

# Novel Catalysts for Improved Remediation of Sulfur-Containing Pollutants

## Market and Background

According to BCC research, the global catalyst market was valued at \$6.8 billion in 2015. With a CAGR of 2.8%, this market is anticipated to exceed \$8.0 billion by 2021. Driving this growth is the global demand for refinery catalysts (including hydrodesulfurization (HDS) catalysts for petroleum refining), a sector expected to reach 2,234.3 metric kilotons within the same period. While HDS is the industrial standard for the removal of sulfur from fuels, it remains an imperfect option due to its use of high temperature and pressure. In addition, this process is not effective for use in the removal of certain heterocyclic sulfur compounds such as dibenzothiophene (DBT) and related compounds. Oxidative desulfurization (ODS) has emerged as a promising alternative desulfurization technology due to its ability to operate at lower temperatures and pressures. However, existing oxidation methods can require use of undesirable organic solvents, expensive precious metals, toxic heavy metals, caustic strong bases and environmentally unfriendly oxidants. As such, there remains a need for development of green catalytic systems capable of efficiently operating under ambient conditions.

## Research and Development Status:

A professor of chemistry at the University of Wisconsin-La Crosse has developed a versatile suite of iron-based catalysts with the potential to promote rapid, efficient oxidation of deleterious sulfur-containing compounds present in crude oil, natural gas, and/or aqueous waste streams. With these novel catalysts, there is no need for corrosive base, elevated temperatures, expensive or dangerous oxidants, or high pressures. Primary catalysts have been shown to successfully catalyze the oxidation of a series of substrates consisting of representative thiols and DBT. Substrates initially present in both solution (including in “model oil”) and the gas phase have been successfully oxidized. Reactions have been carried out at room temperature and in many cases using only molecular oxygen from ambient air as the primary oxidant. Reaction times for 100% conversion range from as little as 40 minutes to seven hours with TON ranging from 700-4500. A summary of exemplary reactions carried out to date can be seen below in Table 1.

## Applications:

- Mercaptan and hydrogen sulfide sweetening. Primary catalysts are capable of:
  - Oxidizing a series of representative thiols and DBT in solution;
  - Oxidizing vapor phase thiols, demonstrating potential utility for removal of mercaptans from natural gas as well as gas-phase effluents from sources such as biodigesters and sewage treatment plants;
  - Catalyzing oxidation of heterocyclic sulfur compounds present in non-polar hydrocarbons to sulfones thereby enabling effective removal via partitioning into a more polar phase; and
  - Oxidizing select thiols in model oil demonstrating ability to catalyze conversion of mercaptans dissolved in non-polar hydrocarbons to more easily separable disulfides.

## Key Benefits

- Low cost and green - primary catalysts are based upon inexpensive, earth abundant and environmentally friendly iron;
- Select catalyst have been successfully immobilized on solid support providing for easier recovery;

- Reactions can be carried out at room temperature, ambient pressure, and without use of harmful solvents or caustic base. Rather, environmentally friendly solvents (e.g. water and alcohol) can be employed.

## Intellectual Property:

A PCT application is pending for this technology. WiSys also holds rights to a US patent ([US10,065,980](#)) covering the composition of matter and method of manufacture of primary catalysts. For more information, please contact Jennifer Souter at [jennifer@wisys.org](mailto:jennifer@wisys.org) or by phone at 608-316-4131.

## Supplementary Data:

**Table 1.** Exemplary catalytic reactions using primary catalysts A and B\*

Sample/Substrate	Product	Reagent	Oxidant	Efficiency
2-mercaptoethanol	2-hydroxyethyl disulfide	Catalyst A, Na+ salt <i>in polar mixed aqueous/organic phase</i>	H <sub>2</sub> O <sub>2</sub>	Near 100% in 3.5hr TON of ~2800
		Catalyst A <i>in polar mixed aqueous/organic phase</i>	O <sub>2</sub>	100% in 2hr, TON of ~1600
		Catalyst A <i>immobilized on ion-exchange resin</i>	O <sub>2</sub>	100% in 12hr, TON of ~2400
		Catalyst A <i>immobilized on amino-modified silica gel</i>	H <sub>2</sub> O <sub>2</sub>	100% in 2hr, TON of ~4500
		Catalyst B <i>in n-propanol solution</i>	H <sub>2</sub> O <sub>2</sub>	100% in 40min, TON of ~1500
		Catalyst B <i>in n-propanol solution</i>	O <sub>2</sub>	100% in 3hr, TON of ~1300
Ethyl mercaptan	Diethyl disulfide	Catalyst A <i>in polar mixed aqueous/organic phase</i>	O <sub>2</sub>	Near 100% in 4hr
		Catalyst B <i>in EtOH</i>	O <sub>2</sub>	Near 100% in 4hr
		Catalyst B <i>in 1-butanol</i>	O <sub>2</sub>	Near 100% in 6hr
Ethyl mercaptan <i>vapor phase</i>		Catalyst B <i>in 1-butanol</i>	O <sub>2</sub>	TBD
Ethyl mercaptan <i>with model oil</i>		Catalyst B <i>bi-phasic solvent system – tetradecane as model oil and EtOH polar phase</i>	O <sub>2</sub>	TBD
n-propyl mercaptan		Catalyst A <i>in polar mixed aqueous/organic phase</i>	O <sub>2</sub>	100% in 7hr
		Catalyst B <i>in EtOH</i>	O <sub>2</sub>	100% in 6hr
Dibenzothiophene	Dibenzothiophene 5,5 dioxide	Catalyst B <i>in mixed acetonitrile/dichloromethane</i>	H <sub>2</sub> O <sub>2</sub>	Near 100% in 8hr, TON of ~700
Dibenzothiophene <i>with model oil</i>		Catalyst B <i>with tetradecane as model oil and EtOH solvent polar phase</i>	H <sub>2</sub> O <sub>2</sub>	TBD

\* all reactions were carried out at room temperature