

**RATIONAL DESIGN OF CATALYST SUPPORT AND  
PROMOTER IN METHANE DEHYDROAROMATIZATION  
REACTION**

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by

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Submitted

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

to the



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*Dedicated to*  
*My Parents*

## CERTIFICATE

This is to certify that the thesis entitled, “**RATIONAL DESIGN OF CATALYST SUPPORT AND PROMOTER IN METHANE DEHYDROAROMATIZATION REACTION**” being submitted by **Mr. Sourabh Mishra** to the Indian Institute of Technology Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by him under our guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi.

The research report and 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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## ABSTRACT

Non-oxidative methane dehydroaromatization (MDA) is the most promising route for direct transformation of natural gas, an abundant source of methane, into value added aromatic hydrocarbons. The process is attractive in terms of decreasing wastage of valuable methane hydrocarbon mostly flared at remote locations and simultaneously reducing greenhouse gas emissions to the atmosphere caused by flaring. In view of commercial aspects, the process is also beneficial as it comprises single step conversion of low cost natural gas into aromatic hydrocarbons and hence can be an alternative towards traditional production of aromatics in petroleum refineries. Limitations with the process are mainly associated to low equilibrium conversion and fast catalyst deactivation. Molybdenum modified zeolite (ZSM-5/MCM-22) has been known as potential catalyst for MDA reaction and is found to be highly selective towards aromatic hydrocarbons. Fast deactivation of Mo-Zeolite catalysts require more insights into the functioning of the catalyst. Further modification in active sites with varying zeolite Si/Al content or addition of secondary metals is desirable in view of investigating the catalyst stability. Coke growth analysis and its nature over MDA catalyst must be in consideration while understanding the deactivation path. In this context, the present work has been constructed performing DFT calculations for methane transformation into C<sub>2</sub> intermediates (ethane and ethylene) and experimental studies for rational design of catalyst support and promoter.

As a first step, DFT calculations were performed in detail for methane activation and C-C coupling steps to generate key C<sub>2</sub> intermediates (ethane and ethylene) on the isolated molybdenum carbide cluster (Mo<sub>4</sub>C<sub>2</sub>). Methane activation barrier was checked at different Mo sites of Mo<sub>4</sub>C<sub>2</sub> cluster to find suitable Mo atom sites towards ethylene formation path possessing lower energy barriers. Further, energy barriers of C-H dissociation and C-C coupling steps were analyzed over Mo<sub>4</sub>C<sub>2</sub> cluster having different residual charge in view of understanding a relation between reducibility and catalyst activity. It was found that more reduced cluster having low

positive charge favours methane dehydrogenation which is a key step in MDA. Reducibility of active Mo sites on the catalyst can be controlled during catalyst preparation or regeneration. Overall, DFT calculations are providing insights into ethane and ethylene formation in MDA route and guidelines towards tailoring the active sites via modification in electronic structure.

In a parallel efforts, effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (SAR) of MCM-22 support was analyzed with respect to the interaction of Mo species with the MCM-22 support, formation of active phases (MoO<sub>x</sub>C<sub>y</sub>/Mo<sub>2</sub>C) and corresponding activity towards MDA reaction. For this, HMCM-22 zeolite of different SAR (30, 40 and 55) was synthesized via conventional hydrothermal method and tested for the reaction with constant 5 wt% Mo loading. Different characterizations; XRD, BET, NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR, <sup>27</sup>Al MAS NMR, XPS and Raman spectroscopy were used to investigate the physiochemical properties of Mo/HMCM-22 with respect to different Si/Al ratio. In MDA activity results, Mo/HMCM-22 was found to be highly active at SAR-30 exhibiting higher methane conversion and benzene formation rate with lower coke content as compared to that at SAR-40 and SAR-55. NH<sub>3</sub>-TPD results confirmed that HMCM-22 at SAR-30 consists of higher concentration of Brønsted acid sites which is beneficial towards Mo anchoring over zeolite channels and aromatization in MDA reaction. Further, <sup>27</sup>Al MAS NMR, Raman spectroscopic and H<sub>2</sub>-TPR results directed that Mo oxide species effectively interacts with MCM-22 framework at SAR-30 compared to other SAR and hence results in higher activity of the catalyst. XPS results of pre-treated Mo/HMCM-22 indicated that higher proportion of active Mo species (MoO<sub>x</sub>C<sub>y</sub>) associated to the zeolite framework occurs at SAR-30 compared to that at SAR-40 and 55. Overall, HMCM-22 possessing higher acidity due to higher Al content at SAR-30 exhibits sufficient anchoring sites for Mo oxide and hence shows an enhanced proportion of associated active Mo sites (oxycarbide/carbide) during pre-treatment which leads a higher activity in MDA reaction.

