COVER PAGE
DEPARTMENT OF ENERGY

Project Title: Understanding of catalytic transformation of shale gas and development of catalysts with high activity and selectivity through experimental exploration and theoretical simulation	
Federal Award Identification Number: DE-SC0014561	
Agency Code: 8900	**Organization:** Office of Basic Energy Sciences
Recipient Award Identification Number: Not Provided	**Project Period:** 09/15/2015 to 09/14/2020
Reporting Period: 09/15/2018 - 06/15/2019	**Budget Period:** 09/15/2018 - 09/14/2019
Report Term: Once per Budget Period	**Submission Date and Time:** 06/15/2019 01:46 PM ET
Principal Investigator Information: Dr. Franklin (Feng) Tao Miller Associate Professor 1501 Wakarusa Drive Lawrence, KS 66045-7568	**Recipient Organization:** University of Kansas Center for Research, Inc. 2385 Irving Hill Road Lawrence, KS 66045-7568 Country: USA
Submitting Official Information: Dr. Franklin (Feng) Tao Miller Associate Professor 1501 Wakarusa Drive Lawrence, KS 66045-7568	

ACCOMPLISHMENTS

1. What are the major goals of the project?

In this project, (1) we will achieve fundamental understanding of catalytic aromatization of shell gas components at a molecular level through the integration of both experimental exploration and theoretical simulation to provide insights for designing catalysts with high activity and selectivity; (2) we will achieve new catalytic processes and catalysts active in directly transforming shale gas compounds to organic oxygenates including alcohol and carboxylic acid with high selectivity at low catalysis temperature, and gain fundamental understanding of these catalytic transformations at a molecular level; (3) we will demonstrate in situ/operando studies of catalysts at high temperature in mixture of reactant gases at a relatively high through new instrumentation; (4) we will illustrate successful studies of surface of a catalyst in liquid during catalysis with X-ray photoelectron spectroscopy; (5) we will develop a new method to quantify gas composition near to surface of catalyst during catalysis toward building a direct correlation between surface of a catalyst tracked with AP-XPS and catalytic performance quantified with inner shell excitation of photoelectrons we just discovered.

2. What was accomplished under these goals?

With the financial support of DOE BES catalysis program, in the first year of this project we have performed fundamental studies of (1) synergy effect of Ga and Pt in ZSM-5 leading to high activity and selectivity for producing benzene through aromatization of ethane, (2) correlation between chemical and coordination environment of Ga and Pt in ZSM-5, and (3) development of methods of measuring composition of gas near to catalyst surface.

Project 1. Synergy effect of Ga and Pt in ZSM-5 leading to high activity and selectivity for producing benzene through aromatization of ethane

Efficient utilization of shale gas has been the main stream of next-generation chemical industrial technology. Change of raw materials of chemical industries from crude oil to shale gas needs a whole library of new catalytic processes. Driven by this change, we have developed projects to synthesize benzene from ethane. In the work of last year, we have extensively studies the synergy effect of Ga and Pt in the last year.

1.1 Structure characterization of synthesized catalysts before catalysis

Before the catalysis, the prepared catalysts were analyzed by various characterization methods to clarify the components and structure of samples. XRD spectra of H-ZSM-5, 0.2wt%Ga-ZSM-5, 0.2wt%Pt-ZSM-5 and 0.2wt%Ga/0.2wt%Pt-ZSM5 were displayed in Figure 1. As shown in Figure 1, the lattice of ZSM-5 still remained after the introduction of Ga, Pt or both Ga and Pt. Pt NPs were formed on ZSM-5 based on TEM images (Figure 2) and XPS after catalysis. This suggests that the active chemical state of Pt is Pt nanoparticles. In terms of Ga, no Ga Ga_2O_3 nanoparticles was observed. It suggests that Ga atoms are singly dispersed. The chemical and coordination environment of Pt and Ga are examined with XPS. As shown in Figure 3, Ga atoms are singly dispersed during catalysis. The lack of Ga atoms was confirmed with a surface-sensitive technique, XPS. Pt atoms are in the format of metallic Pt NPs during catalysis (Figure 4). The fitted r-space of Pt-L3 edge shows that the size of Pt NPs are in the range of 2-3 nm. Thus, Pt atoms are clearly located on surface of ZSM-5. The location of Pt on external surface of Pt nanoparticles was confirmed with XPS. These characterizations show that Pt and Ga are spatially separated on the catalyst of 0.20wt%Pt+0.20wt%Ga/ZSM-5.

1.2 Understanding the role of acid site in the reaction

The Brøwsted acid sites in ZSM-5 was reported to be one important factor participating in the ethane aromatization. Therefore, firstly, control experiments with parent H-ZSM5 and Na-ZSM-5 were performed at a range of temperature from 450^{o}C to 600^{o}C, confirming that parent H-ZSM-5 and Na-ZSM-5 provided the poor activity of the aromatization of ethane. Furthermore, sodium formed ZSM-5 catalysts loaded with 0.2wt%Ga, 0.4wtPt and 0.4wt%Pt/0.2wt%Ga were prepared through IWI method mentioned in the experimental section and performed under identical conditions. As shown in Figure 5c, 5d and 5e, metal anchoring Na-ZSM-5 showed the high selectivity of ethylene transformed from ethane, suggesting that gallium and platinum played an essential role on cleaving the C-H bond of ethane and furtherly dehydrogenating ethane to ethylene.

1.3 Catalytic performance of Ga/ZSM-5 and Pt/ZSM-5

Catalysis performance of ethane aromatization via H-ZSM-5 with various concentration of Ga and Pt at a range from 0.1%

to 1.0% was analyzed at a temperature range from 450°C to 600°C. Figure 6 summarized the conversion of ethane as well as the selectivity and yield of benzene gained from different concentration of Ga/ZSM-5 catalysts and Pt/ZSM-5 catalysts at 600°C. It was observed that generally the Ga/ZSM-5 catalyst exhibited the capability in the high selectivity of benzene despite the less conversion of ethane. Particularly, 0.2wt%Ga/ZSM-5 achieved almost 55% selectivity of benzene and increasing the concentration of gallium did not have a large influence on the activity of conversion from ethane to benzene. On other hand, the Pt/ZSM-5 catalyst was capable of converting more ethane than the Ga/ZSM-5 catalyst while formed more byproduct besides of benzene as well, and the selectivity of benzene was reduced along rising concentration of platinum. Consequently, 0.2wtGa%/ZSM-5, 0.2wtPt%/ZSM-5, and 0.2wt%Ga+0.2wt%Pt/ZSM-5 were designed and studied on the aromatization of ethane to further clarify whether the synergy of bimetallic Ga and Pt sites would exhibit the higher performance of the catalysis.

1.4 Catalytic performance of Ga/Pt-ZSM-5

0.2wt%Ga+0.2wt%Pt/ZSM-5 was prepared via IWI method described in the experimental section and the aromatization of ethane was performed under the same temperature range from 450°C to 600°C. As demonstrated in Figure 7, 0.20g 0.2wt%Ga+0.2wt%Pt/ZSM-5 converted more than 70% of ethane to benzene at 600°C and generated the benzene with a yield of 54%. Compared with those from the same amount of 0.2wt%Ga/ZSM-5 and 0.2wt%Pt/ZSM-5, 0.2wt%Ga/0.2wt%Pt/ZSM-5 demonstrated a distinguished promotion of both conversion of ethane and selectivity of benzene. In addition, from Figure 7d, the yield of benzene from ethane catalyzed by 0.2wt%Ga+0.2wt%Pt/ZSM-5 (almost 55%) was obviously larger than the sum of yields from 0.2wt%Ga/ZSM-5 and 0.2wt%Pt/ZSM-5 (nearly 35%), indicating that the synergetic effects of bimetallic gallium and platinum sites on ZSM-5 played a significant role on participating in the aromatization of ethane.

1.5 Characterization of the three sets of catalysts

In order to the reveal the role of gallium and platinum sites on the aromatization of ethane, various characterization methods were used to study Ga/ZSM-5, Pt/ZSM-5 and Ga+Pt/ZSM-5.

Locations of Ga and Pt sites on ZSM-5

Solid-state NMR and DRIFT pyridine adsorption methods were applied to clarify the position of gallium and platinum anchored on ZSM-5.

The Al^{27} solid-state NMR of used H-ZSM-5, 0.2wt%Ga/ZSM-5, 0.2wt%Pt/ZSM-5 and 0.2wt%Ga/0.2wt%Pt/ZSM-5 were used to detect the modification of aluminum sites in ZSM-5 and all spectra of four samples were plotted in Figure 8. There were two types of aluminum in ZSM-5 including the tetrahedral sites (at 50ppm) associated to the Bronsted acid sites [Al-O(H)-Si] and octahedral sites belonging to the external Lewis acid sites[$Al(OH)_2^+$] or [$Al(OH)_3$]. The shift of the peak in 0.2wt%Ga/0.2wt%Pt/ZSM-5 at 50ppm may suggest the gallium and platinum were bonded with the aluminum of Bronsted acid sites.

In addition, the DRIFT pyridine adsorption of H-ZSM-5, 0.2wt%Ga/ZSM-5, 0.2wt%Pt/ZSM-5 and 0.2wt%Ga+0.2wt%Pt/ZSM-5 were measured under catalytic condition and all spectra were described in Figure 9. The area of peak at 1545 cm^{-1} assigned to the BAS from each sample was calculated by normalizing to the peak of framework at 1860 cm^{-1}. According to the result in Figure 9, the BAS peak area of 0.2wt%Ga/0.2wt%Pt/ZSM-5 was declined considerably to less than half of that of H-ZSM5, suggesting that Bronsted acid sites were replaced by metal atoms.

In summary, through the integration of in-situ and operando characterization of bimetallic catalysts active for aromatization of ethane, we have found that the active phase of Pt and Ga are Pt nanoparticles and singly dispersed Ga atoms anchored in micropores of ZSM-5. Our studies show that Ga and Pt play synergistic role in the aromatization of ethane.

Project 2. Development of methods of composition of gas near to catalyst surface.

We discovered a photoelectron-induced excitation (PEIE) spectroscopy which exams gaseous species near to a solid surface. It is a new excitation spectroscopy related to X-ray photoelectron spectroscopy (XPS). A spectrum of PEIE of gaseous species is observed at the high binding energy side of XPS peak of a solid surface while photoelectrons of the solid surface travel through the gas phase. It consists of discrete peaks contributed from different excitation states formed through different transitions of electrons of gaseous species from occupied to unoccupied orbitals. Intensity of these peaks is proportional to density of gaseous species proximal to a catalyst surface, by which a new analytic method of identification of gaseous species and of quantification of composition of gaseous species proximal to the catalyst surface was established. This finding allows to track surface of a catalyst during catalysis with ambient pressure XPS and simultaneously on-site identify gaseous species and analyze composition of these gaseous species proximal to the catalyst surface with PEIE. This spectroscopy allows for establishing correlation between an authentic catalyst surface during catalysis and its corresponding catalytic performance.

3. What opportunities for training and professional development has the project provided?

In this project, two students are supported in the year of 2015-2016. One postdoc has worked in Tao group and one student in Jiang group. The student in Tao group have extensively worked on the preparation of oxide-based nanocatalysts. The researcher in Tao group has learnt the synthesis of ZSM-5 based bimetallic catalysts and evaluation of catalytic performance. He was also trained in how fundamental understanding of catalysis can be performed through integration of in situ characterization of catalyst structure and measurement of catalytic performance. In addition, the research in Tao group has been trained for operando characterization of the catalyst surface during catalysts by using ambient pressure XPS. He was also trained for exploring new spectroscopy. Student of computational studies has worked on the project under the advisory of co-PI, Jiang. The student has been trained for computational studies. Through him and co-PI, Jiang, they have investigated the reaction mechanism of propane aromatization.

