Financial report of ACS-DNI Project

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Towards Ultimate dispersion: Stable Bi-Layer Single Atom Catalyst for Methane Activation

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1. Progress of the Research:

1.1 Project summary:

Single Atom Catalyst, a.k.a. SAC, represents ultimate dispersion of surface metals, allowing fundamental understanding of catalytic structure-performance relationship into atomic level. Unlike existing SACs, in which single atoms exist in both surface and bulk phase, the innovative SAC model to stabilize single atom over subnano-oxide ligands by enhanced spatial restriction and strong metal-oxide interaction. This unique SAC model is composed of isolated single atoms at outermost layer, a monolayer of reducible oxide and an inert oxide substrate with high surface area. The catalytic reactivity/stability will be evaluated for methane oxidation under realistic conditions (>400 ºC).

This innovative catalytic structure will significantly leverage the mechanistic insights of SAC on three aspects: 1) how to design/stabilize isolated single metal atom under realistic conditions, 2) how to precisely control the domain size of metal clusters and binding configuration of C-H bond breakage, and 3) how to tune the catalytic performance of SAC with homogenous surface vacancy/morphology. The proposed research will provide essential guidance for the design and optimization of sintering-resistant catalyst for methane activation. The proposed research on shale gas utilization is of significance on economic improvement and environmental impacts for West Virginia States with the shrinking coal industry and booming shale gas production.

1.2 Research Tasks and Achievements:

Two graduate student and one postdoc associate have involved in the project. In Year I project, we have developed an effective procedure to prepare stable Pt-SAC, skilled advanced STEM imagining, mastered theoretical background and computational software for methane activation.

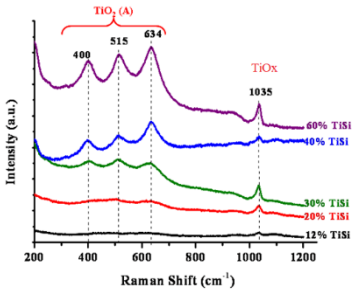
The research achievements for each task/subtask can be break-down as follows:

Task 1: Synthesis Strategy of Unique SAC model:

This subtask focus on the preparation of unique 2D monolayer of reducible oxides. Incipient wetness impregnation were used for preparing various oxides supported over Al_2O_3 as substrate, while sol-gel and pre-wet impregnation methods were prepared for various oxides supported over SiO_2 as substrate. Several bi-layer catalyst has successfully prepared, and their BET areas were summarized as follows:

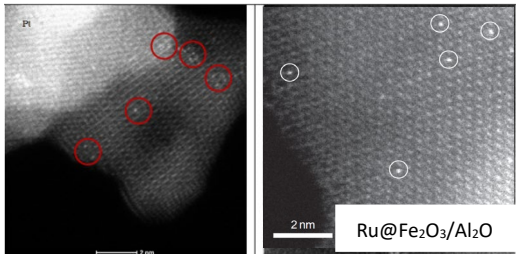
Al_2O_3 substrate (BET 125 m^2/g)	TiO_2/ Al_2O_3	ZrO_2/ Al_2O_3	Fe_2O_3/ Al_2O_3
	114	83	97
SiO_2 substrate (BET 230 m^2/g)	TiO_2/ SiO_2	ZrO_2/ SiO_2	Al_2O_3/ SiO_2
	120	155	112

The surface of Al_2O_3 possess strong Lewis acid sites, while surface SiO_2 is essentially inert because of enriched Si-OH group. Therefore, the preparation of highly-dispersed second-layer monolayer over Al_2O_3 substrate is much more challenge than that over SiO_2 substrate. As shown in above table, surface area of bilayer over Al_2O_3 substrate essentially remain similar as Al_2O_3, while the surface area of bilayer over SiO_2 substrate is approximately half of SiO_2 substrate. This is reasonable and predictable. Moreover, we successfully prepared bilayer SrO_2/TiO_2, which is not included in the original proposal. The main reason is to

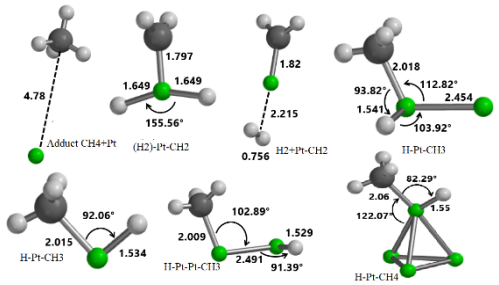


tune surface acidity of TiO_2 (Redox) by SrO_2 (Basic). The BET of novel SrO_2/TiO_2 bilayer SrO_2/TiO_2 is 76 m^2/g

