Putting Depleted Uranium to Use: A New Class of Uranium-Based Catalysts

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ABSTRACT

Uranium oxides are known to have high efficiency and long-term stability when used to destroy volatile organic compounds (VOCs) when compared with some of the commercial catalysts, such as precious metals, TiO_2, and Co_3O_4 catalysts. Two key factors limiting catalytic activities of uranium oxides prepared by conventional methods are small *surface area* and *pore size*. To overcome these limitations, mesoporous uranium oxides and uranium oxide, which are dispersed on mesoporous oxide hosts are synthesized. Some preliminary results in the synthesis and characterization of uranium oxides, which are supported on mesoporous hosts with large surface areas and porosities, are reported in this paper. This work was conducted under the auspices of the U.S. Department of Energy's Depleted Uranium Uses Research and Development Program.

INTRODUCTION

The U.S. Department of Energy (DOE) is responsible for a variety of complex and unique waste materials and environmental problems. More than 2,500 soil and groundwater plumes are contaminated with organic solvents, such as alkanes, aromatics, and chlorinated organic compounds. The organic compounds are not readily degraded by microorganisms and thus persist in environmental media. For the volatile organic compounds (VOCs), pump-and-treat and vacuum-extraction techniques have been developed and are commonly used for remediating soils and groundwater contaminated by VOCs (1–4). Low-temperature (100–287°C) thermal desorption has also been proposed as a cost-effective technology for treating organically contaminated soils, sludge, and other mixed and tank wastes. However, in all these processes, an off-gas containing hazardous VOCs is generated and must be treated to prevent the release of VOCs to the atmosphere. Adsorption by activated carbon is commonly used to treat off-gas VOCs, but the process generates large quantities of secondary hazardous wastes and is therefore undesirable (5). Thermal catalytic combustion is also used to destroy VOCs. Various catalysts that fall into two broad categories—noble metals and metal oxides—have been proposed. Precious-metal catalysts, which are often used in supported forms, show high intrinsic combustion activity; however, they are relatively expensive; are susceptible to poisoning even at low contaminant levels; and, in some cases, show poor stability (6, 7). Metal-oxide catalysts (such as TiO_2 and Co_3O_4) can tolerate relatively high levels of poisons. However, the activity shown by these oxides is generally lower than that of precious metal catalysts. It is therefore recognized that the slow reaction kinetics and low destruction efficiency of VOCs have been limiting steps to remediate VOC-contaminated soils and groundwater or other mixed-waste streams.

A high-activity oxide catalyst, which operates at a relatively low temperature (<450°C), is highly desirable. A uranium-oxide catalyst holds promise, and its efficiency in degrading various organic compounds has been recently demonstrated. Notably, Hutchings and co-workers (7, 8) found that the benzene conversion over a U/SiO_2 catalyst was 100% at 400°C and that CO and CO_2 were produced

with selectivities of 27 and 73%, respectively. The U and or SiO_2 catalyst was also examined for the destruction of butane. With U loaded onto SiO_2 and heated to 500°C, butane oxidation was 100%. This activity was even higher than that shown by using U_3O_8 alone. The high reactivity of U_3O_8 detailed in these studies is of great significance, particularly when compared with the combustion activity of Co_3O_4, which is known to be highly active for many organic substrates (8, 9, 10). Chlorinated organic compounds are known to be particularly stable. However, Hutchings et al. (7, 8) recently reported that uranium-oxide-based catalysts are effective in destroying a range of vapor-phase hydrocarbons and chlorinated organic compounds (such as chlorobenzene and chlorobutane) at a very high flow rate.

Unlike incineration, which is carried out at a high temperatures, typically >1000°C, catalytic oxidation involves combustion at lower temperatures, typically 400–600°C. The lower temperatures required for catalytic oxidation result in lower fuel demand and can therefore be more cost-effective than a thermal incineration process. More importantly, perhaps, catalytic oxidation is not classified as an incineration process, thus eliminating many regulatory operation requirements. Another distinct advantage of catalytic oxidation is that it can operate with very dilute pollutant concentrations (<1%), which cannot be thermally combusted without additional fuel. The catalytic process also exerts more control over the reaction products and is less likely to produce toxic by-products, such as dioxins, which are often produced by high-temperature thermal incineration (7, 8).

