RATIONAL CATALYST DESIGN FOR THE REMOVAL OF ORGANIC CONTAMINANTS FROM WATER

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by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

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Dedicated to my grandparents (ajja and mamama),

parents and Ajay

Certificate

This is to certify that the dissertation entitled "**Rational Catalyst Design for the Removal of Organic Contaminants from Water**" being submitted by **Chaitra Shantharam Shenoy** 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 my supervision and has fulfilled the requirements, which to my 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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Chaitra Shantharam Shenoy

Abstract

The organic contaminants released from various industries, due to their carcinogenic nature and inability to degrade naturally, pose a serious threat to human health and the environment. Of the existing treatment techniques for the removal of these organic pollutants from water, catalytic treatment is a viable practice as it is economically feasible, leads to complete mineralization of the pollutants and can be conducted at moderate reaction conditions. This transformation of organic contaminants is aided by transition metals and thus, it is deemed essential to rationally design the catalysts. In this direction, catalytic reactions (hydrodechlorination (HDC) reaction and oxidation reaction) of various contaminants (trichloroethylene (TCE), 4-chlorophenol (4-CP) and ethylene glycol (EG)) using density functional theory (DFT) simulations combined with microkinetic modeling (MKM) are undertaken. A few experiments are also carried out involving TCE as a model impurity.

In the present work, an attempt is made to gain mechanistic insights on the reactivity of the Pd catalyst, which is the most widely employed catalyst for HDC reactions. Towards this, the HDC reaction of TCE, incorporating DFT calculations, is simulated over different facets (terrace Pd (111) and Pd (100), undercoordinated Pd (211) and Pd (110)) of a Pd catalyst. TCE undergoes dechlorination to form a hydrocarbon intermediate followed by hydrogenation to form ethene or ethane. On the Pd catalyst, TCE binds with a high binding energy (B.E.) of -178 kJ/mol over the Pd (110) surface. The chlorine atoms released as a result of dechlorination tend to block the active sites, thereby poisoning the surface with high binding energies (B.E. > -160 kJ/mol) on all the surfaces. The removal of surface chlorine is facilitated by its reaction with surface hydrogen to form hydrogen chloride. The terrace sites display comparatively lower activation energies for the formation of hydrogen chloride in contrast to the undercoordinated sites, which suggests the ease of removal of Cl as HCl from the terrace sites. The structure sensitivity in the TCE HDC reaction could possibly arise due to the differences in the energetics of Cl removal on different Pd facets.

In addition, to understand the role of the support in the HDC reaction of TCE, few experiments are also conducted by employing Pd metal supported over carbon (Pd/C) and titania ($Pd/TiO_{2(C)}$ and $Pd/TiO_{2(S)}$, wherein the subscripts (C) and (S) stand for commercial and synthesized TiO_2, respectively). TCE HDC follows first order reaction kinetics. In this study, it is observed that on increasing the temperature, the conversion increases over the three catalysts. However, the conversion increases drastically over the TiO_2-supported Pd catalyst compared to the Pd/C catalyst. The variation in the concentration with temperature is utilized to calculate the apparent

activation energies (E_{app}). Herein, the E_{app} over the Pd/C catalyst is calculated to be 21.2 kJ/mol, which is higher than that calculated over the $Pd/TiO_{2(C)}$ catalyst (E_{app} = 13.6 kJ/mol) and $Pd/TiO_{2(S)}$ catalyst (E_{app} = 12.4 kJ/mol). Furthermore, the DFT studies reveal lower adsorption energy of chlorine over Pd_4/TiO_2 compared to the Pd (111) slab, highlighting the role of the titania support.

Addition of a second metal to the parent metal (Pd) has proved to be beneficial as it leads to improved stability, activity and selectivity towards the desired product compared to the parent metal. Herein, a combined DFT and MKM study for the HDC of 4-CP is performed over the terrace (111) sites of the Pd metal and A_3B type alloys with coinage metals (A-Pd, B-Cu, Ag and Au). 4-CP undergoes dechlorination followed by hydrogenation to form phenol. The Pd_3Ag surface displays the lowest barrier (44 kJ/mol) for the C-Cl bond dissociation step compared to the monometallic Pd surface (71 kJ/mol). The trend in the reactivity follows: $Pd_3Ag > Pd_3Au > Pd > Pd_3Cu$. The high turnover frequency (TOF) over the Pd_3Ag surface could be attributed to the ease of C-Cl bond dissociation, whereas the low TOF over the Pd_3Cu surface can be due to the high binding energy of 4-CP molecule. For the C-Cl bond dissociation step, a positive degree of rate control is observed, which suggests that the step is crucial in ascertaining the HDC rate.

