

Uranium-Based Catalysts

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INTRODUCTION

U.S. industry and the U.S. Department of Energy (DOE) must manage a variety of off-gas wastes consisting of complex and halogenated volatile organic compounds (VOCs). The literature indicates that uranium dioxide has a high activity for the catalytic destruction of VOCs and halogenated VOCs [1]. DOE has a surplus of depleted uranium (DU) inventory for which beneficial uses are being sought [2]. The goal of this research, therefore, was to explore the possibility of tailoring DU-based catalysts for use in the catalytic oxidation of VOCs. One possible application is in the cleanup of emissions from soil vapor extraction wells, which are in use to remove VOCs from groundwater at DOE's Hanford and Savannah River sites.

This research consisted of synthesizing potential DU catalysts, as well as testing and structural characterization. A chemical reactor was built to compare the catalytic performance for oxidation of toluene, chlorobenzene, and tri-chloroethylene (TCE). These VOCs were chosen as typical of those found in anticipated applications. In particular, TCE is a major pollutant found in the groundwater plumes at Hanford. Complete destruction of VOCs that contain chlorine is more difficult and thus represents a more stringent catalyst challenge.

APPROACH

Catalysts were synthesized using a variety of methods, most notably a method that includes templated cosynthesis of mesoporous oxides [3]. This method isolates uranium oxide in a highly dispersed form on a mesoporous oxide support, typically silica or titania. Recently, Hutchings and coworkers have demonstrated that doping uranium oxide with transition metal ions can further enhance the catalytic activity of uranium oxide [1]. This observation prompted us to expand the evaluation of various dopant metal ions as potential catalysis promoters for uranium oxide. Dopants (e.g., Cr, Co, K, Fe, V, Ca) were added to the uranium oxide to improve the catalytic activity; catalyst performance was compared with that of conventional catalysts. The effects of post-synthesis calcination temperatures

were also considered. A plug-flow chemical reactor was constructed and used to measure the conversion of the VOC vs catalyst temperature. These data result in so-called "light-off" curves. Conversion generally increases with temperature. From light-off curves for fixed flow rates, the temperature (T_{50}) at which 50% conversion of the VOC to oxidation products (CO_2 and H_2O) occurs is obtained and provides a measure of the catalyst activity. Lower values of T_{50} indicate higher activity. A gas chromatograph and a sampling mass spectrometer were used to measure conversion and reaction by-products. Table I summarizes the results (T_{50}) for several selected catalysts discussed below. X-ray diffraction (XRD), transmission electron microscopy (TEM), and surface area measurements were used to provide information about the phases present in the catalyst.

RESULTS

- Initial catalysts made at Oak Ridge National Laboratory were urania in a mesoporous silica support, $m\text{U-SiO}_2$. These catalysts were made by templated coassembly. XRD measurements indicated that the urania is present as U_3O_8 . TEM measurements indicated that the U_3O_8 particles were dispersed in the silica support. Some less-active catalysts contained a UO_2 phase, suggesting that U_3O_8 is the active phase. Pure U_3O_8 was found to be less active than $m\text{U-SiO}_2$. This seeming anomaly is attributed to the very high surface area that can be achieved in the mesoporous silica support, which causes the urania to be highly dispersed both in the pores and on the external surface. Variation in the U:Si ratio indicates that optimal activity for chlorobenzene oxidation is obtained for U:Si = 1:30.
- Doping chromium oxide into a $m\text{U-SiO}_2$ catalyst (Cr:U:Si = 0.2:1:20) enhances activity slightly, but only if the chromium oxide is added in cosynthesis. Post-impregnation of chromium yields no improvement compared with $m\text{U-SiO}_2$ catalysts, and without uranium, the Cr- SiO_2 catalyst is much less active. Cobalt oxide appears to have comparable activity to the uranium oxide, and doping it into $m\text{U-SiO}_2$ has little synergistic effect.

TABLE I. Summary of Selected Experimental Results, including BET Surface Area and Light-Off Temperatures (T_{50}).

