Infrared spectroscopy of bare single crystal and nano-particle covered surfaces

NEBOJŠA S. MARINKOVIĆ1* and RADOSLAV R. ADŽIĆ2#

1Center for Catalytic Research, Brookhaven National Laboratory, Building 535A, Upton, NY 11973 and Department of Chemical Engineering, University of Delaware, Newark, DE 19716 and 2Department of Chemistry, Brookhaven National Laboratory, Building 555, Upton, NY 11973, USA (e-mail: marinkov@bnl.gov.)

(Received 20 January 2006)

Abstract: Infrared spectroelectrochemistry is the leading technique for in situ investigation of electrode–solution interfaces because it can both identify the species adsorbed at the metal/solution interface, and quantitatively follow their reaction and kinetic behavior. The unique capabilities of the method have been demonstrated by selective examples, including the identification of preferentially adsorbed species on single crystal surfaces of noble metals with hexagonal symmetry, and electrochemical oxidation of CO on bare and Pt-decorated single crystal Ru surfaces.

Keywords: infrared, spectroelectrochemistry, single crystal surfaces, noble metals, CO oxidation, bisulfate adsorption.

Molecular and ionic vibrations from particles adsorbed on metal surface are now routinely investigated by infrared (IR) spectroscopy. Electrochemical studies are usually conducted in situ using a technique termed Subtracively Normalized Interfacial FTIR Spectroscopy (SNIFTIRS), or Potential Difference IR (PDIR) spectroscopy in which the difference in the spectral response of species adsorbed on a surface is measured as a function of the electrode potential, both qualitatively and quantitatively. The technique was firstly used by Pons et al.1 and later modified and improved by various authors.2

One of the systems, most studied by the technique is the adsorption of sulfate/bisulfate on Pt.3 While a matter of great controversy in the past, it is now generally acknowledged that the adsorbed species at a Pt(111) surface is bisulfate, or more precisely, the SO2−4 − H3O+ ion pair.4 This was explained in terms of the behavior of two low-intensity modes at 1050 and 945 cm−1 which were clearly resolved only after careful optimization of the IR accessory, thus dramatically improving the sensitivity of the technique for spectrochemical studies.5

* Invited lecture at the Meeting of the Electrochemical Section of the Serbian Chemical Society, held on 29 December 2005.
# Serbian Chemical Society active member.
doi: 10.2298/JSC0609945M
Another frequently studied system is the oxidation of CO on a Pt electrode surface. Its so-called linear configuration (CO_L) with the carbon monoxide adsorbed through the carbon atom oriented perpendicularly to the electrode surface was seen in both perpendicular (p) and parallel (s) light, although the surface selection rule precludes the existence of bands with a dipole moment that lies parallel to the plane of surface.\(^2\) This was explained in terms of the low polarizator discriminating power due to the polarizer extinction coefficients.\(^6\)

Work on other metal surfaces with a hexagonal atom arrangement similar to that of Pt(111) revealed fundamental differences in the adsorption of both CO and (bi)sulfate species. While inactive for CO oxidation, the well-ordered Ag(111) surface showed adsorption bands with frequencies over 100 cm\(^{-1}\) lower than those on Pt(111) which increased in frequency at more positive potentials.\(^7\) It was concluded that the predominant adsorbed species was sulfate, due to the fact that the IR band was seen in both acidic and neutral sulfate-containing media, as well as on the basis of \textit{ab-initio} calculations of the behavior of bands upon approaching a strongly positively charged substrate.\(^8\) Ag ad-atoms electrochemically deposited on Pt(111) showed an intermediate behavior between Pt and Ag, with identical hexagonal arrangement of the surface atoms. Two commensurate layers of Ag on Pt(111) showed similar adsorption characteristics to those of bulk Ag(111), thus being inactive for CO oxidation and adsorbing sulfate. The behavior of a Ag monolayer was closer to that of Pt(111), in that it oxidized CO and adsorbed bisulfate.\(^9\) The unusual electrochemical behavior, as well as the lattice constant difference of the Ag/Pt(111) layers with respect to that of bulk Ag, shown by high-resolution surface X-ray scattering\(^10\) were explained by a considerable charge transfer from the Ag adlayers to Pt, which resulted in an increased adatom–adatom repulsion in the system.