Raman spectra has collected for bilayer supports with collaboration of Oak Ridge National Lab (supported by PI's NSF project). As shown in Figure above over $TiOx/SiO_2$, nano-dispered $TiOx/SiO_2$ was observed. The monolayer dispersion was achieved at 60% TiOx content, while crystalline TiO_2 presented as anatase form. The 1035 cm^{-1} band was finally assigned as Ti=O double bond of TiO_2, instead of quartz windows. More characterization, such as *in-situ* Raman and XPS (not in-situ) are in process.

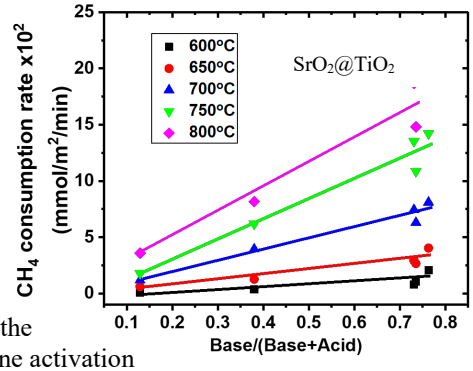


After success synthesis and systematic study of 2D bilayer, single Pt atom will be anchored. Two kinds of highly-dispersed Pt and Ru are prepared. Single-atom dispersion of Pt and Ru after 300 °C reduction has been successfully achieved. Moreover, Ru SAC (right) indicated excellent thermal stability at 500 °C for 4 hours, but SAC-Pt (left) indicated particle agglomeration by forming 2D-raft structure. We are optimizing prepared procedure by adding various surfactant.



Task 2: Atomic/electronic Structure of Novel SAC:
DFT calculation were performed to understand the CH_4 activation over Pt, Ru catalysts with Pt/Ru clusters. As shown in right figures, the bonding configurations, including bond length and coordination angles have been optimized. Because we have successfully Pt/Ru SAC, detailed calculation for bigger metal clusters will not pursued. The next step will be the improvement of established model for bi-layer catalysts.

Task 3: Structure/Performance Relationship on Methane Oxidation:
Activity measurements have been conducted for prepared catalyst with fixed-bed reactor. In year-1 project, we have finished methane conversion measurement of all bi-layer catalyst. As shown in right figure, the linear relationship of methane conversion has been successfully established with the number of basic sites over SrO_2/TiO_2 catalysts. The amount of basic sites were quantitatively measured by in-situ NH_3-adsoprtion, while acidic sites was measured by in-situ CO_2 adsorption experiments. were Adjusting the partial pressure of CH_4 observed linear increase of catalytic reactivity, while the pressure of oxygen do not significantly influence methane conversion. Thus, the catalytic kinetics of bilayer catalyst follows the determing step of methane activation over single active site, instead of Langmuir-Hinshelwood mechanism.



<u>*Research Plan for Year-2 project:*</u> As reported above, all research tasks have been partially completed. The major challenges hurdled the proposed project, including single-atom preparation, DFT calculation, kinetic fitting have been overcame. With the deeper understanding on surface structure of innovative SAC catalyst, we are confident that all research goals will be achieved. The Year-2 research is to:
+improve thermal stability of Pt-SAC catalyst
+detailed electronic/molecular characterization of prepared catalyst
+catalytic evaluation so as to generate structural-performance

2. Impact on PI's Career and Students:
Based on current achievement, two extension projects have been developed: PI has awarded WV's high-educational challenge grants (5M total), teaming with WVU and Marshall University; 2) PI, teamed with several WVU's mechanical engineering faculties has submitted proposal for DOE's advanced heavy-duty natural gas vehicles program. Regarding the student, both students, Lei and Haines have been well-trained in fixed-bed reactor, GC/MS detection, and various advanced characterization, such as SEM/TEM, BET, in-situ FTIR/Raman, XRD, XPS etc. It should be specially mentioned that Lei and Haines have performed experiments on ORNL, partially supported by ACS project. The access to ORNL's HAADF-STEM (one of ten in US) and Spallation Neutron Source of neutron scattering (one of two in US) experiment are invaluable experience for student educational outreaches.