4. How have the results been disseminated to communities of interest?

In the last year, we have published four papers which were supported by DOE-BES project. We have reported (1) Tang, Y.; Wei, Y.; Wang, Z.; Zhang, S.; Li, Y.; Nguyen, L.; Li, Y.; Zhou, Y.; Shen, W.; **Tao, F.***, and Hu, P.*. "Synergy of Single-Atom Ni_1 and Ru_1 Sites on CeO_2 for Dry Reforming of CH_4." ***J. Am. Chem. Soc.***, 2019,141,7283-7293.), (2) Tang, Y.; Li, Y.; Fung, V.; Jiang, D., Huang, W.; Zhang, S.; Iwasawa, Y.; Sakata, T.; Nguyen, L.; Zhang, X.; Frenkel, A.I. and **Tao, F.*** "Single rhodium atoms anchored in micropores for efficient transformation of methane under mild conditions". ***Nature Comm***. 2018, 9: 1231. **DOI: 10.1038/s41467-018-03235-7**.), (3) Fung, V. ; **Tao, F.***; and Jiang, D.*. "Low-temperature activation of methane on anchored single atoms: descriptor and prediction." ***Phys. Chem. Chem. Phys.***, 2018, 20, 22909-22914. **DOI:**10.1039/C8CP03191F. (4) Nguyen, L.; Tao, P.; Liu, H.; Al-Hada, M.; Amati, M.; Sezen, H.; Gregoratti, L.; Tang, Y.; House, S.D.; and **Tao, F**.*. "X-ray Photoelectron Spectroscopy Studies of Nanoparticles Dispersed in Static Liquid." ***Langmuir***, **2018**, *34* (33), 9606–9616. **DOI:** 10.1021/acs.langmuir.8b00806. (5) Nguyen, L.; Tao, P.; Liu, H.; Al-Hada, M.; Amati, M.; Sezen,H.; Tang, Y.; Gregoratti, L.; **Tao, F.***. "XPS studies of the surface of metal catalyst nanoparticles in a flowing liquid." ***Chem. Commun*.**, 2018, **54**, 99,81-9984. Advance Article. **DOI**: 10.1039/C8CC03497D. (6) Nguyen, L.; **Tao, F.***, et al. "Understanding Catalyst Surfaces during Catalysis through Near Ambient Pressure X-ray Photoelectron Spectroscopy." ***Chem. Rev.*** 2019. **DOI**: 10.1021/acs.chemrev.8b00114.

Other than the dissemination of the above work in the format of publications, we have also presented these pieces of work on a few conferences. PI, Tao was invited to present the work on 12th Natural Gas Conversion meeting on San Antonie in TX and 2018 Fall meeting of ACS and 2019 Spring meeting of ACS.

5. What do you plan to do during the next reporting period to accomplish the goals?

We plan to perform the following studies in the reporting period:

(1) Design new catalysts highly active for synthesis of aromatic moelcules from methane

Methane is the main component of shale gas. Catalytic transofmation of methane to benzene is still a process to be develop toward industrialization. The main challenges remained are the low activity, selectivity and stability. We plan to design a robust catalyst with high activity and selectivity for producing benzene. The main approach will use is a two-step process. Mo3C nanoparticles supported on SiO2 are prepared first and then SiO2 was used as the only source of silica for synthesis of zeolite. As the access area of a Mo3C nanoparticles is limited by the cross section of a micropore of a zeolite, there is no space for the growth of coke layer on Mo3C.

(2) Design of catalysts highly active for oxidative coupling of methane

Oxidative coupling of methane has been another process to utilize methane. It is a promising process but has not been commercialized due to the lack of catalyst with high yield for producing ethane or ethylene. We plan to design a catalyst with high activity and selectivity by integrating thermal catalysis and electrocatalysis. Through electrocatalysis, we can dissociate H2O into H2 and O2; the consumption of H2O should break the limit of equilibrium of OCM and thus increase the conversion of CH4 and yield of ethylene.

(3) Develop a method to measure the catalytic product proximate to surface of a catalyst

So far the techniques with the capability of measuring catalytic performance are mainly GC and mass spectrometer. Their detectors are always far from surface of a catalyst with macroscopic distance in terms of mm or above. It is definitely necessary to measure the products formed right at the surface of a catalyst. So far there is no such a technique. We plan to use the excitation spectroscopy of photoelectrons to characterize the gas molecules which are above the surface of a catalyst.

(4) Understanding aromatization of ethane at a molecular level

We plan to perform computational studies of the aromatization of ethane at a molecular level. It is important to understand the mechanism of aromatization at a molecular level so that a new catalyst can be rationally designed.

Extended description of accomplishments

With the financial support of DOE BES catalysis program, in the first year of this project we have performed fundamental studies of (1) synergy effect of Ga and Pt in ZSM-5 leading to high activity and selectivity for producing benzene through aromatization of ethane, (2) correlation between chemical and coordination environment of Ga and Pt in ZSM-5, and (3) development of methods of measuring composition of gas near to catalyst surface.

Project 1. Synergy effect of Ga and Pt in ZSM-5 leading to high activity and selectivity for producing benzene through aromatization of ethane

Efficient utilization of shale gas has been the main stream of next-generation chemical industrial technology. Change of raw materials of chemical industries from crude oil to shale gas needs a whole library of new catalytic processes. Driven by this change, we have developed projects to synthesize benzene from ethane. In the work of last year, we have extensively studies the synergy effect of Ga and Pt in the last year.

1.1 Structure characterization of synthesized catalysts before catalysis

Before the catalysis, the prepared catalysts were analyzed by various characterization methods to clarify the components and structure of samples. XRD spectra of H-ZSM-5, 0.2wt%Ga-ZSM-5, 0.2wt%Pt-ZSM-5 and 0.2wt%Ga/0.2wt%Pt-ZSM5 were displayed in Figure 1. As shown in Figure 1, the lattice of ZSM-5 still remained after the introduction of Ga, Pt or both Ga and Pt. Pt NPs were formed on ZSM-5 based on TEM images (Figure 2) and XPS after catalysis. This suggests that the active chemical state of Pt is Pt nanoparticles. In terms of Ga, no Ga Ga2O3 nanoparticles was observed. It suggests that Ga atoms are singly dispersed. The chemical and coordination environment of Pt and Ga are examined with XPS. As shown in Figure 3, Ga atoms are singly dispersed during catalysis. The lack of Ga atoms was confirmed with a surface-sensitive technique, XPS. Pt atoms are in the format of metallic Pt NPs during catalysis (Figure 4). The fitted r-space of Pt-L3 edge shows that the size of Pt NPs are in the range of 2-3 nm. Thus, Pt atoms are clearly located on surface of ZSM-5. The location of Pt on external surface of Pt nanoparticles was confirmed with XPS. These characterizations show that Pt and Ga are spatially separated on the catalyst of 0.20wt%Pt+0.20wt%Ga/ZSM-5.

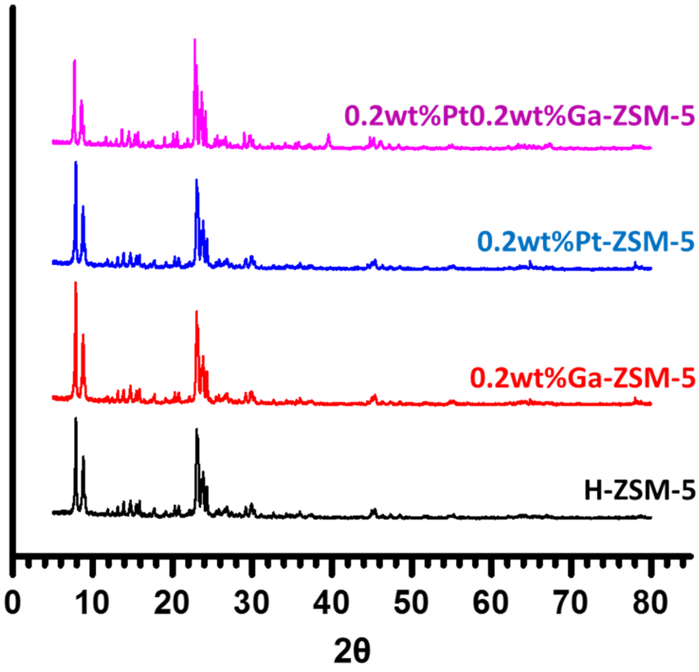


Figure 1. XRD patterns of HZSM-5, 0.20wt%Ga/HZSM-5, 0.20wt%Pt/HZSM-5, 0.20wt%Ga+0.20wt%Pt/HZSM-5.

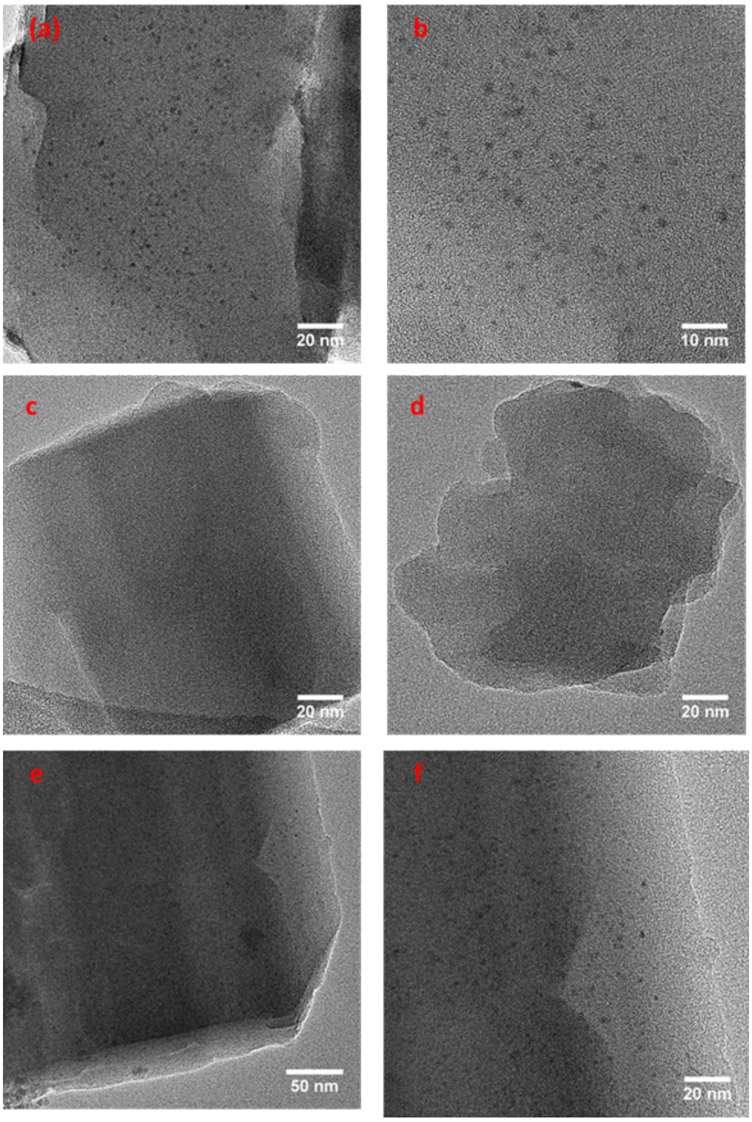
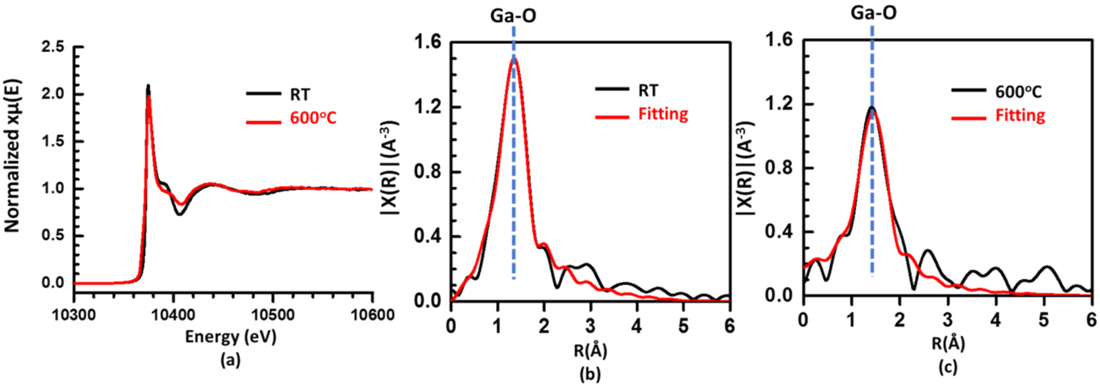
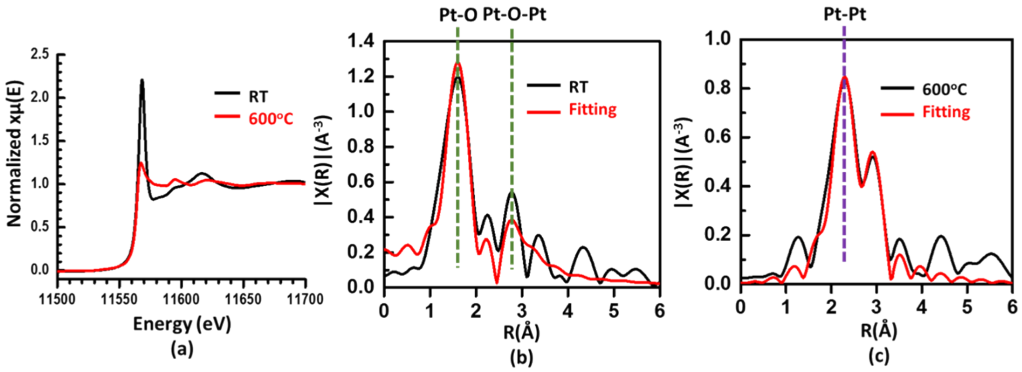