In the third study, Mo/HMCM-22 (SAR-30) catalyst was upgraded with addition of Cr in view of investigating the effect of chromium as a promoter towards MDA activity. Experimental

results revealed that Cr addition (0.5Cr/5Mo/HMCM-22) significantly improves the catalytic activity showing higher benzene production rate and methane conversion with time on stream as compared to 5Mo/HMCM-22 catalyst. The spent Cr added catalyst showed lower coke content (15.9 wt%) compared to spent Mo/HMCM-22 (19.3 wt%) as confirmed by TGA results. Higher reduction temperature corresponding to  $\text{Mo}^{6+}$  to  $\text{Mo}^{4+}$  transformation and reduced surface acidity on Cr addition indicated an effective interaction of Mo species over MCM-22 crystals as confirmed by  $\text{H}_2$ -TPR and  $\text{NH}_3$ -TPD respectively. HR-TEM results of calcined and pre-treated catalysts further indicated an improved distribution of Mo species over MCM-22 crystals on Cr addition leading to higher activity towards MDA reaction. Coke associated large  $\text{Mo}_2\text{C}$  particles were observed with non-promoted (Mo/HMCM-22) catalyst during the course of reaction (120 min of TOS) as supported by HR-TEM results and also responsible for its lower activity. XPS results inferred that the formation of active Mo sites ( $\text{MoO}_x\text{C}_y/\text{Mo}_2\text{C}$ ) associated to zeolite channels was more pronounced with Cr added catalyst during pre-treatment and reaction. In addition, more disordered carbonaceous species originated over Mo/HMCM-22 ( $I_D/I_G = 1.27$ ) compared to that on Cr added catalyst ( $I_D/I_G = 0.93$ ) and hence indicates variation in coking during the reaction. Overall, Cr added catalyst showed higher activity possessing superior physiochemical properties as compared to Mo/HMCM-22 catalyst.

As coke deposition is considered a major obstacle in MDA route, mode of coke growth analysis over MDA catalyst is thus needed. In the fourth study, coke deposition analysis over 0.5Cr/5Mo/HMCM-22 catalyst was performed at different time intervals for the three different temperatures (600, 700 and 800 °C). TGA and Raman spectroscopic studies were performed to evaluate the coke content and quality of carbonaceous species over spent catalysts collected at different intervals. Raman results directed that with the increase in TOS, more disordered carbon accumulates over the catalyst surface based on  $I_D/I_G$  ratio. High temperature range also favours the formation of disordered carbonaceous species. Further, a monolayer-multilayer model was applied to predict the coke formation rate over the catalyst. In optimized results, first order

kinetics was found with coke formation in monolayer which indicates that monolayer coking depends on a single site which is in support towards MDA catalytic path. A higher activation energy (105.43 kJ/mol) was found for monolayer coking as compared to that for multilayer coking (47.67 kJ/mol). Low activation energy for multilayer coking indicated a strong dependency of coking rate in multilayer on the coke concentration in monolayer. This indicates that coke precursors in monolayer acts as an active site towards multilayer coking over the catalyst. Observed results support the hypothesis of MDA path as carbide associated coking facilitates severe coking with the progress of reaction.

