



# CLSI PROPOSAL SUBMISSION

## GENERAL USER

Proposal #14-3680  
06B1-1 (SXRMB)

Date Submitted: 2011-03-01  
Cycle 14 (July 2011 - December 2011)

<b>Title of Proposal:</b>	Role of citric acid in the sulfidation behaviour of Ni in hydrotreating catalysts
<b>Type of Proposal:</b>	General User
<b>Proposal Duration:</b>	2 cycles (12 months)
<b>Subject of Research</b>	Material and Chemical Sciences
<b>Industrial Partners Involved?</b>	Yes, Syncrude
<b>Five Key Words</b>	Chelating Ligand, Sulfidation, NiMoS phase, hydrotreating, EXAFS
<b>Funding Sources</b>	NSERC

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**BRIEF DESCRIPTION**

Canadas Athabasca basin is blessed with the largest deposits of crude bitumen which is the feedstock for extremely heavy crude oil. With modern unconventional oil production technology, at least 10% of these deposits, or about 170 billion barrels (27109 m3) were considered to be economically recoverable at 2006 prices, making Canada's total oil reserves the second largest in the world, after Saudi Arabia. However the presence of large amounts of impurities like sulfur, nitrogen, and other metals make it an extremely low quality feedstock. In order to meet the challenging task of producing a fuel which can meet the most stringent of environmental regulations, hydrotreatment of the feedstock assumes a lot of importance. Conventional hydrotreatment catalysts consist of MoS<sub>2</sub> promoted by Co or Ni and almost always supported on Al<sub>2</sub>O<sub>3</sub>. The active phase MoS<sub>2</sub>, the promotional effect of Ni(Co) and the metal support interaction of Mo and Al<sub>2</sub>O<sub>3</sub> has been the focus of a lot of research around the globe. The catalytically active phase of nickel and molybdenum catalysts consists of small hexagonal MoS<sub>2</sub> slabs with promoter ions dispersed over the edges, the so-called Ni(Co)-Mo-S phase. There are two types of NiMoS phases with distinctly different activities, NiMoS Type I and Type II, the latter exhibiting about two times higher activity than the former [8]. Type I sites refer to the active sites of Ni or Co located at the edges of the first layer of MoS<sub>2</sub>, whereas Type II refers to Co or Ni located at the second or overlaying layers of MoS<sub>2</sub>. It is, accordingly expected that highly active NiMo catalysts are composed of a highly dispersed NiMoS type II phase. Improper sulfidation of the oxide based catalysts leads to the formation of separate phases of Ni<sub>3</sub>S<sub>2</sub> and MoS<sub>2</sub> on the support. Previous works have attributed this to the different sulfiding temperatures of Ni and Mo which prevents the complete formation of the catalytically active NiMoS phase on the surface of the support. It has also been shown that the diculty of suldation of some relevant bulk compounds increases from NiO > MO<sub>3</sub> > NiMO<sub>4</sub> > NiAl<sub>2</sub>O<sub>4</sub>. In order to improve the formation of the so called NiMoS phase and lower the Ni<sub>3</sub>S<sub>2</sub>, phase a

higher temperature sulfidation of the Ni species to a temperature similar to that of Mo is required. In addition there is also a need to reduce the formation of spinel type  $\text{NiAl}_2\text{O}_4$  structures which are formed when Ni escapes into the  $\text{Al}_2\text{O}_3$  framework. The use of Ni salts of various chelating ligands as precursors have shown promising results. Chelation of Ni with ligands like Nitriloacetic acid (NTA), Ethylene diamine tetraacetate (EDTA), Citric acid (CA) etc increases the sulfiding temperature of NiO and minimizes the formation of spinels. In this context, the application of X-ray absorption spectroscopy to study the sulfidation of Ni in presence of chelating ligands holds great potential in understanding the mechanism of formation of the active NiMoS phase for hydrotreatment reactions.