Figure 2. TEM images of 0.20wt%Ga/HZSM-5 (a and b), 0.20wt%Pt/HZSM-5 (c and d), and 0.20wt%Ga+0.20wt%Pt/HZSM-5 (e and f).



sample	Bond	CN	R(Å)
0.2wt%Pt+0.2wt%Ga/ZSM-5 RT	Ga-O	4.92±0.84	1.817±0.016
0.2wt%Pt+0.2wt%Ga/ZSM-5 600C	Ga-O	3.37±0.34	1.924±0.026

Figure 3. XAS studies of 0.20wt%Ga/HZSM-5. (a) XANES of 0.20wt%Ga/HZSM-5 at RT and after catalysis at 600°C. (b) r-space spectra of 0.20wt%Ga/HZSM-5 before catalysis. (c) r-space spectra of 0.20wt%Ga after catalysis at 600°C. The lower panel is the table of the parameters used for fitting r-space spectra of 0.20wt%Ga/HZSM-5 at RT (b) or after catalysis at 600°C (c).



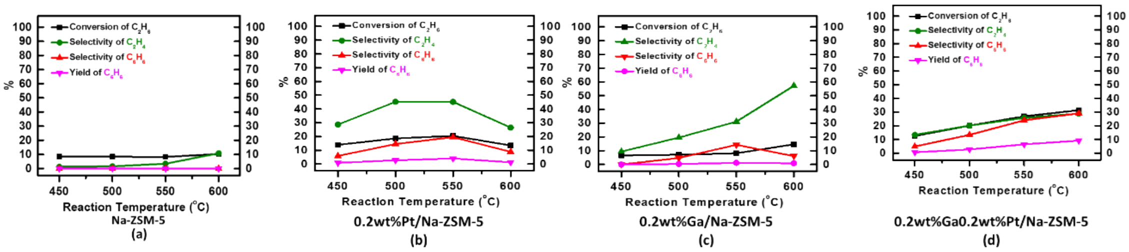
sample	Bond	CN	R(Å)
0.2wt%Pt/0.2wt%Ga/ZSM-5 RT	Pt-O	4.07 ± 1.74	2.006±0.038
	Pt-O-Pt	1.76 ± 1.5	2.846±0.080
0.2wt%Pt/0.2wt%Ga/ZSM-5 600C	Pt-Pt	8.84 ± 1.77	2.750±0.012

Figure 4. XAS studies of 0.20wt%Pt /HZSM-5. (a) XANES of 0.20wt%Pt/HZSM-5 at RT and after catalysis at 600°C. (b) r-space spectra of 0.20wt%Pt/HZSM-5 before catalysis. (c) r-space spectra of 0.20wt%Pt after catalysis at 600°C. The lower panel is the table of the parameters used for fitting r-space spectra of 0.20wt%Pt/HZSM-5 at RT (b) or after catalysis at 600°C (c).

1.2 Understanding the role of acid site in the reaction

The Brøwsted acid sites in ZSM-5 was reported to be one important factor participating in the ethane aromatization. Therefore, firstly, control experiments with parent H-ZSM5 and Na-ZSM-5 were performed at a range of temperature from 450°C to 600°C, confirming that parent H-ZSM-5 and Na-ZSM-5 provided the poor activity of the aromatization of ethane. Furthermore, sodium formed ZSM-5 catalysts loaded with 0.2wt%Ga, 0.4wtPt and

0.4wt%Pt/0.2wt%Ga were prepared through IWI method mentioned in the experimental section and performed under identical conditions. As shown in Figure 5c, 5d and 5e, metal anchoring Na-ZSM-5 showed the high selectivity of ethylene transformed from ethane, suggesting that gallium and platinum played an essential role on cleaving the C-H bond of ethane and furtherly dehydrogenating ethane to ethylene.



Na-ZSM-5 (a)

0.2wt%Pt/Na-ZSM-5 (b)

0.2wt%Ga/Na-ZSM-5 (c)

0.2wt%Ga0.2wt%Pt/Na-ZSM-5 (d)

Figure 5. Catalytic performance of Na-ZSM-5 (a), 0.20wt%Pt/Na-ZSM-5 (b), 0.20wt%Ga/Na-ZSM-5 (c), and 0.20wt%Ga+0.20wt%Pt/Na-ZSM-5 (d).

1.3 Catalytic performance of Ga/ZSM-5 and Pt/ZSM-5

Catalysis performance of ethane aromatization via H-ZSM-5 with various concentration of Ga and Pt at a range from 0.1% to 1.0% was analyzed at a temperature range from 450°C to 600°C. Figure 6 summarized the conversion of ethane as well as the selectivity and yield of benzene gained from different concentration of Ga/ZSM-5 catalysts and Pt/ZSM-5 catalysts at 600°C. It was observed that generally the Ga/ZSM-5 catalyst exhibited the capability in the high selectivity of benzene despite the less conversion of ethane. Particularly, 0.2wt%Ga/ZSM-5 achieved almost 55% selectivity of benzene and increasing the concentration of gallium did not have a large influence on the activity of conversion from ethane to benzene. On other hand, the Pt/ZSM-5 catalyst was capable of converting more ethane than the Ga/ZSM-5 catalyst while formed more byproduct besides of benzene as well, and the selectivity of benzene was reduced along rising concentration of platinum. Consequently, 0.2wtGa%/ZSM-5, 0.2wtPt%/ZSM-5, and 0.2wt%Ga+0.2wt%Pt/ZSM-5 were designed and studied on the aromatization of ethane to further clarify whether the synergy of bimetallic Ga and Pt sites would exhibit the higher performance of the catalysis.

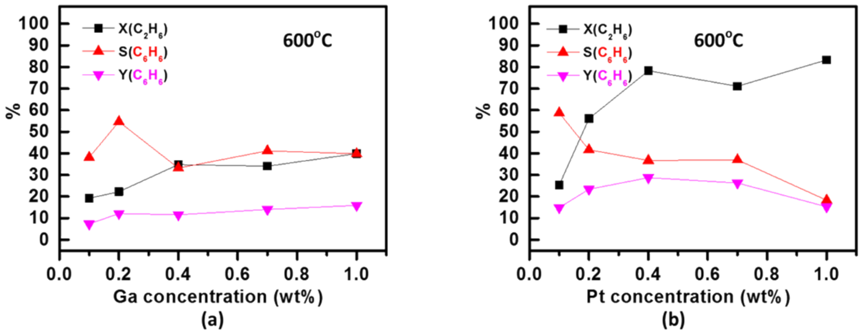
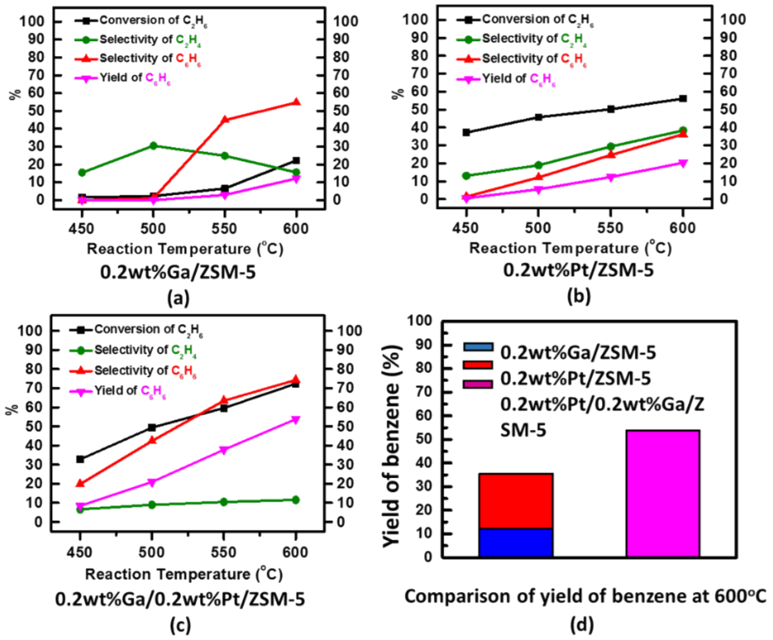


Figure 6. Catalytic performance of Ga/ZSM-5 with different loading (a) and Pt/ZSM-5 with different loading.

1.4 Catalytic performance of Ga/Pt-ZSM-5

0.2wt%Ga+0.2wt%Pt/ZSM-5 was prepared via IWI method described in the experimental section and the aromatization of ethane was performed under the same temperature range from 450°C to 600°C. As demonstrated in Figure 7, 0.20g 0.2wt%Ga+0.2wt%Pt/ZSM-5 converted more than 70% of ethane to benzene at 600°C and generated the benzene with a yield of 54%. Compared with those from the same amount of 0.2wt%Ga/ZSM-5 and 0.2wt%Pt/ZSM-5, 0.2wt%Ga/0.2wt%Pt/ZSM-5 demonstrated a distinguished promotion of both conversion of ethane and selectivity of benzene. In addition, from Figure 7d, the yield of benzene from ethane catalyzed by 0.2wt%Ga+0.2wt%Pt/ZSM-5 (almost 55%) was obviously larger than the sum of yields from 0.2wt%Ga/ZSM-5 and 0.2wt%Pt/ZSM-5 (nearly 35%), indicating that the synergetic effects of bimetallic gallium and platinum sites on ZSM-5 played a significant role on participating in the aromatization of ethane.



0.2wt%Ga/ZSM-5 (a)

0.2wt%Pt/ZSM-5 (b)

0.2wt%Ga/0.2wt%Pt/ZSM-5 (c)

Comparison of yield of benzene at 600°C (d)

Figure 7. Catalytic performance of 0.20wt%Ga/ZSM-5 (a), 0.20wt%Pt/ZSM-5 (b), and 0.20wt%Ga+0.20wt%Pt/ZSM-5 (c), and yield of the three catalysts at 600oC under the same catalytic condition (d). This figure clearly confirmed the synergy effect of aromatization of ethane on Ga and Pt of 0.20wt%Ga+0.20wt%Pt/ZSM-5.