## सार

गैर-ऑक्सीडेटिव मीथेन डीहाइड्रोएरोमैटाइजेशन (MDA) प्राकृतिक गैस के प्रत्यक्ष परिवर्तन के लिए सबसे आशाजनक मार्ग है, जो मीथेन का एक प्रचुर स्रोत है, मूल्य वर्धित सुगंधित हाइड्रोकार्बन में। यह प्रक्रिया कीमती मीथेन हाइड्रोकार्बन की बर्बादी को कम करने के मामले में आकर्षक है, जो ज्यादातर दूरदराज के स्थानों पर भड़कती है और साथ ही साथ वातावरण में ग्रीनहाउस गैस उत्सर्जन को कम करती है। वाणिज्यिक पहलुओं को ध्यान में रखते हुए, यह प्रक्रिया भी फायदेमंद है क्योंकि इसमें कम लागत वाली प्राकृतिक गैस का सुगंधित हाइड्रोकार्बन में एकल चरण रूपांतरण शामिल है और इसलिए पेट्रोलियम रिफाइनरियों में सुगंधित पदार्थों के पारंपरिक उत्पादन के लिए एक विकल्प हो सकता है। प्रक्रिया के साथ सीमाएं मुख्य रूप से कम संतुलन रूपांतरण और तेजी से उत्प्रेरक निष्क्रियता से जुड़ी हैं। मोलिब्डेनम संशोधित जिओलाइट (ZSM-5/MCM-22) को MDA प्रतिक्रिया के लिए संभावित उत्प्रेरक के रूप में जाना जाता है और इसे सुगंधित हाइड्रोकार्बन के प्रति अत्यधिक चयनात्मक पाया जाता है। Mo-Zeolite उत्प्रेरकों को तेजी से निष्क्रिय करने के लिए उत्प्रेरक के कामकाज में अधिक अंतर्दृष्टि की आवश्यकता होती है। उत्प्रेरक स्थिरता की जांच के मद्देनजर अलग-अलग जिओलाइट Si/Al सामग्री या द्वितीयक धातुओं के अतिरिक्त सक्रिय साइटों में और संशोधन वांछनीय है। निष्क्रियता पथ को समझते समय कोक वृद्धि विश्लेषण और MDA उत्प्रेरक पर इसकी प्रकृति को ध्यान में रखा जाना चाहिए। इस संदर्भ में, वर्तमान कार्य का निर्माण  $C_2$  मध्यवर्ती (ईथेन और ईथिलीन) में मीथेन परिवर्तन के लिए DFT गणना करते हुए किया गया है और उत्प्रेरक समर्थन और प्रमोटर के तर्कसंगत डिजाइन के लिए प्रयोगात्मक अध्ययन किया गया है।

पहले चरण के रूप में, मीथेन सक्रियण और C-C युग्मन चरणों के लिए DFT गणनाओं को पृथक मोलिब्डेनम कार्बाइड क्लस्टर ( $Mo_4C_2$ ) पर प्रमुख  $C_2$  मध्यवर्ती (ईथेन और ईथिलीन) उत्पन्न करने के लिए विस्तार से किया गया था।  $Mo_4C_2$  क्लस्टर के विभिन्न Mo साइटों पर मीथेन सक्रियण

अवरोध की जाँच की गई ताकि कम ऊर्जा अवरोधों वाले ईथिलीन निर्माण पथ की ओर उपयुक्त Mo परमाणु साइटों का पता लगाया जा सके। इसके अलावा, रिड्यूसिविलिटी और उत्प्रेरक गतिविधि के बीच संबंध को समझने के मद्देनजर विभिन्न अवशिष्ट चार्ज वाले Mo<sub>4</sub>C<sub>2</sub> क्लस्टर पर C-H पृथक्करण और C-C युग्मन चरणों की ऊर्जा बाधाओं का विश्लेषण किया गया था। यह पाया गया कि कम धनात्मक आवेश वाले अधिक कम क्लस्टर मीथेन डिहाइड्रोजनीकरण का पक्ष लेते हैं जो MDA में एक महत्वपूर्ण कदम है। उत्प्रेरक की तैयारी या पुनर्जनन के दौरान उत्प्रेरक पर सक्रिय Mo साइटों की कमी को नियंत्रित किया जा सकता है। कुल मिलाकर, DFT गणना MDA मार्ग में ईथेन और ईथिलीन के गठन में अंतर्दृष्टि प्रदान कर रही है और इलेक्ट्रॉनिक संरचना में संशोधन के माध्यम से सक्रिय साइटों को सिलाई करने की दिशा में दिशानिर्देश प्रदान कर रही है।