## SCIENTIFIC MERIT

### Our Research

Our research has focused on synthesis of catalysts with higher intrinsic activities for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions of heavy gas oil (HGO) derived from the Athabasca oil sands. The current proposal is intended for the study of the temperature dependent sulfidation mechanism of Nickel oxide in presence of citric acid which acts as a chelating ligand. Ni K edge EXAFS will allow us to determine the coordination number and bond lengths of the respective Nickel species formed during the sulfidation process. The NiMo/ $\text{Al}_2\text{O}_3$  catalysts sulfided at 3 different temperatures of 150 oC, 250 oC and 350 oC will be used in the Ni K edge EXAFS study. A detailed study at varying temperature will enable us to accurately determine the transition of Ni(citrate) complex to the NiMoS phase by observing the changes in the coordination number and bond lengths of the Ni and neighbouring atoms. Varying molar ratios of Citric acid and Ni will also be used as a parameter, to determine the effects of addition of citric acid on the structure of the Ni complex formed. In addition, the effects of a chelating ligand on the formation of inactive species like  $\text{Ni}_3\text{S}_2$  and  $\text{NiAl}_2\text{O}_4$ . The obtained spectra for Ni K edge will also be compared with various pure reference materials like  $\text{Ni}_3\text{S}_2$ , NiO and Nickel citrate.

Our initial XAS work with the above mentioned catalyst systems involving the Mo K edge EXAFS at the HXMA beamline, CLS, Canada has already given us a better understanding of the chemical nature of Mo atom in the sulfided state as well as the oxide phase. Fitting of the Mo K edge spectra with theory, revealed that formation of NiMoS was best observed when the CA/Ni ratio was 0.7. Further studies of the etrmined fits showed that using excess citric acid led to the formation of Mo(citrate) complex which proved to be detrimental to the formation of active sites. The coordination number of Mo-S and Mo-Mo was found to be 5.6 and 5.4 respectively for the best performing catalyst.

On the basis of the coordination numbers and bond lengths, a slight deviation from pure hexagonal structure of  $\text{MoS}_2$  was observed in case of our catalyst system. As a follow up to our work with Mo K edge at the HXMA beamline, a Ni K edge EXAFS study will help us determine the geometry around the Ni atom in oxide as well as sulfide phase. From this study we hope to identify and elucidate the transitional structures of Ni in presence of a chelating ligand during sulfidation.

### Hypothesis to be tested

The use of citric acid as a chelating ligand to form Ni complex will help increase the sulfidation of Ni to a sulfidation temperature close to that of Mo. The simultaneous sulfidation of the Ni and Mo species will help generate very active NiMoS phase by increasing the type II sites. In addition the formation of inactive species like  $\text{Ni}_3\text{S}_2$  and spinel structures can be reduced. Ni K edge XAFS will allow us to identify the species present during sulfidation at different temperatures. The coordination numbers and bond lengths obtained from the fits will also help us in predicting the ratio of Type I to Type II NiMoS phase present in the catalyst.

### Potential impact of results

The Canadian oil sand resource, which is spread across 77,000  $\text{km}^2$  mostly in northern Alberta, holds about 1.7 trillion barrels of bitumen. Of this vast non-conventional bitumen deposits, about 300 billion barrels can be recovered. Syncrude Canada Ltd. and Suncor Ltd. currently produce 250,000 and 110,000 bbl/day of synthetic crude oil from oil sands, and they will double their production capacity in the next 2-3 years. This expansion, combined with more stringent fuel specifications, means that there is a critical need for improved hydrotreating technologies to reduce S and N levels in the fuels derived from bitumen. In addition, the needed technology is unique to the oil sands operation of Western Canada since the organic compounds associated with the S and N are much larger heterocycles than in conventional oils, making their reactivities different. Consequently, there is a need to develop new catalyst and process technology that is focused on treating bitumen-derived HGO, so that it can be applied to the Canadian oil sands industry. If successful, the proposed catalyst and process development work will have a major impact on efficient removal of N and S atoms from heavy gas oil derived from Athabasca bitumen. This will in fact benefit Canada by efficient utilization of its vast oil sand resource. Moreover, the proposed research will help mitigate the  $\text{SO}_x$  and  $\text{NO}_x$  responsible for acid rains and green house effects, thus complementing Kyoto agreement that Canada is committed to. Therefore this proposal has high potential in providing both economic and environmental benefits to Canada.

