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Title: Structure and Stability of Oxyfluorides and Oxychlorides and Their Relations to Catalytic Activities in Oil Refining Reactions

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Introduction: Metal oxides play very important roles in petroleum refining processes either as catalysts or supporters. Their role and efficiency in the catalysis processes strongly depend on their stability, their atomic and electronic structures and properties. These important features are usually tuned by changing or alloying the metal cations. On the other hand, engineering the anions, such as blending F into the structure may greatly enhance the stability and tune the electronic structures and properties of materials. Due to the difficulties in synthesizing mixed anion compounds, it will be greatly helpful if we can know in advance the stability and the properties of the target compounds. In this project, we will apply the automatic structure search method based on DFT calculations and particle swarm optimization (PSO) algorithm to explore the stability and the structures of metal oxyfluorides and study their possible catalytic activities in oil refining. Our main goal is to systematically study the structure evolution and the corresponding property change with increasing fluorine or chlorine composition.

Current Results: We first conducted a series DFT based structure searches for Fe-O-F and Al-O-F compounds at ambient pressure as well as 10 GPa. We assume all compounds compose of Fe_2O_3 (Al_2O_3) and FeF_3 (AlF_3). The compositions include FeOF, Fe_2OF_4, $Fe_3O_2F_5$, Fe_3O_4F, Fe_3OF_7, $Fe_4O_3F_6$, $Fe_4O_5F_2$ for Fe-O-F compounds, and AlOF, $Al_4O_3F_6$, $Al_4O_5F_2$, $Al_5O_6F_3$, Al_3O_4F, $Al_3O_2F_5$ for Al-O-F. Once the most stable structure is found for each composition, we calculated the convex hull that can reveal the stability of the compounds. As shown in Fig. 1, all mixed anion compounds are not thermodynamically stable for both Fe-O-F and Al-O-F systems. However, FeOF and Fe2OF4 are significantly more stable than other compositions. They are only 0.02 eV/atom and 0.04 eV/atom above the convex hull; therefore they can be obtained as metastable compounds. In contrast to Fe-O-F system, AlOF is the only Al-O-F compound showing low enough formation energy.

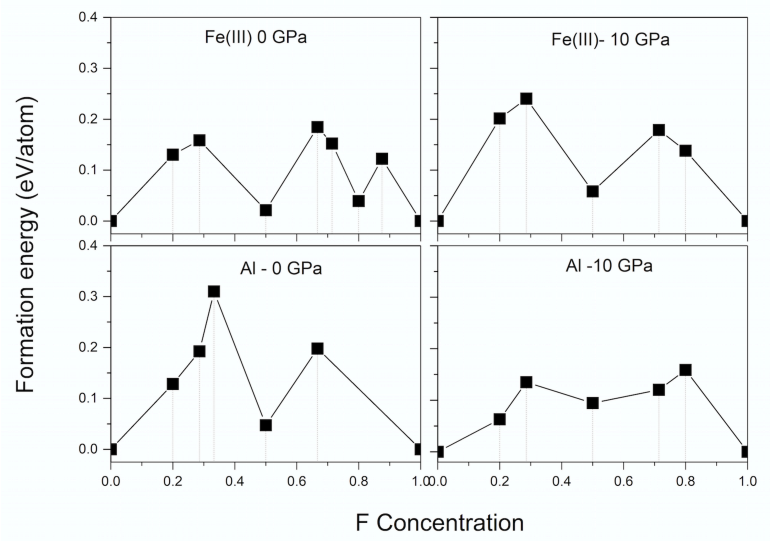

Figure 1. The calculated convex hulls for Fe-O-F and Al-O-F compounds under 0 GPa and 10 GPa.

