EXPERIMENTAL METHODS IN CATALYSIS
(CA5030)

Application of XPS technique in studying the Chemical state of species, Surface composition, deactivation and reactivation of active surface:

Submitted by

Rahul Bagdi
(CY19D033)

Department of Chemistry
Indian Institute of Technology, Madras

X-ray photoelectron spectroscopy:

Electron spectroscopy for chemical analysis (ESCA), also known as X-ray photoelectron spectroscopy (XPS), is a widely used method for measuring the chemical composition of solid surfaces, characterizing polymer surfaces. X-ray photoelectron spectroscopy (XPS) is able to detect all elements except hydrogen. (The 1s electrons of H are valence electrons and as such participate in chemical bonding due to this reason hydrogen has no core electrons and, therefore, core−electron XPS is impossible.)

In XPS, a surface is irradiated with low-energy X-rays (usually Al and Mg K∝), which results in the ejection of core level electrons. Photon energy of the X-rays is transferred to an electron in the inner shell, enabling it (the photoelectron) to escape from the sample surface. An analyzer measures the kinetic energy of the photoelectron, which is equal to the electron's binding energy. Knowledge of the binding energy allows identification of the element. The chemical bond of an atom to other elements shifts the bonding energy of the photoelectron to higheror lower values. This shift in binding energy provides structural information about a molecule.

Let understand with an example-

The chemical structure of silver, nickel and bimetallic silver–nickel nanoparticles, i.e. Ag, Ni and Ag-Ni NPs, with sizes ≤35 nm, obtained by derived seed-mediated growth method on transparent and conductive indium tin oxide (ITO) substrates, has been studied by a comparative X-ray photoelectron spectroscopy (XPS) analysis of Ag 3d, Ni 2p and O1s core levels. XPS indicates that the surface of Ag NPs is not oxidized, while Ni NPs are clearly oxidized to **nickel oxide** and **hydroxide**.
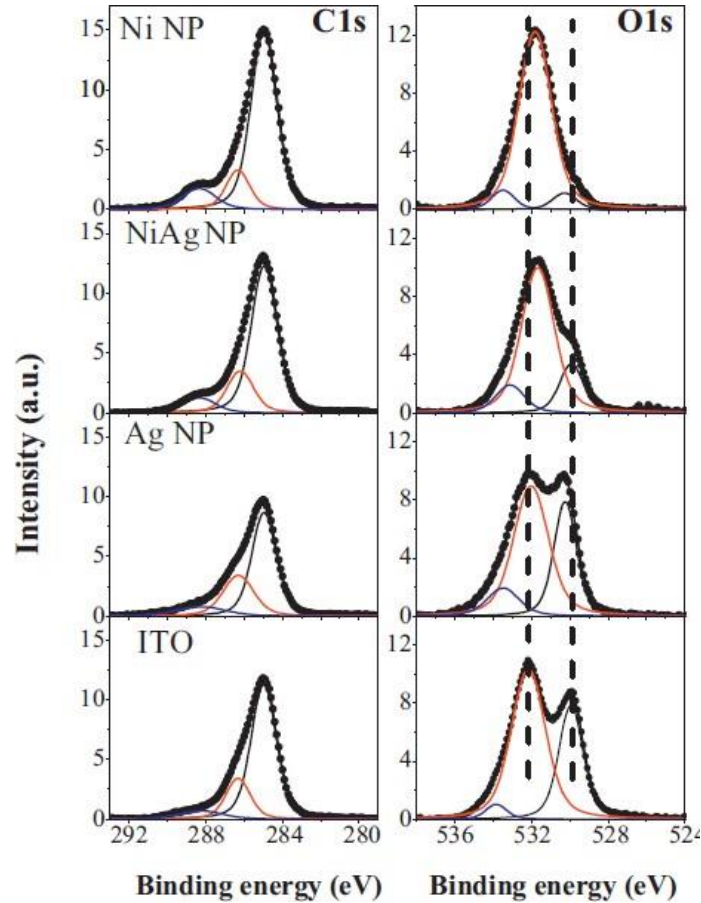
Fig. 1. C1s and O1s XPS spectra of ITO substrate and Ag, Ag-Ni and Ni nanoparticles as labelled.

XPS has been used to determine the oxidation states of Ag and Ni at the outer layers of the Ag, Ni and Ag-Ni NPs samples. Fig. 1 shows O1s and C1s spectra, and their deconvolution, form ITO substrate as well as for Ag, Ni and Ag-Ni NPs deposited on it.

