Assignment – 2

Subject : Experimental Methods in Catalysis

Topic : The Oxidation states of metal ions as revealed by XPS

-By

CH. Naga Lakshmi,

R.No-ch20d502(IIT Tirupati)

X-ray photoelectron spectroscopy is a very useful surface analysis technique especially for metals. The change in binding energy, the chemical shift, can be used to determine the **oxidation** state of the metal. X-rays are absorbed by the atoms, and a single K shell electron is emitted. The binding energy of the electron is dependent on the environment and oxidation state of the atom.

The oxidation states of metal ions as revealed by XPS :- Applications

MgO catalyses both the dehydration and dehydrogenation of alcohols. The selectivity has been found to vary greatly for different preparations. Vinek et al. [1] have studied the surface of MgO prepared from $Mg(OH)_2$ and $MgCO_3$ and observed changes on sample ageing. Fig. 1 shows the O 1s spectra from MgO prepared from $Mg(OH)_2$ and after ageing for several months (Xm), from commercial MgO (com) and from MgO derived from $MgCO_3$ (car). Clearly the O 1s peak has two components, due to the oxide and terminal OH groups (or $Mg(OH)_2$). The number of the latter depends (a) on preparative route and (b) on sample age. The catalytic conversion data for butan-2-ol showed marked changes in behaviour on catalyst ageing, which could be reversed by high temperature calcination. The data show that as a surface hydroxide layers grow on the MgO the basicity of the surface decreases and the selectivity of the catalyst changes from dehydrogenation (formation of butanone) to dehydration (formation of butene).
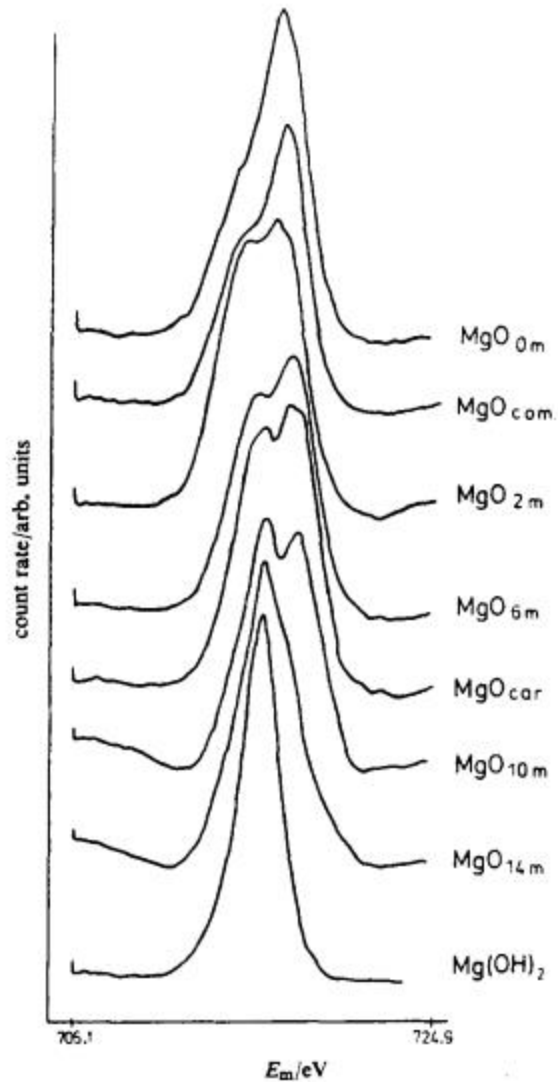
Fig. 1. O 1s spectra of different MgO samples and Mg(OH)$_2$. No charging corrections have been applied. Reproduced with permission from ref. [1]

