DEVELOPMENT OF SINGLE-SITE METAL-ORGANIC FRAMEWORK- CATALYSTS FOR SUSTAINABLE ORGANIC TRANSFORMATIONS

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by

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Submitted

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Dedicated to My Parents

Certificate

This is to certify that the thesis entitled "Development of single-site metal-organic framework-catalysts for sustainable organic transformations" being submitted by Neha Antil to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. Neha Antil has worked under my supervision and has fulfilled all the requirements for the submission of her Ph.D. thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of a Ph.D. degree. The work embodied in this thesis has not been submitted, in part or full, to other Universities or Institutes for the award of any degree or diploma.

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Abstract

This thesis entitled "Development of single-site metal-organic framework-catalysts for sustainable organic transformations" presents the details of the synthesis of earth-abundant metal-based catalysts supported on metal-organic frameworks, their characterizations, and applications in various catalytic reactions. The thesis focuses on the utility of developed catalysts in asymmetric catalysis, hydrogenation catalysis, and methane oxidation.

Chapter 1: This chapter provides a brief overview of Metal-Organic Frameworks (MOFs), their characteristics, and potential applications. The significance of MOFs as single-site heterogeneous catalysts in numerous industrially significant catalysis processes, such as hydrogenations, oxidations, and asymmetric synthesis, is also covered in detail. With the help of the previously described examples, various methods that have been used to create MOF-based catalysts are explained in this section. The value of base metal catalysts is also discussed.

Chapter 2: This chapter has a detailed description of general techniques followed in the research work. This chapter includes a description of the chemicals used in this work. The experimental procedures for the purification of reagents and products, drying of solvents, and handling of air and moisture-sensitive compounds have been stated. It has details of the instrument techniques utilized for the characterization of catalysts and compounds, and also the sample preparation for the same. It also has the details of the software used in theoretical research.

Chapter 3: The development of chemoselective and heterogeneous earth-abundant metal catalysts is essential for sustainable chemical synthesis. We report a highly efficient, chemoselective, and reusable single-site nickel(II) hydride catalyst based on robust and porous aluminum MOF (DUT-5) for the hydrogenation of nitro and nitrile compounds to the corresponding amines. The nickel hydride catalyst was prepared by the metalation of aluminum hydroxide SBUs of DUT-5 having the formula of $Al(\mu_2\text{-}OH)(bpdc)$ (bpdc = 4,4'-biphenyldicarboxylate) with $NiBr_2$ followed by the reaction with $NaEt_3BH$. DUT-5-NiH has shown excellent functional group tolerance in the hydrogenation of various aromatic and aliphatic nitro and nitrile compounds under 1 bar H_2, and could be recycled and reused at least 10 times. By changing the reaction conditions of the hydrogenation of nitriles, symmetric or unsymmetric secondary amines were also afforded selectively. The experimental and computational studies suggested reversible nitrile coordination to nickel

followed by 1,2-insertion of the coordinated nitrile into nickel-hydride bond occurring in the turnover limiting step.

Chapter 4: DUT-5-NiH catalyst synthesized in chapter 3 was an active catalyst for chemoselective hydrogenolysis of carbon−oxygen (C−O) bonds in aryl ethers to afford hydrocarbons under atmospheric hydrogen pressure in the absence of any base, which is important for the generation of fuels from biomass. The reaction kinetic studies suggested that the initial rate of hydrogenolysis has first-order dependency on the substrate and catalyst and zero order dependency on the pressure of hydrogen. This work highlights the potential of DUT-5-NiH catalysts for the production of biofuels from biomass.

Chapter 5: Chemoselective deoxygenation of carbonyls and alcohols using hydrogen by heterogeneous base-metal catalysts is crucial for the sustainable production of fine chemicals and biofuels. We report an aluminum MOF (DUT-5) node supported cobalt(II) hydride, which is a highly chemoselective and recyclable heterogeneous catalyst for deoxygenation of a range of aromatic and aliphatic ketones, aldehydes, primary and secondary alcohols, including biomass-derived substrates under 1 bar H_2. The single-site cobalt catalyst (DUT-5-CoH) was easily prepared by post-synthetic metalation of the SBUs of DUT-5 with $CoCl_2$ followed by the reaction of $NaEt_3BH$. X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge spectroscopy (XANES) indicated the presence of Co^{II} and Al^{III} centers in DUT-5-CoH and DUT-5-Co after catalysis. The coordination environment of the cobalt-center of DUT-5-Co before and after catalysis was established by extended X-ray fine structure spectroscopy (EXAFS) and density functional theory (DFT). The kinetic and computational data suggest reversible carbonyl coordination to cobalt preceding the turnover-limiting step, which involves 1,2-insertion of the coordinated carbonyl into the cobalt-hydride bond. The unique coordination environment of the cobalt ion ligated by oxo-nodes within the porous framework and the rate-independency on the pressure of H_2 allow the deoxygenation reactions to occur chemoselectively under ambient hydrogen pressure.

