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Title of the research project :

Design of innovative nano-carbide/nitride catalysts as substitute for noble metals for selk

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Research Unit

Name : Laboratoire de Réactivité de Surface

Code (ex. UMR xxxx) :

UMR 7197

Doctorate School

Thesis supervisor's doctorate school (candidate's futur
doctoral school) : ED 397

PhD student currently supervised by the thesis supervisor (number, year of the first inscription) :

1, 2021



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Description of the research project (ENGLISH):

Ce texte sera diffusé en ligne : il ne doit pas excéder 3 pages et est écrit en interligne simple.

Ce texte est à l'adresse d'étudiantes et étudiants chinois, il doit donc être rédigé en anglais.

Détailler le contexte, l'objectif scientifique, la justification de l'approche scientifique ainsi que l'adéquation à l'initiative/l'Institut.

Le cas échéant, préciser le rôle de chaque encadrant ainsi que les compétences scientifiques apportées. Indiquer les publications/productions des encadrants en lien avec le projet.

Préciser le profil d'étudiant(e) recherché.

avis favorable



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Design of innovative nano-carbide/nitride catalysts as substitute for noble metals for selective hydrogenation

Scientific context

Polyethylene (PE) and polypropylene (PP) are the world leading thermoplastic polyolefins in terms of market size; over 150 million tons in 2015 with a growing demand. Light alkenes are the key chemicals for the synthesis of these industrial polymers but, in order to avoid the poisoning of the catalysts used for polymerization reactions, impurities such as alkynes and dienes must be removed. For example, the acetylene concentration in ethylene streams must be less than 5 ppm for polymer synthesis. Catalytic semi-hydrogenation is the main current process for reducing impurities by transforming them into light alkenes without over-hydrogenation into alkanes or oligomer formation.

Positioning

Palladium-based catalysts are recognized as the most efficient systems for industrial semi-hydrogenation reactions. However, their selectivity towards alkenes decreases drastically at high conversion of alkynes or dienes. Moreover, Pd is a noble metal with limited resources (0.015 ppm in the earth crust) and its production is concentrated in a small number of countries (Russia and South Africa), giving rise to highly fluctuating prices and geopolitical concerns (Pd is on the list of the critical raw material of the European Union). Replacing Pd for selective hydrogenation could decrease the dependency to these rare metal resources. In addition, it would allow one to reduce the cost by decreasing the noble metal loading or by developing new non-noble metal catalysts. Transition metal carbide or nitride (TMC or TMN) catalysts (Mo or W) are attractive alternatives due to their metallic functionality from readily available metals. TMC and TMN attracted the attention in the 80's following the discovery by Boudart^[1] that metal carbides and nitrides exhibit catalytic properties very similar to platinum-group metals. Nowadays, carbide/nitride catalysts have experienced a large renewed interest due to their exceptional selectivity in hydrodeoxygenation (HDO) of biomass-derived oxygenates.^[2] However, they have been relatively poorly studied in the case of selective hydrogenation reactions, despite showing interesting catalytic performances.^{[3],[4],[5]}

Objectives

TMC-based catalysts are a very promising earth-abundant and cheap alternative to Pd based catalysts for selective hydrogenation. Nevertheless, the elaboration of this type of catalysts relies often on coarse thermal synthesis routes. The synthesis of TMC and TMN is generally carried out by exposure of a metal precursor (oxide or salt) to a carburizing (CH_4 or C_2H_6 ... + H_2) or nitriding mixture (NH_3 or N_2 + H_2) at high temperature (600-900°C). These solid/gas synthesis procedures generally lead to materials with relatively small specific surfaces (bulk carbides and nitrides) or whose composition is poorly defined (supported oxycarbides or oxynitrides) due to their high reactivity to oxygen.

New synthetic routes have recently been developed, using sol-gel methods, in order to obtain transition metal carbides and nitrides with particularly interesting textural and structural properties. The so-called sol-gel methods ("urea glass route" and related methods using biopolymers such as chitosan or alginates) can produce carbides and nitrides of a large number of transition metals (Mo, W, Ti, Ga, V, Fe...) in the form of nanoparticles.^[6] These methods are simple, use non-toxic reagents such as urea or chitosan, and are performed under an inert gas (N_2) and not under potentially explosive or toxic atmospheres. The source of carbon and nitrogen is urea or a biopolymer.

In this project, we propose to develop new synthesis routes in order to obtain nano-TMC or TMN-based catalysts, both bulk and supported on a support, using these sol-gel methods. The catalytic performance of these new formulations will be evaluated in two reactions: 1) the selective hydrogenation of acetylene in an excess of ethylene and 2) the selective hydrogenation of butadiene in the presence of an excess of propene.

