

## 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 °C).

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:

In previous report (April 2019), two graduate student and one postdoc associate was reported in the project during the period of (May 2019-April 2019). 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. Unfortunately, those graduate students have quitted from the project due to their family issues. Thus, one new graduate students (Mr. Thong Luong) started working on the project since August 2019. Meanwhile, a new postdoc associate will be assigned for the project since Dec 2019.

The research achievements of Mr. Thong Luong during the period of Aug-Dec 2019 can be break-down as follows:

###### *Task 1: Synthesis Strategy of Unique SAC model:*

In the previous report, SAC-Pt @bilayer supports were successfully prepared. Those bi-layer support include two series of sample: TiO<sub>2</sub>, ZrO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> over Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> over SiO<sub>2</sub>. In this period, we attempted to prepared unique 2D monolayer of SAC-catalyst supported over nano-rod Al<sub>2</sub>O<sub>3</sub>. Our hypothesis is to promote combustion kinetic of methane by enhancing mass/heat transfer from crystalline catalytic structure. Sol-gel method were used for preparing Al<sub>2</sub>O<sub>3</sub> nano-rod as substrate, while sol-gel and pre-wet impregnation methods were prepared for SAC-Pt over Al<sub>2</sub>O<sub>3</sub> nano-support. The high-resolution SEM are reported here.

As shown in the Fig 1, the nano-rod Al<sub>2</sub>O<sub>3</sub> samples have been successfully prepared with average diameter of 10nm. Dispersed 1 wt% Pt nanoparticle evenly dispersed over the nano-rod with uniformed size (left images). With higher resolution, the Pt clusters presented as island-structure with average 2-4nm. For each island, about 30 single-

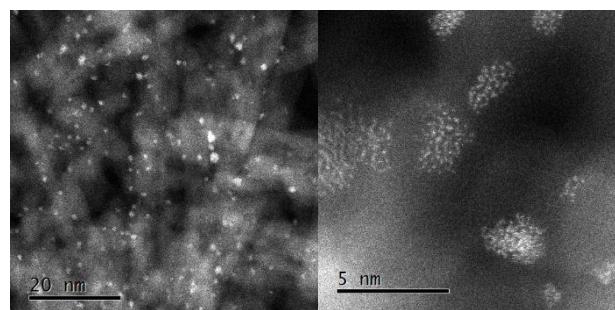


Figure 1: Highly-dispersed 1% Pt over Nano-rod Al<sub>2</sub>O<sub>3</sub>

Pt atoms were observed. Compared to SAC-Pt over bilayer support, it should be specially noted that individual Pt is presented as single atom, as well secondary cluster of structure along with the nano-Al<sub>2</sub>O<sub>3</sub> rod. The BET area of SAC-Pt/ nano-rod Al<sub>2</sub>O<sub>3</sub> is 220 m<sup>2</sup>/g, which is higher than previous SAC over bilayer supports.

*Task 2: Atomic/electronic Structure of Novel SAC:*

Surface composition and oxidation state of SAC-Pt over bilayer supports (TiO<sub>2</sub>, ZrO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> over Al<sub>2</sub>O<sub>3</sub>) were examined by XPS analysis. All catalyst demonstrated multiple oxidation states, but with different surface concentrations. As shown in the table, SAC-Pt/TiO<sub>2</sub>@Al<sub>2</sub>O<sub>3</sub> are mainly Pt(0) with Pt(II), while SAC-Pt/ZrO<sub>2</sub>@Al<sub>2</sub>O<sub>3</sub> and SAC-Pt/Fe<sub>2</sub>O<sub>3</sub>@Al<sub>2</sub>O<sub>3</sub> are presented with Pt(IV). The enriched Pt(II) over SAC-Pt/Fe<sub>2</sub>O<sub>3</sub>@Al<sub>2</sub>O<sub>3</sub> are contributed to strong SMSI between PtO<sub>x</sub> and Fe<sub>2</sub>O<sub>3</sub>. More characterization and DFT calculation are necessary to illustrate detailed fundamental insights.

	Pt (0)	Pt (II)	Pt(IV)
SAC-Pt/ TiO <sub>2</sub> @Al <sub>2</sub> O <sub>3</sub>	65.5	34.5	0
SAC-Pt/ ZrO <sub>2</sub> @Al <sub>2</sub> O <sub>3</sub>	55.3	28.0	16.7
SAC-Pt/ Fe <sub>2</sub> O <sub>3</sub> @Al <sub>2</sub> O <sub>3</sub>	10.0	69.0	21.0

*Task 3: Structure/Performance Relationship on Methane Oxidation*

One of potential application of SAC catalyst is for environmental control of automotive exhaust, especially under cold start condition. With the collaboration of WVU's automotive and energy test facility, we performed cold start experiments with SAC-Pt/nano-rod catalyst. The student was trained and perform testing independently. As shown in the Figure 2, 50% CH<sub>4</sub> conversion achieved at 329 °C during heating, and 304 °C during cooling process of the engine. Similar experiments were conducted with addition of CO and NO to simulate the realistic exhaust gas, the reaction temperatures for 50% CH<sub>4</sub> conversion was increased to 348°C and 332 °C during heating and cooling cycles, respectively. We have built implemental kinetic model for heating/cooling cycles. Assuming the overall process is catalytic reaction-control, activation energy for heating process is calculated as 101 KJ/mol for methane oxidation, and 115 KJ/mol for the oxidation of realistic exhaust gas. The increase of activation energy, and decrease of catalytic kinetics were contribute to competitive adsorption of NO species, while the influence of CO is negligible.

Research Plan for Year-2 project: 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:  
+detailed electronic/molecular characterization of prepared catalyst  
+catalytic evaluation for generating structural-performance relationship  
A new postdoc is hiring for improving DFT calculation. We expect the academic quality of this research could be significantly improved with theoretical simulation/

## 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, Luong has been well-trained in fixed-bed reactor, GC/MS detection, and in the training process for various advanced characterization, such as SEM/TEM, in-situ FTIR/Raman, XRD, XPS etc.

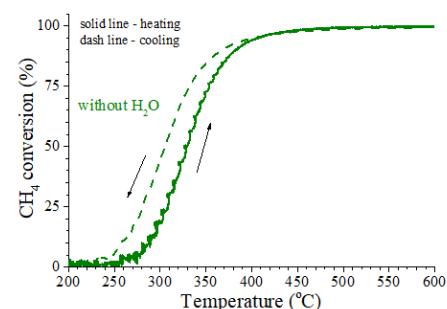


Figure 2. Cold-starting test of 1% SAC-Pt/nano-rod: 0.05% CH<sub>4</sub> and 8% O<sub>2</sub>

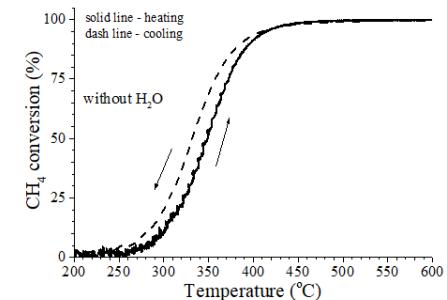


Figure 3. Cold-starting test of 1% SAC-Pt/nano-rod: 0.05% CH<sub>4</sub>, 8% O<sub>2</sub>, 0.03% CO and 0.05% NO