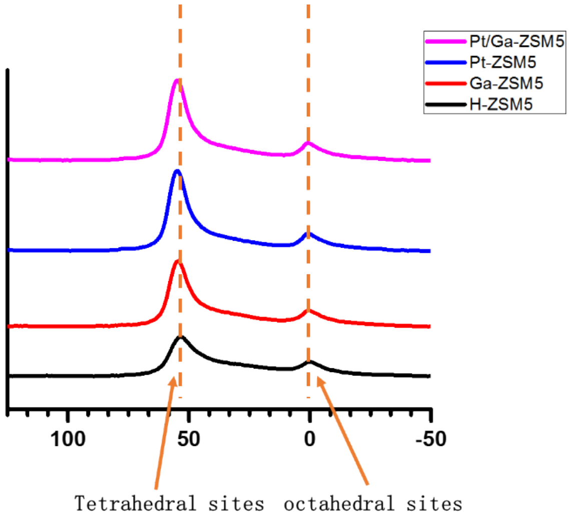
1.5 Characterization of the three sets of catalysts

In order to the reveal the role of gallium and platinum sites on the aromatization of ethane, various characterization methods were used to study Ga/ZSM-5, Pt/ZSM-5 and Ga+Pt/ZSM-5.

Locations of Ga and Pt sites on ZSM-5

Solid-state NMR and DRIFT pyridine adsorption methods were applied to clarify the position of gallium and platinum anchored on ZSM-5.

The Al^{27} solid-state NMR of used H-ZSM-5, 0.2wt%Ga/ZSM-5, 0.2wt%Pt/ZSM-5 and 0.2wt%Ga/0.2wt%Pt/ZSM-5 were used to detect the modification of aluminum sites in ZSM-5 and all spectra of four samples were plotted in Figure 8. There were two types of aluminum in ZSM-5 including the tetrahedral sites (at 50ppm) associated to the Bronsted acid sites [Al-O(H)-Si] and octahedral sites belonging to the external Lewis acid sites[Al(OH)$_2^+$] or [Al(OH)$_3$]. The shift of the peak in 0.2wt%Ga/0.2wt%Pt/ZSM-5 at 50ppm may suggest the gallium and platinum were bonded with the aluminum of Bronsted acid sites.



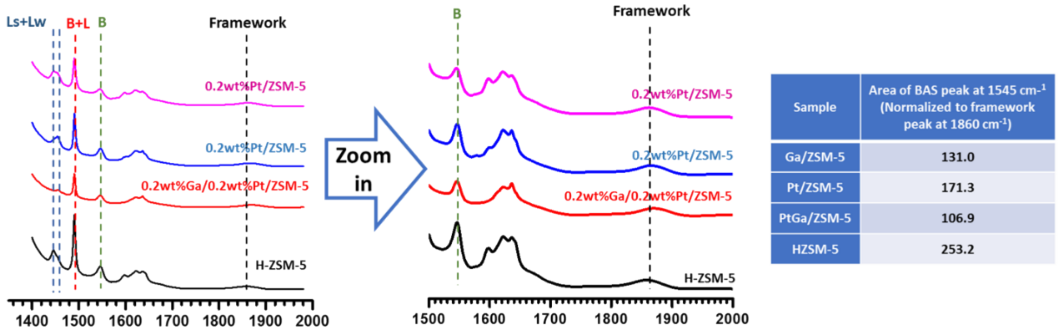
Tetrahedral sites octahedral sites

Figure 8. ^{27}Al NMR studies of 0.20wt%Ga/ZSM-5, 0.20wt%Pt/ZSM-5, 0.20wt%Pt0.20wt%Ga/ZSM-5.

In addition, the DRIFT pyridine adsorption of H-ZSM-5, 0.2wt%Ga/ZSM-5, 0.2wt%Pt/ZSM-5 and 0.2wt%Ga+0.2wt%Pt/ZSM-5 were measured under catalytic condition and all spectra were described in Figure 9. The area of peak at 1545 cm^{-1} assigned to the BAS from each sample was calculated by normalizing to the peak of framework at 1860 cm^{-1}. According to the result in Figure 9, the BAS peak area of 0.2wt%Ga/0.2wt%Pt/ZSM-5 was declined considerably to less than half of that of H-ZSM5, suggesting that Bronsted acid sites were replaced by metal atoms.

In situ XAFS

Furthermore, the operando XANES and EXAFS experiments of 0.2wt%Ga/0.2wt%Pt/ZSM-5 were performed in Spring8 National Lab via using the home-made high temperature reactor cell in Dr. Tao's group. The spectrum was analyzed through Athena (Demeter) software and the result was plotted as energy space and R space of Ga K-edge (Figure 3) and Pt L3-edge (Figure 4), respectively. The fitting of R space was conducted through Artemis (Demeter) software to study the coordination environment of gallium and platinum on ZSM-5 under the catalytic condition.



Sample	Area of BAS peak at 1545 cm^{-1} (Normalized to framework peak at 1860 cm^{-1})
Ga/ZSM-5	131.0
Pt/ZSM-5	171.3
PtGa/ZSM-5	106.9
HZSM-5	253.2

Figure 9. Pyridine IR of 0.20wt%Pt+0.20wt%Ga/ZSM-5

As seen from Figure 3, the first peak at approximately 1.3 Å (before phase correction) was associated to the first shell Ga-O bond of gallium oxide, and the lack of second shell of Ga-(O)-Ga bond indicated that the gallium was singly dispersed on ZSM-5 before the catalysis and also maintained to be singly dispersed under the catalytic condition at 600°C. Additionally, the coordination number of oxygen atoms surrounding the core gallium atom was reduced from 5 oxygen atoms to 3 oxygen atoms, which was consistent to the reducing aromatization condition. In another hand, from Figure 10, at room temperature it was clearly seen that the peak at around 1.5 Å (before the phase correction) was assigned to the first shell Pt-O bond of platinum oxide, confirming the platinum was bond with oxygen atoms, while under the catalysis at 600^{o}C, the formation of platinum nanoparticle was observed, identified via the assignment of the peak around 2-3 Å to Pt-Pt bond of metallic platinum.

In summary, through the integration of in-situ and operando characterization of bimetallic catalysts active for aromatization of ethane, we have found that the active phase of Pt and Ga are Pt nanoparticles and singly dispersed Ga atoms anchored in micropores of ZSM-5. Our studies show that Ga and Pt play synergic role in the aromatization of ethane.

Project 2. Development of methods of composition of gas near to catalyst surface.

We discovered a photoelectron-induced excitation (PEIE) spectroscopy which exams gaseous species near to a solid surface. It is a new excitation spectroscopy related to X-ray photoelectron spectroscopy (XPS). A spectrum of PEIE of gaseous species is observed at the high binding energy side of XPS peak of a solid surface while photoelectrons of the solid surface travel through the gas phase. It consists of discrete peaks contributed from different excitation states formed through different transitions of electrons of gaseous species from occupied to unoccupied orbitals. Intensity of these peaks is proportional to density of gaseous species proximal to a catalyst surface, by which a new analytic method of identification of gaseous species and of quantification of composition of gaseous species proximal to the catalyst surface was established. This finding allows to track surface of a catalyst during catalysis with ambient pressure XPS and simultaneously on-site identify gaseous species and analyze composition of these gaseous species proximal to the catalyst surface with PEIE. This spectroscopy allows for establishing correlation between an authentic catalyst surface during catalysis and its corresponding catalytic performance.

2.1 Excitation of gas phase molecules

Photoelectrons can be generated from sub-shells of a catalyst surface such as Ag 3d5/2 of a Ag foil or Ag nanoparticles by X-ray such as Al Kα. Before scattering with gas phase molecules, Ag 3d5/2 photoelectrons have specific kinetic energies of about 1116.3 eV under the assumption that work function of the energy analyzer is 2.0 eV. Thus, these photoelectrons can be considered as an electron beam with a specific kinetic energy (116.3 eV) although they leave surface along different directions. Upon they leave surface, they travel through the gas phase between the catalyst surface and aperture. In their trip to the aperture. They may excite species such as molecules or radicals in gas phase, by which the gaseous species transit from their ground state to excitation states.

2.2 Science in the excitation of gas phase molecules by photoelectrons

Such an excitation to gaseous species causes the original photoelectrons, Ag 3d5/2 to lose certain amount of kinetic energy. This excitation can be described with the equation: e_{E_0} + A $\rightarrow e_{E_f}$+ $A^{*(n)}$, where e_{E_0} is the photoelectrons such as Ag 3d5/2 with original kinetic energy (E_o), 1116.3 eV before exciting a gas molecule; A is a gaseous species at its ground state proximal to surface of the catalyst; here “proximal” is defined to a region near to the catalyst surface with a distance ≤0.3 mm. $A^{*(n)}$ is the gaseous species at an excited state after being excited by photoelectrons such as Ag 3d5/2; n labels one of the excitation states of gaseous species ; e_{E_f} is the photoelectron after losing certain amount of kinetic energy to excite the gaseous species; kinetic energy of these photoelectrons after exciting the gas molecule is E_f.

Thus, $\Delta E\ (=E_0 - E_f)$ is the lost energy of the original photoelectrons; the lost energy, ΔE was used to excite molecule A from its ground state, A to an excitation state, $A^{*(n)}$.

It is important to note that the above excitation process is distinctly different from the photoionization of gaseous molecules in XPS studies of gas molecules. For instance, electrons of subshell of an atom of a molecule such as O_2 are ejected and thus leave the atoms of this molecule to vacuum level; then, the atom of the molecule lose photoelectron(s) and thus become positively charged: $h\nu + M \rightarrow M^{n+} + ne$. Different from the photoionization of gaseous species in photoelectron spectroscopy, here the process, $e_{E_0} + A \rightarrow e_{E_f} + A^{*(n)}$ is a photoelectron-induced excitation to molecules; in the excitation, electrons of valence shell of gaseous species transit to an unoccupied orbital, making the molecule transit to an excitation state *instead of being ionized*. Here we report the first observation of spectra of electron transitions of a molecule from occupied orbitals of gaseous species to unoccupied orbitals *excited by photoelectrons of XPS*. Thus, here it is called photoelectron-induced excitation (PEIE) spectroscopy.

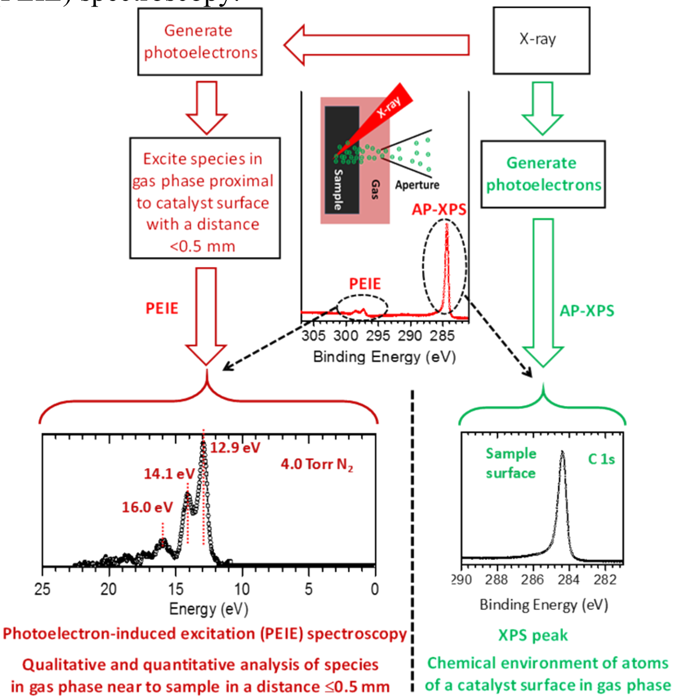


Figure 10. Correlation between XPS and PEIE.