Pressure shows very strong effects to Fe-O-F and Al-O-F systems. It significantly destabilize the

F rich compound Fe_2OF_4, making FeOF the only one that is close to the convex hull. For Al-O-F, all the compounds are destabilized by pressure. While the mechanism is not clear, our assumption is that the packing efficiency is generally low in mixed anion compounds. Therefore the volume is large for those compounds, which increases their enthalpy of formation. This assumption is currently being investigated by first principles calculations.

Structures obtained from our DFT based crystal structure search and the crystal structure database reveal interesting features and changes upon anion mixing. For Fe-O-F system, all compounds including the binary Fe_2O_3 and FeF_3 consist of Fe centered octahedra. The FeOF structure found by PSO method has a symmetry group of Cc2m. All Fe atoms in this structure bond with 3 O and 3 F atoms. However, they form two types of octahedra depending on locations of the O and F atoms. They connect by sharing O or F atoms at the vertices, and form an alternating pattern in order to reduce the strain. Some of the available structures of FeOF consist of only one type of the FeO_3F_3 octahedron. Interestingly, one structure with symmetry of P2/m exhibits FeO_4F_2 and FeO_2F_4 octahedra. However, our calculations show that the energy of this structure is slightly higher. AlOF structure is very different to FeOF. It contains both 4-fold and 6-fold coordinated Al. All the octahedra contain 3 O and 3 F atoms, whereas all the tetrahedra contain 3 O and 1 F atoms.

Based on the Fe-O-F and Al-O-F structures obtained by the PSO method, we start to study the electronic structures and the catalytic activities of these compounds. We will first focus on the magnetic ordering of FeOF and its dependence to the structure. In the next step, the d band center and occupation will be calculated for various structures. Furthermore, we will study the electronic structure of surfaces of FeOF. Although the chemical surroundings are very similar to all the Fe atoms in FeOF, they could be quite different for Fe locating on the surfaces.

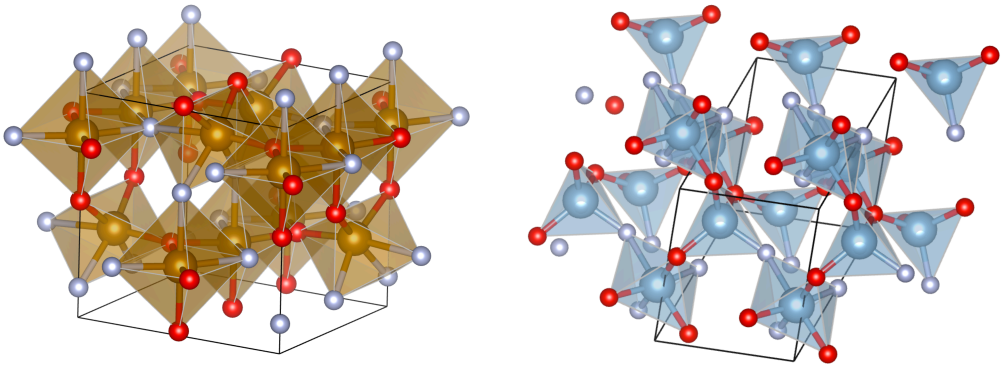

Figure 2. Lowest energy FeOF (left) and AlOF (right) structures obtained by PSO crystal structure search method. The large gold and blue balls represent Fe and Al atoms, and the small red and silver balls represent the O and F atoms.

Impact to our group: This ACS PRF fund enables us to fully support a graduate student. Under this support, the student learned basic theories and practical skills of first principles calculations and automatic crystal structure search. With the help and guidance of the PI, the student conducted a series of structure searches for many compositions of Fe-O-F and Al-O-F, and studied the stability and the structure features of these mixed anion compounds. The student has been well trained and she is now mentoring 2 undergraduate students. Thus, more progresses will be made in the next academic year. 1) We will complete the study of the stability, structure and property relation study for Fe-O-F and write one manuscript; 2) 1 graduate and 2-4 undergraduate students will be trained and involved in this project; 3) 1 graduate student and possibly 1 undergraduate student will attend the APS and/or ACS meetings.