Cross and Pyke [2] have made a detailed study of the surface composition of tin-antimony mixed oxide catalysts as a function of catalyst composition and calcination conditions. There is clear Sb enrichment and the plateau intensities agree with the bulk composition. The gradient exists through a layer 50 A. For the identically calcined range of catalyst compositions $Sn_{1-x}Sb_xO_2$ the surface: bulk Sb atom ratio decreased exponentially from 4.6 to 1.0 (x = 0 to 1). The effect of increasing calcination temperature was found to depend on bulk composition. For x < 0.6 the surface Sb concentration decreases above 700°C. Fig. 2 shows the relationship between surface and bulk composition of catalysts calcined to constant weight at 1000°C.Under these conditions it is known that catalysts containing more than 4 at.% Sb segregate into rutile-like and Sb_2O_4

structures, the Sb204 being slowly lost through volatiisation. Fig. shows that the surface composition corresponding to this equilibrium situation is 25 at.% of S. For the closed packed planes of the rutile lattice higher concentrations would lead to Sb ions being in adjacent sites thereby providing the Sb_2O_4 nucleus. The XPS data therefore provides an understanding of the processes leading to surface compositional changes and it is encouraging to find that a good correlation exists between the surface Sb concentration for these catalysts and their selectivity for the oxidative dehydrogenation of I -butene to butadiene [3].
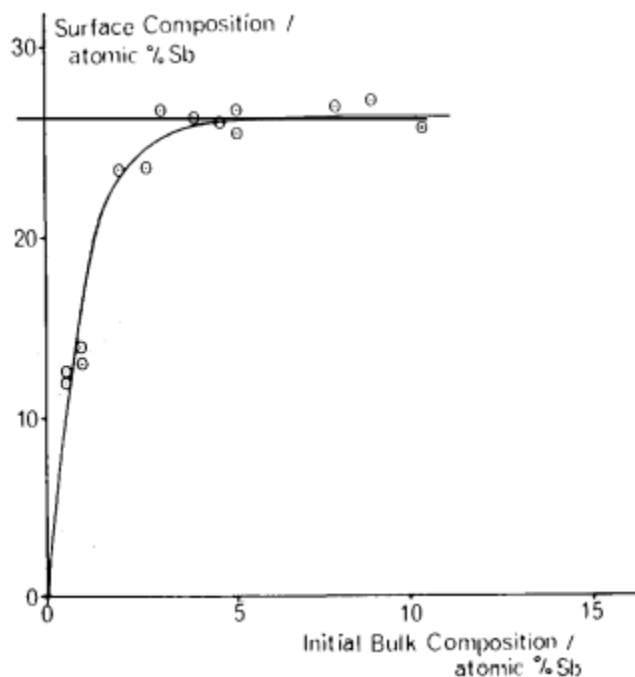

Fig. 2 Surface composition of catalysts after prolonged calcination in air at 1000°C to constant weight. Reproduced, with permission from ref. [2].

The surface chemical composition of the 55Ni15Cu (Sol.) catalysts and it Pd modified catalysts were probed by X-ray photoelectron spectroscopy (XPS) by Ali Rategarpanah et al. [4]. The O 1 s spectra as shown in Fig. 3 can be deconvoluted into three peaks at 530.60, 532.20 and 532.80 eV which were assigned to lattice oxygen (O_{latt}) bonded with metals in the mixed oxides, adsorbed oxygen species (O_{ads}) on the surface defective sites and adsorbed water, respectively. However, in the addition of Pd, no hydroxyl species were detected while the O_{ads} has increased obviously. This result indicated that loading Pd on the catalyst facilitated the formation of surface defective sites which act as active sites to adsorb and dissociate reactant molecules during the reaction. Fig. 3b demonstrated Ni 2p spectra which can be fitted with Ni^{2+}, Ni^{3+} and satellite peaks.
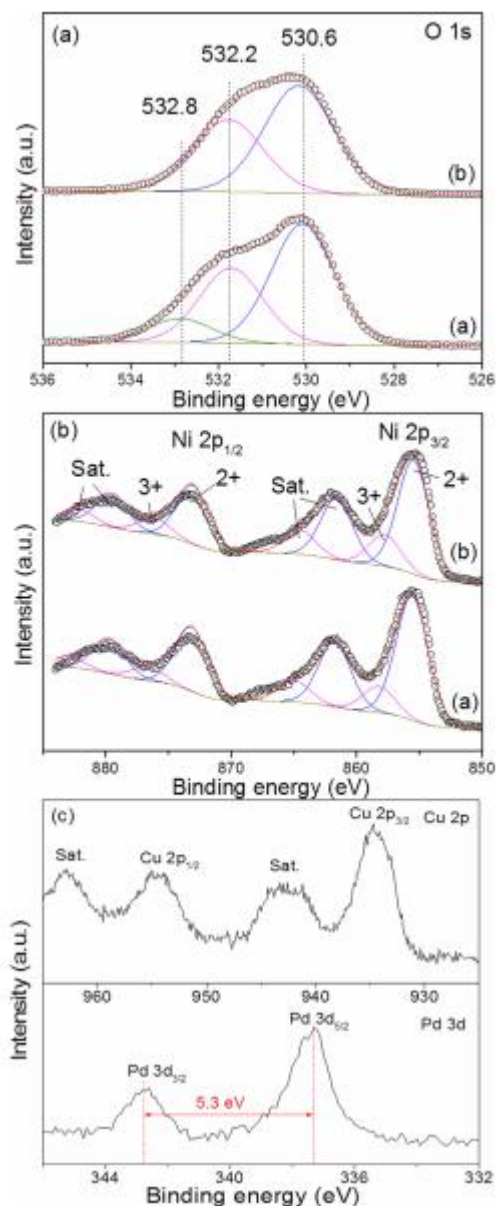
Fig. 3 XPS spectra of (A) O1s, (B) Ni 2p of (a) Ni-Cu/MgO·Al$_2$O$_3$ and (b) Ni-CuPd/MgO·Al$_2$O$_3$ and (c) Cu 2p and Pd 3d of Ni-Cu-Pd/MgO·Al$_2$O$_3$ catalysts. Reproduced with permission from ref. [4]