The overall goal of our research is to synthesize a new class of mesoporous uranium oxide and mesoporous sol-gel catalysts, which are loaded with uranium oxides to destroy a range of volatile organic contaminants, including alkanes, aromatics, and chlorinated organic compounds, through the reutilization of spent (or depleted) uranium. *This study is motivated (a) by the high-efficiency and long-term performance of uranium-oxide-based catalysts in degrading many contaminant organic substrates as compared with some precious metal catalysts, and (b) by the needs for efficient disposal or reutilization of spent uranium at many DOE facilities.* Current uranium-oxide catalysts (e.g. U_3O_8 and UO_3), prepared by conventional solid-state syntheses, have very small surface areas (<1 m^2/g). A large surface area is essential to increase the surface-adsorption capacity of VOCs on catalysts, which is a pre-condition for any efficient heterogeneous catalytic reactions. Furthermore, conventional uranium-oxide catalysts are basically nonporous materials, implying that the bulk of the uranium-oxide catalysts are not involved in catalytic reactions because they are inaccessible to reactant molecules. Accordingly, any increase in surface area will greatly increase the catalytic efficiency of the uranium oxides in the destruction of VOCs. Here, we report the synthesis and characterization of two mesoporous hosts loaded with uranium oxides for the destruction of VOCs. These new materials have much higher surface areas than those of conventional uranium catalysts. Two methodologies have been developed for synthesizing uranium oxides supported on mesoporous materials. The first method is based on the ion-exchange reaction, while the second one is a co-assembly synthesis.

Experimental

Chemicals: The chemicals used in the synthesis were tetramethylothosilicate, which was obtained from Gelest, Inc.; sodium hydroxide (50 wt %) and cetyltrimethylammonium chloride (CTAC) 25 wt %, which were obtained from Aldrich Inc.; uranyl nitrate hexahydrates, which were purchased from Alfa Inc; nitric acid (69%), hydrochloric acid (37%), and anhydrous methanol, which were obtained from J. T. Baker, Inc. The absolute ethyl alcohol was purchased from AAPER Alcohol and Chemical, Inc. All chemicals were used as received.

Mesoporous silica loaded with uranium oxide via ion-exchange reaction: Ordered mesoporous silica was synthesized according to procedures in the literature (11). The typical procedure involved mixing cetryltrimethylammonium bromide (CTAB), tetramethylothosilicate (TMOS), water, and base (NaOH).

The molar ratio of CTAB:TMOS:H_2O:NaOH was 0.12:1:130:0.7. The mixture was then heated at 100°C for 24 h. The white, solid product was recovered by filtration. The residue was then stirred in ethanol containing 0.1 *M* uranyl nitrate for 4 h. The resulting gel was calcined at 600°C for 4 h.

Synthesis of mesoporous uranium catalysts via co-assembly route: A very simple technique was developed to produce monolithic, uranium-containing glasses, which provided fairly high surface areas and a sharp pore-size distribution. The synthesis of these glasses involved mixing 1 mL of a surfactant (CTAB) in acidic solution, 1 mL methanol, 1 mL of a uranyl solution, and 1 mL of a silicon source (TMOS). Once these four starting materials were mixed, a transparent yellow solution was formed. These solutions were covered and allowed to dry in air. The surfactant templates were removed through calcination at 400 or 600°C for 4 h.

Characterization: Nitrogen adsorption isotherms were measured on a Micromeritics Gemini 2375™ surface-area analyzer. The ultraviolet and visible spectra were measured with a Cary 14H scanning spectrophotometer, which had been converted by On-Line Instrument Systems (OLIS) for data acquisition via a personal computer (PC). X-ray scattering plots of the mesoporous supports were measured on the 10-m, small-angle X-ray scattering (SAXS) camera at the SAXS user facility of the Oak Ridge National Laboratory.