The study of (bi)sulfate adsorption and CO oxidation was extended to catalytically important metals, such as ruthenium. While the electrochemical behavior of polycrystalline Ru was characterized in the eighties,\(^11\) the first study of a single crystal Ru surfaces appeared only at the turn of the millennium.\(^12\) Because Ru crystallizes in a hexagonal close-packed system, its (0001) plane has an identical arrangement of atoms as the (111) orientation of cubic structures. SNIFTIRS measurements revealed that bisulfate is the predominant adsorbed species on Ru(0001), and that its adsorption extends even the whole potential range from the onset of H\(_2\) evolution to Ru oxidation. Bisulfate vibration frequencies are higher at this surface than on any face-centered cubic metal with the (111) orientation and proceed with an unusually small tuning rate, ascribed to a small change in bisulfate coverage on the Ru surface with potential.\(^13\) Thus, it appears that noble metals with unfilled d-orbitals (Pt, Pd, Rh, \textit{etc.}) preferentially adsorb bisulfate species, while those with filled d-orbitals (Cu, Ag, and Au) predominantly adsorb sulfate species.

A comparison of CO oxidation on well-ordered Ru surfaces with the (10\(\overline{1}0\)) and (0001) orientations revealed that the more open Ru single crystal structure
showed a facile oxidation of CO and only linearly bonded CO_L, in contrast to the slow reaction on Ru(0001) and IR bands of both CO_L and triply-coordinated CO on Ru(0001).\textsuperscript{14} The spontaneous deposition of Pt produces island-like structures on both single crystal Ru surfaces. While a Pt-modified Ru(0001) structure clearly shows two bands due to CO_L, corresponding to CO adsorption on two different atom clusters,\textsuperscript{15} a single broad peak for CO_L on bimetallic Pt/Ru(10\textit{T}0) surface may result from the addition of the red-shifted CO_L peak for Pt and that for the Ru(10\textit{T}0) substrate.

It should be emphasized that IR spectro-electrochemistry was crucial for the understanding of the processes in all the above systems because it is one of the rare \textit{in situ} techniques that can both identify the species adsorbed at the metal/solution interface, and quantitatively follow their reaction and kinetic behavior. The popularity of the technique has been steadily growing since its discovery, and has now become a standard addition to every electrochemical laboratory.

ИЗВОД

ИНФРАЦВЕНА СПЕКТРОСКОПИЈА НА МОНОКРИСТАЛНИМ И ПОВРШИНАМА ПРЕКРИВЕНИМ НАНО-ЧЕСТИЦАМА

НЕБОЈША С. МАРИНКОВИЋ,1 и РАДОСЛАВ Р. АДИЋ2

1Center for Catalytic Research, Brookhaven National Laboratory, Building 535A, Upton, NY 11973 and Department of Chemical Engineering, University of Delaware, 150 Academy St, Newark, DE 19716, SAD i 2Department of Chemistry, Brookhaven National Laboratory, Building 555, Upton, NY 11973, SAD

Инфрацрвена спектро-електрохемска техника заузима водеће место међу методама за испитивање система метална електроде – раствор \textit{in situ}, зато што може да идентификује честице које су адсорбоване на површини електроде или у присељеног слоју, као и што омогућује квалитативно праћење реакције и кинетичко понашање система. Јединствене способности ове технике су приказана на примерима као што су могућности идентификације адсорбоване честице на монокристалним површинама племенитих метала са хексагоналном симетријом и праћење електрохемијске оксидације угљен-моноксида на монокристалним и површинама рутенијума прекривеним нано-честицама платине.

(Примљено 20. јануара 2006)

REFERENCES

1. J. Daschbach, H. Dale, S. Pons, \textit{Appl. Spectrosc.} 40 (1986) 489