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NOTE

Molybdate and Tungstate Doped Porous Carbons as Hydrogen Peroxide Activation Catalysts for Sulfide Oxidations

The use of porous carbons as catalyst supports is an emerging area in catalysis (1–3). These carbons are themselves redox active catalysts (1a) and addition of metals and metal oxides lead to synergistic interactions which catalyze a variety of reactions, e.g., the low temperature oxidation of methanol (1c), the deep oxidation of chlorinated hydrocarbons (1d), the deep oxidation of hydrocarbons, and the decomposition of NO (1h).

Recently, we have reported (4) that porous carbons, pore filled with solid NaOH, retain nearly all the NaOH when stirred for 5–10 min in water. These materials are effective base catalysts for Michael reactions, the reaction of chalcone with nitromethane, and vapor phase aldol condensations. Recent reports also indicate that metal substituted polyoxometallates are effective catalysts for the oxidation of mustard analogs by *t*-butylhydroperoxide (5) and can be supported (5c) on porous carbons to produce heterogeneous catalysts.

Porous carbons have found applications in the adsorption of chemical warfare (cw) agents from personnel and small equipment (6). It would be desirable if the absorbed materials could be destroyed catalytically. A catalytic adsorbent could find widespread utility in decontamination as well as in cw agent stockpile reduction. The reaction chemistry of nerve agents is similar to that of insecticides, so catalytic adsorbents could also find applications in the remediation of these contaminants.

Mustard (HD; $(ClCH_2CH_2)_2S$) is destroyed by oxidation (6) and G-nerve agents are destroyed by hydrolysis which is base catalyzed by nucleophilic attack at phosphorus (6). For environmental concerns, H_2O_2 and O_2 constitute the most desirable oxidants. Unfortunately, in most systems the basic conditions favorable for catalysis of hydrolysis reactions inhibit oxidations by peroxide.

Molybdenum and tungsten compounds activate hydrogen peroxide in homogeneous solution to oxidize a variety of substrates including organic sulfides (7). MoO_4^{2-} is also a remarkable nucleophile (8) with a second-order rate constant 35 times that of phosphate for the hydrolysis of *p*-nitro-phenylacetate in spite of phosphate having a 1000-fold larger basicity. This research demonstrates that absorbent carbons, pore filled with molybdate and tungstate ions, are very effective catalysts for the oxidation of sulfides with 30% aqueous H_2O_2. The novel feature of these catalysts is that they carry out oxidations under basic conditions where G-agents would also undergo catalyzed hydrolysis.

Catalyst preparation: $Na_2MoO_4 \cdot 2H_2O$, $Na_2WO_4 \cdot 2H_2O$, $Cu(NO_3)_2$, and $Ni(NO_3)_2$ were obtained from Fisher and used as received. Phosphotungstic acid was synthesized. All solvents and reactants were obtained from Fisher. Ambersorb 572 (lot 2125), donated by Rohm and Haas was soaked in 6 *M* HCl overnight, rinsed with water several times, soxhlet extracted with methanol for 6 h, and dried in vacuum overnight at 110°C before pore filling.

Supported catalysts were prepared using two methods. Catalysts were prepared by refluxing the support, metal, an solvent (CCl_4, toluene, or acetonitrile) under nitrogen for 24 h. Typically, the support : metal ratio was 100 : 1 by mass. Catalysts also were prepared by dissolving the metal compound into an appropriate solvent and pore filling the support (i.e., adding solution until the solid was barely moist). Typically, about 1 ml of solution per gram of solid is required and this is comparable to the total pore volume of the solid. In both methods, the prepared catalysts were then dried in a vacuum oven at 105–110°C for at least 16 h. As shown in Table 1, Na_2MoO_4 pore filled A-572 resulted in complete oxidation of EtSPh in 6 min compared to 90% conversion for the same composition catalytic adsorbent prepared by refluxing. Pore filling was the method used in all experiments unless indicated otherwise.

$CuMoO_4$/A-572 was prepared by pore filling A-572 with Na_2MoO_4 dissolved in water and drying the solid in a vacuum oven. This was followed by pore filling Na_2MoO_4/A-572 with aqueous $Cu(NO_3)_2$, washing with water several times to remove $NaNO_3$, and drying in a vacuum oven at 110°C for 24 h.