Fabrication of Mesoporous Support Hosts

Recent breakthroughs (11–15) in catalyst synthesis have resulted in a novel methodology for preparing mesoporous inorganic materials with extremely *high surface areas and ordered mesostructure*. Mesoporous silicon, aluminum, and transition metal oxides have been prepared. The essence of this new methodology is the use of molecular assemblies of surfactants or related substances as structure directors during formation of oxides. The original method was developed by scientists at Mobil Oil Research and Development for synthesis of ordered mesoporous silica (11). The mechanism for the organization of such mesostructure involves electrostatic interactions and charge-matching between micellar assemblies of quaternary ammonium cations and anionic silicate oligomer species, as shown schematically in Fig. 1. Stucky et al. (12) have developed a model that uses the cooperative organization of inorganic and organic molecular species into three-dimensional arrays. Based on this model, there are three main methodologies for synthesizing high-surface-area mesoporous materials: (1) $I^{!}\ S^{+}$, where charged surfactant molecules interact with inorganic oxide precussors via coulombic interactions; (2) $I^{+}\ X^{!}\ S^{+}$, where positively charged surfactant molecules interact with positively charged inorganic oxide precussors through a negatively charged mediator $X^{!}$; (3) I° S°, where neutral surfactant molecules interact with inorganic oxide precussors via hydrogen bonds. The interaction between inorganic precursors and organic surfactants is not limited to the electrostatic interaction, but also includes interaction of hydrogen bonding or mediated by the counter-

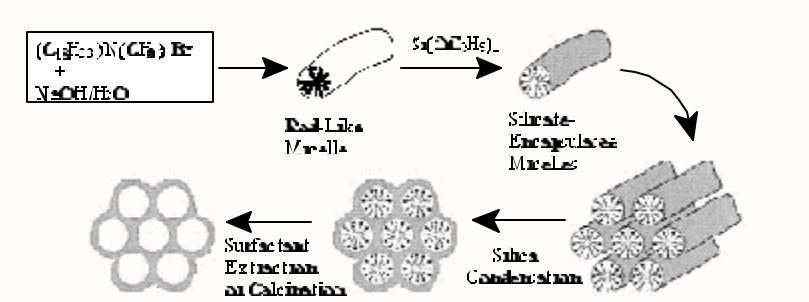

Fig. 1. Surfactant self-assembly synthesis of mesoporous materials.

charged ions. The surfactants used in synthesis can be cationic, anionic, or neutral, depending on the charge of the inorganic precussors. Almost all transition metal oxides can be prepared into high-surface-area mesoporous forms (16, 17).

Unlike microporous catalysts, which can interact only with reactants on outer surfaces, mesoporous materials have larger pore openings, which allow for access to the inner pore surfaces. This feature will result in a much higher catalytic efficiency for mesoporous catalysts. In addition, the mass transport of organic vapors in these materials is far more efficient than that in conventional microporous catalysts, such as zeolites, because of their unique mesoporous pore diameters (20 Å–100 Å). These considerations prompted us to synthesize a new class of uranium oxides supported in mesoporous hosts (e.g., SiO_2 and TiO_2) for the destruction of VOCs.

