

**FIRST-PRINCIPLES DESIGN OF TRANSITION METAL
CATALYSTS FOR SELECTIVE TRANSFORMATION OF
HYDROCARBONS**

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by

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*To my sun, my father – Jalid,
my moon, my mother – Rumana,
and
all the stars that light up my sky*

Certificate

This is to certify that the dissertation entitled “**First-Principles Design of Transition Metal Catalysts for Selective Transformation of Hydrocarbons**” being submitted by **Fatima Jalid** to the Indian Institute of Technology Delhi, for fulfilment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering is a record of bona-fide research work carried out by her. She has worked under our supervision and has fulfilled the requirements, which to our knowledge, has reached the requisite standard for the submission of the thesis. The results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.



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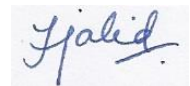
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A handwritten signature in blue ink, appearing to read 'Fatima Jalid', on a light blue background.

Fatima Jalid

Abstract

Heterogeneous catalytic reactions of hydrocarbon molecules are directed towards selective activation of chemical bonds present in the reactant molecule to carry out desired transformations into a target product. For instance, in alcohols and alkanes, C-C, C-O, C-H, and O-H bonds are selectively cleaved over the active sites of a transition metal catalyst surface to produce aldehydes, ketones, alkene and other functionalities. Active sites on the metal catalyst surfaces could also be engineered for selectively activating a specific chemical bond in the hydrocarbon molecule. For example, the high reactivity of the step site as compared to the terrace sites could lead to differential product selectivity. In addition, the metal catalyst surface could be doped with another metal to form a bimetallic alloy surface, so as to achieve the desired reactivity at the active site. All of these engineering options present a molecule level toolbox for the rational design of the catalyst surface. Herein, this molecular level design approach is elucidated in the study of an array of transition metal catalysts, using theoretical *ab initio* density functional theory (DFT) based microkinetic modeling, for four specific reactions; decomposition of ethanol, non-oxidative dehydrogenation (NODH) of ethanol, CO₂ assisted dehydrogenation of ethane and biogas reforming (BGR). A microkinetic model (MKM) thus developed is utilized to design novel composition of bimetallic alloys and to provide key insights into the rate controlling steps and intermediates, which in-turn can further be utilized to engineer the reaction itself. Using the MKM, the entire reaction energetics are expressed in terms of descriptors – the carbon and the oxygen binding energy on the surface of the catalyst.

In the first reaction, the propensity of cleaving the C-O bond versus the C-C bond in the decomposition of ethanol is studied over the step sites of transition metal catalysts. This is done with a broader objective to predict the trend in the reactivity of the metal and bimetallic catalysts for C-O bond activation of larger molecules; such as biomass-derived phenolic compounds via hydrodeoxygenation (HDO) reaction, using the MKM developed for a simple model molecule such as ethanol. Co is shown to be the most active catalyst to produce ethane followed by Ru, Ir, Rh, and Ni, at 523 K. In the design of a bimetallic alloy for the C-O bond activation, three specific alloy catalysts, CoNi, CoFe, and NiFe are calculated to exhibit the maximum turnover for the deoxygenated product with high selectivity at temperatures around 523 K.

In the second reaction, NODH of ethanol is studied for the theoretical design of bimetallic alloys that are likely to show high selectivity for the production of acetaldehyde. At 473 K, Pt is the most active catalyst followed by Cu and Pd for the NODH reaction. Interestingly, as noted from MKM analysis, surfaces of most of the metal catalysts are observed to be covered by the intermediate species; CH₃CO, except that of Cu. The surface of Cu is predominantly covered by the stable intermediate CH₃CH₂O, due to the difficulty of activating the C-H bond on Cu. A rational design idea is thus proposed for alloying Cu with metals having higher dehydrogenation capability, so as to increase turnover of the aldehyde. Four bimetallic alloys; CuNi, CuPd, CuPt, and CuRh are finally selected which

are calculated to show higher selectivity and conversions towards the aldehyde product for the NODH reaction. To speed up the in-situ screening process, Machine Learning (ML) based model is constructed for screening of Cu based alloys for NODH reactions and Ni and Co based alloys for ethanol decomposition reaction. ML model is showing similar predictions of reactivity trends in the MKM. Product selectivity and reactivity trends of primary and secondary alcohols in the NODH reaction on Cu based catalyst are further analysed using DFT calculations of propanol and isopropanol. Secondary alcohol is calculated to undergo NODH with significantly lower activation energies.