Chapter 6: The development of heterogeneous, chemoselective, and tandem catalytic systems using abundant metals is vital for the synthesis of fine and commodity chemicals. We report a robust and recyclable single-site cobalt-hydride catalyst based on a porous aluminum MOF (DUT-5) for chemoselective hydrogenation of arenes. The DUT-5 node supported cobalt(II) hydride (DUT-5-CoH) is a versatile solid catalyst for chemoselective hydrogenation of a range of non-polar and polar arenes, including heteroarenes such as pyridines, quinolines, isoquinolines, indoles, and furans to afford cycloalkanes and saturated heterocycles in excellent yields. DUT-5-CoH exhibited an excellent functional group tolerance and could be reusable at least five times without decreased activity. The same MOF-Co catalyst was also efficient for tandem hydrogenation-hydrodeoxygenation of aryl carbonyl compounds, including biomass-derived platform molecules such as furfural and hydroxymethylfurfural to cycloalkanes. In the case of hydrogenation of cumene, our spectroscopic, kinetic, and density functional theory (DFT) studies suggest the insertion of trisubstituted alkene intermediate into the Co–H bond occurring in the turnover limiting step. Our work highlights the potential of MOF-supported single-site base-metal catalysts for the sustainable and environment-friendly industrial production of chemicals and biofuels.

Chapter 7: The development of highly efficient and enantioselective heterogeneous catalysts based on earth-abundant elements and inexpensive chiral ligands is essential for environment-friendly and economical production of optically active compounds. We report a strategy of synthesizing chiral amino alcohol-functionalized MOF to produce highly enantioselective single-site base-metal catalysts for asymmetric organic transformations. The chiral MOF (vol-UiO) was prepared by grafting of chiral amino alcohol such as L-valinol within the pores of aldehyde-functionalized UiO-MOF via formation of imine linkages. The metalation of vol-UiO with $FeCl_2$ in THF gives amino alcohol coordinated octahedral Fe^{II} species of vol-FeCl(THF)$_3$ within the MOF as determined by X-ray absorption spectroscopy. Upon activation with $LiCH_2SiMe_3$, vol-UiO-Fe catalyzed hydrosilylation and hydroboration of a range of aliphatic and aromatic carbonyls to afford the corresponding chiral alcohols with enantiomeric excesses up to 99%. Vol-UiO-Fe catalysts have high turnover numbers of up to 15000 and could be reused minumum 10 times without any loss of activity and enantioselectivity. The spectroscopic, kinetic and computational studies suggest iron-hydride as the catalytic species, which undergoes enantioselective 1,2-insertion of carbonyl to give iron-alkoxide intermediate. The subsequent σ-bond metathesis between Fe–O bond and Si–H bond of silane produces chiral silyl ether. This work highlights the importance of MOFs as the tunable molecular material for designing chiral solid catalysts based on inexpensive natural feedstocks such as chiral amino acids and base-metals for asymmetric organic transformations.

Chapter 8: Developing highly efficient catalysts for chemoselective oxidation of methane to methanol under mild conditions is a grand challenge. We report a successful design and synthesis of a heterogeneous single-site cobalt-hydroxide catalyst [Ce-UiO-Co(OH)] supported by the nodes of a cerium MOF (Ce-UiO-66 MOF), which is efficient in partial methane oxidation using hydrogen peroxide at 80 °C, giving an extraordinarily high methanol yield of 2166 $mmolg_{cat}^{-1}$ in 99% selectivity with a TON of 3250. Ce-UiO-Co catalyst is significantly more active and selective than its iso-structural zirconium analogue Zr-UiO-Co in methane to methanol conversion. Experimental and computational studies suggest the formation of $Co^{III}(\eta^2$-hydroperoxide) intermediate coordinating with one μ_4-O^- and two neutral carboxylate oxygens of Ce^{+4} oxo nodes within the pores of Ce-UiO-66, which undergoes σ-bond metathesis with methane C–H bond in the turn-over limiting step of the catalytic cycle. The significantly lower activation energy of Ce-UiO-Co than Zr-UiO-Co is due to the highly electron-deficient nature of the cobalt ion of the $Co(\eta^2$-$O_2H)$ species supported by the Ce-UiO nodes, which promotes facile C–H activation of methane via σ-bond metathesis. This MOF-based catalyst design holds promise in developing molecular electrophilic abundant metal catalysts for chemoselective functionalization of saturated hydrocarbons.