Catalyst	Composition Ratio	BET Surface Area (m^2/g)	Toluene T_{50} (EC)	Cl-benzene T_{50} (EC)	TCE T_{50} (EC)
U_3O_8	Pure U_3O_8	0.1	520	N/A	N/A
<i>m</i> U-SiO ₂	U:Si = 1:10	N/A	460	N/A	N/A
<i>m</i> U-SiO ₂	U:Si = 1:20	233	410	420	N/A
<i>m</i> U-SiO ₂	U:Si = 1:30	267	N/A	410	N/A
<i>m</i> U-SiO ₂	U:Si = 1:40	336.7	N/A	470	N/A
<i>m</i> U-SiO ₂	U:Si = 1:50	267	N/A	490	N/A
<i>m</i> (Cr-U)-SiO ₂	U:Cr:Si = 1:0.2:20	203.8	375	N/A	N/A
imp. Cr / <i>m</i> U-SiO ₂	U:Cr:Si = 1:0.2:20	253.4	418	N/A	N/A
<i>m</i> -Cr-SiO ₂	Cr:Si = 0.2:20	207	470	N/A	N/A
<i>m</i> (Co-U)-SiO ₂	U:Co:Si = 1:0.23:20	242	440	N/A	N/A
imp. Co / <i>m</i> U-SiO ₂	U:Co:Si = 1:0.23:20	223	420	N/A	N/A
<i>m</i> -Co-SiO ₂	Co:Si = 1:85	224	420	N/A	N/A
<i>m</i> -TiO ₂ (350EC)	Ti	127.81	365	500	N/A
<i>m</i> -TiO ₂ (600EC)	Ti	18.21	425	N/A	N/A
<i>m</i> -TiO ₂ (800EC)	Ti	2.95	550	N/A	N/A
<i>m</i> -U-TiO ₂ (350EC)	U:Ti = 1:20	249.6	330	375	465
<i>m</i> -U-TiO ₂ (600EC)	U:Ti = 1:20	108.62	325	375	465
<i>m</i> -TiO ₂ (800EC)	U:Ti = 1:20	25.14	345	375	465
<i>m</i> (U-Ti)-SiO ₂	U:Ti:Si = 1:1:20	429	390	N/A	N/A
<i>m</i> (U-Ti)-SiO ₂	U:Ti:Si = 1:1:20	341.6	385	N/A	N/A
<i>m</i> (U-Ti)-SiO ₂	U:Ti:Si = 1:1:20	205.3	380	N/A	N/A

- Iron, magnesium, and calcium were tried as dopants. Generally these decreased the activity for chlorobenzene conversion.
- Potassium is used as a promoter for some catalysts. Addition of potassium by cosynthesis to the *mU*-SiO₂ destroyed the surface area and strongly deactivated the catalysts, regardless of whether potassium was added as a bromide, oxalate, or nitrate salt. Even post-impregnation of high-surface-area *mU*-SiO₂ with potassium salts caused loss of surface area and activity, indicating that potassium is a strong poison for DU catalysts.
- Titanium dioxide (TiO₂) is also an active catalyst for oxidation, and addition of urania has a synergistic interaction, which leads to a very active catalyst. Using templated cosynthesis of uranium and titanium (U:Ti = 1:20) yields a mesoporous catalyst with a T₅₀ of 325°C for toluene oxidation. Mesoporous TiO₂ is not stable at high temperatures, because of crystallization, which leads to mesopore collapse. Interestingly, urania stabilizes the TiO₂ mesoporous framework, leading to much higher surface area and inhibiting deactivation caused by sustained temperatures as high as 800°C. The activity of the *mU*-TiO₂ catalyst was shown to be stable for days on-line, and its activity is comparable to that of 0.1% Pt-Al₂O₃. Therefore, *mU*-TiO₂ is competitive with the more expensive precious metal commercial catalyst.
- Another approach to achieve the Ti-U synergy was to dope a *mU*-SiO₂ sample with titanium in smaller concentrations (U:Ti:Si = 1:1:20). This approach gave catalysts with activities slightly improved compared with *mU*-SiO₂ but not as effective as the *mU*-TiO₂ catalysts. These catalysts were also stable at high temperature.
- The *mU*-TiO₂ catalyst was tested for chlorinated VOCs, which are not readily oxidized even when platinum catalysts are used. This catalyst was active, although higher temperatures were required to obtain comparable conversions. Measured values for T₅₀ were 325, 375, and 465°C for toluene, chlorobenzene, and TCE, respectively. The only carbon-containing by-product besides CO₂ was benzaldehyde. Conversion to benzaldehyde depended upon temperature but was generally <10%. Since TCE contains a low H:Cl ratio, the chlorine-containing by-product must be Cl₂ or unwanted oxidized forms of chlorine (e.g., carbonyl chloride), rather than the desired HCl. The effect of water on the conversion was tested

because it may promote formation of HCl. This is also important because, in an application for soil vapor extraction, the reactant stream will be saturated in water. Addition of water as high as 7 vol % did not interfere with catalytic conversion and appeared to enhance HCl:Cl₂ product ratios.

The details of this research from October 2000 to July 2003 can be found in Ref. 4.

SUMMARY

A catalyst formulation based upon a mixed Ti-U oxide (Ti:U = 1:20) has been found to be competitive with noble metal catalysts for the catalytic oxidation of VOCs and chlorinated VOCs. It is stable to deactivation and operates effectively in the presence of large amounts of water. With development of methods to cast this catalyst onto honeycomb support, it is anticipated that it could be a suitable catalyst for destruction of VOCs emitted from soil vapor extraction wells or in other applications.

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