cluster. (H) is a SEM image of WO_3/SiO_2-3, also representative of the WO_3/SiO_2-1–5 materials.

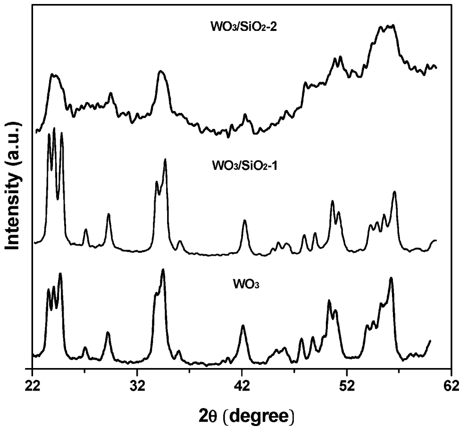


Fig. 2 Powder diffractogram of WO_3, WO_3/SiO_2-1, and WO_3/SiO_2-2.

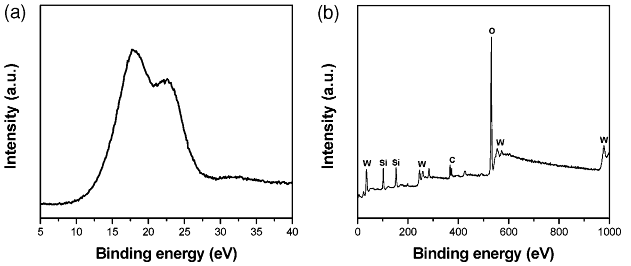


Fig. 3 XPS analysis of WO_3/SiO_2-1 displaying (A) the binding energy region 5–40 eV, and (B) the whole spectrum of the material, with peaks of W, Si, C, and O indicated.

Elemental analysis of the surface of WO_3/SiO_2-1 with XPS gives the following composition: Si, 64.0; W, 4.1; O, 27.9 and C, 4.0. Thus, only a small fraction of the loaded tungsten is present at or near the surface.

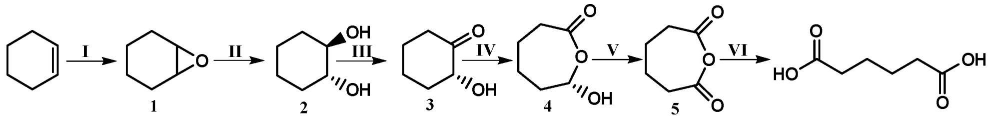
As indicated by the diffraction pattern with peaks at 2θ 1.12°, 1.94° and 2.22° the SiO_2–B and WO_4/SiO_2, which are prepared from an alkoxide precursor, have long range hexagonal order this is also indicated by the TEM micrographs in Fig. 1. The mesoporous materials prepared from a chloride precursor, as well as the Al_2O_3/SiO_2 prepared from an alkoxide precursor, do not show long range order. The SAXS diffractogram of the materials prepared with chloride precursors typically display a first high intensity peak but lack the diffraction pattern typical for hexagonal long range order. These materials can therefore be regarded as largely disordered, possibly with segments of long range hexagonal order.

The pore size distributions obtained with the BJH method show that the SiO_2 and the WO_4/SiO_2 materials have the relatively narrow size distributions typical of long range ordered mesoporous material. The analysis indicates that Al_2O_3 is the most disordered material. Its pore size distribution is broad, ranging from 2 to 27 nm. The other mesoporous oxide materials have pore size distributions of 2–15 nm. Mean pore size values, as well as values of pore volume and specific surface area of the different oxides, are collected in Table 2. All the mesoporous materials display physisorption adsorption isotherms that resemble a type IV, according to the IUPAC classification.[5] The type of hysteresis differs between the materials. Al_2O_3, TiO_2 and Al_2O_3/SiO2 display adsorption hysteresis of type H_3, characteristic of aggregates with plate-like particles and slit-shaped pores.[5] SiO_2–B, WO_3 and WO_4/SiO_2 have a hysteresis loop more of type H_1, indicating that these materials consist of agglomerates of uniform spheres. Such materials often have a narrow pore size distribution.[5] WO_3/SiO_2-1–5 and SiO_2–A have a hysteresis loop resembling type H_4, which means that the materials have narrow slit-like pores.[5] The adsorption isotherms are given in the supplementary data section (ESI †).

