Combined elevated pressure reactor and ultrahigh vacuum surface analysis system

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A combined elevated pressure reactor/ultrahigh vacuum (UHV) surface analytical system has been designed for studies of heterogeneous catalytic reactions. The reaction cell is separated from the surface analysis chamber by a differentially pumped sliding seal. This feature allows simple in situ sample transfer capabilities from the surface analysis region to the reactor cell and also facilitates the introduction and repair of the sample and/or holder with no significant perturbation of the UHV analysis chamber vacuum. The pumping arrangements provide for rapid evacuation of the reaction cell as well as maximum sensitivity with respect to the detection of reaction products.

During the last two decades significant progress has been made toward bridging the gap between surface science and traditional catalysis by the utilization of combined high-pressure reaction cell–ultrahigh vacuum (UHV) surface analysis systems. The use of these systems enables kinetic measurements to be carried out at reaction conditions comparable to those used in technical catalytic reactors. Furthermore, these combined systems allow in situ surface analysis under reaction conditions utilizing photon spectroscopic techniques, e.g., infrared reflection absorption spectroscopy (IRAS), and pre- and post-reaction surface analysis using a wide array of surface analytical tools including Auger electron spectroscopy (AES), high-resolution electron energy-loss spectroscopy (HREELS), low-energy electron diffraction (LEED), temperature programmed desorption (TPD), and photoelectron spectroscopies.

One of the major problems encountered in constructing a combined high-pressure reactor–UHV analysis chamber system is isolation of the two regions of the apparatus. These parts of the system have to be connected in such a way as to assure that no appreciable pressure rise occurs in the UHV chamber while operating the high-pressure catalytic reactor. Several approaches have been used to achieve this goal. Khan et al. utilized an arrangement in which the sample is held in a fixed position and a horizontally moving cup encloses the sample with a gold-wire seal. The fixed position of the sample, however, allows limited access to the surface analytical techniques. A system with a high-pressure reactor cell operational up to 100 atmospheres was constructed by Blakely et al. The sample is rotatable in this arrangement and a hydraulically operated movable reactor cup is sealed to the sample manipulator via a copper gasket. In each of the above configurations the walls of the high-pressure reactor are exposed to the UHV environment following the kinetic experiments, potentially leading to contamination of the UHV chamber. Contamination of the UHV chamber by residual reactants and products, particularly hydrocarbons, via degassing from the reactor walls was considerably decreased by the construction of a system reported by Goodman et al. A horizontally translatable sample rod allows surface analysis of the sample, metal and gas dosing as well as elevated pressure reactions up to ~2 atm. The main limitations of this system are the large reactor volume and the high reactor wall surface area, primarily due to the retraction bellows utilized. Contamination of the UHV chamber by outgassing of reactants/products from the reactor walls can best be eliminated by isolating the reactor from the surface analysis chamber with a UHV gate valve. However, this constraint, without the modification described in this article, requires transfer of the sample from one manipulator through the isolation valve to a second manipulator.

Spring loaded Teflon seals are currently widely used in various UHV applications. Teflon is an excellent material for vacuum devices since it is bakeable up to 520 K and its outgassing properties are comparable to those of metal surfaces. The use of Teflon in vacuum seals requires some precautions because of its high expansion coefficient which can result in its deformation during bakeout. The use of multiple Teflon seals with differential pumping provides a very satisfactory solution to any leakage and outgassing problems typically encountered with moving Teflon surfaces. Vajo et al. reported a differentially pumped sample manipulator in which Teflon O-rings were used to seal the manipulator shaft. In their high-pressure reactor–UHV chamber system Campbell and Paffett utilized Teflon seals to isolate a high-pressure reaction cell from a UHV surface analysis chamber.

In this article we describe a combined elevated pressure reactor cell UHV surface analysis chamber system that is being used to study the kinetics of surface catalyzed reactions. The emphasis is on the elevated pressure reactor cell and its connection to both the UHV chamber and the gas handling/gas analysis system.

This combined elevated pressure reactor cell–UHV surface analysis chamber system is similar, in many respects, to that described by Campbell and Goodman and is shown in Fig. 1 in a side view. The sample manipulator is mounted on an X-Y motion (Huntington) stage allowing ±0.5 in. horizontal movement of the sample. The X-Y
motion is connected to the UHV chamber via a 6 in. - 2 ½ in. reducing flange. An identical sample manipulator to that used in Ref. 7 was employed here. This manipulator allows an 18 in. vertical travel of the sample rod located along the center line of the UHV chamber. The octagonal upper level of the UHV surface analysis chamber is equipped with a cylindrical mirror analyzer (CMA) for AES, LEED, a quadrupole mass spectrometer (QMS), and a capillary gas doser. The octagonal chamber with a volume of about 100 ft³ is also connected to a pumping system through one of its 8 in. flanges. The pumping system consists of a titanium sublimation pump (TSP), a 200 l/s ion pump (Perkin Elmer), a 170 l/s turbomolecular pump (Balzers), and a roughing pump (Alcatel). The horizontal arrangement of the pumping system and the conductance of the connecting tubing (6 in. diameter between the chamber and the ion pump, 4 in. diameter between the ion pumps and the turbomolecular pump) ensures rapid evacuation of the UHV chamber. Except during the bakeout of the system the turbomolecular pump is utilized to evacuate the elevated pressure reaction cell and the double differentially pumped sliding seal described below. The bottom cylindrical part of the UHV chamber accommodates eight 2 ½ in. flanges which house metal dosers, an Ar-ion sputter gun, a tungsten filament for electron beam heating, and a nude ionization vacuum gauge. The arrangement of the main chamber is shown in Fig. 2 in a top cut-away view.

