

# Laboratory astrochemistry: catalytic reactions of organic molecules over olivine-type silicates and SiC

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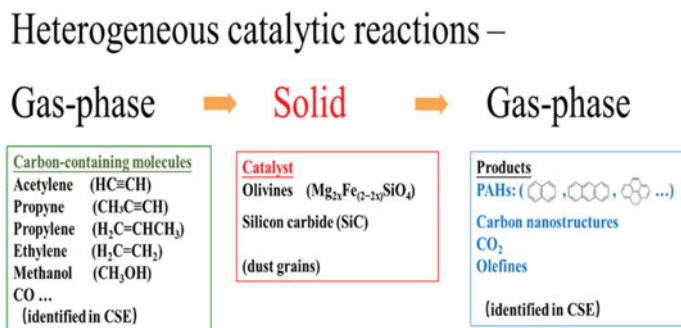
**Abstract.** A series of catalytic reactions has been performed in our laboratory using olivine-type silicates (OTS) and SiC as catalysts for the conversion of carbon-containing molecules (such as acetylene, CO and methanol) to small organic molecules (C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>3</sub>, CH<sub>3</sub>O) and also polycyclic aromatic hydrocarbons (PAHs). Experimentally, small-to-medium-sized gas-phase compounds such as PAHs, reaction intermediates and hydrocarbon compounds were detected in situ using the time-of-flight mass-spectrometry technique. Solid deposition on the catalyst surface was examined by high-resolution transmission electron microscopy and thermo-gravimetric analysis techniques. Our laboratory results show that the conversion of acetylene to PAHs, the CO disproportionation reaction for producing CO<sub>2</sub> and carbon deposition (graphitic and carbon nanostructures), and also the transformation of methanol to hydrocarbon compounds can easily be achieved with OTS as a catalyst. Furthermore, the conversion of acetylene to PAHs could also be achieved by SiC as the catalyst. It is proposed that these catalytic reactions mimic similar chemical processes in circumstellar envelopes (CSEs).

**Keywords.** Catalytic reaction, surface chemistry, dust grains: silicon carbide, olivine-type silicates.

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## 1. Introduction

Astrochemistry is a subject that blends astronomy and chemistry in which each area of research mutually enhances and enriches the other in the interaction. Chemical processes in interstellar and circumstellar regions may be classified into two categories: gas-phase reactions and surface reactions. For general gas-phase reactions, when atoms and molecules in the gas-phase collide, and can overcome any activation barrier, product species can be formed. In low temperature regions ( $T \sim 10$  K), chemical reactions are triggered by cosmic-ray ionization and proceed mainly via ion-molecule reactions in the gas-phase (Öberg, 2016). It is essential to have fundamental chemical knowledge of molecular collisions, and photochemical and reaction dynamics processes to understand such reactions in the universe. For grain surface reactions, atoms and molecules that strike grains and are efficiently adsorbed onto the grain surface. As far as the adsorption processes are concerned, both physisorption and chemisorption can in principle occur. Physisorbed species can migrate on a grain surface and react when they meet. Chemisorbed species, on the other hand, stick tightly to the surface even at temperatures of several hundred Kelvin, and this suppresses any diffusion process. The strong interaction between adsorbed species and the surface can eventually lead to cleavage of chemical bonds of the adsorbed species and that proceeds as an initial step of a catalytic reaction. There has