Further, to understand the effect of the catalyst particle size on the oxidation reaction of EG, different transition metals and nanoclusters are screened by building a MKM. EG oxidizes to form glycolic acid and oxalic acid. Two different routes are explored for this oxidation reaction – direct metal-assisted oxidation route and the O and OH-assisted oxidation route. The transition metals display considerably higher TOF via the O and OH-assisted route compared to the metal-assisted route (TOF is 4 to 5 orders of magnitude lower). A high selectivity towards glycolic acid is reported over all the nanoclusters and transition metals via the O and OH-assisted route compared to oxalic acid formation. In addition, on moving from metal surfaces to nanoclusters, that is, reducing the size of the catalyst, the Au_{13} nanocluster is observed to lie at the top of the volcano plot with a high selectivity towards glycolic acid.

In all, this dissertation presents a brief outline on developing catalytic materials for the removal of organic contaminants in water, accomplished by employing theoretical tools, that can aid in the rational design of catalysts by providing mechanistic insights and trends in the activity and selectivity of the catalysts.

सार

विभिन्न उद्योगों से निकलने वाले कार्बनिक प्रदूषक, जो कैंसरजन्य प्रकृति के होते हैं और स्वाभाविक रूप से नष्ट नहीं हो सकते, मानव स्वास्थ्य और पर्यावरण के लिए गंभीर खतरा पैदा करते हैं। जल से इन कार्बनिक प्रदूषकों को हटाने के लिए उपलब्ध उपचार तकनीकों में, उत्प्रेरक उपचार एक व्यावहारिक विकल्प है क्योंकि यह आर्थिक रूप से किफायती है, प्रदूषकों का पूर्ण खनिजीकरण करता है और इसे मध्यम प्रतिक्रियात्मक परिस्थितियों में किया जा सकता है। इन कार्बनिक प्रदूषकों के रूपांतरण में संक्रमण धातुएँ सहायक होती हैं, और इसलिए उत्प्रेरकों की तार्किक रूप से डिज़ाइनिंग आवश्यक मानी जाती है।

इस दिशा में, कार्बनिक प्रदूषकों (ट्राइक्लोरोएथिलीन (TCE), 4-क्लोरोफेनोल (4-CP) और एथिलीन ग्लाइकोल (EG)) की हाइड्रोडिक्लोरीनेशन (HDC) और ऑक्सीकरण प्रतिक्रियाओं का अध्ययन डेंसिटी फंक्शनल थ्योरी (DFT) सिमुलेशन और माइक्रोकाइनेटिक मॉडलिंग (MKM) के संयोजन से किया गया है। कुछ प्रयोगात्मक अध्ययन भी किए गए हैं, जिनमें TCE को एक मॉडल अशुद्धि के रूप में लिया गया है।

इस कार्य में, Pd उत्प्रेरक की प्रतिक्रियाशीलता पर यांत्रिक अंतर्दृष्टि प्राप्त करने का प्रयास किया गया है, जो HDC प्रतिक्रियाओं के लिए सबसे व्यापक रूप से प्रयुक्त उत्प्रेरक है। इसके लिए, TCE की HDC प्रतिक्रिया को विभिन्न Pd सतहों (टैरेस Pd (111) और Pd (100), अंडरकोऑर्डिनेटेड Pd (211) और Pd (110)) पर DFT गणनाओं को शामिल करते हुए सिमुलेट किया गया है। TCE डी-क्लोरीनेशन के बाद हाइड्रोजन के साथ अभिक्रिया करता है और इथीन या इथेन बनाता है। Pd उत्प्रेरक पर TCE Pd (110) सतह पर -178 kJ/mol की उच्च बाइंडिंग ऊर्जा के साथ बंधता है। डी-क्लोरीनेशन के फलस्वरूप मुक्त हुए क्लोरीन परमाणु सक्रिय स्थलों को अवरुद्ध करते हैं, जिससे सतह जहर का शिकार होती है, क्योंकि इनकी बाइंडिंग ऊर्जा सभी सतहों पर अधिक होती है (B.E. > -160 kJ/mol)। सतह पर हाइड्रोजन के साथ क्लोरीन की प्रतिक्रिया से हाइड्रोजन क्लोराइड बनती है, जिससे क्लोरीन हटाना संभव होता है। टैरेस साइट्स पर HCl बनने की सक्रियण ऊर्जा अंडरकोऑर्डिनेटेड साइट्स की तुलना में कम पाई गई, जिससे टैरेस साइट्स पर Cl को HCl के रूप में हटाना अधिक आसान प्रतीत होता है। इससे यह स्पष्ट होता है कि TCE HDC प्रतिक्रिया में Pd सतहों की संरचनात्मक संवेदनशीलता Cl को हटाने की ऊर्जा में अंतर के कारण उत्पन्न हो सकती है।