समानांतर प्रयासों में, MCM-22 समर्थन के SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> अनुपात (SAR) के प्रभाव का विश्लेषण MCM-22 समर्थन के साथ Mo प्रजातियों की बातचीत, सक्रिय चरणों के गठन (MoO<sub>x</sub>C<sub>y</sub>/Mo<sub>2</sub>C) और MDA की ओर संबंधित गतिविधि के संबंध में किया गया था। प्रतिक्रिया। इसके लिए, विभिन्न SAR (30, 40 और 55) के MCM-22 जिओलाइट को पारंपरिक हाइड्रोथर्मल विधि के माध्यम से संश्लेषित किया गया था और लगातार 5 wt% Mo लोडिंग के साथ प्रतिक्रिया के लिए परीक्षण किया गया था। विभिन्न लक्षण वर्णन; XRD, BET, NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR, <sup>27</sup>Al MAS NMR, XPS और रमन स्पेक्ट्रोस्कोपी का उपयोग विभिन्न Si/Al अनुपात के संबंध में Mo/HMCM-22 के भौतिक रासायनिक गुणों की जांच के लिए किया गया था। MDA गतिविधि परिणामों में, SAR-40 और SAR-55 की तुलना में कम कोक सामग्री के साथ उच्च मीथेन रूपांतरण और बेंजीन गठन दर को प्रदर्शित करते हुए SAR-30 में Mo/HMCM-22 अत्यधिक सक्रिय पाया गया। NH<sub>3</sub>-TPD परिणामों ने पुष्टि की कि SAR-30 में HMCM-22 में ब्रॉस्टेड एसिड साइटों की उच्च सांद्रता होती है जो कि जिओलाइट चैनलों पर Mo एंकरिंग और MDA प्रतिक्रिया में सुगंध के लिए फायदेमंद है। इसके अलावा, <sup>27</sup>Al MAS NMR, रमन स्पेक्ट्रोस्कोपिक और H<sub>2</sub>-TPR परिणामों ने निर्देशित किया कि Mo ऑक्साइड प्रजाति

अन्य SAR की तुलना में SAR-30 पर MCM-22 ढांचे के साथ प्रभावी ढंग से बातचीत करती है और इसलिए उत्प्रेरक की उच्च गतिविधि होती है। पूर्व-उपचारित Mo/HMCM-22 के XPS परिणामों ने संकेत दिया कि जिओलाइट ढांचे से जुड़े सक्रिय Mo प्रजातियों ( $\text{MoO}_x\text{C}_y$ ) का उच्च अनुपात SAR-40 और 55 की तुलना में SAR-30 में होता है। कुल मिलाकर, HMCM-22 में उच्च अम्लता होती है। SAR-30 में उच्च अल सामग्री के कारण Mo ऑक्साइड के लिए पर्याप्त एंकरिंग साइट प्रदर्शित होती है और इसलिए पूर्व-उपचार के दौरान संबद्ध सक्रिय Mo साइटों (ऑक्सीकार्बाइड/कार्बाइड) का एक बड़ा हुआ अनुपात दिखाता है जो MDA प्रतिक्रिया में एक उच्च गतिविधि की ओर जाता है।