The tungstate loading in the silica materials (WO_3/SiO_2-1–5) affects the adsorption-desorption isotherms. There is a clear trend towards lower BET surface area (and smaller pore volume) with increasing ratio of WO_3 to SiO_2. This is a relevant piece of information because these mixed oxide materials are particularly interesting as media for the oxidation reaction studied in this work, as will be discussed in the next section.

The reaction mechanism and oxidation reaction in a mesoporous slurry

The conversion of cyclohexene to adipic acid with hydrogen peroxide as oxidizing agent is a multistep oxidation reaction that goes through at least five identified intermediates: 1,2-epoxycyclohexane (1), 1,2-cyclohexanediol (2), 2-hydroxycyclohexanone (3), 7-hydroxyoxepan-2-one (4) and oxepane-2,7-dione (adipic anhydride, 5), see Scheme 1. Four



Scheme 1 Reaction pathway for the oxidation of cyclohexene to adipic acid.

different types of reactions are involved in the conversion: epoxidation (I), hydrolysis (II, VI), alcohol oxidation (III, V) and Baeyer–Villiger rearrangement (IV). The rate limiting step in the reaction is believed to be the hydrolytic ring opening (II) of epoxide 1.[9b,d] A metal catalyst, typically a derivative of tungstic acid (H_2WO_4), is required together with an acidic ligand.[9a] An uncomplexed metal catalyst, as well as the use of a basic or neutral ligand, has been found to give low yield of adipic acid.[9a,d] The acidic condition is believed to be required in the two hydrolysis steps (II, VI).[9b,d]

Hydrogen peroxide exhibits both nucleophilic and electrophilic properties.[19] The O–O bond in hydrogen peroxide is easily polarized and 10^4 times more nucleophilic than water.[19] Moreover the O–O bond is relatively weak, approximately 213 kJ, and starts to dissociate at 35 °C.[19,20] Therefore, a self-consumption of hydrogen peroxide is expected at higher temperatures, in particular in the absence of organic substrates.

It has been found that a variety of tungsten oxide species can coordinate to silanol groups at the surface forming stable tungsten-containing mixed oxides.[18] Fig. 4 shows different coordination modes for tungsten oxides. The XPS data, see previous section, shows that the WO_3/SiO_2 materials contain tungstate of different oxidation states.

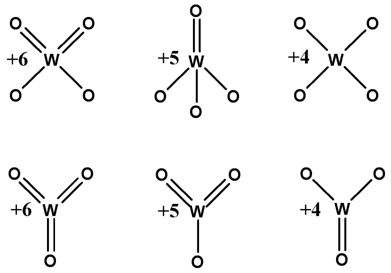
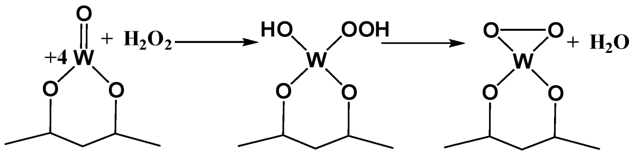


Fig. 4 Possible oxidation states for WO_4 and WO_3.

As discussed above in connection to Fig. 3, tungsten seems to be present as W(IV), W(V) and W(VI) oxides on the surface. Tungstates are known to act as catalytic centers for the oxidation reaction.[7]

A postulated mechanism for formation of a highly reactive peroxy complex generated from hydrogen peroxide is shown in Scheme 2.[10]



Scheme 2 Formation of a silica-bound peroxotungstate complex.

Conversion of cyclohexene into adipic acid was selected as a reference reaction to evaluate the catalytic performance of the different mesoporous materials. Hydrogen peroxide is primarily present in the water-filled pores of the mesoporous particles, which were suspended in the apolar reactant, cyclohexene. The reaction is a typical case where the use of a mesoporous material can overcome problems associated with reactant incompatibility. The water-hydrocarbon system used as reaction medium has both safety and environmental benefits compared with the existing synthetic procedures.[21]

The reaction needs an excess of hydrogen peroxide and in the literature 4.4 equivalents of hydrogen peroxide to cyclohexene has been reported to be sufficient.[9b] However, in this work 4.6 equivalents of hydrogen peroxide were used, which ensures that cyclohexene is the limiting reactant. Fig. 5 shows the disappearance of cyclohexene as a function of time for a range of systems investigated. It can be seen that without a catalyst such as sodium tungstate hydrogen peroxide is not a useful oxidant for cyclohexene. Reaction in a slurry of mesoporous silica gives only marginal consumption of the starting material. The results also show that a soluble oxidation catalyst may readily be replaced by catalytic sites built into the frame of the mesoporous material. This immediately opens possibilities for facile reuse of the catalyst, which is important for industrial applications of the process.