Homogeneous catalyzed oxidations: Sodium tungstate and molybdate were used as catalysts in homogeneous oxidations of EtSPh. Solvent (1.5 ml), 0.1 ml EtSPh, and 0.2 ml H_2O_2 (30%) were added to about 0.008 g of the catalyst in a 6 inch test tube. The solution was stirred magnetically for 6 min at ambient temperature and pressure. The corresponding sulfoxide and sulfone were measured using an

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TABLE 1

Catalyzed Oxidations of $C_2H_5SC_6H_5$

Catalyst[a]	Solvent[b]	% Conversion to sulfone[c]
None, soln	CH_3CN	1–3 even after 30 min
None, soln	50/50	10
None, soln	CH_3CN	3
Na_2MoO_4, soln	CH_3CN	100
Na_2MoO_4	CH_3CN	100–90 lch–100
Na_2MoO_4, R	CH_3CN	93–90 lch
$CuMoO_4$	CH_3CN	100–55 lch–99–40 lch-99
$NiMoO_4$	CH_3CN	100–50 lch–99–99
Na_2WO_4, soln	CH_3CN	100
Na_2WO_4, soln	buffer	95
Na_2WO_4	CH_3CN	100–90 lch–100–98–98
Na_2WO_4	50/50	98
Na_2WO_4	t-C_4H_9OH	100–99–99
Na_2WO_4, SOX	CH_3CN	100–70 lch
Na_2WO_4, 0.5% KOH	CH_3CN	100–50 lch–98
$H_3PO_4 \cdot 12WO_3$	CH_3CN	95–99

[a] Unless indicated, the catalyst (1% by mass) was supported on A-572 by pore filling; soln refers to a homogeneous reaction with no support. None refers to control reactions. R indicates the catalyst was prepared by refluxing in CH_3CN under N_2 for 24 h and drying at 110°C. SOX refers to a catalyst that was washed by soxhlet extraction with CH_3OH overnight.

[b] Buffer refers to an aqueous solution of sodium tetraborate, pH 9, and 50/50 refers to an equal mixture of this buffer and CH_3CN.

[c] Reactions are typically carried out for 6 min. In all instances, the product of the reaction is ethylphenylsulfone, $EtSO_2Ph$. Dashes indicate repeat experiments with the same adsorbent catalyst after filtering off the product solution and washing with CH_3CN. Lch indicates that the product solution was separated from the catalyst and a homogeneous oxidation carried out with the filtrate. For example, the seventh entry from the top indicates 100% oxidation with the solid catalyst with 55% by the leachate. This is followed by 99% oxidation with the solid catalyst followed by 40% by the leachate. This is followed by 99% oxidation by the solid catalyst.

SRI 8610-FID gas chromatograph with an Alltech AT-1000 15 m × 0.54 mm ID capillary column.

Heterogeneous catalyzed oxidations: 0.5 g of supported catalyst (1% loading by mass unless otherwise specified), 1.5 ml solvent (e.g., CH_3CN), 0.1 ml EtSPh, and 0.2 ml H_2O_2 (30%) were added into a 6 inch test tube. The reaction mixture was stirred for 6 min at ambient temperature and pressure. The liquid above the support was filtered through a glass wool filter to remove any solid and the solution was analyzed as described in the homogeneous oxidation procedure. The conditions used led to complete conversion to sulfone in all instances.

To test for leaching and repeat catalyst evaluation, the product from an oxidation reaction was filtered through glass wool. The solid was washed with CH_3CN and used in a subsequent oxidation reaction following the above procedure.

To test for leaching, 0.1 ml of EtSPh and 0.2 ml of H_2O_2 (30%) were added to the solution that had been analyzed and after 6 min of stirring, the solution was again analyzed by G.C for sulfoxide and sulfone.

The oxidations were carried out by adding Ambersorb 572 (A-572) (0.5 g) containing the catalyst (1% by mass in the support) to a solution of the sulfide (0.1 ml; 0.7 mmol) in solvent (1.5 ml) containing 0.2 ml of 30% H_2O_2 (2.0 mmol). The solution was stirred for 6 min under ambient conditions, filtered, and analyzed by G.C. In a random selection of experiments with active catalysts, the solid beads were crushed, extracted, and found to contain adsorbed sulfone, but no sulfide. Table 1 summarizes the results for catalyzed oxidation of the mustard simulant, $C_2H_5SC_6H_5$ (EtSPh).

