Title
CRADA Final Report: Optimized Catalysts for the Cracking of Heavier Petroleum Feedstocks

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CRADA Final Report
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1. Parties:
   Lawrence Berkeley National Laboratory and Catalytica Advanced Technologies, Inc.

2. Title of the Project:
   Optimized Catalysts for the Cracking of Heavier Petroleum Feedstocks

3. Summary of the specific research and project accomplishments:

Catalysts lower the energy required for chemical reactions to proceed and are widely used in petroleum refining and chemical manufacturing. The useful lifetime and, thus, the value of an industrial catalyst are limited by a process known as deactivation in which the efficiency of the catalyst declines over time. Understanding this deactivation process is essential for developing new catalysts with longer useful lifetimes. In this project a new surface science tool, ultraviolet (UV) Raman spectroscopy, was used to identify chemical species on the surfaces of catalysts *in-situ* under actual reaction conditions. In collaboration with Catalytica this tool was applied to a series of important industrial catalysts.

An important technical objective was the construction of laboratory scale versions (with UV optical access) of industrial reactors such as fluidized and fixed bed reactors. Fixed and fluidized bed reactors with UV optical access were designed, constructed, and tested to 300 C. It was demonstrated that UV Raman spectra could be obtained from a number of industrial catalysts (no spectra could be obtained with the standard Raman method of using visible excitation). Initial *in-situ* work concentrated on catalysts used for petroleum reforming (Pt supported on alumina). The generation of coke was monitored *in-situ* during the conversion of cyclohexene to cyclohexane and benzene in a temperature range of 20 – 120 C. The conversion of other hydrocarbons was also investigated.

4. Deliverables:

Deliverable Achieved	Party (LBNL, Participant, Both)	Delivered to Other Party?
Completion of chamber construction (milestone)	LBNL	N/A
Completion of operational chamber for *in-situ* reaction studies (milestone)	LBNL	N/A
First *in-situ* UV-Raman spectrum obtained at elevated temperature (>300 C), (milestone)	LBNL, Catalytica	N/A
First *in-situ* UV-Raman spectrum obtained under "cracking" conditions (milestone)	LBNL	N/A
Annual reports to DOE (deliverables)	LBNL	Yes

5. Identify publications or presentations at conferences directly related to the CRADA?

C. R. Tewell, F. Malizia, J. W. Ager III, and G. A. Somorjai, "An Ultraviolet-Raman Spectroscopic Investigation of Magnesium Chloride-ethanol Solids with a 0.47 to 6 Molar Ratio of C_2H_5OH to $MgCl_2$," J. Phys. Chem B **106**, 2946-2949 (2002). LBNL-48568. Describes operation of UV-Raman system.

"In-situ ultraviolet Raman spectroscopy of advanced catalysts," National Laboratory Catalysis Workshop, Argonne, IL. October, 2000. Invited talk by J. W. Ager III

"In-situ ultraviolet Raman spectroscopy of advanced catalysts," Fall Meeting of the Materials Research Society, Boston, MA. December, 2000. Contributed talk by J. W. Ager III.

6. List of Subject Inventions and software developed under the CRADA:

None

7. A final abstract suitable for public release:

Catalysts lower the activation energy required for chemical reactions to proceed and are widely used in petroleum refining and chemical manufacturing. The useful lifetime and, thus, the value of an industrial catalyst are limited by a process known as deactivation in which the efficiency of the catalyst declines over time. Understanding this deactivation process is essential for developing new catalysts with longer useful lifetimes. In this project a new surface science tool, ultraviolet (UV) Raman spectroscopy, was used to identify chemical species on the surfaces of catalysts *in-situ* under actual reaction conditions. In collaboration with Catalytica this tool was applied to study deactivation in a series of important industrial catalysts. In the specific case of "reforming" catalysts are used to dehydrogenate and cyclize n-hexane and n-heptane to form benzene and toluene for the production of high octane gasoline, the buildup and polymerization of carbonaceous reaction byproducts on the surface of the catalyst was studied *in-situ* by this new method. The information on catalyst reaction and deactivation mechanisms has been found to be useful to the industrial partner in improving their catalysts. These improvements could have a major impact on the efficiency of petroleum refining and gasoline production. In addition, the new surface science tools developed by this project will have general applicability to the study of catalysis and to the field of surface science in general.

8. Benefits to DOE, LBNL, Participant and/or the U.S. economy.

Catalysts by their very nature serve to lower the activation energy required for a chemical reaction and are the dominant vehicle of chemical energy conversion. For this reason, catalysis research has long been supported by the Department of Energy. The Berkeley Lab work that forms the background of this project, namely the research into the mechanism of petroleum refining catalysts and the development of new *in-situ* surface characterization tools, was supported by DOE funding of the Surface Science and Catalysis Program. This project benefited from the unique facilities and expertise derived from many years of DOE support of this program. This project has introduced a new and flexible surface characterization tool, which is of direct benefit to the LBNL program and to DOE.

In addition, this project has given the Surface Science and Catalysis Program at LBNL the opportunity to apply a new and powerful surface science tool directly to the study of industrial catalysts of considerable scientific and commercial interest. In return for in-kind contribution of catalysis fabrication and testing expertise, Catalytica has had the opportunity to have its catalysts studied with a new surface science tool. The enhanced understanding of deactivation processes on their real catalyst will assist them in producing new and more efficient catalysts for their business lines. Initially, the benefits accruing from catalysts improved by this project would be in the petrochemical industry, but follow-on work outside of this project is likely to yield improved catalysts for applications in other industrial sectors, including fine chemical and pharmaceutical manufacturing.

9. Financial Contributions to the CRADA:

DOE Funding to LBNL	$658k
Participant Funding to LBNL	$ 10k
Participant In-Kind Contribution Value	$776k
Total of all Contributions	$1,444k