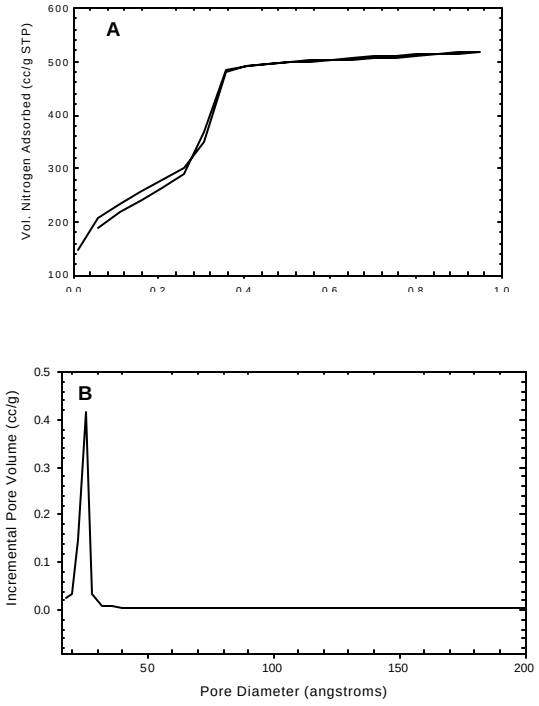

Fig. 2. (A) N_2 adsorption isotherm. (B) Pore-size distribution of ordered mesoporous silica. This distribution was calculated from N_2 adsorption isotherm based on the Barret-Joyner-Halenda (BJH) method.

Figure 2 gives the N_2 adsorption isotherm and pore-size distribution of the calcined mesoporous silica prepared through surfactant template synthesis. The corresponding B.E.T. surface areas, total pore volumes, and pore diameters are 1,080 m^2/g, 0.81 cm^3/g, and 25 Å, respectively. The isotherm of the mesoporous silica has a step around 0.1–0.4 P/P_0 (Fig. 2A), which is characteristic of mesoporous materials. Figure 3 gives the small-angle X-ray scattering of the calcined mesoporous silica host. The narrow scattering peak indicates the long-range order organized by the surfactant templates. The position of the main scattering peak (2 Å = 2°) agrees well with the corresponding pore size determined by N_2 adsorption experiment. A transmission electron microscopy image of this material is shown in Fig. 4. The hexagonally-packed pores (25 Å) can be easily seen from this image.

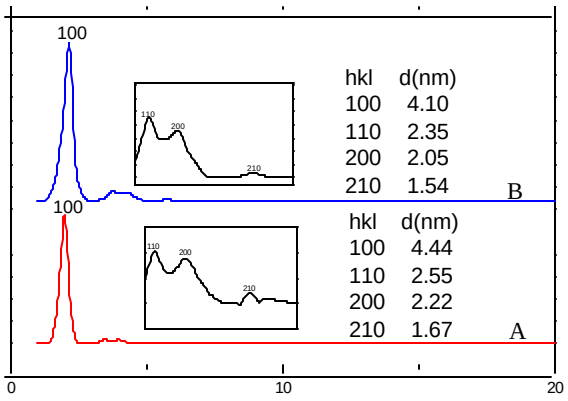

Fig. 3. Small-angle X-ray scattering of as-synthesized mesoporous silica (A) and calcined mesoporous silica (B).

Methodology for Synthesizing Uranium Oxides Catalyst

The most common method used to synthesize supported catalytic systems is impregnation of catalysts on inorganic supports. The supported material may be prepared in a variety of ways, but all suffer major problems: (a) no control of the

location of catalytic particles on support surfaces, (b) potential aggregation of particles, and (c) polydispersion of particle sizes. Large-particle-size distributions limit the tunability and selectivity of the nanoparticle catalysts and make it difficult to correlate experimental test results with particle sizes. The particles isolated on external surfaces of the supports are susceptible to aggregation, which eventually destroys the ultradispersion and catalytic efficiency. To overcome these limitations, one of the objectives for this research is to develop a systematic methodology to synthesize and disperse stable uranium-oxide catalysts on ordered mesoporous silica and related materials through the controlled transport of precursors via ion-exchange reactions.

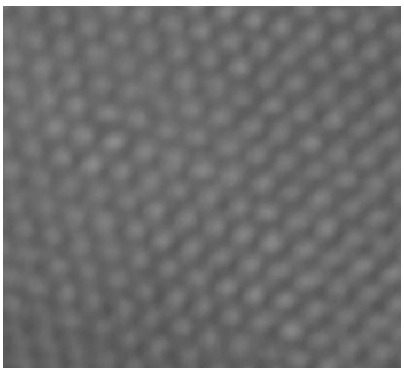

Fig. 4. Transmission electron microscope (TEM) image of SiO_2-ordered nanopores (25 Å).