The elevated pressure reaction cell is connected to the bottom of the UHV chamber through a 4 ½ in. flange positioned at the center of the base plate. The reaction cell is separated from the UHV chamber by a gate valve (MDC, GV-1500M) that is always in the closed position except for elevated pressure kinetic studies. The ability to completely separate the UHV chamber from the reaction cell is a very important feature of our system that eliminates any significant contamination of the main UHV chamber from outgassing of the reactor wall following an elevated pressure reaction. The gate valve is located between the UHV chamber and the double differentially pumped sliding seal (shown in Fig. 4). The housing of the sliding seal is a 2 ½ in. double-sided flange machined to securely hold three spring-loaded Teflon seals (Furon, AR-10103) and three Teflon spacers. The Teflon seals and spacers are firmly held in position by a snapring. The flange is double differentially pumped via a roughing pump between the lower two seals (next to the reaction cell) and via a turbomolecular pump between the upper two seals (next to the UHV chamber). This configuration prevents pressure increases in the UHV chamber during elevated pressure kinetic experiments in
the reaction cell up to 1000 Torr. The Teflon sliding seals are sufficiently vacuum tight that double differential pumping is generally unnecessary; pumping with the turbomolecular pump is adequate to prevent leakage into the UHV chamber.

Two precautions have to be exercised in the use of the Teflon sliding seals. First, the manipulator rod has to be mirror polished; any longitudinal scratch can result in significant leakage that ultimately leads to an unacceptable level of gas loss from the reaction chamber as well as an unacceptable pressure increase in the UHV chamber. Second, the position of the vertical translational sample rod (see in Ref. 7) has to be carefully centered prior to insertion of the sample rod into the seal assembly. Deviation from the center position of the sample holder rod can cause irreparable damage to the Teflon seals or the polished rod surface. In our system accurate centering of the sample holder rod is accomplished by utilizing a viewport located at the bottom of the reaction cell.

Another advantage of using the manipulator and reaction cell configuration described here is that only a small fraction of the sample holder rod is actually in contact with the reaction gas mixture. This is also important in preventing significant contamination of the UHV chamber following transfer of the sample into the UHV chamber for surface analysis or sample preparation.

The elevated pressure reaction cell consists of a 1\(\frac{1}{2}\) in. tee and a \(\frac{1}{2}\) in. nipple with a total volume of \(\sim 500 \text{ ml}\). The tee is connected to a gate valve (MDC, GV-1500M) which separates the reaction cell from the vacuum line to the turbomolecular pump. The nipple is easily removable providing convenient access to the manipulator tip and sample. This arrangement makes it possible to mount and repair the sample without breaking vacuum in the UHV chamber. Via the horizontal gate valve the reaction cell can be pumped rapidly to \(10^{-8}\) Torr following a high-pressure experiment. Vacuum pressures in the reactor cell region are monitored by a nude ionization gauge.

Through a double-sided flange the reaction cell is connected to a gas handling system, a gas chromatograph (GC), and a pressure gauge (MKS, 94BH). A sampling system has been constructed for accurate and sensitive GC analysis (shown in Fig. 1). The main element of this system is a sample loop located between the reaction cell and the GC, and positioned in-line with a roughing pump. Upon completion of an elevated pressure reaction experiment, the reactant/product gas mixture is pumped through the sample loop which is, in turn, immersed in a cold bath. The temperature of the bath can be modified by the choice of coolant depending on the reaction under study. Injection of samples for GC analysis can be achieved by rapid warming of the loop. This arrangement also allows consecutive injection of samples onto the separation column. For example, the sample loop can be cooled initially with liquid nitrogen which condenses all the products. By warming the loop with a dry ice/acetone slurry to \(-78\, ^\circ\text{C}\), samples with higher vapor pressures can be injected. Compounds with low boiling points are retained in the sample loop and are subsequently analyzed by warming the GC loop, for example, with hot water.

The combined elevated pressure reaction cell-UHV surface analysis chamber system described above has been used successfully in studying reaction kinetics of several heterogeneous catalytic processes. The synthesis of methanol was studied using a CO/CO\(_2\)/H\(_2\) reactant gas mixture on a Cu(100) single-crystal surface. Applying the described gas analysis procedure quantities of methanol produced as low as \(10^{12}\) molecules were analyzed. This quantity corresponds to a turnover frequency of \(\sim 10^{-7}\) s\(^{-1}\).

The system was also utilized to study the catalytic properties of model Cu/Rh(100) bimetallic catalysts for CO oxidation and methane activation on clean and oxidized Ni(100) surfaces.

A very similar high-pressure cell with two CaF windows has also been constructed and mounted to a UHV surface analysis chamber described in Ref. 11 to carry out infrared reflection absorption spectroscopy studies at elevated pressures. This system has been used to study CO adsorption on metal surfaces and to investigate the nature of adsorbed species on metal surfaces during catalytic CO-O\(_2\) and CO NO reactions under elevated pressures. 13

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