In this report, Ag 3d5/2 or Ag 3d3/2 of Ag foil, Au 4f 7/2 or Au 4f5/2 of Au foil, C 1s of HOPG, or Pt 4f7/2 or Pt 4f5/2 of Pt foil were used as a mono-energetic electron source to excite gaseous species, generating a PEIE spectrum (or called an excitation spectrum). It is found this excitation spectroscopy can be used to study gaseous species such as molecules or radicals proximal to a catalyst surface through analyzing energy diagram of molecular orbital of these gaseous species and quantifying composition of the gas mixture to a catalyst surface. With PEIE spectroscopy along with AP-XPS, the surface of a catalyst during catalysis and the identity and composition of gaseous species proximal to a catalyst surface (< 0.3 mm) during catalysis can be simultaneously tracked. Experimentally, practice of PEIE of gaseous species proximal to a catalyst surface does not need additional experimental setup other than an existing AP-XPS. The intrinsic correlation of AP-XPS and PEIE was schematically shown in Figure 10. An extended XPS spectrum shown in the middle of Figure 10 consists of the XPS spectrum (also called parent peak) and PEIE spectrum. Collection of such an extended spectrum allows for tracking surface and analyzing gaseous species proximal to the catalyst surface with the feature of both spatial proximity and temporal simultaneity.

In our studies, four solid surfaces including Ag foil (99.999%, Aldrich), Au foil (99.999%, Aldrich), and Pt foil (99.999%, Aldrich), and HOPG (99.999%, SPI) were used for generation of photoelectrons including C 1s, Ag $3d_{5/2}$/Ag $3d_{3/2}$, Au $4f_{7/2}$/Au $4f_{5/2}$, Pt $4f_{7/2}$/Pt $4f_{5/2}$, respectively. These photoelectrons were used as source to excite gaseous species. Gases were introduced into reaction cell of the AP-XPS system and flow through aperture of the reaction cell. The pressure of gas around the catalyst in the reaction cell of AP-XPS during data collection was marked in each of the following figures. Flow rate in the reaction cell is 4 ml/min. As the travel distance of photoelectrons in gas is about 0.3 mm. PEIE analyzes gaseous species (products, reactants, radicals and others) near to a catalyst surface within a distance of ≤0.3 mm when the catalyst surface during catalysis is being tracked with AP-XPS.

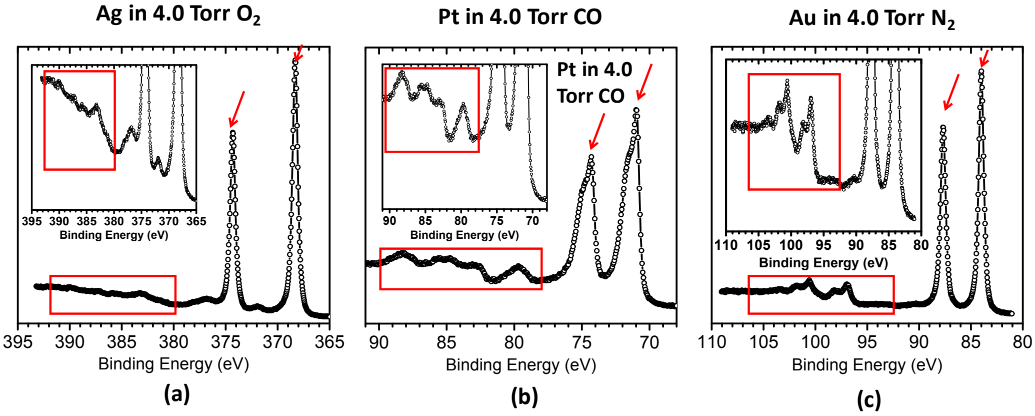


Figure 11. Extended spectra of (a) Ag $3d_{3/2}$ and Ag $3d_{5/2}$ in 4.0 Torr O_2, (b) Pt $4f_{5/2}$ and Pt $4f_{7/2}$ in 4.0 Torr CO, (c) Au $4f_{5/2}$ and Au $4f_{7/2}$ in 4.0 Torr N_2. Each spectrum includes both the parent photoelectron peaks (regular XPS peak) marked with red arrows and high-binding energy region marked with red box which consists of discrete peaks with unusually high binding energies (UHBE). The inset in each figure is the spectral enlargement for better observation.

Capability of qualitatively identifying gas phase molecules

Figure 11 presents the extended XPS spectra of Ag 3d of Ag foil in O_2 at 4.0 Torr, Pt 4f of Pt foil in CO gas at 4.0 Torr, and Au 4f of Au foil in N_2 at 4.0 Torr. The peaks marked with red arrows are parent peaks of Ag 3d3/2 and Ag 3d5/2, Pt 4f5/2 and Pt 4f7/2, and Au 4f5/2 and Au 4f7/2, these parent peaks appear at low binding energy (BE) side of these extended spectra; they are contributed from photoelectrons which did not excite gaseous species or did not lose kinetic energy after scattering gas molecules. As marked with red boxes in Figure 1, new peaks at high energy side of the extended spectrum were observed. Compared to their parent peak(s) marked with red arrow(s), their positions are several to a couple of tens of eVs higher but their intensities are much lower; thus, they were not readily observed. Notably, there is lack of any peaks at high BE side of parent peaks when these samples are in high vacuum environment. Thus, these new peaks in red boxes at high BE side must result from the interaction between photoelectrons and gas molecules. Each of these new peaks must contribute from photoelectrons with specific kinetic energy. As kinetic energies of these photoelectrons contributing to these peaks in the red box are lower than parent peak(s) by different amounts of energy (Figure 11), they derived from different losses of kinetic energy of some of these parent photoelectrons. Definitely, these discrete peaks in the red boxes cannot be attributed to different chemical shifts of atoms in different chemical environments since their binding energies in terms of peak positions are higher than their parent peak by several eV or larger. Here we temporarily term these discrete peaks as unusually high binding energy peaks (UHBE).

To check whether the positions of UHBE peaks at high BE side are determined by identity of gaseous molecules or not, the same studies were done by introducing different gases (CH_4, CO, and N_2) and then exciting these gas molecules with the *same* electron source, C 1s photoelectrons of HOPG. In Figures 12a-12d, the *energy gap* between the parent peak (C 1s of

HOPG at 284.5 eV) and the lowest UHBE peak marked with a red double arrow, is obviously different when a different gas was used. This is also true since the energy gap is different for a different gas. For instance, CO, O_2 and N_2 excited by the same electron source Au 4f7/2 of Au foil are quite different.

On the other hand, similar set of UHBE peaks of N_2 was observed although different electron sources (C 1s in Figure 2d and Au 4f7/2 or Au 4f5/2 in Figure S5c) were used to excite. The energy gap between the first peak UHBE of N_2 and their corresponding parent peaks of Au 4f5/2 in Figure S5c, 12.9 eV is the same as the gap (12.9 eV) between the first peak of UHBE and the parent peak (C 1s) in Figure 2d. These studies confirmed that UHBE peaks of a specific gas are solely determined by the gas molecules instead of the excitation source. In other words, an excitation spectrum of specific represent the identity of this gaseous species.

To further explore the origin of these UHBE peaks of an extended spectrum, a difference spectrum of excitation was generated by the following steps. By using C 1s photoelectrons of HOPG to excite molecular transitions, UHBEs of 3.0 Torr CH_4, 4.0 Torr CO, 4.0 Torr O_2, or 4.0 Torr of N_2 and their corresponding parent peaks, C 1s were collected from the same AP-XPS system using the same data acquisition parameters (Figures 12a-12d). The intensity of C 1s parent peak obtained from a gas phase at a pressure, p (Figures 12a-12d) was normalized to the intensity of C 1s of the HOPG in UHV. This normalization generated a calibration factor for the intensity of UHBEs of Figures 12a-12d, $f_{C\,1s\,parent\,(p)} = \frac{I_{C\,1s\,parent\,(in\,UHV)}}{I_{C\,1s\,parent\,(p)}}$. Then, the extended spectrum of gaseous species including parent peaks and UHBEs was normalized by using the equation: $I_{calibrated\,UHBE} = \frac{I_{UHBE}}{f_{C1s\,parent\,(p)}}$. Upon this calibration, the intensity of UHBE peaks of the same gas at different pressure are comparable.   Upon all peaks of the extended

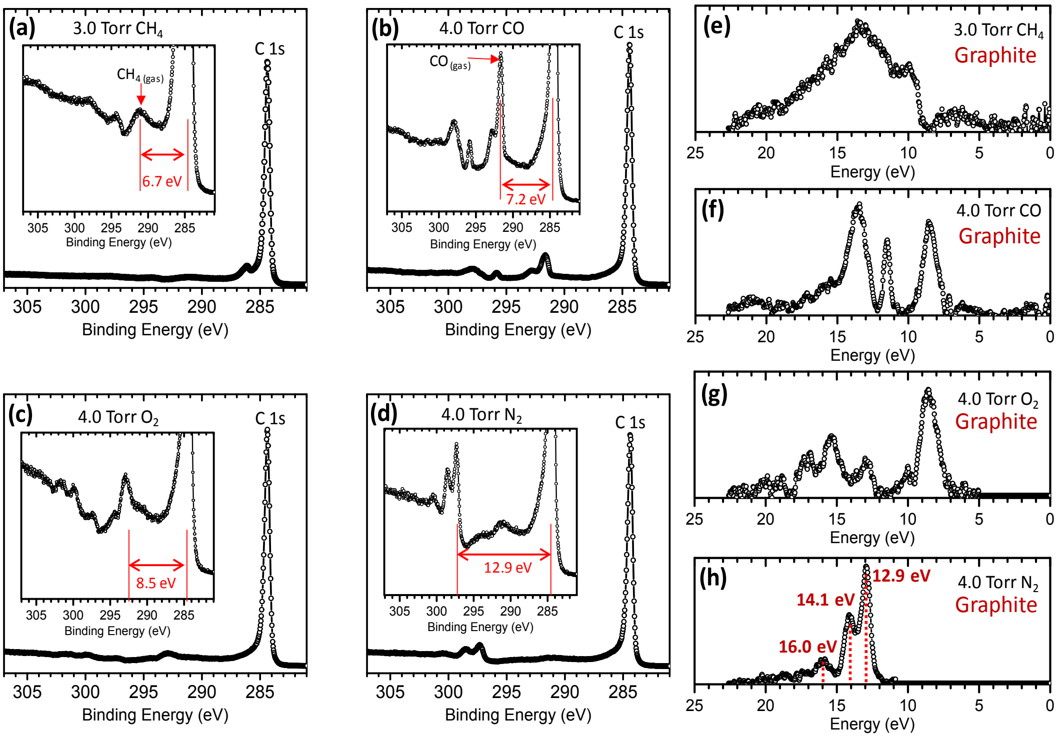


Figure 12. Extended spectra of C 1s of HOPG in different gases (a-d) and the corresponding difference spectra (e-h) generated from the corresponding extended spectra of C 1s of (a-d) by calibration and subtraction, respectively. The method of generation of difference spectrum is described in the main text. (a) 3.0 Torr CH_4; (b) 4.0 Torr CO; (c) 4.0 Torr O_2; (d) 4.0 Torr N_2; (e) difference spectra of 3.0 Torr CH_4; (f) difference spectra of 4.0 Torr CO; (g) difference spectra of 4.0 Torr O_2; and (h) difference spectra of 4.0 Torr N_2.