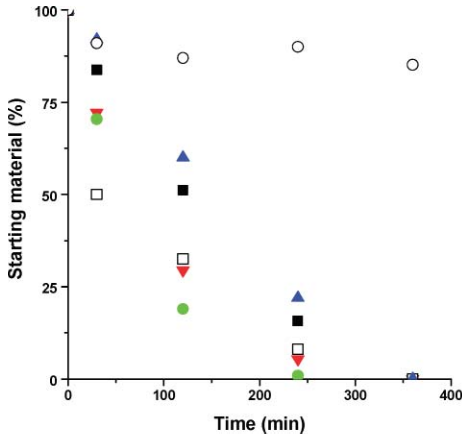


Fig. 5 Cyclohexene consumption profiles for reactions with different types of mesoporous materials: ○ SiO_2–B; ▲ TiO_2, 5.01 mmol, ■ SiO_2–B with 0.045 mmol Na_2WO_4; ▼ Al_2O_3 with 0.045 mmol Na_2WO_4; ☐ WO_3, 1.73 mmol and ● WO_4/SiO_2, 0.016 mmol (representing the WO_3/SiO_2-1–5 materials).

There is no major difference in the consumption of cyclohexene between the different types of materials. For instance, the reactivity does not follow the value of the interfacial area of the materials. The figure clearly shows that as long as a suitable metal catalyst is present, in immobilized or free state, cyclohexene oxidation to the intermediate epoxide 1 is rapid.

The yield of the target product, adipic acid, was monitored after 24 h reaction. This analysis revealed important and interesting differences between the different reaction systems, see Table 3. Almost complete conversion of cyclohexene into adipic acid was obtained when a slurry of mesoporous WO_3 was used as reaction medium. Nearly quantitative yield was also obtained with the mixed oxide WO_3/SiO_2 provided the WO_3 to SiO_2 ratio was high enough.

Reaction with SiO_2–A and B with added tungstate catalyst gave a moderately good yield of adipic acid, 44 and 55%, respectively. Al_2O_3/SiO_2, also with added tungstate catalyst, gave 17% yield but only Al_2O_3 with added catalyst did not give any adipic acid at all. The reason why Al_2O_3 gives such a poor yield is not clear. It is the material with the largest pore size but the material with the second largest pore size is WO_3, which was the oxide that gave the highest conversion of cyclohexene to adipic acid of all the materials. A possible reason for the poor performance of Al_2O_3 could be that it has the highest point of zero charge of all the investigated oxides, in the range 8.0–8.5. Thus, at the conditions used for the reaction the pore walls carry a net positive charge. This could be detrimental for the reaction because such positively charged surface sites may tie up the tungstate anion, WO_4^{2-}, which is added (as its sodium salt) as catalyst. The catalyst may become inactivated by adsorption to the walls of the mesoporous structure. It can be seen from Table 3 that the main product when Al_2O_3 is used, alone or as a mixed oxide with SiO_2, together with the tungstate catalyst is the intermediate diol 2. Evidently, it is the oxidation of this diol to the hydroxyketone 3 that fails in the alumina system.

According to the literature, titania is an efficient catalyst for oxidation of cyclohexene to adipic acid.[11] In this work TiO_2 was much inferior to WO_3, however, and gave a very low yield of adipic acid. As can be seen from Table 3, there seems to be a threshold value of WO_3 in the WO_3/SiO_2 material for the reaction to proceed well. WO_3/SiO_2-3, which gives almost quantitative yield of adipic acid, contains 5 mol% WO_3 while WO_3/SiO_2-4, which gives a poor yield, contains 2.5 mol% WO_3. Table 3 also shows the turnover frequency (TOF), calculated as mole of adipic acid generated per mole of catalytically active metal (W or Ti). As can be seen, the highest activity is obtained with the materials that have high surface area and low loading of catalytically active sites.