सारांश:

"टिकाऊ कार्बनिक परिवर्तनों के लिए एकल-साइट धातु-कार्बनिक फ्रेमवर्क-उत्प्रेरक का विकास" नामक यह थीसिस धातु-कार्बनिक चौखटे, उनके लक्षण वर्णन और विभिन्न उत्प्रेरक प्रतिक्रियाओं में अनुप्रयोगों पर समर्थित पृथ्वी-प्रचुर मात्रा में धातु-आधारित उत्प्रेरक के संश्लेषण का विवरण प्रस्तुत करती है। थीसिस असममित उत्प्रेरण, हाइड्रोजनीकरण उत्प्रेरण और मीथेन ऑक्सीकरण में विकसित उत्प्रेरक की उपयोगिता पर केंद्रित है।

अध्याय 1: यह अध्याय धातु-कार्बनिक फ्रेमवर्क (MOF), उनकी विशेषताओं और संभावित अनुप्रयोगों का एक संक्षिप्त अवलोकन प्रदान करता है। हाइड्रोजनीकरण, ऑक्सीकरण और असममित संश्लेषण जैसे कई औद्योगिक रूप से महत्वपूर्ण उत्प्रेरण प्रक्रियाओं में एकल-साइट विषम उत्प्रेरक के रूप में एमओएफ का महत्व भी विस्तार से कवर किया गया है। पहले वर्णित उदाहरणों की मदद से, MOF-आधारित उत्प्रेरक बनाने के लिए उपयोग की जाने वाली विभिन्न विधियों को इस खंड में समझाया गया है। आधार धातु उत्प्रेरक के मूल्य परभी चर्चा की गई है।

अध्याय 2: इस अध्याय में अनुसंधान कार्य में अपनाई जाने वाली सामान्य तकनीकों का विस्तृत विवरण है। इस अध्याय में इस कार्य में उपयोग किए जाने वाले रसायनों का वर्णन शामिल है। अभिकर्मकों और उत्पादों की शुद्धि, सॉल्वैंट्स के सुखाने, और हवा और नमी के प्रति संवेदनशील यौगिकों की हैंडलिंग के लिए प्रयोगात्मक प्रक्रियाओं को कहा गया है। इसमें उत्प्रेरक और यौगिकों के लक्षण वर्णन के लिए उपयोग की जाने वाली उपकरण तकनीकों का विवरण है, और इसके लिए नमूना तैयारी भी है। इसमें सैद्धांतिक अनुसंधान में उपयोग किए जाने वाले सॉफ़्टवेयर का विवरण भी है।

अध्याय 3: टिकाऊ रासायनिक संश्लेषण के लिए कीमोसेलेक्टिव और विषम पृथ्वी-प्रचुर मात्रा में धातु उत्प्रेरक का विकास आवश्यक है। हम नाइट्रो और नाइट्राइल यौगिकों के हाइड्रोजनीकरण के लिए इसी अमाइन के लिए मजबूत और झरझरा एल्यूमीनियम एमओएफ (DUT-5) के आधार पर एक अत्यधिक कुशल, केमोसेलेक्टिव और पुन: प्रयोज्य एकल-साइट निकल (द्वितीय) हाइड्राइड उत्प्रेरक की रिपोर्ट करते हैं। निकल हाइड्राइड उत्प्रेरक को DUT-5 के एल्यूमीनियम हाइड्रॉक्साइड SBU के धातुकरण द्वारा तैयार किया गया था, जिसमें Al(μ_2-OH)(bpdc) (bpdc = 4,4’-biphenyldicarboxylate) का सूत्र था, जिसके बाद एनआईबीआर$_2$ के साथ NaEt$_3$BH बीएच के साथ प्रतिक्रिया हुई थी। DUT-5-NiH 1 बार H_2 के तहत सुगंधित और एलिफैटिक नाइट्रो और नाइट्राइल