साथ ही, TCE की HDC प्रतिक्रिया में सपोर्ट की भूमिका को समझने के लिए कुछ प्रयोग भी किए गए, जिनमें Pd को कार्बन (Pd/C) और टाइटेनिया (Pd/TiO_2(C) और Pd/TiO_2(S), जहाँ (C) और (S) क्रमशः वाणिज्यिक और संश्लेषित टाइटेनिया को दर्शाते हैं) पर सहारा दिया गया है। TCE HDC प्रथम क्रम की अभिक्रिया गति का पालन करता है। इस अध्ययन में पाया गया कि तापमान बढ़ाने पर तीनों उत्प्रेरकों पर रूपांतरण में वृद्धि होती है, परंतु TiO_2-समर्थित Pd उत्प्रेरकों पर यह वृद्धि Pd/C की तुलना में कहीं अधिक होती है। तापमान के साथ सांद्रता में अंतर का उपयोग कर के प्रकट सक्रियण ऊर्जा (E_{app}) की गणना की गई है। Pd/C उत्प्रेरक के लिए E_{app} = 21.2 kJ/mol, जबकि Pd/TiO_2(C) के लिए E_{app} = 13.6 kJ/mol और Pd/TiO_2(S) के लिए E_{app} = 12.4 kJ/mol पाया गया। DFT अध्ययन यह भी दिखाते हैं कि Pd_4/TiO_2 पर क्लोरीन का एडसॉर्प्शन Pd (111) सतह की तुलना में कम होता है, जो टाइटेनिया सपोर्ट की भूमिका को रेखांकित करता है।

मूल धातु (Pd) में एक द्वितीय धातु जोड़ना लाभकारी सिद्ध हुआ है क्योंकि इससे उत्प्रेरक की स्थिरता, सक्रियता और चयनात्मकता बेहतर होती है। इस संदर्भ में, 4-CP की HDC प्रतिक्रिया के लिए Pd (111) टैरेस साइट्स और कॉइनज धातुओं (Pd-Cu, Pd-Ag और Pd-Au) के A_3B प्रकार के मिश्रधातु सतहों पर DFT और MKM का संयुक्त अध्ययन किया गया है। 4-CP डीक्लोरीनेशन के बाद फिनोल में परिवर्तित होता है। Pd_3Ag सतह पर C-Cl बॉन्ड टूटने की ऊर्जा अवरोध सबसे कम (44 kJ/mol) पाया गया, जो मोनोमेटालिक Pd सतह (71 kJ/mol) की तुलना में काफी कम है। प्रतिक्रियात्मकता की प्रवृत्ति इस प्रकार है: Pd_3Ag > Pd_3Au > Pd > Pd_3Cu। Pd_3Ag सतह पर उच्च टर्नओवर फ्रिक्वेंसी (TOF) C-Cl बंध के आसानी से टूटने के कारण है, जबकि Pd_3Cu पर TOF कम है क्योंकि 4-CP अणु की बाइंडिंग ऊर्जा अधिक होती है। C-Cl बंध टूटने के चरण पर प्रतिक्रिया दर नियंत्रण की सकारात्मक डिग्री पाई गई है, जो दर्शाती है कि यह चरण HDC दर निर्धारित करने में निर्णायक है।

इसके अलावा, EG के ऑक्सीकरण प्रतिक्रिया में उत्प्रेरक कण आकार के प्रभाव को समझने हेतु विभिन्न संक्रमण धातुओं और नैनोकणों का MKM मॉडलिंग द्वारा अध्ययन किया गया है। EG का ऑक्सीकरण ग्लायकोलिक अम्ल और ऑक्सालिक अम्ल में होता है। इस ऑक्सीकरण के दो मार्ग अध्ययन किए गए: प्रत्यक्ष धातु-सहायित मार्ग और O एवं OH-सहायित मार्ग। O और OH-सहायित मार्ग पर सभी संक्रमण धातुओं पर TOF धातु-सहायित मार्ग की तुलना में 4–5 गुणा अधिक पाया गया। सभी नैनोकणों और धातुओं पर ग्लायकोलिक अम्ल के लिए उच्च चयनात्मकता देखी गई। जब धातु सतहों से नैनोकणों की ओर बढ़ा गया (अर्थात उत्प्रेरक आकार घटाया गया), तब पाया गया कि Au_{13} नैनोकण वोल्केनो प्लॉट के शीर्ष पर स्थित है और ग्लायकोलिक अम्ल के प्रति उच्च चयनात्मकता दर्शाता है।

अंततः, यह शोध कार्य जल में मौजूद कार्बनिक प्रदूषकों को हटाने हेतु उत्प्रेरक पदार्थों के विकास की रूपरेखा प्रस्तुत करता है, जिसे सैद्धांतिक उपकरणों के उपयोग से पूरा किया गया है। यह दृष्टिकोण उत्प्रेरकों की तार्किक डिज़ाइनिंग में सहायक हो सकता है, क्योंकि यह गतिविधि और चयनात्मकता में प्रवृत्तियों और यांत्रिक अंतर्दृष्टियों को उजागर करता है।

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