Ion Exchange Reaction Method. The ion-exchange reaction, shown in Eq. 1, has been extensively used to prepare novel intercalate materials. The general reaction mechanism can be expressed as follows:

$$m(S\text{-}O^-)M_1^+ + M_2^{m+} = (S\text{-}O^-)_mM_2^{m+} + mM_1^+ , \quad (1)$$

where (S-O$^-$) is a surface anionic group of inorganic materials such as the galleries of pillared materials, M_1^+ is a singly charged cation in as-synthesized materials, M_2^{m+} is a new cationic species, and m is the number of surface sites involved in the ion exchange which needs to be intercalated into the preceding materials. Ordered nanoporous materials synthesized by the use of cationic surfactants have the same structural feature as those of ionic intercalate materials. In this case, the (S-O$^-$) groups correspond to the SiO^- anions on the nanopore surface, while M_1^+ is a cationic surfactant ion, cetyltrimethylammonium (CTA^+). The CTAs are organized in the form of a cylindrical micellar structure with hydrophilic positive ends Coulombically interacting with negatively charged silica pore surfaces. The weak Coulombic interaction can be easily broken or replaced by another cation through ion exchange. In fact, this exchange reaction has been used to remove surfactant molecules from the ordered inorganic materials synthesized through the surfactant-templating method (19). The surfactant ions can be removed using HCl, NaCl, NH_4Cl, etc. For example, Badiei and Bonneviot (19) have used the ion-exchange reaction between CTA^+ and a copper complex to load Cu^{2+} into as-synthesized mesoporous silica.

Ion-Exchange Experimental Results. We have recently demonstrated the use of the ion-exchange reactions to deliver molecular imprints inside the mesopores (20). Therefore, the surfactant ions in the mesopores can be used as a unique vehicle to transport metal ions inside the mesopores. Accordingly, UO_2^{2+} can be loaded *inside* the mesopores through this ion-exchange reaction. The unique property of this ion-exchange technique is that metal ions are transported *only* inside the pores. Very few metal ions are expected in outer surfaces of the oxide substrates because there are no cationic surfactants in these places. The transported metal ions can then be used as sources for nanoparticle-catalyst assemblies inside the nanopores. Since the metal ions are located inside the nanopores, the sizes of the nanoparticles assembled are precisely controlled by the pore diameters, and each pore can be viewed as an independent nanocatalytic reactor. This nanoparticle oxide growth can be viewed as a template growth process (21). These oxide nanoparticles are monodispersed and accessible to chemical reactions. Figure 5 shows a

schematic diagram of the protocol used in such synthesis. A light-yellow powder containing uranyl ions

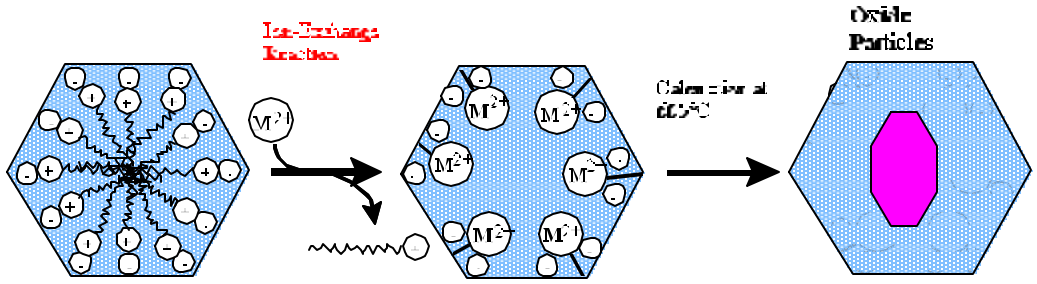

Fig. 5. Synthetic procedure for uranium oxide supported on MCM-41.

was obtained through this synthesis. Fluorescence spectroscopic measurement showed an intense green emission, whose band maximum is at 520 nm. This emission indicates the presence of uranyl species on the mesoporous silica.