यौगिकों के हाइड्रोजनीकरण में उत्कृष्ट कार्यात्मक समूह सहिष्णुता के साथ एक व्यापक सब्सट्रेट गुंजाइश है, और इसे कम से कम 10 बार पुनर्नवीनीकरण और पुन: उपयोग किया जा सकता है। नाइट्राइल्स के हाइड्रोजनीकरण की प्रतिक्रिया स्थितियों को बदलकर, सममित या असमान माध्यमिक अमाइनों को भी चुनिंदा रूप से वहन किया गया था। प्रयोगात्मक और कम्प्यूटेशनल अध्ययनों ने निकल के लिए प्रतिवर्ती नाइट्राइल समन्वय का सुझाव दिया, जिसके बाद टर्नओवर सीमित चरण में होने वाले निकल-हाइड्राइड बॉन्ड में समन्वित नाइट्राइल के 1,2-सम्मिलन का पालन किया गया।

अध्याय 4: अध्याय 3 में संश्लेषित DUT-5-NiH उत्प्रेरक किसी भी आधार की अनुपस्थिति में वायुमंडलीय हाइड्रोजन दबाव के तहत हाइड्रोकार्बन को वहन करने के लिए एरिल ईथर में कार्बन-ऑक्सीजन (C-O) बांड के केमोसेलेक्टिव हाइड्रोजनोलिसिस के लिए एक सक्रिय उत्प्रेरक था, जो बायोमास से ईंधन की पीढ़ी के लिए महत्वपूर्ण है। प्रतिक्रिया गतिज अध्ययनों ने सुझाव दिया कि हाइड्रोजनोलिसिस की प्रारंभिक दर में सब्सट्रेट और उत्प्रेरक पर पहला आदेश निर्भरता और H_2 के दबाव पर शून्य आदेश निर्भरता है। यह काम बायोमास से जैव ईंधन के उत्पादन के लिए DUT-5-NiH उत्प्रेरक की क्षमता पर प्रकाश डालता है।

अध्याय 5: विषम आधार-धातु उत्प्रेरक द्वारा हाइड्रोजन का उपयोग करके कार्बोनिल्स और अल्कोहल का केमोसेलेक्टिव डीऑक्सीजनेशन ठीक रसायनों और जैव ईंधन के टिकाऊ उत्पादन के लिए महत्वपूर्ण है। हम एक एल्यूमीनियम MOF (DUT -5) नोड समर्थन कोबाल्ट (द्वितीय) हाइड्राइड की रिपोर्ट करते हैं, जो 1 बार H_2 के तहत बायोमास-व्युत्पन्न सबस्ट्रेट्स सहित सुगंधित और एलिफैटिक केटोन्स, एल्डिहाइड, प्राथमिक और माध्यमिक अल्कोहल की एक श्रृंखला के डीऑक्सीजनेशन के लिए एक अत्यधिक केमोसेलेक्टिव और पुनर्नवीनीकरण विषम उत्प्रेरक है। एकल-साइट कोबाल्ट उत्प्रेरक (DUT-5-CoH) को आसानी से सीओसीएल 2 के साथ DUT -5 के SBU के पोस्ट-सिंथेटिक मेटलेशन द्वारा तैयार किया गया था, जिसके बाद एनएईटी 3 बीएच की प्रतिक्रिया हुईथी। एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (XPS) और एक्स-रे अवशोषण निकट-किनारे स्पेक्ट्रोस्कोपी (XANES) ने उत्प्रेरण के बाद DUT-5-Co और DUT-5-Co में Co^{II} और Al^{III} केंद्रों की उपस्थिति का संकेत दिया। उत्प्रेरण से पहले और बाद में DUT-5-Co के कोबाल्ट-केंद्र का समन्वय वातावरण विस्तारित एक्स-रे ठीक संरचना स्पेक्ट्रोस्कोपी (EXAFS) और घनत्व कार्यात्मक सिद्धांत (DFT) द्वारा स्थापित किया गया था। गतिज और कम्प्यूटेशनल डेटा टर्नओवर-सीमित चरण से पहले कोबाल्ट

के लिए प्रतिवर्ती कार्बोनिल समन्वय का सुझाव देते हैं, जिसमें CoH बॉन्ड में समन्वित कार्बोनिल का 1,2-सम्मिलन शामिल है। झरझरा ढांचे के भीतर ऑक्सो-नोड्स द्वारा लिगेटेड कोबाल्ट आयन का अद्वितीय समन्वय वातावरण और एच 2 के दबाव पर दर-निर्भरता परिवेश हाइड्रोजन दबाव के तहत डीऑक्सीजनेशन प्रतिक्रियाओं को केमोसेलेक्टिव रूप से अनुमति देती है।