It suggested the presence of mixed oxidation state of Ni, further confirming the presence of defects in the catalysts. Additionally, the XPS spectra of Cu 2p and Pd 3d were shown in Fig. 3c. The coexist of Cu 2p$_{1/2}$, Cu 2p$_{3/2}$ with two conspicuous shake-up satellite peaks indicated that the oxidation composite of Cu is Cu^{2+}. The binding energy position for Pd 3d$_{3/2}$ and Pd 3d$_{5/2}$ are 342.60 and 337.30 eV with a 3d spin-orbital splitting of 5.30 eV. The energy values correlate well with the literature for the positions of two valent palladium, Pd^{2+}.

A Pt-Re surface alloy was studied by Duke et. al.[5] during CO oxidation via AP-XPS. These results show a surface reconstruction during CO oxidation. Initially Re is subsurface, but during CO oxidation it is driven to the surface to assist in O_2 dissociation. Additionally, Re was shown to decrease CO binding as little to no surface CO is observed at 450K, whereas on pure Pt, CO remains on the surface until 500K. Interestingly, Pt alloyed with Re instead of Sn has an opposite interaction that ends in the same result: Re is drawn to the surface to weaken CO binding and enhance O_2 oxidation for the Pt-Re alloy.

M.A. Panafidin et.al. [6] studied on XPS method for the chemical state of silver, it should be taken into account that the binding energy of the $Ag3d_{5/2}$ peak only slightly changes depending on the oxidation state of silver, which prevents one from drawing unequivocal conclusions regarding changes in the chemical (charge) state of silver on the support surface. The signals in the region of high binding energies in Ag3d and Pd3d photoelectron spectra (~368.9 and 337.0 eV, respectively) registered immediately after the deposition of Pd or Ag onto the modified HOPG surface have been assigned to mono- or bimetallic clusters localized on the defects of the planar support. The portion of these states for each of the samples did not change for different conditions of treatment and was 15–25% of the general integral intensity. These states are thermally stable under the experimental conditions (at 200–450°C). Moreover, new states of palladium and silver appear after heating to 300°C (Fig. 4), and their signals are shifted toward lower binding energies by 0.2–0.4 eV relative to the values typical for metallic palladium and silver.