In contrast to Cu as a catalyst for NODH, the objective to rationally design a Pt-based bimetallic alloy surface is different. Since the Pt surface is covered with CH_3CO species, the target here is to control the dehydrogenation activity of the surface by alloying Pt with a lesser active metal, so as to stop the reaction at the desired aldehyde (CH_3CHO) product before undergoing subsequent dehydrogenation on the surface. In addition, from an economic perspective, a price filter is added to design cheaper bimetallic catalysts than that of pure Pt. Four specific Pt-based bimetallic alloys are finally proposed; PtCu, PtZn, PtGa, and PtGe for obtaining high yield of the NODH products.

In the third reaction, aforementioned *ab initio* design principles are further implemented for developing catalyst materials for a sustainable process of ethane to ethylene conversion, combined with CO_2 reduction, without the requirement of an external hydrogen source. As a benchmark of the theoretical parameters, MKM confirmed to the high reactivity of NiFe catalyst for this reaction, calculating high selectivity towards ethylene and significant CO_2 conversion similar to the reported trend in a recent experimental study. In addition, the *ab initio* MKM is providing mechanistic insight into the reaction where C-C hydrogenolysis reaction at the step (211) surface is observed to produce high amount of coke, leading to catalyst deactivation.

As a final application of the molecular level engineering toolbox, the MKM is applied to understand the reaction pathways in the reforming reaction of biogas at 973K over the terrace (111) and step (211) sites of transition metal catalysts. Out of all the catalysts studied, Co and Ru are calculated to show moderate turnover for consumption of methane and significantly smaller coke formation, thus exhibiting the potential to act as stable catalysts for the reaction. The H_2/CO ratio calculated on terrace sites of Co and Ru is closest to that required for FT reactions. Steam reforming of methane is observed to be the dominant reforming route for all the catalysts studied.

Overall, the dissertation is outlining the implementation of DFT calculations and *ab initio* MKM in comprehensive modeling of complex reaction networks for conclusive predictions of catalyst reactivity which may provide help in rational catalyst design.

सार

हाइड्रोकार्बन मॉलिक्यूल को लक्ष्य उत्पाद में परिवर्तित करने के लिए विषम उत्प्रेरक प्रतिक्रियाओं के द्वारा प्रतिक्रियाशील अणु में मौजूद रासायनिक बंधन के चयनात्मक सक्रियण की ओर निर्देशित किया जाता है। उदाहरण स्वरूप, अल्कोहल और एल्केन्स में C-C, C-O, C-H और O-H बंधन को संक्रमण धातु उत्प्रेरक सतह के सक्रिय स्थलों पर चयनात्मक रूप से तोड़ा जाता है ताकि एलिडहाइड, केटोन्स, एल्केन एवं अन्य अभिक्रियाशील समूह के पदार्थों का उत्पादन किया जा सके। धातु उत्प्रेरक सतहों पर active sites को इंजीनियर कर हाइड्रोकार्बन अणु में एक विशिष्ट रासायनिक बंधन को सक्रिय किया जा सकता है। उदाहरण के लिए, terrace sites की तुलना में step sites की उच्च प्रतिक्रियाशीलता अंतर उत्पाद चयनात्मकता को जन्म दे सकती है। इसके अलावा, धातु उत्प्रेरक सतह को एक अन्य धातु के साथ द्विधात्विक मिश्र धातु की सतह बनाने के लिए dope किया जा सकता है, ताकि सक्रिय स्थल पर वांछित प्रतिक्रिया संभव हो सके। ये सभी इंजीनियरिंग विकल्प उत्प्रेरक सतह के तर्कसंगत डिजाइन के लिए एक अणु स्तरीय टूलबॉक्स प्रस्तुत करते हैं। इस के साथ, विभिन्न प्रकार के संक्रमण धातु उत्प्रेरक का अध्ययन आणविक स्तर के डिजाइन दृष्टिकोण से चार विशिष्ट प्रतिक्रियाओं- इथेनॉल के अपघटन, इथेनॉल के गैर-ऑक्सीडेटिव डिहाइड्रोजनीकरण (NODH), CO₂ ने इथेन और बायोगैस रेफॉर्मिंग (BGR) के निर्जलीकरण के लिए, Density functional theory (DFT) आधारित microkinetic मॉडलिंग का उपयोग करके किया जा सकता है। इस प्रकार विकसित किया गया एक माइक्रोकैनेटिक मॉडल (MKM) का उपयोग द्विधात्विक मिश्र धातुओं को डिजाइन तथा नियंत्रित करने वाले चरणों और मध्यवर्ती में प्रमुख अंतर्दृष्टि प्रदान करने के लिए किया जाता है, जो कि प्रतिक्रिया को स्वयं इंजीनियर करने के लिए आगे उपयोग किया जा सकता है। MKM का उपयोग करते हुए, पूरी प्रतिक्रिया ऊर्जावान विवरणों के संदर्भ में व्यक्त की जाती है - उत्प्रेरक की सतह पर कार्बन और ऑक्सीजन बंधन ऊर्जा।