**Figure 1.** Schematic of heterogeneous catalytic processes of interest in our laboratory.

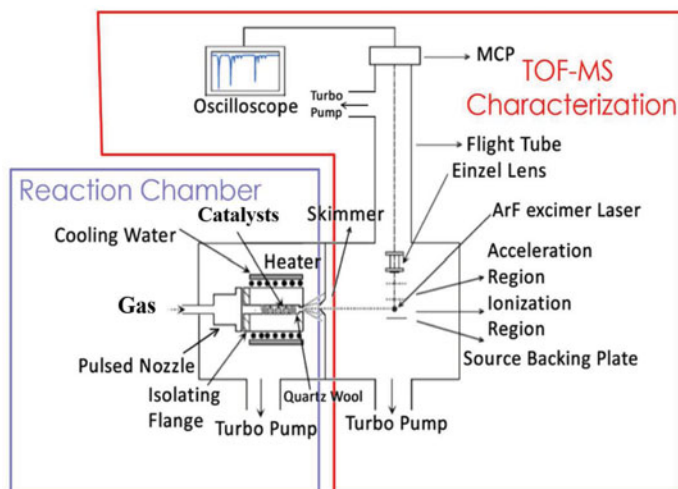
been some work concerning the study of physisorbed species on grain surfaces that are relevant to astrochemical processes (Pirronello *et al.* 1997, Herbst *et al.* 2005). However, only a handful of papers reported chemisorption processes or catalytic reactions that are of importance in astrophysical environments (Kress *et al.* 2001, Ferrante *et al.* 2000).

We have worked on heterogeneous catalytic reactions that are of significance in astrochemistry and explore new connections between circumstellar gas-phase molecules and grains. Recent studies of the circumstellar envelopes (CSEs) of evolved stars indicate that gaseous materials, the high near-zone temperature and high molecular density environment support a rich and complex chemistry (Ziurys, 2006). More than sixty different organic chemical compounds have been identified in the CSEs of stellar objects and many of them are exotic species with more than eight atoms. As far as circumstellar dust grains are concerned, there is evidence indicating the existence of olivine-type silicate (OTS) (forsterite, olivine, pyroxene) dust grains in oxygen-rich envelopes, and for the carbon-rich envelopes, silicon carbide (SiC) grains are an important component (Draine, 2003, Henning, 2010). The physical conditions in the circumstellar shell: the inner CSE is warm (the temperature can be up to 1500 K), and the number density of molecules is also high (around  $n \approx 10^{10} \text{ cm}^{-3}$ ). With the presence of carbon-containing chemicals, solid grains as catalysts and the right physical conditions in a CSE, it is expected that catalytic reactions would be of significance in such astrophysical environments. Figure 1 shows schematically a summary of the catalytic processes studied in our laboratory with relevance to astrochemistry. Carbon-containing gas-phase molecules, catalysts and product species have all been identified in CSEs. In order to understand better the conversion reactions of organic molecules in circumstellar environments, this work is conducted in a hypothetical-deductive model of reasoning. The coexistence of the reagent, catalyst and product species suggests that there could indeed be a connection between them.

## 2. Experimental

### 2.1. Characterization of catalysts

The catalysts used in this work are solid SiC and olivine-type silicates. A range of characterization techniques were used to examine the catalysts before and after catalytic reaction (Ertl *et al.* 2008). The structure of the crystalline solid material and the size of the crystals were determined using X-Ray Diffraction (XRD). In addition, energy dispersive X-ray (EDX) spectroscopy was employed to measure the elemental composition and undertake chemical characterization of the catalyst. The organic molecules adsorbed on the catalytic surface were observed and analyzed using Fourier transform infrared (FT-IR) spectroscopy. In this work, various different forms of solid carbon deposition



**Figure 2.** Schematics of the TOF-MS instrument used in this work.

on the catalytic surface were commonly observed. High-resolution transmission electron microscopy (HRTEM) was employed to examine the carbon deposits. The HRTEM images, with a spatial resolution below  $2\text{\AA}$  provided information on the structure of the deposited material. Furthermore, various thermal techniques such as thermal gravimetric analysis (TGA) and temperature-programmed desorption (TPD) proved to be useful in identifying the different forms of carbon deposition on the catalyst surfaces.