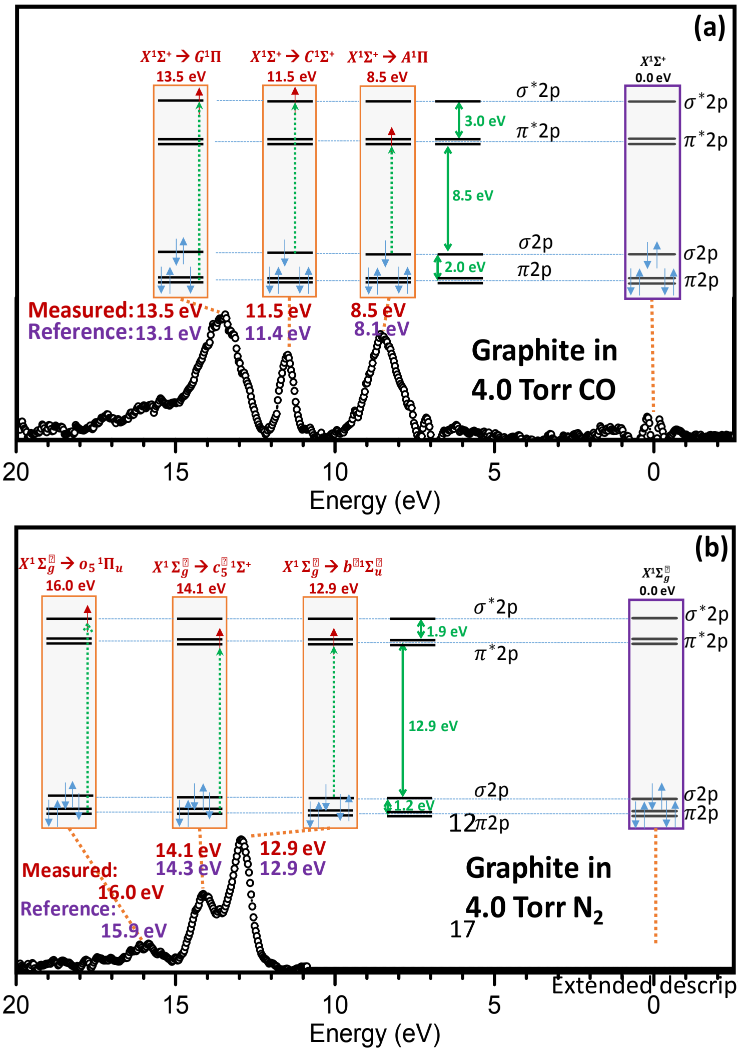
spectrum are calibrated, the parent C 1s peak was subtracted by C 1s peak obtained at UHV; this subtraction removed the parent C 1s peak of each calibrated spectrum (Figures 12a-12d). Upon this subtraction, only the calibrated UHBEs remain; those peaks comprise of a difference spectra of excitation.

In this difference spectrum, the binding energy of parent C 1s peak was set to 0 eV (Figures 2e-2h). By setting the position of parent peak to 0 eV, the peak positions of UHBEs of difference spectrum of the same gas generated with different sources are same (Figure 12h). With this treatment, difference spectra of CH_4, CO, O_2, and N_2 were generated (Figures 12e-12h). Notably, each difference spectrum only consists of UHBEs. Different from the UHBEs in originally extended C 1s spectrum (Figure 12a-12d), energy positions of these UHBEs in a difference spectrum are now referred to the C 1s parent peak (Figures 12a-12h). Thus, typically positions of these peaks in a difference spectrum (Figure 12e-12h) are in the range of 0-25 eV. To carry on physical meaning of these difference spectra, here they are called photoelectron-induced excitation spectra (PEIE) or simply called excitation spectroscopy. For instance, the excitation spectrum of N_2 gas mainly includes a set of peaks at 12.9 eV, 14.1 eV, and 16.0 eV (Figure 12h).

These UHBE peaks in an excitation spectrum can be assigned to different excitation states of gas molecules formed by electronic transitions between different molecular orbitals. Thus, an energy diagram of unoccupied and occupied orbitals of the gas molecules can be built through position of these UHBE peaks. For instance, Figures 13a and 13b present the excitation spectra of CO and N_2 molecules obtained by using C 1s photoelectrons as the electron source to excite, respectively. These peak positons in these difference spectra represent the amounts of kinetic energy consumed to achieve these excitations. The observed peak positions in the excitation spectrum of Figure 13a at 8.5 eV, 11.5 eV, and 13.5 eV are marked with their corresponding excitation states $G^1\Pi$, $C^1\Sigma^+$, $A^1\Pi$, respectively; these excitation states formed through transition of one electron of π_{2p} orbital of ground state $X^1\Sigma^+$ to σ^*_{2p}, one electron of σ_{2p} orbital of ground state $X^1\Sigma^+$ to σ*2p, and one electron of σ_{2p} orbital of ground state $X^1\Sigma^+$ to π^*_{2p} as shown in yellow boxes in Figure 13a. The energy gaps between these excitation states and the ground state are quite consistent with the energy differences: 8.15 eV, 11.4 eV, and 13.1 eV, respectively, reported in literature. [17,18] This consistence suggests the assignments of these excitation states in Figure 13a are reasonable. The three different excitation states were formed through electronic transitions: HOMO→LUMO, HOMO→LUMO+1, and HOMO-1 → LUMO+1, respectively, based on the reported energy levels of occupied and unoccupied orbitals.[17,18] Here these observed electron transitions in excitation spectroscopy allow us to build an energy diagram of unoccupied and occupied orbitals of CO as shown in pink box at the right side of Figure 3a. Similarly, the three peaks at 12.9 eV, 14.1 eV and 16.0 eV in the excitation spectrum of N_2 (Figure 13b) were assigned to the energies needed to excite N_2 from its ground state to three excitation states $b'\,{}^1\Sigma_u^+$, $c_5'\,{}^1\Sigma^+$ and $o_5\,{}^1\Pi_u$, respectively. The three excitation states were formed through electronic transitions: HOMO → LUMO, HOMO-1 → LUMO, and HOMO-1 → LUMO+1, respectively. These assignments allow us to generate the energy diagram consisting of occupied and unoccupied orbitals of N_2 as shown in the pink box at the right side of Figure 13b. The energy diagram of N_2 built with PEIE is well consistent with energy levels of molecular orbitals reported in references.[17,18]

Compared to identification of occupied orbitals using ultraviolet photoelectrons spectroscopy (UPS) and characterization of unoccupied orbitals using inverse photoemission spectroscopy (IPES)[19-21], here the photoelectron-induced excitation (PEIE) spectroscopy offers the capability of simultaneous identification of both occupied and unoccupied orbitals of molecules. In other words, the unique feature of the PEIE spectroscopy is the capability of identifying energy levels of *both* occupied and unoccupied orbitals to obtain a complete energy diagram of species in gas phase. It is expected that the successful identification of gaseous species in gas phase offers opportunity to identify radicals formed in the proximal region of a catalyst surface in gas phase during catalysis at high temperature such as dehydrogenation oxidation of ethane and propane at 500-700°C, oxidative coupling of methane at 750-900°C, direct dehydrogenation of ethane or aromatization to benzene at 600-800°C[22-28] since (1) radicals are expected to be important intermediates of high-temperature catalysis and (2) in fact formation of radicals was experimentally confirmed in some reactions.[29-35] Unfortunately, most characterization techniques cannot directly access to radical-based intermediates in a gaseous phase because typically radicals only exist in the proximal region of a catalyst surface in a gas phase during high temperature catalysis. The photoelectrons released from a catalyst surface through the photoionization of XPS excite molecules or radicals of the gas phase proximal to the catalyst surface, forming a photoelectron-induced excitation spectrum in terms of UHBE peaks. Clearly, tracking surface of a catalyst and spontaneously identifying gaseous species proximal to catalyst surface during catalysis can be done with an existing lab-based or synchrotron-based AP-XPS without any additional instrumentation. Interestingly, information of catalyst surface from parent peaks and signature of gaseous species (reactant, products, radical at high temperature) are shown in one spectrum such as one extended spectrum of Ag 3d, Pt 4f, or Au 4f.

Figure 13. Assignment of peaks of photoelectron-induced excitation (PEIE) spectra (or called excitation spectra or difference spectra) of CO and N_2 formed by exciting electrons of an occupied orbital of CO and N_2 to a partially occupied orbital or to unoccupied orbitals of a gaseous species. (a) Excitation spectrum of 4.0 Torr CO excited by C 1s photoelectrons of HOPG. (b) Excitation spectrum of 4.0 Torr N_2 excited by C 1s photoelectrons of graphite. Yellow boxes give electron configurations of three excitation states. Pink boxes give electron configurations and energy level of occupied and unoccupied orbitals gained from these identified transitions here; the energy levels of π 2p, σ 2p, π*2p, and σ*2p were deduced from the peak positions of these observed excitation states.



PRODUCTS - DETAILS

PUBLICATIONS DETAIL

1. Journal Article: C-C coupling on single-atom based heterogeneous catalyst	
Journal: J. Am. Chem. Soc.	
Publication Date: 12/19/2018	**Publication Status:** Accepted
Volume: Not Provided	**First Page Number or eLocation ID:** Not Provided
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Zhang, X.; Sun, Z.; Wang, B.; Tang, Y.; Nguyen, L.; Li, Y.; Tao, F.*	
Publication Identifier Type: Not Provided	**Publication Identifier:** ja-2017-09314c
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

2. Journal Article: Heterogeneous Catalysis: more than skimming the surface	
Journal: Nature Chemistry	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 8	**First Page Number or eLocation ID:** 902
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao. F.*; Tang, Y.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1038/nchem.2630
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

3. Journal Article: *Understanding Complete Oxidation of Methane on Spinel Oxides at a Molecular Level*	
Journal: Nat. Commun.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 6	**First Page Number or eLocation ID:** 7798
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.*; Shan, J.; Nguyen, L.; Wang, Z. Y.; Zhang, S. R.; Zhang, L.; Wu, Z. L.; Huang, W. X.; Zeng, S.; Hu. P.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1038/ncomms8798

Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

4. Journal Article: *Integrated In Situ Characterization of a Molten Salt Catalyst Surface: Evidence of Sodium Peroxide and Hydroxyl Radical Formation*	
Journal: Angew. Chem. Int. Ed	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 56	**First Page Number or eLocation ID:** 10403
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Takanabe, K.; Khan, A. M.; Tang, Y.; Nguyen, L.; Ziani, A.; Jacobs, B. W.; Elbaz, A. M. ; Sarathy, S. M.; Tao, F.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acscatal.7b01469
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

5. Journal Article: *Oxygen Mobility in Pre-Reduced Nano- and Macro-Ceria with Co Loading: An AP-XPS, In-Situ DRIFTS and TPR Study*	
Journal: Catal. Lett.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 147	**First Page Number or eLocation ID:** 2863
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Sohn, H.; Celik, G.; Gunduz, S.; Dogu, D.; Zhang, S.; Shan, J.; Tao, F.;* Ozkan, U. S.*	
Publication Identifier Type: DOI	**Publication Identifier:** doi:10.1007/s10562-017-2176-4
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

6. Journal Article: Size-and shape-dependent catalytic performances of oxidation and reduction reactions on nanocatalysts	
Journal: Chem. Soc. Rev.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: Not Provided	**First Page Number or eLocation ID:** Not Provided
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Cao, S.; Tao, F.,* Tang, Y. Li, Y.; Yu, J.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1039/c6cs00094k

Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

7. Journal Article: Water–Gas Shift on Pd/a-MnO2 and Pt/a-MnO2	
Journal: Catal. Lett.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 145	**First Page Number or eLocation ID:** 1571
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Shan, J.; Nguyen, L.; Zhang, S. R.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1007/s10562-015-1549-9
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

8. Journal Article: Development of a reaction cell for in-situ/operando studies of surface of a catalyst under a reaction condition and during catalysis	
Journal: Rev. Sci. Instrument	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 87	**First Page Number or eLocation ID:** 064101
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Nguyen, L.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1063/1.4946877
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

9. Journal Article: Understanding oxidative dehydrogenation of ethane on Co3O4 nanorods from density functional theory	
Journal: Catal. Sci. Technol	
Publication Date: Not Provided	**Publication Status:** Published
Volume: Not Provided	**First Page Number or eLocation ID:** Not Provided
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Fung, V.; Tao, F.; Jiang, D	
Publication Identifier Type: DOI	**Publication Identifier:** c6cy00749j

Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

10. Journal Article: Formation of Second-generation Nanoclusters on Metal Nanoparticles Driven by Reactant Gases	
Journal: Nano Lett.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 16	**First Page Number or eLocation ID:** 5001
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.*, Nguyen, L.; Zhang, S.; Li, Y.; Tang, Y.; Zhang, L.; Frenkel, A. I.; Xia, Y.; Salmeron, M. B.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acs.nanolett.6b01718
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

11. Journal Article: Selective Epoxidation of Cyclohexene with Molecular Oxygen on Catalyst of Nanoporous Au Integrated with MoO3 Nanoparticles	
Journal: Appl.Catal. A	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 529	**First Page Number or eLocation ID:** 131
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Dou, J.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1016/j.apcata.2016.10.010
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

12. Journal Article: Size- and Shape-Dependent Catalytic Performances of Oxidation and Reduction Reactions on Nanocatalysts	
Journal: Chem. Soc. Rev	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 45	**First Page Number or eLocation ID:** 4747
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Cao, S.; Tao, F.*; Tang, Y.; Li, Y.; Yu, J.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1039/C6CS00094K

Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

13. Journal Article: Atomic-Scale Structural Evolution of Rh(110) during Catalysis	
Journal: ACS Catal.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 7	**First Page Number or eLocation ID:** 664
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Nguyen, L.; Liu, L.; Assefa, S.; Wolverton, C.; Schneider, W. F.;* Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acscatal.6b02006
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

14. Journal Article: Effect of Cobalt on Reduction Characteristics of Ceria under Ethanol Steam Reforming Conditions: AP-XPS and XANES Studies	
Journal: J. Phys. Chem. C	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 120	**First Page Number or eLocation ID:** 14631
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Sohn, H.; Soykal. I.; Zhang, S.; Shan, J.; Tao, F.*; Miller, J. T.; Ozkan, U. S.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acs.jpcc.6b02490
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

15. Journal Article: Catalysis on singly dispersed bimetallic sites	
Journal: Nature Communications	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 6	**First Page Number or eLocation ID:** 7798
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.*; Shan, J.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1038/ncomms8798

Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

16. Journal Article: *Elucidating the Copper-Hagg Iron Carbide Synergistic Interactions for Selective CO Hydrogenation to Higher Alcohols*	
Journal: ACS Catal.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 7	**First Page Number or eLocation ID:** 5500
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Lu, Y.; Zhang, R. G. ; Cao, B. B.; Ge, B. H. ; Tao, F.; Shan, J. J.; Nguyen, L.; Bao, Z. H.; Wu, T. P.; Pote, J. W.; Wang, B. J.; Yu, F.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acscatal.7b01469
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

17. Journal Article: *General Structure–Reactivity Relationship for Oxygen on Transition-Metal Oxides*	
Journal: J. Phys. Chem. Lett.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 8	**First Page Number or eLocation ID:** 2206
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Fung,V.; Tao,F.; Jiang,D	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acs.jpclett.7b00861
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

18. Journal Article: Oxidation of Cyclohexene Catalyzed by Nanoporous Au(Ag) in Liquid Phase	
Journal: Catal. Lett.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 147	**First Page Number or eLocation ID:** 442
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Dou, J.; Tang, Y.; Nguyen, L.; Tong, X.; Thapa, P. S.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1007/s10562-016-1883-6

Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

19. Journal Article: Development of a reaction cell for in-situ/operando studies of surface of a catalyst under a reaction condition and during catalysis	
Journal: Rev. Sci. Instrument.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 87	**First Page Number or eLocation ID:** 064101
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Nguyen, L.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1063/1.4946877
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

20. Journal Article: Tuning Catalytic Performance through a Single or Sequential Post-Synthesis Reaction(s) in a Gas Phase	
Journal: ACS Catal.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 7	**First Page Number or eLocation ID:** 191
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Shan, J.; Zhang, S.; Choksi, T.; Nguyen, L.; Bonifacio, C.; Li, Y.; Zhu, W.; Tang, Y.; Zhang, Y; Yang, J; Greeley, J; Frenkel, A; Tao, F*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acscatal.6b02054
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

21. Journal Article: Excavation of precious metal-based alloy nanoparticles for efficient catalysis	
Journal: Angew. Chem. Int. Ed	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 55	**First Page Number or eLocation ID:** 15212
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.*	

Publication Identifier Type: DOI	**Publication Identifier:** 10.1002/anie.201606324
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

22. Journal Article: *Tuning Catalytic Selectivity of Oxidative Catalysis through Deposition of Nonmetallic Atoms in Surface Lattice of Metal Oxide*	
Journal: ACS Catal.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 6	**First Page Number or eLocation ID:** 4218
Issue: 7	**Publication Location:** Not Provided
Author(s): Liu, J.; Zhang, S.; Zhou, Y.; Fung, V.; Nguyen, L.; Jiang, D.; Shen, W.; Fan, J.; Tao, F.*,	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acscatal.5b02900
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

23. Journal Article: Direct Neutron Spectroscopy Observation of Cerium Hydride Species on a Cerium Oxide Catalyst	
Journal: J. Am. Chem. Soc.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 139	**First Page Number or eLocation ID:** 9721
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Wu, Z. L.; Cheng, Y. Q.; Tao, F.; Daemen, L.; Foo, G. S.; Nguyen, L.; Zhang, X. Y.; Beste, A.; Ramirez-Cuesta, A. J.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/jacs.7b05492
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

24. Journal Article: **In-situ characterization by Near-Ambient Pressure XPS of the catalytically active phase of Pt/Al2O3 during NO and CO oxidation**	
Journal: Appl. Catal. B.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 220	**First Page Number or eLocation ID:** 506

Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Bergamn, S.; Granestrand, J.; Tang, Y.; Paris, R. S.; Nilsson, M.; Tao, F.; Tang, C.; Pennycook, S. J.; Pettersson, L. J.; Bernasek, S. L.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1016/j.apcatb.2017.08.047
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

25. Journal Article: Operando chemistry of catalyst surfaces during catalysis	
Journal: Chem. Soc. Rev.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 46	**First Page Number or eLocation ID:** 2001
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Dou, J.; Sun, Z.; Opalade, A. A.; Wang, N.; Fu, W. S.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1039/c6cs00931j
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

26. Journal Article: Catalysis at Multiple Length Scales: Crotonaldehyde Hydrogenation at Nanoscale and Mesoscale Interfaces in Platinum-Cerium Oxide Catalysts	
Journal: J. Phys. Chem. C	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 121	**First Page Number or eLocation ID:** 13765
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Mueanngern, Y.; Yang, X.; Tang, Y.; Tao, F.; Baker, L. R.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acs.jpcc.7b03886
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

27. Journal Article: *Low-temperature transformation of methane to methanol on single sites anchored on internal surface of microporous silicate in liquid*	
Journal: Angew. Chem. Int. Ed.	
Publication Date: Not Provided	**Publication Status:** Published

Volume: 55	**First Page Number or eLocation ID:** 13441
Issue: Not Provided	**Publication Location:** DOI: 10.1002/anie.201604708
Author(s): Huang, W.; Zhang, S.; Tang, Y.; Li, Y.;Nguyen, L.; Shan. J.; Xiao, D.; Gagne, R.; Frenkel, A. I.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1002/anie.201604708
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

28. Journal Article: In-situ studies of NiFe2O4 surface during complete oxidation of methane	
Journal: Surf. Sci	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 648	**First Page Number or eLocation ID:** 156
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Zhang, S.; Shan, J.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1016/j.susc.2015.12.011
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

29. Journal Article: Preferential Oxidation of CO in H2 on Pure Co3O4-x and Pt/Co3O4-x	
Journal: ChemCatChem	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 7	**First Page Number or eLocation ID:** 2346
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Nguyen, L.; Zhang, S.; Yoo, S. J.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1002/cctc.201500320
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

30. Journal Article: In situ studies of surface of NiFe2O4 catalyst during complete oxidation of methane	
Journal: Surf. Sci.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 648	**First Page Number or eLocation ID:** 156

Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Zhang, S.; Shan, J.; Nie, L.; Nguyen, L.; Wu, Z.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1016/j.susc.2015.12.011
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

31. Journal Article: Stabilization of Iron-Based Catalysts against Oxidation: An In Situ Ambient-Pressure X-ray Photoelectron Spectroscopy (AP-XPS) Study	
Journal: ACS Catal.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 7	**First Page Number or eLocation ID:** 3639
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Hong, Y.; Zhang, S. R.; Tao, F.; Wang, Y.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acscatal.7b00636
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

32. Journal Article: Interactions of gaseous molecules with X-ray photons and photoelectrons in studies of catalyst surface in gas phase	
Journal: PhydchemchemPhys	
Publication Date: Not Provided	**Publication Status:** Under Review
Volume: Not Provided	**First Page Number or eLocation ID:** Not Provided
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.*, Nguyen, L.	
Publication Identifier Type: Not Provided	**Publication Identifier:** Not Provided
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

33. Journal Article: Reduction of Nitric Oxide with Hydrogen on Catalysts of Singly Dispersed Bimetallic Sites Pt_1Co_m and Pd_1Co_n	
Journal: ACS Catal.	
Publication Date: Not Provided	**Publication Status:** Published

Volume: 6	**First Page Number or eLocation ID:** 840
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Nguyen, L.; Zhang, S.; Wang, L.; Li, Y.;Yoshida, H.; Patlolla, A.; Takeda, S.; Frenkel, A.*; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acscatal.5b00842
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

34. Journal Article: Room-temperature catalytic oxidation of formaldehyde on catalysts	
Journal: Catal. Sci. Technol	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 6	**First Page Number or eLocation ID:** 3649
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Nie, L.; Yu, J.; Jaroniec, M.; Tao, F.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1039/C6CY00062b
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

35. Journal Article: Understanding oxidative dehydrogenation of ethane on Co_3O_4 nanorods from density functional theory	
Journal: Catal. Sci. Technol.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 6	**First Page Number or eLocation ID:** 6861
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Fung, V.; Tao, F.; Jiang, D.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1039/C6CY00749J
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

36. Journal Article: The Dynamics of CrO_3-Fe_2O_3 Catalysts during the High Temperature Water-Gas Shift Reaction: Molecular Structures and Reactivity
Journal: ACS Catal.