There is a large difference between WO_3 and the WO_3/SiO_2-1–5 materials on the one side and WO_4/SiO_2 on the other side. Both give full conversion of cyclohexene but only WO_3 and WO_3/SiO_2-1–5 are capable of catalyzing oxidation of cyclohexanediol (intermediate 2). This difference in catalytic activity may be related to the observation that whereas WO_3/SiO_2-1–5 contains crystalline WO_3 groups, the oxotungsten silica, WO_4/SiO_2, seems to lack crystallinity. Futhermore, it could be that WO_3 and the WO_3/SiO_2 materials have the majority of the active sites on the framework while in WO_4/SiO_2 the active sites are largely hidden into the bulk of the material. It is interesting to note the high conversion into adipic acid obtained with WO_3 only despite the fact that this material has a large pore size and a low surface area. In this case there is evidently no correlation between surface area and catalytic efficiency.

As illustrated in Scheme 1, oxidation of cyclohexene to adipic acid involves several consecutive steps. Cyclohexene and the first intermediate, epoxide 1, are hydrophobic species with very low solubility in water. The other intermediates are somewhat more polar and the end product, adipic acid, is water soluble. The first two steps, the epoxidation (I) and the hydrolytic opening of the oxirane ring (II) are therefore likely to be true interfacial reactions, *i.e.*, occurring at the pore openings where the polar and the apolar regions meet. The subsequent reaction steps (III–VI) may occur at the interface but since the intermediates 2–5 have a certain solubility in water these reactions may also take place in the aqueous phase, *i.e.*, inside the pores of the mesoporous material. If this is the case, the incompatability problem should only be an issue for the steps I and II of Scheme 1.

Table 2 lists a number of characteristic properties of the mesoporous materials. It has not been possible to correlate parameters such as pore size or surface area with yield of adipic acid, as given in Table 3. The chemical composition of the material seems to be much more important than the internal structure.

One should be aware that the number of parameters that may influence the reaction is large when comparing such a wide range of different catalysts and this work only takes into account the parameters that we have regarded to be the most important. We have, for instance, not taken particle size into account. It is conceivable that a smaller particle size will result in more active sites per unit weight of catalyst being exposed, which may well lead to a higher reaction rate. This could be a topic for a future study. Likewise, we have made no attempt to assess the effect of ions in the reaction medium. Some of the solid catalysts contain sodium and chloride ions, and such electrolytes may effect the acid–base properties of the materials. A typical example where this type of consideration is relevant is in the comparison between the WO_3 and the Na_2WO_4 materials.

The most important finding of this work is that the mesoporous material with chemically incorporated WO_3 catalyst constitutes a very reactive system, even more reactive than mesoporous silica with added soluble catalyst. This observation opens for facile reuse of the material, which from a process point of view is very important. The next section addresses this issue.

Reuse of mesoporous catalyst

A very attractive feature of having the catalytically active site covalently built into the mesoporous material, as in mesoporous WO_3 and WO_3/SiO_2-1–5, is that reuse of the catalyst is simplified as compared to the situation when a soluble catalyst is added, such as when mesoporous SiO_2–A or SiO_2–B is used together with added Na_2WO_4. In order to test the reusability of the catalyst, mesoporous WO_3 and the WO_3/SiO_2-1–5 materials with varying ratio of the two oxides were subjected to recycling.

After a completed 24 h reaction the solid material was removed from the reaction mixture by filtration, washed and reused. Fig. 6 shows analysis results from the two consecutive runs. As can be seen, WO_3, as well as the two mixed oxides with the highest content of WO_3 (WO_3/SiO_2-1 and WO_3/SiO_2-2) work at least as well in the second run as in the first. However, WO_3/SiO_2-3, which was an active catalyst in the first run, performed poorly in the second run. Thus, it seems that the threshold value of WO_3 content for making the mixed oxide an active oxidation catalyst has become higher.