अध्याय 6: प्रचुर मात्रा में धातुओं का उपयोग करके विषम, केमोसेलेक्टिव और अग्रानुक्रम उत्प्रेरक प्रणालियों का विकास ठीक और वस्तु रसायनों के संश्लेषण के लिए महत्वपूर्ण है। हम एरेनेस के केमोसेलेक्टिव हाइड्रोजनीकरण के लिए एक झरझरा एल्यूमीनियम एमओएफ (DUT -5) के आधार पर एक मजबूत और पुनर्नवीनीकरण योग्य एकल-साइट कोबाल्ट-हाइड्राइड उत्प्रेरक की रिपोर्ट करते हैं। DUT -5 नोड समर्थित कोबाल्ट (द्वितीय) हाइड्राइड (DUT-5-CoH) गैर-ध्रुवीय और ध्रुवीय एरेन की एक श्रृंखला के केमोसेलेक्टिव हाइड्रोजनीकरण के लिए एक बहुमुखी ठोस उत्प्रेरक है, जिसमें उत्कृष्ट पैदावार में साइक्लोएल्केन और संतृप्त हेटरोसाइकिल को बर्दाश्त करने के लिए पाइरिडिन, क्विनोलिन, आइसोक्विनोलिन, इंडोल और फुरान जैसे हेटरोरेन शामिल हैं। DUT-5-CoH ने एक उत्कृष्ट कार्यात्मक समूह सहिष्णुता का प्रदर्शन किया और कम गतिविधि के बिना कम से कम पांच बार पुन: प्रयोज्य हो सकता है। वही एमओएफ-सीओ उत्प्रेरक एरिल कार्बोनिल यौगिकों के अग्रानुक्रम हाइड्रोजनीकरण-हाइड्रोडिऑक्सीजनेशन के लिए भी कुशल था, जिसमें बायोमास-व्युत्पन्न प्लेटफ़ॉर्म अणु जैसे फरफुरल और हाइड्रॉक्सीमेथिलफर्फुरल से साइक्लोएल्केन्स शामिल थे। क्यूमिन के हाइड्रोजनीकरण के मामले में, हमारे स्पेक्ट्रोस्कोपिक, गतिज और घनत्व कार्यात्मक सिद्धांत (DFT) अध्ययन टर्नओवर सीमित चरण में होने वाले को Co-H बॉन्ड में ट्राइसब्स्टीट्यूटेड एल्केन इंटरमीडिएट के सम्मिलन का सुझाव देते हैं। हमारा काम रसायनों और जैव ईंधन के टिकाऊ और पर्यावरण के अनुकूल औद्योगिक उत्पादन के लिए एमओएफ समर्थित एकल-साइट बेस-मेटल उत्प्रेरक की क्षमता पर प्रकाश डालता है।

अध्याय 7: ऑप्टिकल रूप से सक्रिय यौगिकों के पर्यावरण के अनुकूल और किफायती उत्पादन के लिए पृथ्वी-प्रचुर तत्वों और सस्ती चिरल लिगैंड्स के आधार पर अत्यधिक कुशल और एन्टिओसेलेक्टिव विषम उत्प्रेरक का विकास आवश्यक है। हम असममित कार्बनिक परिवर्तनों के लिए अत्यधिक एंटिओसेलेक्टिव सिंगल-साइट बेस-मेटल उत्प्रेरक का उत्पादन करने के लिए चिरल एमिनो अल्कोहल-कार्यात्मक एमओएफ को संश्लेषित करने की रणनीति की रिपोर्ट करते हैं। चिरल MOF (vol-UiO) को चिरल एमिनो अल्कोहल जैसे एल-वैलिनोल के ग्राफ्टिंग द्वारा तैयार किया गया