Publication Date: Not Provided	**Publication Status:** Published
Volume: 6	**First Page Number or eLocation ID:** 4786
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Keturakis, C.; Zhu, M.; Gibson, E.; Daturi, M.; Tao, F.; Frenkel, F.; Wachs, I.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acscatal.6b01281
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

37. Journal Article: Atomic-Scale Observations of Catalyst Structures under Reaction Conditions and during Catalysis	
Journal: Chem. Rev.	
Publication Date: Not Provided	**Publication Status:** Published
Volume: 116	**First Page Number or eLocation ID:** 3487
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.,* Crozier, P.*	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/cr5002657
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

38. Journal Article: Reactor for tracking catalyst nanoparticles in liquid at high temperature under a high-pressure gas phase with X-ray absorption spectroscopy	
Journal: Rev. Sci. Instrument	
Publication Date: Not Provided	**Publication Status:** Accepted
Volume: Not Provided	**First Page Number or eLocation ID:** Not Provided
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Nguyen, L.; Tao, F.*	
Publication Identifier Type: Not Provided	**Publication Identifier:** Not Provided
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

39. Journal Article: Efficient transformation of methane on Rh cationic sites anchored in microporous silicate at low temperature

Journal: Nature Communications	
Publication Date: Not Provided	**Publication Status:** Under Review
Volume: Not Provided	**First Page Number or eLocation ID:** Not Provided
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.*; Li, Y.; Tang, Y.; Fung, V.; Nguyen, L.; Huang, W.; Zhang, X.; Zhang, S.; Jiang, D.	
Publication Identifier Type: Not Provided	**Publication Identifier:** Not Provided
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

40. Journal Article: *Formation of Second-generation Nanoclusters on Metal Nanoparticles Driven by Reactant Gases*	
Journal: Nano Letters	
Publication Date: Not Provided	**Publication Status:** Published
Volume: Not Provided	**First Page Number or eLocation ID:** Not Provided
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.*, Nguyen, L.; Zhang, S.; Li, Y.; Tang, Y.; Zhang, L.; Frenkel, A. I.; Xia, Y.; Salmeron, M. B.,	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acs.nanolett.6b01718
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

41. Journal Article: **Study of nanoparticles in liquid with photoelectron spectroscopy**	
Journal: Nano Lett.	
Publication Date: Not Provided	**Publication Status:** Under Review
Volume: Not Provided	**First Page Number or eLocation ID:** Not Provided
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.; Nguyen,L.; Tao, P.; Al-Hada, M.; Amati, M.; Sezen, H.; Gregoratti , L.; Tang, Y.	
Publication Identifier Type: Not Provided	**Publication Identifier:** Not Provided
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

42. Journal Article: Surface Structure of Model Catalysts in Reactant Gases

Journal: J. Phys. Chem. B	
Publication Date: Not Provided	**Publication Status:** Published
Volume: Not Provided	**First Page Number or eLocation ID:** Not Provided
Issue: Not Provided	**Publication Location:** Not Provided
Author(s): Tao, F.;* Ralston, W. A.; Liu, H.; Somorjai, G. A.	
Publication Identifier Type: DOI	**Publication Identifier:** 10.1021/acs.jpcb.7b06950
Acknowledgement of DOE Support: Yes	**Peer Reviewed:** Yes

INTELLECTUAL PROPERTIES DETAIL

1. Patent: Si-Doped Co3O4 with High Selectivity for Oxidative Dehydrogenation of Ethane to Ethylene

Patent Abstract: Catalytic selectivity for producing an ideal product is a key topic for chemical transformations through heterogeneous catalysis. Tuning catalytic selectivity by integrating the second metal to form an alloy has been well demonstrated in literature. Here we report a method totune catalytic selectivity in oxidative catalysis on another category of heterogeneous catalysts, transition metal oxides. By choosing oxidative dehydrogenation (ODH) of ethane to ethylene as a probe reaction, we demonstrated that doping nonmetallic atoms to surface lattice of catalyst of a transition metal oxide can enhance catalytic selectivity through suppression of complete oxidation of the reactant molecules. Catalysts of Co3O4 with doped silicon atoms (Six-Co3O4) maintaining the spinel structure of pure Co3O4 exhibit much higher selectivity for the production of ethylene through ODH of ethane compared to pure Co3O4 at 600 oC by 40%. The suppression of activity of surface lattice oxygen atoms was evidenced by the observation that the surface lattice oxygen atoms of Six- Co3O4 cannot exchange oxygen atoms with gas phase oxygen at a low temperature while pure Co3O4 can. The difference in releasing surface lattice oxygen atoms and dissociating molecular oxygen between pure Co3O4 and Six-Co3O4 was supported by DFT calculations. The calculated activation barriers for dissociation of molecular O2 and energy barriers for hopping surface oxygen vacancies of Six-Co3O4 are obviously higher than those of pure Co3O4, respectively. These experimental exploration and computational studies established a correlation between increase of catalytic selectivity and suppression of the activity of surface lattice oxygen atoms/oxygen vacancies. This correlation suggests an approach for increasing catalytic selectivity of oxidative catalysis through suppressing activity of surface lattice oxygen atoms/vacancies via doping atoms of a non-metallic element. This new approach was further confirmed by the observed higher catalytic selectivity for production of ethylene on Ge0.2-Co3O4 than pure Co3O4.

Country/Transnational Patent Office: United States (USA)	**Patent Number:** 62/339,227
Application Date: 05/01/2016	**Date Issued:** 06/06/2016
Application Status: Submitted	

TECHNOLOGIES AND TECHNIQUES DETAIL

1. Description:

Tracking surface chemistry of a catalyst during catalysis is significant for fundamental understanding of catalytic performance of the catalyst since it allows for establishing an intrinsic correlation between surface chemistry of an active catalyst and its corresponding catalytic performance. Ambient pressure XPS (AP-XPS) can be used for in-situ studies of surfaces of different materials or devices in a gas or liquid phase. To simulate the gaseous environment of a catalyst in a fixed-bed reactor through in-situ/operando studies, a flowing gaseous environment of reactants around the catalyst is necessary. Here we report the development of a new flowing reaction cell for simulating in-situ study of a catalyst surface under a reaction condition in gas of one reactant or during catalysis in a mixture of reactants of a catalytic reaction. The reaction cell is installed in a high vacuum (HV) or ultrahigh vacuum (UHV) environment of a chamber. The flowing gas in the reaction cell is separated from the HV or UHV environment through well sealings at three interfaces between the reaction cell and X-ray window, sample door and aperture of front cone of an energy analyzer. Catalyst in the cell is heated through infrared laser beam introduced through a fiber optics interfaced with the reaction cell through a homemade feedthrough. The highly localized heating on the sample holder and Au-passivated internal surface of the reaction cell effectively minimize any unwanted reactions potentially catalyzed by the reaction cell. The incorporated laser heating allows a fast heating and a high thermal stability of the sample at a high temperature. With this cell, a catalyst at 800^{o}C in a flowing gas can be tracked readily.

OTHER PRODUCTS DETAIL

There are no other products to report.

PARTICIPANTS AND OTHER COLLABORATING ORGANIZATIONS

PARTICIPANTS DETAIL

1. Participant: Victor Fung		
Project Role: Postdoctoral (scholar, fellow or other postdoctoral position)	**Person Months Worked**: 6	**Funding Support (if other than this award)**: Not Provided
Contribution to the Project: Performed DFT calculations.		
International Collaboration: No		
International Travel: No		

2. Participant: Prof. De-en Jiang		
Project Role: Co-Investigator	**Person Months Worked**: 1	**Funding Support (if other than this award)**: Not Provided
Contribution to the Project: Performed DFT calculations.		
International Collaboration: No		
International Travel: No		

3. Participant: Yuting Li		
Project Role: Graduate Student (Research Assistant)	**Person Months Worked**: 6	**Funding Support (if other than this award)**: Not Provided
Contribution to the Project: Prepared catalysts and evaluated catalytic performance.		

International Collaboration: No
International Travel: No

4. Participant: Luan Nguyen		
Project Role: Postdoctoral (scholar, fellow or other postdoctoral position)	**Person Months Worked**: 6	**Funding Support (if other than this award)**: Not Provided
Contribution to the Project: Characterized catalysts and analyzed data and wrote publications.		
International Collaboration: No		
International Travel: No		

5. Participant: Dr. Franklin (Feng) Tao		
Project Role: Principal Investigator/Project Director	**Person Months Worked**: 1	**Funding Support (if other than this award)**: Not Provided
Contribution to the Project: Supervised this project, prepared some of the catalysts, analyzed some data and wrote publications and other research work related to this fund.		
International Collaboration: No		
International Travel: No		

PARTNERS DETAIL

1. Partner: University of California-Riverside, Riverside, CA, USA
Partner Contribution: Collaborative Research
Description of the Contribution: Performed DFT calculations.

OTHER COLLABORATORS DETAIL

There are no other collaborators to report.

IMPACT

1. What is the impact on the development of the principal discipline(s) of the project?

Significance of fundamental studies of high temperature catalysis with ambient pressure X-ray photoelectron spectroscopy
High-temperature catalysis is defined to the catalysis performed at a temperature higher than 600C. In fact, most transformation of light hydrocarbons are performed at high temperature. Different from intermediate temperature or low temperature catalysis, high temperature catalysis involves reaction in gas phase other than the catalysis performed on surface. Detection of radicals in gas phase is significant for understanding high temperature catalysis such as aromatization. The fundamental studies we have performed in the last years have provided a promising method to identify radicals formed at high temperature.

Significance in development of in situ/operando studies of catalysis
Understanding of catalysis through the correlation between surface chemistry of a catalyst during catalysis has been the main approach for building correlation between surface. Through the DOE-BES project, we have carried out pioneering work. PI, Tao was invited by Chemical Reviews to write an article for the community of catalysis. The paper was just published in Chemical Reviews (Nguyen, L.; Tao, F. et al. "Understanding Catalyst Surfaces during Catalysis through Near Ambient Pressure X-ray Photoelectron Spectroscopy." ***Chem. Rev.*** 2019. **DOI**: 10.1021/acs.chemrev.8b00114.)

2. What is the impact on other disciplines?

We have made efforts on the development of a new generation lab-based ambient pressure XPS which is definitely benefited to other disciplines. For example, environmental science and technology can use this type of analysis technology to track how a target (a material such as metal or oxide) could be changed in gas phase of contaminant and explore how concentration and temperature of gaseous contamination could poison a target.
In addition, this technique can be used to surface science community and the field of corrosion and passivation since they can use these design and techniques to explore the surface of a materials or device in gas phase and track how the surface of a materials or device response the external environment. Other than these disciplines, they can be definitely used for studying surface of electrodes of fuel cell and battery in gas phase.

3. What is the impact on the development of human resources?

Two graduate students were trained in this project in different aspect of experimental studies of heterogeneous catalysis, preparation of catalysts, and in-situ characterization of catalysts, and even computational studies. The financial support of this project allowed students to concentration on the scientific training and testing hypothesis and developing their own ideas. This award definitely helped in education of next generation manpower of catalysis.

4. What is the impact on physical, institutional, and information resources that form infrastructure?

N/A

5. What is the impact on technology transfer?

Technology transfer is benefited from this project. In this project, we have developed a technology/catalyst which can increase catalytic selectivity and yield for production of benzene through aromatization of ethane. We have applied patent for the preparation of this catalysts and the application of this catalysts to the production of benzene.

6. What is the impact on society beyond science and technology?

Shale gas is an abundant energy resource. Maturation of horizontal drilling and hydraulic fracturing technology brings this energy resource from shale to global society in a safe and reliable manner. It has unlocked vast energy resource located in shale and other tight rocks in many states of the USA. In the last decade, the domestic energy renaissance has offered tremendous economic benefits to the USA including lower energy costs, less dependence on foreign energy sources, and enhanced domestic manufacturing activity. Based on the prediction of ExxonMobil that the portion of shale gas in all energy supplies of USA will increase to about 30% in 2020. According to International Energy Agency and ExxonMobil, US will become completely energy-independent and in fact the largest global oil/gas producer by 2030. One transformational energy application clearly observed is the replacement of coal-fired power plants by natural gas power plants in many parts of the US. The next transformation is expected to be the production of ethylene from natural gas since shale gas will replace petroleum to a large extent. Thus, an emerging switch is the replacement of existing hydrocarbon cracking process with efficient, different processes to produce ethylene from shale gas.

Aromatization of ethane has been one of the most important channels for utilization of shale gas. There were a large number of studies of aromatization of ethane in the last three decades. Motivated by the increase of shale gas in energy sector in this decade and continuous increase in next decades, aromatization of ethane has attracted new attention of catalysis community in recent years. Our work in the first year has targeted on utilization of ethane to produce the most important industrial intermediate, benzene through new design of catalysts. Through developing efficient catalysts to catalytically transform ethane to benzene, the most important intermediate of chemical industries, we are working for switching the dependence of chemical industries on petroleum to shale gas since shale gas is inexpensive and quite abundant in USA. From this point of view, our research does help in developing a shale gas-based chemical industries.

7. Foreign Spending

Not Provided

CHANGES - PROBLEMS

1. Changes in approach and reasons for change
No change.
2. Actual or anticipated problems or delays and actions or plans to resolve them
3. Changes that have a significant impact on expenditures
4. Significant changes in use or care of human subjects, vertebrate animals, and/or biohazards
5. Change of primary performance site location from that originally proposed
6. Carryover Amount
Estimated carryover amount for the next budget period: $0.00