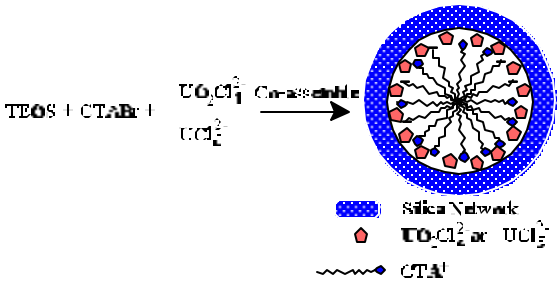

Fig. 6. Co-assembly synthesis of uranium oxide supported on mesoporous silica.

Co-Assembly Synthesis Method. Another synthetic method that we have explored is co-assembly. This approach is very like that of $I^+ X^! S^+$ scheme synthesis of mesoporous supports (12). The mediator, ($X^!$ in this case) is the anionic complex of uranyl, depending on precursor uranium oxidation states. The halide complexes of uranyl are $UO_2X_4^{2-}$ (X = Br^-, Cl^-). These complexes are known to be very stable and the dominant species under high halide concentration. Concentrated halide acids are used to mediate and catalyze sol-gel reactions of inorganic precursors, such as tetraethylorthosilicon (TEOS). The overall reaction is shown schematically in Fig. 6. The surfactant templates were removed by calcination. It is well known in sol-gel chemistry that acid-induced, sol-gel processes normally give rise to transparent monolithic products.

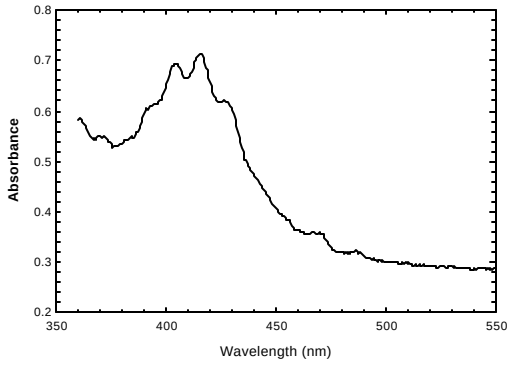

Fig. 7. UV-vis absorption spectrum of mesoporous, uranyl-doped silica glass.

Co-Assembly Experimental Results. As expected, transparent, monolithic, mesoporous materials were produced using the co-assembly synthetic route. The surface area and pore volume of these monolithic catalysts are around 500 m^2/g and 0.4 cm^3/g, respectively. Figure 7 gives ultraviolet visual spectrum of a typical uranyl-doped mesoporous silica, synthesized by the co-assembly method. The characteristic

absorption band around 400 nm can be attributed to the charge-transfer electronic transition of the uranyl group. The mesoporous materials obtained in this way are expected to have the mesopores coated with uranium oxides. Theoretically, all pore surfaces of the mesoporous supports can be used in the catalysts.

CONCLUSIONS

Two methods have been developed to prepare uranium-oxide catalysts supported on mesoporous oxide hosts. The first method makes use of the ion-exchange reaction to efficiently load uranyl ions inside the nanopores of MCM-41. The second method, co-assembly, is used to synthesize the mesoporous uranium catalyst via a $UO_2X_4^{2-}$ mediator. The structural properties of these new catalytic systems were characterized by ultraviolet-visible fluorescence, x-ray diffraction, and nitrogen-adsorption measurements. The surface area of mesoporous catalysts is .650 times greater than conventional catalysts. Consequently, these mesoporous uranium catalysts are expected to be much more efficient than conventional catalysts. The chemical reactor tests of these catalytic systems are underway.

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