## 2.2. Apparatus and experimental condition

A schematic of the time-of-flight mass-spectrometer (TOF-MS) used for these studies is shown in Fig. 2 (Zhao *et al.* 2016). This homebuilt instrument consists of a source chamber with a quartz tube fixed-bed reactor, an ionization chamber, a TOF tube and a detection chamber. The feeding device is connected to the reactor and reactant gas is introduced via an electronically-controlled pulsed valve. A skimmer with a small aperture is used to separate the source chamber and ionization chamber, the background vacuum pressure of the chambers being typically  $2 \times 10^{-6}$  Torr. A two-stage TOF lens assembly (including source backing plate, ionization and acceleration region) and an ion-beam focusing Einzel lens setup are located inside the ionization chamber, where ionization of the gaseous species is achieved through multi-photon processes. The detection chamber is connected to the TOF tube and a multi-channel plate (MCP) detector is used to detect the arrival of ions. For each experiment, the same amount of catalyst is placed inside the quartz tube reactor. The reagent gas is introduced in pulsed mode to the reactor at a repetition rate of 10 Hz with a pulse duration of around 250–300 microsecond. The catalytic reaction was studied in the 100 to  $750^{\circ}\text{C}$  temperature range. The gaseous reagent, intermediates and products from the reaction are all injected directly into the ionization chamber through the skimmer and ionized by a 193 nm ArF excimer laser to generate molecular ions, which are then accelerated by high voltage and travel through a standard TOF field-free region. The signals recorded by the MCP detector are forwarded to a 300 MHz oscilloscope for averaging.

In order to further confirm the catalytic reactions and to obtain a sufficient amount of solid deposit, separate experiments using a continuous flow of reagent molecule under atmospheric pressure were conducted in a separate apparatus. A quartz tube reactor is housed in a furnace and the catalyst placed inside the quartz tube. After the catalyst

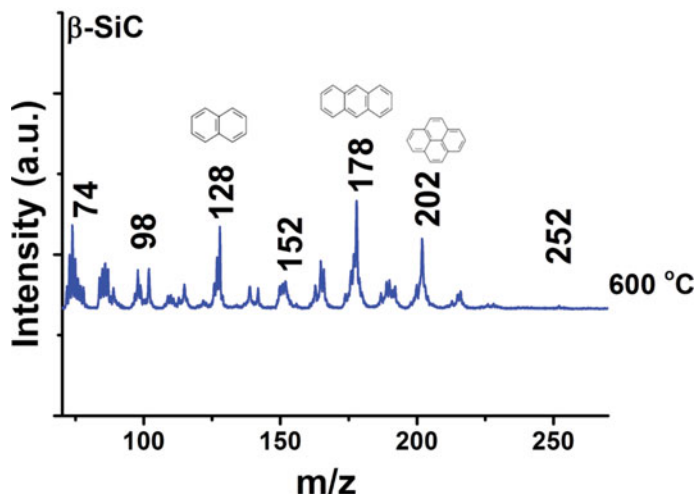


Figure 3. The formation of PAHs over SiC at 600°C.

is pretreated in argon, reagent gas is allowed to flow for a short period of time, and the effluent gas after passing through the catalyst is directed to go through a cold trap to condense any volatile compounds. The trapped species and the solid carbon deposits are, subsequently, analyzed using gas chromatography-mass spectrometry (GC-MS).

### 3. Results and discussion

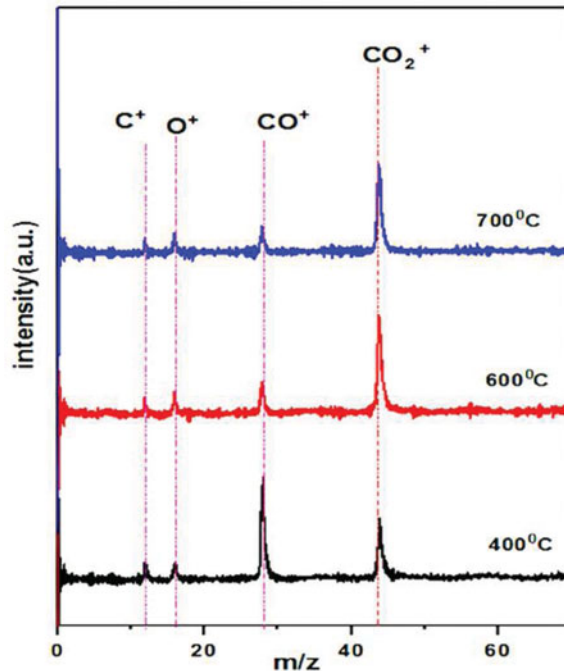
We have studied catalytic reactions that are of significance in astrophysical environments, including acetylene on SiC, carbon monoxide disproportionation on OTS and methanol on OTS. The individual experiments conducted are summarized below:

#### 3.1. Catalytic conversion of acetylene to PAHs over SiC Grains

Polycyclic aromatic hydrocarbons (PAHs) play an important role in astrochemistry. Despite the fact that the formation chemistry of PAHs has been widely discussed, a complete mechanism for cosmic PAH formation is still lacking or disputed. Our experimental work on catalytic conversion reactions of acetylene on a solid SiC grain surface provides an alternative or additional channel for the formation of PAHs. It is found that catalytic conversion reactions of acetylene on a solid SiC grain surface lead to the formation of polycyclic aromatic hydrocarbons (PAHs) and are expected to mimic chemical processes in some astrophysical environments. Gas-phase PAHs and intermediates were detected in situ using TOF-MS and their formation confirmed using GC-MS in separate experiments by flowing acetylene gas through a fixed-bed reactor. The formation of PAHs was found to be optimum around 600 °C. Figure 3 shows the formation of PAHs at this temperature (Zhao *et al.* 2016).

#### 3.2. Catalytic CO disproportionation reactions over olivine-type-silicates

The catalytic carbon monoxide disproportionation (COD) reaction over OTS leads to formation of carbon dioxide gas and solid carbon allotropes on the surface of catalyst (Dai *et al.* 1996). Figure 4 illustrates the breaking down of CO and the formation of CO<sub>2</sub>. The deposited carbon has nanotube, graphene and graphitic structure. These carbon nanotube and graphitic structures have important implications in astrochemistry, as cleavage can produce lower molecular mass PAHs and mimic chemical processes in



**Figure 4.** TOF mass spectrum of the COD reaction.

some evolved stellar environments. The catalytic COD reaction thus provides a top-down mechanism for forming smaller PAHs.

### 3.3. Catalytic conversion of methanol to PAHs over olivine-type-silicates

Catalytic reactions of methanol on olivine-type-silicates produce hydrocarbons and organic molecules, which indicates that there are important relationships among these organic molecules. The observed gas-phase molecules include  $C_2H_4$ ,  $C_3H_3$ ,  $CH_3O$ ,  $CO$ , naphthalene, anthracene, pyrene etc., their mass-to-charge ratios were confirmed by using deuterated methanol. The reactions provide a link between dust particles and organic molecules, which may have implications for the chemistry in the CSE (Olah *et al.* 2016).

### 3.4. Future experiments

The catalytic reaction experiments performed thus far were with a single gas as reagent (acetylene, carbon monoxide, methanol etc.) on OTS and SiC catalysts. We are also interested in catalytic reactions using initial gas mixtures such as  $CO/H_2$ ,  $C_2H_2/CO$ ,  $CO/NH_3$  etc. to examine whether other organic and nitrogen-containing molecules, and potentially prebiotic molecules, can be synthesized from these reactions.

### 3.5. Astrophysical implications

Interest in investigating chemistry involving olivine-type silicates and silicon carbide is due to the fact that the dust grains are ubiquitously present throughout interstellar and circumstellar media and because an important chemical role of cosmic dust particles can be as in terrestrial heterogeneous catalysis, to accelerate certain astrochemical reactions. For example, concerning the high abundance of large interstellar PAHs, a number of theories are based on bottom-up chemical processes initiated through gas-phase reactions or surface reactions (Zhao *et al.* 2016), in which there is a merging of small, possibly radical

or ionized, PAH molecules into larger units as a result of collisions. A more recent theory is based on the completely opposite top-down principle, whereby PAHs form in interstellar space from decomposition of graphitic layers covering the surface of the particles leading to release of PAH molecules (Merino *et al.* 2014). In astrophysical environments, surface aromatic materials could indeed be generated initially from catalytic reactions such as those explored here experimentally, and eventually break down into smaller parts thus forming the PAHs that have been observed.

#### 4. Acknowledgements

The work described here was supported by a grant from the University Research Committee of the University of Hong Kong. PJS thanks the Leverhulme Trust for award of a Research Fellowship.

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