The first three entries in Table 1 are blank runs. The effectiveness of the molybdate catalyst is seen in the homogeneous oxidation where complete oxidation occurs with 0.033 mmol of catalyst in less than 6 min under ambient conditions. When $Na_2MoO_4 \cdot 2H_2O$ is added to A-572 by either reflux or pore filling techniques, a very effective catalyst results. The 0.02 mmol of molybdate in the 0.5 g of catalyst oxidize 0.7 mmol of sulfide to sulfone in 6 or less minutes giving at least 70 turnovers per minute for the heterogeneous reaction. In one experiment, complete conversion was observed in 3 min exceeding 140 turnovers per minute. The final solutions were not analyzed for residual H_2O_2, but a minimum value for the peroxide efficiency is 70% in those runs where 95–100% sulfone is obtained. The solution is filtered off the catalyst producing a clear filtrate. With a fresh 0.1 ml of sulfide and 0.2 ml of H_2O_2 added to this filtered solution, the traces of molybdate that have leached off the catalyst lead to 90% oxidation of the sulfide in 6 min. Thus, even at molybdate concentrations too low to detect by visible spectroscopy efficient catalysis occurs. When the filtered solid carbon catalyst is reused, 100% oxidation of sulfide is again observed in 6 min at ambient temperatures. The catalyst prepared by pore filling is slightly more active than the catalyst prepared by reflux (see above). No apparent difference in leaching results with either method of preparation.

In an attempt to minimize leaching of the catalyst into solution, the $Na_2MoO_4 \cdot 2H_2O$/A-572 catalyst was pore filled with stoichiometric amounts of $Cu(NO_3)_2$ and a second batch with $Ni(NO_3)_2$ to prepare the less soluble $CuMoO_4$ and $NiMoO_4$. Complete oxidation of the substrate with H_2O_2 occurs in 6 min and the filtered solution resulted in 50% oxidation of a new charge of sulfide by peroxide. The solid $CuMoO_4$ and $NiMoO_4$ catalysts from the first oxidation were reused a second and third time. Complete oxidation of the new charges of sulfide resulted in all instances, establishing the point that oxidation is catalyzed by molybdate in the solid carbon.

Results similar to $Na_2MoO_4 \cdot 2H_2O$ were obtained with $Na_2WO_4 \cdot 2H_2O$. The doped carbon gives over 95 turnovers per minute. This catalyst was also shown to be active in the solvent t-C_4H_9OH and in a 50/50 CH_3CN : buffer solvent. When pore filled $Na_2WO_4 \cdot 2H_2O$ is soxhlet extracted overnight with methanol, the amount of tungstate that leaches into solution during the first oxidation is decreased. In this case, only 70% sulfide oxidation occurred in the homogeneous oxidation using the filtrate. However, the reuse of the catalytic adsorbent leads to complete oxidation of sulfide to sulfone in 6 min under ambient conditions. This result indicates that the amount of leachate in the 1.5 ml of solvent used in an oxidation run is very small and the catalyst could be used many times before the dopant was lost by leaching. This result also demonstrates that a heterogeneous reaction occurs.

The reaction of leachate from the catalyst prepared by a second pore filling of the Na_2WO_4 catalyst with 0.5% KOH is less than that without KOH addition. This could be due to less effective catalytic activity in basic CH_3CN or to less leaching of WO_4^{2-}. The relevant point from our standpoint is that even with strong base present, efficient catalysis of the peroxide oxidation of EtSPh occurs with the doped carbon under ambient conditions. A 1% loading of phosphotungstic acid ($H_3PO_4 \cdot 12WO_3$) in A-572 also produced an effective oxidation catalyst. Under reaction conditions, the phosphotungstic acid is probably a precursor for lower molecularity peroxometalates (9).

$Na_2MO_4 \cdot 2H_2O$ ($M =$ Mo or W) exists as aggregates in aqueous solution at a pH of 6 or lower. The species $MO(OH)_5^-$ forms first and as the pH is lowered, the next species detected in the case of molybdenum is $Mo_7O_{24} \cdot xH_2O^{6-}$. The species that exist on the surface of the carbon are unknown. With OOH^- able to replace OH^- in these species, it is expected that coordination activates peroxide so that direct nucleophilic attack by sulfide and sulfoxide are the oxygen atom transfer mechanisms. In the reported (10) classification scheme for metal complex activation of O_2 and peroxides, this corresponds to the Class IVb mechanism. Alternatively, a one electron oxidation of the sulfide and reduction of the molybdenum or tungsten species can generate a sulfur cation radical (5a, 11) that is subsequently converted to sulfoxide. One electron oxidation of the sulfoxide would then occur to give the sulfone. This reaction would be included in the Class V category (10).

Molybdate and tungstate doping of A-572 leads to catalytic absorbents for oxidative and base catalyzed reactions. Freshly prepared catalysts leach small amounts of dopant into solution. Reuse or extensive washing diminishes leaching while maintaining excellent catalytic activity. These results demonstrate that a heterogeneous reaction occurs. With only 0.02 mmol of $Na_2MoO_4 \cdot 2H_2O$ in 0.5 g of carbon in the original catalyst, very little tungstate or molybdate is required for effective catalysis. The new and reused catalysts exhibit turnovers per minute of 70–95 and peroxide efficiencies of at least 70%.

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