पहली प्रतिक्रिया में, इथेनॉल के अपघटन में सी-ओ बॉन्ड बनाम सी-सी बांड को क्लीयरिंग करने की प्रवृत्ति का संक्रमण धातु उत्प्रेरक के चरण स्थलों पर किया जाता है। यह बड़े अणुओं के सी-ओ बांड सक्रियण के लिए धातु और द्विधात्विक उत्प्रेरक की प्रतिक्रिया में प्रवृत्ति की भविष्यवाणी करने के लिए एक व्यापक उद्देश्य के साथ किया जाता है; हाइड्रोमाक्सीजिनेशन (एचडीओ) प्रतिक्रिया के माध्यम से बायोमास-व्युत्पन्न फेनोलिक यौगिकों जैसे कि इथेनॉल जैसे सरल मॉडल अणु के लिए विकसित एमकेएम का उपयोग करना। सह को 523 K रु, ईआर, आरएच और नी के बाद इथेन का उत्पादन करने के लिए सबसे सक्रिय उत्प्रेरक दिखाया गया है। सीओ बॉन्ड सक्रियण के लिए एक द्विधात्विक मिश्र धातु के डिजाइन में, तीन विशिष्ट मिश्र धातु उत्प्रेरक, कोनी, सीओएफई, और NiFe की गणना 523 K के तापमान पर उच्च चयनात्मकता के साथ डीऑक्सीजेनेटेड उत्पाद के लिए अधिकतम कारोबार को प्रदर्शित करने के लिए की जाती है।

दूसरी प्रतिक्रिया में, इथेनॉल के एनओडीएच का अध्ययन द्विधात्विक मिश्र धातुओं के सैद्धांतिक डिजाइन के लिए किया जाता है, जो एसिटालडीहाइड के उत्पादन के लिए उच्च चयनात्मकता दिखाने की संभावना है। 473 K पर, NODH प्रतिक्रिया के लिए Cu और Pd के बाद Pt सबसे सक्रिय उत्प्रेरक है। दिलचस्प है, जैसा कि एमकेएम विश्लेषण से उल्लेख किया गया है, अधिकांश धातु उत्प्रेरक की सतहों को मध्यवर्ती प्रजातियों द्वारा कवर किया गया है; CH₃CO, Cu को छोड़कर। Cu की C-H बॉन्ड को सक्रिय करने में कठिनाई के कारण Cu की सतह मुख्य रूप से स्थिर मध्यवर्ती CH₃CH₂O द्वारा कवर की जाती है। एक तर्कसंगत डिजाइन विचार इस प्रकार मिश्र धातु के लिए प्रस्तावित है जिसमें धातुओं के साथ डीहाइड्रोजनीकरण की क्षमता अधिक होती है, ताकि एलिडहाइड का कारोबार बढ़ सके। चार द्विधात्विक मिश्रधातु; CuNi, CuPd, CuPt, और CuRh अंत में चुने गए हैं जो NODH प्रतिक्रिया के लिए एलिडहाइड उत्पाद के प्रति उच्च चयनात्मकता और रूपांतरण दिखाने के लिए गणना की जाती है। इन-सीटू स्क्रीनिंग प्रक्रिया को तेज करने के लिए, मशीन

लर्निंग (एमएल) आधारित मॉडल का निर्माण NODH प्रतिक्रियाओं के लिए Cu आधारित मिश्र धातुओं की जांच और इथेनॉल अपघटन प्रतिक्रिया के लिए Ni और Co आधारित मिश्र धातुओं के लिए किया गया है। एमएल मॉडल एमकेएम में प्रतिक्रियात्मक रुझान के समान पूर्वानुमान दिखा रहा है। घन आधारित उत्प्रेरक पर एनओडीएच प्रतिक्रिया में प्राथमिक और माध्यमिक अल्कोहल के उत्पाद चयनात्मकता और प्रतिक्रियात्मक रुझान, प्रॉपेनॉल और आइसोप्रोपानॉल के डीएफटी गणना का उपयोग करके आगे का विश्लेषण किया जाता है। द्वितीयक अल्कोहल की गणना एनओडीएच को कम सक्रियता ऊर्जा के साथ करने के लिए की जाती है।