था, जो इमिन लिंकेज के गठन के माध्यम से एल्डिहाइड-फंक्शनलाइज्ड UiO-MOF के छिद्रों के भीतर था। THF में एफईसीएल 2 के साथ vol-UiO का धातुकरण एक्स-रे अवशोषण स्पेक्ट्रोस्कोपी द्वारा निर्धारित MOF के भीतर वॉल्यूम- vol-FeCl(THF)$_3$ की एमिनो अल्कोहल समन्वित ऑक्टाहेड्रल Fe^{II} प्रजातियां देता है। LiCH$_2$SiMe$_3$ के साथ सक्रियण पर, vol-UiO-Fe ने 99% तक एनेन्टिओमेरिक अतिरिक्तता के साथ संबंधित चिरल अल्कोहल को वहन करने के लिए एलिफैटिक और सुगंधित कार्बोनिल्स की एक श्रृंखला के हाइड्रोसिलिलेशन और हाइड्रोबोरेशन को उत्प्रेरित किया। वॉल्यूम-यूआईओ-फे उत्प्रेरक में 15000 तक की उच्च टर्नओवर संख्या होती है और गतिविधि और एंटिओसेलेक्टिविटी के किसी भी नुकसान के बिना 10 बार न्यूनतम का पुन: उपयोग किया जा सकता है। स्पेक्ट्रोस्कोपिक, गतिज और कम्प्यूटेशनल अध्ययन उत्प्रेरक प्रजातियों के रूप में लौह-हाइड्राइड का सुझाव देते हैं, जो लौह-अल्कोक्साइड मध्यवर्ती देने के लिए कार्बोनिल के एन्टिओसेलेक्टिव 1,2-सम्मिलन से गुजरता है। सिलेन के Fe–O बॉन्ड और Si–H बॉन्ड के बीच बाद के σ-बॉन्ड मेटाथेसिस चिरल सिलिल ईथर का उत्पादन करता है। यह काम MOF के महत्व को सस्ती प्राकृतिक फीडस्टॉक्स जैसे चिरल एमिनो एसिड और असममित कार्बनिक ट्रांसफॉर्मेटियो एनएस के लिए आधार-धातुओं के आधार पर चिरल ठोस उत्प्रेरक को डिजाइन करने के लिए ट्यून करने योग्य आणविक सामग्री के रूप में उजागर करताहै।

अध्याय 8: हल्के परिस्थितियों में मेथनॉल के लिए मीथेन के केमोसेलेक्टिव ऑक्सीकरण के लिए अत्यधिक कुशल उत्प्रेरक विकसित करना एक बड़ी चुनौती है। हम एक विषम एकल-साइट कोबाल्ट-हाइड्रॉक्साइड उत्प्रेरक [Ce-UiO-Co(OH)] के सफल डिजाइन और संश्लेषण की रिपोर्ट करते हैं जो एक सीरियम MOF (Ce-UiO-66 MOF) के नोड्स द्वारा समर्थित है, जो 80 डिग्री सेल्सियस पर हाइड्रोजन पेरोक्साइड का उपयोग करके आंशिक मीथेन ऑक्सीकरण में कुशल है, जिससे 2166 mmolg$_{cat}^{-1}$ की असाधारण उच्च मेथनॉल उपज मिलती है 3250 के TON के साथ 99% चयनात्मकता में। Ce-UiO-Co उत्प्रेरक मेथनॉल रूपांतरण के लिए मीथेन में अपने आईएसओ-संरचनात्मक ज़िरकोनियम एनालॉग Zr-UiO-Co की तुलना में काफी अधिक सक्रिय और चयनात्मक है। प्रायोगिक और कम्प्यूटेशनल अध्ययनों से पता चलता है कि Co^{III}(η^2-hydroperoxide) मध्यवर्ती समन्वय एक μ_4-O$^-$ और Ce-UiO-66 के छिद्रों के भीतर Ce^{+4} ऑक्सो नोड्स के दो तटस्थ कार्बोक्सिलेट ऑक्सीजन के साथ समन्वय करता है, जो उत्प्रेरक चक्र के टर्न-ओवर सीमित चरण में मीथेन सी C–H एच बॉन्ड के साथ σ-बॉन्ड मेटाथेसिस से गुजरता है। Zr-UiO-Co की तुलना में Ce-UiO-Co की काफी कम सक्रियण ऊर्जा Ce-UiO-Co नोड्स द्वारा समर्थित सह Co(η^2-O$_2$H)) प्रजातियों के कोबाल्ट आयन की अत्यधिक इलेक्ट्रॉन-कमी प्रकृति के कारण है, जो σ-बॉन्ड मेटाथेसिस के माध्यम से मीथेन

के सहज C–H यह एमओएफ-आधारित उत्प्रेरक डिजाइन संतृप्त हाइड्रोकार्बन के केमोसेलेक्टिव फंक्शनलाइजेशन के लिए आणविक इलेक्ट्रोफिलिक प्रचुर मात्रा में धातु उत्प्रेरक विकसित करने में वादा करता है।

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