तीसरे अध्ययन में, MDA गतिविधि के लिए एक प्रमोटर के रूप में क्रोमियम के प्रभाव की जांच के मद्देनजर Mo/HMCM-22 (SAR-30) उत्प्रेरक को Cr के अतिरिक्त के साथ उन्नत किया गया था। प्रायोगिक परिणामों से पता चला कि Cr जोड़ 0.5Cr/5Mo/HMCM-22 उत्प्रेरक की तुलना में 5Mo/HMCM-22 स्ट्रीम पर समय के साथ उच्च बेंजीन उत्पादन दर और मीथेन रूपांतरण दिखाते हुए उत्प्रेरक गतिविधि में काफी सुधार करता है। खर्च किए गए Cr जोड़े गए उत्प्रेरक ने TGA परिणामों द्वारा पुष्टि की गई Mo/HMCM-22 (19.3 wt%) की तुलना में कम कोक सामग्री (15.9 wt%) दिखाई।  $\text{Mo}^{6+}$  से  $\text{Mo}^{4+}$  परिवर्तन के अनुरूप उच्च कमी तापमान और Cr जोड़ पर सतह की अम्लता में कमी ने MCM-22 क्रिस्टल पर Mo प्रजातियों की प्रभावी बातचीत का संकेत दिया, जैसा कि क्रमशः  $\text{H}_2$ -TPR और  $\text{NH}_3$ -TPD द्वारा पुष्टि की गई थी। कैल्क्लाइंड और पूर्व-उपचारित उत्प्रेरकों के HR-TEM परिणामों ने Cr अतिरिक्त पर MCM-22 क्रिस्टल पर Mo प्रजातियों के बेहतर वितरण का संकेत दिया, जिससे MDA प्रतिक्रिया की दिशा में उच्च गतिविधि हुई। कोक से जुड़े बड़े  $\text{Mo}_2\text{C}$  कणों को प्रतिक्रिया के दौरान गैर-प्रवर्तित (Mo/HMCM-22) उत्प्रेरक के साथ देखा गया (120 मिनट TOS) जैसा कि HR-TEM परिणामों द्वारा समर्थित है और इसकी निचली गतिविधि के लिए भी जिम्मेदार है। XPS परिणामों ने अनुमान लगाया कि जिओलाइट चैनलों से जुड़े सक्रिय Mo

साइटों ( $\text{MoO}_x\text{C}_y/\text{Mo}_2\text{C}$ ) का गठन पूर्व-उपचार और प्रतिक्रिया के दौरान Cr जोड़ा उत्प्रेरक के साथ अधिक स्पष्ट था। इसके अलावा, Cr जोड़े गए उत्प्रेरक ( $I_D/I_G = 0.93$ ) की तुलना में Mo/HMCM-22 ( $I_D/I_G = 1.27$ ) से अधिक अव्यवस्थित कार्बनयुक्त प्रजातियों की उत्पत्ति हुई और इसलिए प्रतिक्रिया के दौरान कोकिंग में भिन्नता का संकेत मिलता है। कुल मिलाकर, Cr जोड़ा उत्प्रेरक ने Mo/HMCM-22 उत्प्रेरक की तुलना में बेहतर भौतिक रासायनिक गुणों वाले उच्च गतिविधि को दिखाया।

चूंकि कोक निक्षेपण को MDA मार्ग में एक बड़ी बाधा माना जाता है, इसलिए MDA उत्प्रेरक पर कोक वृद्धि विश्लेषण के तरीके की आवश्यकता है। चौथे अध्ययन में, तीन अलग-अलग तापमानों (600, 700 और 800 °C) के लिए अलग-अलग समय अंतराल पर 0.5Cr/5Mo/HMCM-22 उत्प्रेरक से अधिक कोक जमाव विश्लेषण किया गया था। TGA और रमन स्पेक्ट्रोस्कोपिक अध्ययन विभिन्न अंतरालों पर एकत्र किए गए खर्च किए गए उत्प्रेरकों पर कोक सामग्री और कार्बोनीस प्रजातियों की गुणवत्ता का मूल्यांकन करने के लिए किए गए थे। रमन परिणामों ने निर्देशित किया कि TOS में वृद्धि के साथ,  $I_D/I_G$  अनुपात के आधार पर उत्प्रेरक सतह पर अधिक अव्यवस्थित कार्बन जमा हो जाता है। उच्च तापमान रेंज भी अव्यवस्थित कार्बोनेसियस प्रजातियों के निर्माण का पक्षधर है। इसके अलावा, उत्प्रेरक पर कोक गठन दर की भविष्यवाणी करने के लिए एक मोनोलेयर-बहुपरत मॉडल लागू किया गया था। अनुकूलित परिणामों में, मोनोलेयर में कोक गठन के साथ प्रथम क्रम केनेटीक्स पाया गया जो इंगित करता है कि मोनोलेयर कोकिंग एक active साइट पर निर्भर करता है जो MDA उत्प्रेरक पथ के समर्थन में है। बहुपरत कोकिंग (47.67 kJ/mol) की तुलना में मोनोलेयर कोकिंग के लिए एक उच्च सक्रियण ऊर्जा (105.43 kJ/mol) पाई गई। बहुपरत कोकिंग के लिए कम सक्रियण ऊर्जा ने मोनोलेयर में कोक सांद्रता पर बहुपरत में कोकिंग दर की एक मजबूत निर्भरता का संकेत दिया। यह इंगित करता है कि मोनोलेयर में कोक अग्रदूत उत्प्रेरक के ऊपर बहुपरत कोकिंग की दिशा में एक सक्रिय साइट के रूप में कार्य करता है। देखे गए परिणाम MDA पथ