The simplicity and versatility of these sol-gel synthesis methods should allow us to design nano-TMC and TMN either as pure single phase such as molybdenum carbides and nitrides (Mo_2C and Mo_2N) but also as innovative phases (W_2N , WC , Fe_3C , Ni_3C ...) which have not been reported so far. In addition, in a more exploratory way, the preparation of ternary phases ($\text{Ni}_3\text{Mo}_3\text{N}$, Fe_2MoC , FeWN_2 ...) can also be considered.

The main objective of the project is to design innovative carbide and nitride nanocatalysts with optimized metallic properties for selective hydrogenation of alkynes and dienes. The synthesis route will involve simple, non-toxic procedures in order to develop cost-effective and earth-abundant alternatives to Platinum-Group Metal catalysts (namely Pd). Molecular-scale investigation of these new catalysts in *operando/in situ* conditions will be carried out in order to derive structure/activity relationships.

The research will be organized along the three following work packages.

WP1. Catalyst design.

WP1 will consist in the synthesis of new carbide/nitride catalysts including monometallic Mo or W carbide/nitrides as well as bimetallic systems (Fe_2MoC , FeWN_2 ...) and more original ones such as Fe_3C or Ni_3C in order to tune the hydrogenation selectivity.

- Benchmark systems will be first prepared through Temperature-Programmed Carburizing/Nitriding reactions largely applied in the literature.^[7] This classic and robust method will produce an array of reference catalysts but with little flexibility on the composition and particle size.

- Second, an original pathway of synthesizing TMC/TMN with a sol-gel like urea glass method^[8] will give us an increased flexibility in the composition and particle size leading to an advanced design of nanocatalysts. Oxide-supported TMC and TMN phases will be prepared via the same route. This original one-pot procedure has never been reported to our knowledge.

WP2. Catalytic reactions.

The TMC/TMN materials prepared will be tested in the selective hydrogenation of acetylene in an excess of ethylene and in the selective hydrogenation of butadiene in the presence of an excess of propene. The reactions conditions mimic the front-end process of purification of a stream of alkene (ethylene or propene) containing traces of alkyne or alkadiene (acetylene or butadiene) in the presence of a high concentration of H_2 . Propene has been chosen for replacing butene for analytical reasons.

WP3. Operando catalyst characterization with Synchrotron-based techniques.

Catalyst optimization will be performed through an ambitious molecular-scale investigation of the reactivity of new catalysts in *operando/in situ* conditions in order to pinpoint structure/activity relationships using advanced synchrotron-based techniques. This approach is almost inexistent for Mo/W carbides where most of the studies are dealing with *ex situ* and/or macroscopic (i.e. XRD) techniques. X-ray Absorption Spectroscopy (XAS) will be used to correlate the nature of precursor, preparation route and activation treatment with the catalytic nanostructure.^[9] Innovative experiments will also be performed with X-ray Raman scattering (XRS), a highly valuable technique that allows to bridge the pressure gap by

recording C and N K-edge XANES spectra in the presence of a gas atmosphere.^[10] It will yield unprecedented insight into the carbon/nitrogen speciation.

Implication of the scientific coordinator and co-supervisors

The coordinator will be Xavier Carrier, Professor at LRS (Laboratoire de Réactivité de Surface, Sorbonne Université). He has a confirmed experience in handling fundamental and applied projects and he was recently the scientific leader at LRS of two large ANR projects: SLIMCAT (Solid-Liquid Interfaces at Molecular-scale for Catalysis, PRC, 2014-2018) and ROCK (Quick-EXAFS spectrometer for chemical kinetics, EQUIPEX with the synchrotron Soleil, 2010-2020). He is managing the group "Surface Science and Solid-Liquid Interfaces" at LRS which has a strong expertise in the investigation of interfacial phenomena for catalysis through a well-recognized molecular approach. His research targets the molecular design of heterogeneous catalysts with a strong focus on catalyst preparation^[11] and characterization methods.^[9] He has co-authored 3 book chapters on the subject^[11] and he is founder and three-times organizer of *CatPrep* (European Summer School on Catalyst Preparation).

The group has been a pioneer in the development of Mo/W carbides for catalysis.^[12] WP1 will be managed by C. Guibert specialist of soft-matter and colloidal synthesis^[13] for innovative preparation routes and it will include C. Sayag and L. Delannoy, both experts in the design of carbide-based catalysts through temperature-programmed methods.^[14] The expertise of L. Delannoy^[15] and C. Sayag^[16] for investigation of gas-phase catalytic reactions will be dedicated to WP2 while WP3 will benefit from the combined expertise of X. Carrier^[9] and C. Guibert^[17] in synchrotron-based characterization methods.

Background of the PhD candidate

We are looking for a motivated PhD candidate with a background in materials chemistry, spectroscopy and catalysis. Knowledge in synchrotron-based characterization methods would be an asset but is not mandatory.

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