### Likelihood of success

We are confident that we will be able to better explain the detailed nature of the chemical interaction between Ni and citric acid in the catalyst precurosr. Understanding of the Nickel-citrate complex will help us synthesize catalysts with higher intrinsic NiMoS sites while minimizing the formation of inactive  $\text{Ni}_3\text{S}_2$  phases during the sulfidation process. Our previous experience while

working with Mo K edge EXAFS of the same catalyst system has familiarized us with data analysis associated with EXAFS.

## EXPERIMENT PROCEDURE

We will be carrying out EXAFS experiments for Ni K edge on catalysts Ni(citrate)Mo/Al<sub>2</sub>O<sub>3</sub> and standards (Ni<sub>3</sub>S<sub>2</sub>, Nickel citrate, NiAl<sub>2</sub>O<sub>4</sub>). The catalysts to be studied are in various states including: oxides and sulfides. Both fresh and spent catalysts will be analyzed. We intend to analyze about 20 samples from 1 graduate and one post doctoral fellow. The catalysts are prepared by impregnating (different techniques) the support (Alumina) with a solution containing the active metal species (Ni, Mo) and citric acid as a chelating ligand. They are then dried and calcined to obtain the oxide catalyst samples. Reaction of the oxide catalyst sample with butanethiol forms the sulfide catalyst.

The spent catalysts to be used in the experiments are as a result of reaction of the fresh catalysts with heavy gas oil over long periods of time (30 days on the average). These long periods of exposure to the heavy gas oil results in the deposition of carbon and sulfur species on the catalysts surfaces. The solid samples will be ground into powder prior to the analyses. The XANES and EXAFS will give us information such as the oxidation states, coordination numbers, bond distances and chemical environment at atomic level. This information will help in designing new catalytic systems without conducting many experiments.

We have requested two days beamtime to be able to complete experiments on our samples. Our experience from previous synchrotron experiments indicates that we need to perform three repeats for each sample. Counting unforeseen problems likely to be encountered, two days will be required to complete the proposed analyses.

## SUITABILITY

Synchrotron radiation analysis is a technique that is able to give detailed local structural information of catalytic material. Our previous experience and reports in the open literature show synchrotron analyses as powerful tools to study catalytic and sorbent material surfaces and to provide information regarding the local structure and binding of elements. Secondly, the fact that CLS has the right beamlines for our samples, close proximity of the CLS compared to other synchrotron radiation centers, the state of the art equipment, and the benefit of using the center for academic research purposes make the CLS an obvious choice. We intend to use the SXRMB (700-10000 eV) for the analysis of Ni K edge. The other beamlines are outside our range of interest for this experiment.

## PAST PRODUCTIVITY - Shifts received in the past two years:

Access Mechanism	Cycle 11	Cycle 12	Cycle 13	Cycle 14
General User	0	0	0	3
Total Shifts	0	0	0	3

a) Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) of different NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts containing boron and phosphorus were performed at the Synchrotron Radiation Centre (CRC), Madison, WI. The measurements were carried out in fluorescence yield mode on the Canadian Double Crystal Monochromator (DCM) and Canadian Grasshopper Monochromator (GM) beam lines. For both kinds of measurement, catalyst samples were pressed into self supported wafers and then put into soft X-ray beam. P K-edge EXAFS was performed using Canadian DCM beam line. S and P K-edge XANES analysis of all catalysts were performed for the energy range of 2460-2520 eV and 2140-2200 eV, respectively using Canadian DCM beam line. B K-edge XANES analysis of all catalysts containing boron was performed for the energy range of 180-225 eV using Canadian GM. In all cases the spectra around the edge jump were fitted by a linear function of standard compounds. Standard procedures were used to extract the EXAFS data from the absorption spectra using WINXAS software. A paper entitled X-ray absorption near edge structure and X-ray photo electron spectroscopy analyses of NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts containing boron and phosphorus are published in Journal of Molecular Catalysis A: Chemical (2005), 234(1-2). EXAFS and XANES of molybdenum (L3 edge), sulphur (K edge), and nickel (K edge) edges has been conducted using SXRMB beamline at CLS. We has presented one poster on this work in the CLS user meeting 2010, Saskatoon. Two manuscripts for publication are under preparation based on the SXRMB beam line research. We have also got experience in analysing different activated carbon catalysts for specifying sulphur species were performed at the Synchrotron Radiation Center (CRC), Madison, WI. In addition, PGM beamline was used for some modified coal-based activated carbons in CLS in last two years. Recent works (Jan 11th 2011) include 3 shifts at the HXMA beamline at CLS allotted to us by Dr., Dr. Thomas Ellis, Director of Research, Experimental from his discretionary time. Results of Mo K Edge EXAFS of the above catalyst systems are very promising. The analysis of the results are complete and are in the process of submission to a peer reviewed journal.

b) n/a

## BEAMLINE REQUIREMENTS

<b>Beamline:</b>	06B1-1 (SXRMB)
<b>CLS Staff Contacted:</b>	Dr. Yongfeng Hu
<b>Endstation:</b>	XAFS
<b>Technique:</b>	X-ray Absorption spectroscopy

<b>Equipment:</b>	Total electron yield (sample drain current measurement) Total fluorescence yield (micro-channel-plate detector, in vacuum) Transmission yield
<b>Wavelength / Energy Range:</b>	1700-10000 eV
<b>Spotsize on Sample:</b>	mm
<b>Energy Resolution:</b>	deltaE/E

<b>SCHEDULING REQUIREMENTS</b>	
<b>Total # shifts for entire proposal:</b>	6
	<b>Anticipated Timeline</b>
<b>Cycle</b>	<b># of 8-hour shifts requested</b>
Cycle 14 - July - December, 2011	3
Cycle 15 - January - June, 2012	3
<b>Specific scheduling requirements:</b>	
<b>Preferred dates (current cycle)</b>	
<b>Unacceptable dates (current cycle)</b>	

## SAFETY AND MATERIALS

### Chemical Information

Are you bringing any hazardous chemical materials to the CLS? Yes

### Chemical Materials

Name	CAS/UN #	State	Quantity	Units	Known Hazards
Nickel citrate		solid	0.2-0.3	g	irritant
Nickel Oxide		solid	0.2-0.3	g	irritant
Ni3S2 - Nickel sulfide		solid	0.2-0.3	g	Toxic, irritant

Will any sample preparation be done while at the CLS? No

Will any chemical waste be generated while at the CLS? No

### Biological Information

Are you bringing any biological materials to the CLS? No

Does this research involve human tissue and/or biological fluids? No

Does this research involve the study of aboriginal people's culture? No

### Does this research involve:

Live animals? No

Animal tissue and/or biological fluids from live animals? No

Does your work involve Genetically Modified Organisms, Genetically Modified Microorganisms or Transgenic Organisms? No

### Radioactive Material Information

Are you bringing anything radioactive? No

### Nano Material Information

Are you bringing any nanomaterials to the CLS? No

### Pesticide Information

Are you bringing pesticides to the CLS? No

### Non-Hazardous Material Information

Name	Quantity	Units	State
Ni-CitrateMo/Al2O3 catalysts	20	gms	solid

### EQUIPMENT

Are you bringing any equipment to the CLS to assist you with this experiment? No

### ANCILLARY FACILITIES REQUESTED