की परिकल्पना का समर्थन करते हैं क्योंकि कार्बाइड से संबंधित कोकिंग प्रतिक्रिया की प्रगति के साथ गंभीर कोकिंग की सुविधा प्रदान करता है।

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## NOMENCLATURE

$\Delta_r G^\circ$	Standard Gibbs free energy (kJ/mol)
$\Delta_r H^\circ$	Standard heat of reaction (kJ/mol)
$X_{CH_4}$	Methane conversion
W	Weight of the catalyst (g)
$F_{CH_4}$	Methane flow rate (mL/min)
D	Internal diameter of reactor
$d_p$	Catalyst particle size
$E_a$	Activation energy (kJ/mol)
$E_{TS}$	Energy of transition state (kJ/mol)
$E_{IS}$	Energy of reactant state (kJ/mol)
$E_{ads}$	Adsorption energy (kJ/mol)
$E_{diss}$	Dissociation energy (kJ/mol)
$S_{BET}$	BET surface area (m <sup>2</sup> /g)
$S_{micro}$	Micropore surface area (m <sup>2</sup> /g)
$S_{ext}$	External surface area (m <sup>2</sup> /g)
$V_{micro}$	Micropore volume (cm <sup>3</sup> /g)
$I_D$	Intensity of D band in Raman spectra
$I_G$	Intensity of G band in Raman spectra
$C_C$	Total concentration of coke over catalyst surface (mg/mg <sub>cat</sub> )
$C_m$	Concentration of coke in monolayer (mg/mg <sub>cat</sub> )
$C_M$	Concentration of coke in multiple layers (mg/mg <sub>cat</sub> )
$C_{max}$	Maximum concentration of coke in monolayer (mg/mg <sub>cat</sub> )
$T_{ref}$	Reference temperature (°C)

### Acronyms

$\varepsilon$	Function for error optimization
$k_m$	Rate constant for monolayer coking ( $s^{-1}$ )
$k_M$	Rate constant for multilayer coking ( $\frac{mg\ cat}{mg\ coke} s^{-1}$ )
$E_{A_m}$	Activation energy for monolayer coking (kJ/mol)
$E_{A_M}$	Activation energy for multilayer coking (kJ/mol)
n, q	Reaction order
Rg	Ideal gas constant (8.314 J/mol K)

### Greek letters

$\lambda$	X-ray wavelength (1.54 Å)
$\theta$	Diffraction angle
MDA	Methane dehydroaromatization
DFT	Density functional theory
DNP	Double numerical plus polarization
GGA	Generalized gradient approximation
PW91	Perdew and Wang 91
SCF	Self-consistent field
TS	Transition state
LST	Linear synchronous transit
QST	Quadratic synchronous transit
HMI	Hexamethyleneimine
SAR	Silica alumina ratio ( $SiO_2/Al_2O_3$ )
MCM-22	Mobil Composition of Matter-22
ZSM-5	Zeolite Socony Mobil-5
MWW	Framework code (International zeolite association)
MFI	Framework code (International zeolite association)

AHM	Ammonium heptamolybdate
BET	Brunauer-Emmett-Teller
MAS-NMR	Magic angle spinning-Nuclear magnetic resonance
MHz	Megahertz
FESEM	Field Emission Scanning Electron Microscope
EDX	Energy-dispersive X-ray spectroscopy
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
TPO	Temperature programmed oxidation
HR-TEM	High Resolution-Transmission electron micrographs
TGA	Thermal Gravimetric Analysis
TCD	Thermal Conductivity Detector
FID	Flame Ionization Detector
GHSV	Gas hourly space velocity