A probable explanation for the decreased efficiency of the WO_3/SiO_2-3 catalyst is that the pore system has been

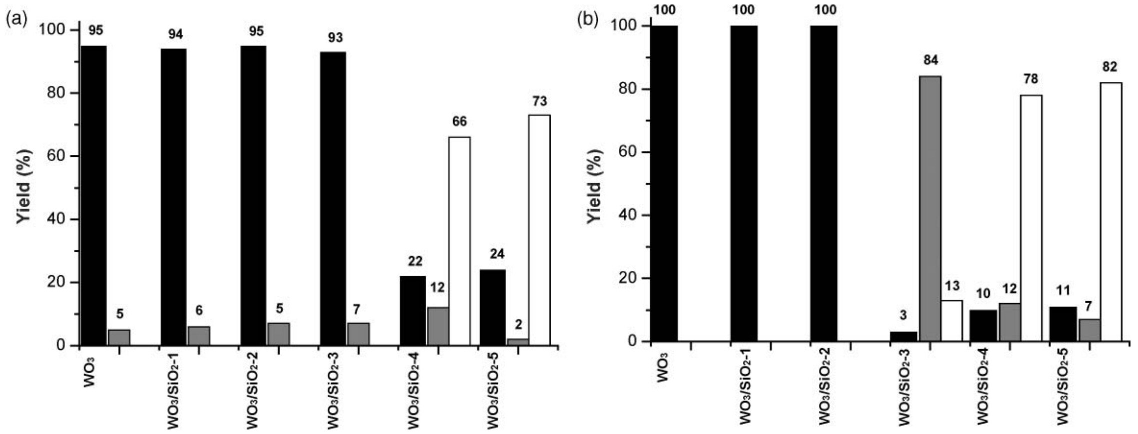


Fig. 6 Recycling experiments with WO_3 and the WO_3/SiO_2-1–5 mixed oxides as catalytically active materials. (A) and (B) show the product compositions after the first and the second run, respectively. Black- adipic acid, grey- diol 2, and white- other.

contaminated by organic residues from the first run, and that these residues have blocked catalytically active sites. Such deactivation of solid catalysts is well-known, for instance with zeolites.[22] Since mesoporous materials have considerably larger pore sizes than zeolites, one may expect them to retain their activity better in consecutive experiments but this will probably depend on the type of residue formed and thus vary from one reaction to another. The residues can probably be removed by calcination but the recovered catalysts in these experiments were not calcined.

The WO_3 material was subjected to a more extensive experiment with respect to reuse, see Fig. 7. After the first run, the only species that was detectable by the NMR analysis was adipic acid and the yields given therefore refer to that compound. As can be seen, the yield dropped between the second and the third run but stayed approximately constant after that.

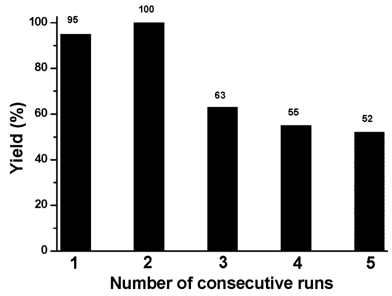


Fig. 7 Yield of adipic acid obtained after five consecutive runs using WO_3 as catalyst.

If clogging of the catalyst is the main reason for deactivation on repeated use, one may expect that a large pore size would be beneficial. At first, WO_3, which is good from a reusability point of view, seems to prove this point since it has a large pore size (11.5 nm). However, WO_3/SiO_2-1 and WO_3/SiO_2-2 also gave good results in the initial reusability test; see Fig. 6, and these materials have much smaller pore sizes. Thus, the results indicate that it is the relative amount of WO_3 at the surface of the material, not the pore size that dictates not only the catalytic activity in the first run but also the recyclability.

Conclusions

In this paper it has been demonstrated that the conversion of cyclohexene into adipic acid can be performed in suspensions of mesoporous oxides such as SiO_2, TiO_2, and WO_3, as well as in oxide mixtures such as WO_3/SiO_2, Al_2O_3/SiO_2 and WO_4/SiO_2. A catalytically active metal oxide catalyst, tungstate or titania, must be present, either as an integrated part of the porous oxide or as an externally added salt. Moderately good yield was obtained with SiO_2 and externally added Na_2WO_4. The corresponding system with SiO_2 replaced by Al_2O_3 gave no yield at all of adipic acid.

The most efficient systems were those where the catalytically active species were built into the framework, either as the sole oxide material or in combination with silica. WO_3 was found to be far superior to TiO_2. With WO_3 only and with WO_3/SiO_2 mixtures with high enough WO_3 content the yield of adipic acid after 24 h reaction was almost quantitative. This material could also be reused with reasonably retained activity. The degree of order of the mesoporous material and the pore size and the pore volume of the material seemed not to be important for the outcome of the reaction.

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