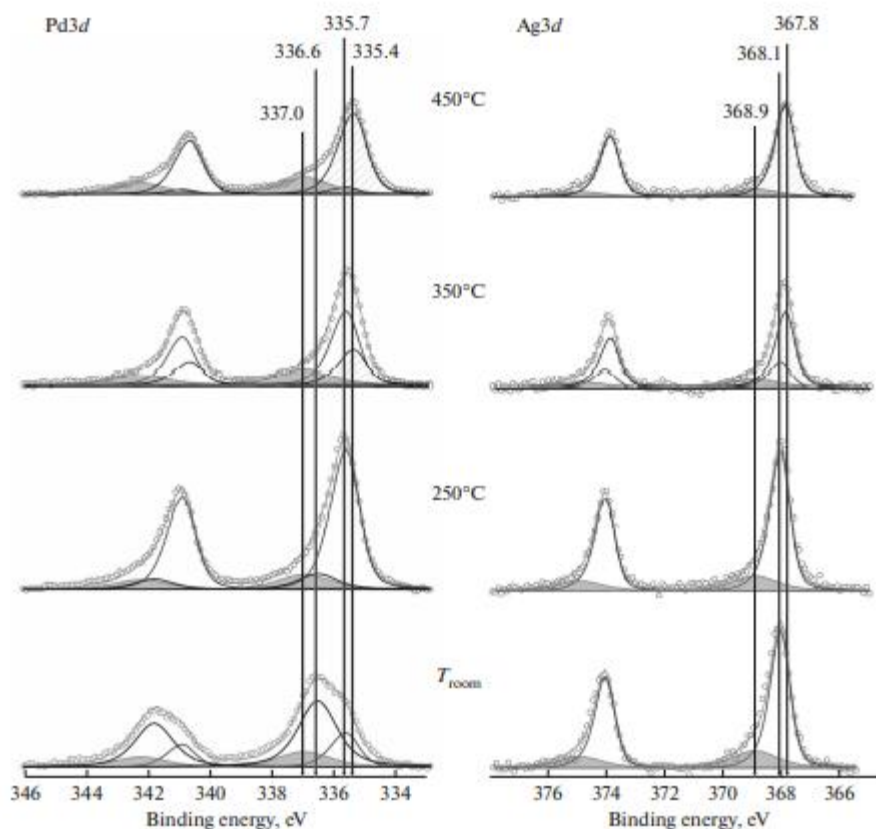
Fig. 4 XPS spectra Pd3d and Ag3d for the Ag–Pd-2 sample recorded at room temperature and after heating at 250, 350, and 450°C. The kinetic energy of electrons in the measurements was 300 eV. Reproduced with permission from ref. [6]

Svintsitskiy et al.[7] studied CO oxidation over oxygen deficient CuO NPs (NPs). This study was performed in one of the first laboratory NAP-XPS apparatuses, therefore the reaction pressure during the in situ experiments was limited to 10^{-5} mbar. Nevertheless, based on Cu LMM and Cu 2p spectral analysis, the authors detected surface reduction of Cu^{2+} to Cu^+ , suggesting that CuO is transformed into Cu_4O_3 under certain reaction conditions. They also defined O^- as the most active oxygen species on the surface of copper suboxides during the reaction. Later, Eren's group et al.[8] compared the reactivity of CO with oxygen chemisorbed on three different low-index surface planes of copper single crystals. In order to determine the reaction rates, the O 1s NAP-XPS peak intensity was measured as a function of time, pressure, and temperature. Eventually, it was found that Cu(111) is the most active surface plane for the CO reaction followed by Cu(100), while Cu(110) is the less active crystallographic plane.

References:

1. H. Vinek, J. Latzel, H. Noller and M. Ebel, I. Chem. Soc. Faraday Trans. 174 (1978) 2092
2. Y.M. Cross and D.R. Pyke, J. Catalysis 58 (1979) 61.
3. J.H. Herniman, D.R. Pyke and R. Reid, J. Catalysis 58 (1979) 68
4. Ali Rategarpanah, F. Meshkani, Y.wang, H. Arandiyan, Energy Conversion and management 166 (2018) 268.
5. Duke, A.S, Journal of Physical Chemistry 119 (2015) 381.
6. M.A.Panafidin, A.V.Bukhtiyarov, Kinetics and catalysis 59 (2018) 776.
7. D. A. Svintsitskiy, T. Y. Kardash, O. A. Stonkus, E. M. Slavinskaya, A. I. Stadnichenko, S. V. Koscheev, A. P. Chupakhin and A. I. Boronin, J. Phys. Chem. C 117 (2013) 14588
8. B. Eren, L. Lichtenstein, C. H. Wu, H. Bluhm, G. A. Somorjai and M. Salmeron, J. Phys. Chem. C 119 (2015), 14669.