एनओडीएच के उत्प्रेरक के रूप में घन के विपरीत, पं-आधारित द्विधात्विक मिश्र धातु की सतह को तर्कसंगत रूप से डिजाइन करने का उद्देश्य अलग है। चूंकि Pt की सतह CH_3CO प्रजाति से आच्छादित है, इसलिए यहां टारगेट को कम सक्रिय धातु के साथ Pt करके मिश्रधातु की सतह की डिहाइड्रोजनीकरण गतिविधि को नियंत्रित करना है, ताकि बाद में डिहाइड्रोजनीकरण से गुजरने पर वांछित एल्डिहाइड (CH_3CHO) उत्पाद पर प्रतिक्रिया को रोका जा सके। सतह। इसके अलावा, एक आर्थिक दृष्टिकोण से, शुद्ध पं। की तुलना में सस्ता द्विध्रुवीय उत्प्रेरक डिजाइन करने के लिए एक मूल्य फ़िल्टर जोड़ा जाता है। चार विशिष्ट पं-आधारित द्विध्रुवीय मिश्र अंत में प्रस्तावित हैं; NODH उत्पादों की उच्च उपज प्राप्त करने के लिए PtCu, PtZn, PtGa, और PtGe।

तीसरी प्रतिक्रिया में, बाहरी हाइड्रोजन स्रोत की आवश्यकता के बिना, सीओ 2 में कमी के साथ, एथिलीन रूपांतरण के लिए एथेन रूपांतरण की एक स्थायी प्रक्रिया के लिए उत्प्रेरक सामग्री विकसित करने के लिए उक्त इनिटियो डिजाइन सिद्धांतों को आगे लागू किया जाता है। सैद्धांतिक मापदंडों के एक बेंचमार्क के रूप में, एमकेएम ने इस प्रतिक्रिया के लिए NiFe उत्प्रेरक की उच्च प्रतिक्रियाशीलता की पुष्टि की, एक हालिया प्रयोगात्मक अध्ययन में रिपोर्ट किए गए रुझान के समान एथिलीन और महत्वपूर्ण CO_2 रूपांतरण के लिए उच्च चयनात्मकता की गणना की। इसके अलावा, अब इनिटियो एमकेएम प्रतिक्रिया में यंत्रवत अंतर्दृष्टि प्रदान कर रहा है जहां सी-सी हाइड्रोजनोलिसिस प्रतिक्रिया कदम (211) सतह पर कोक की उच्च मात्रा का उत्पादन करने के लिए मनाया जाता है, जो उत्प्रेरक निष्क्रियता की ओर जाता है।

आणविक स्तर के इंजीनियरिंग टूलबॉक्स के अंतिम आवेदन के रूप में, एमकेएम को छत पर (111) और संक्रमण धातु उत्प्रेरकों के चरण (211) स्थलों पर बायोगैस की सुधारकारी प्रतिक्रिया को समझने के लिए लागू किया जाता है। अध्ययन किए गए सभी उत्प्रेरकों में से, सह और आरयू की गणना मीथेन की खपत के लिए मध्यम कारोबार और काफी छोटे कोक गठन के लिए की जाती है, इस प्रकार प्रतिक्रिया के लिए स्थिर उत्प्रेरक के रूप में कार्य करने की क्षमता प्रदर्शित होती है। सीओ और आरयू के छत स्थलों पर गणना की गई एच 2 / सीओ अनुपात एफटी प्रतिक्रियाओं के लिए आवश्यक है। मीथेन के स्टीम सुधार को अध्ययन किए गए सभी उत्प्रेरकों के लिए प्रमुख सुधार मार्ग माना जाता है।

कुल मिलाकर, शोध प्रबंध उत्प्रेरक अभिकर्मक की निर्णायक भविष्यवाणियों के लिए जटिल प्रतिक्रिया नेटवर्क के व्यापक मॉडलिंग में डीएफटी गणना और अब इनिटियो एमकेएम के कार्यान्वयन को रेखांकित कर रहा है जो तर्कसंगत उत्प्रेरक डिजाइन में मदद प्रदान कर सकता है।

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