In order to determine the chemical environment and oxidation state of silver atoms on the different kind of NPs, we have to performed XPS measurement at the Ag 3d core levels. The Ag 3d5/2–3/2 spectra for Ag and Ag-Ni NPs are showed in Fig. 2. The Ag 3d5/2 and Ag 3d3/2 core level binding energies for Ag NPs sample appear at 368.1 and 374.1 eV. It is known that XPS core levels can be influenced by silver nanoparticles size and the core levels shifts to higher binding energies for small Ag nanoparticles.
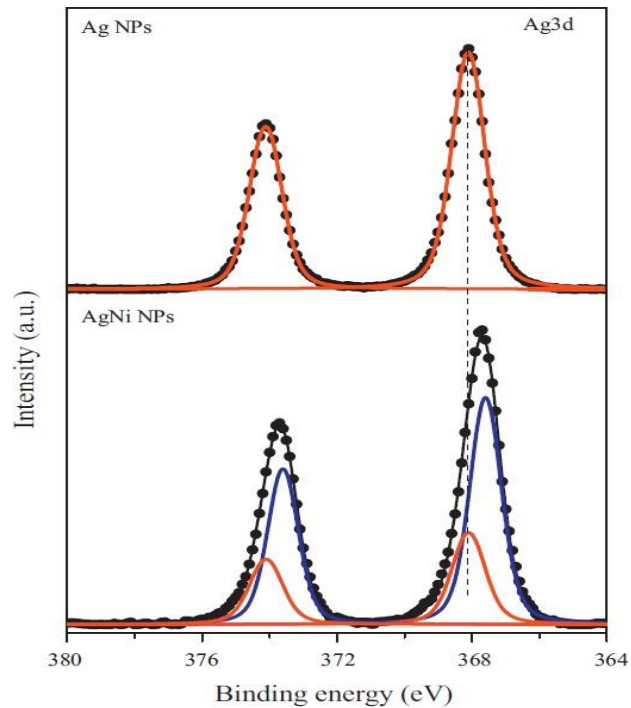
Fig. 2. Ag 3d XPS spectra of Ag and Ag-Ni nanoparticles on ITO substrates.

The binding energy of Ag 3d core levels for Ag-Ni NPs shifts towards lower binding energy values suggesting the existence of silver oxidation states.

The XPS spectra of Ni 2p3/2 and Ni 2p1/2 core levels and its satellites peaks for the Ni containing samples, i.e. Ni and Ag-Ni NPs. The Ni 2p3/2 and Ni 2p1/2 peaks appear at ≈855.9 eV and 873.6 eV, respectively and the corresponding satellite peaks are observed at 860.9 and 880.3 eV, respectively. The differences between both Ni 2p XPS spectra are in Ni metal and in NiO binding energy region, indicated by arrows in Fig.3.
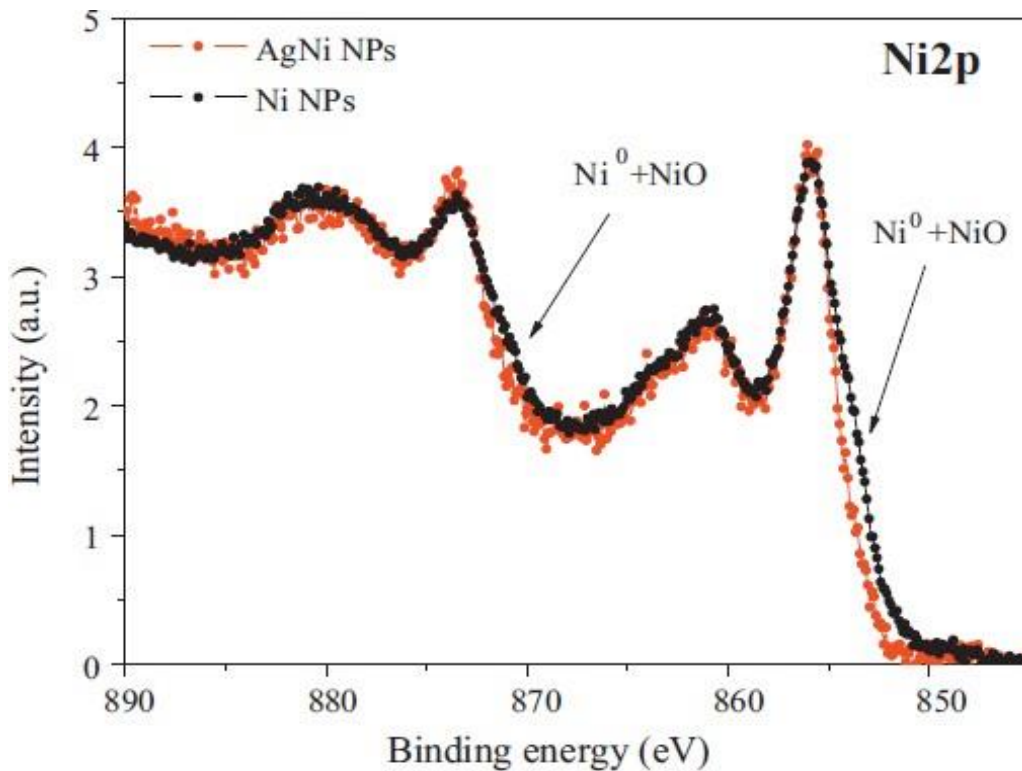
Fig. 5. XPS spectra of Ni 2p3/2 and Ni 2p1/2 core levels for Ni and Ag-Ni nanoparticles.

Fig.4a. shows the XPS spectrum of Ni 2p after Shirley background removal for Ni NPs sample. The figure also includes a normalized Ni 2p spectrum from metallic nickel with a Ni 2p3/2 peak at 852.6ev that has been subtracted to the Ni 2p spectra, as well as the difference spectrum.
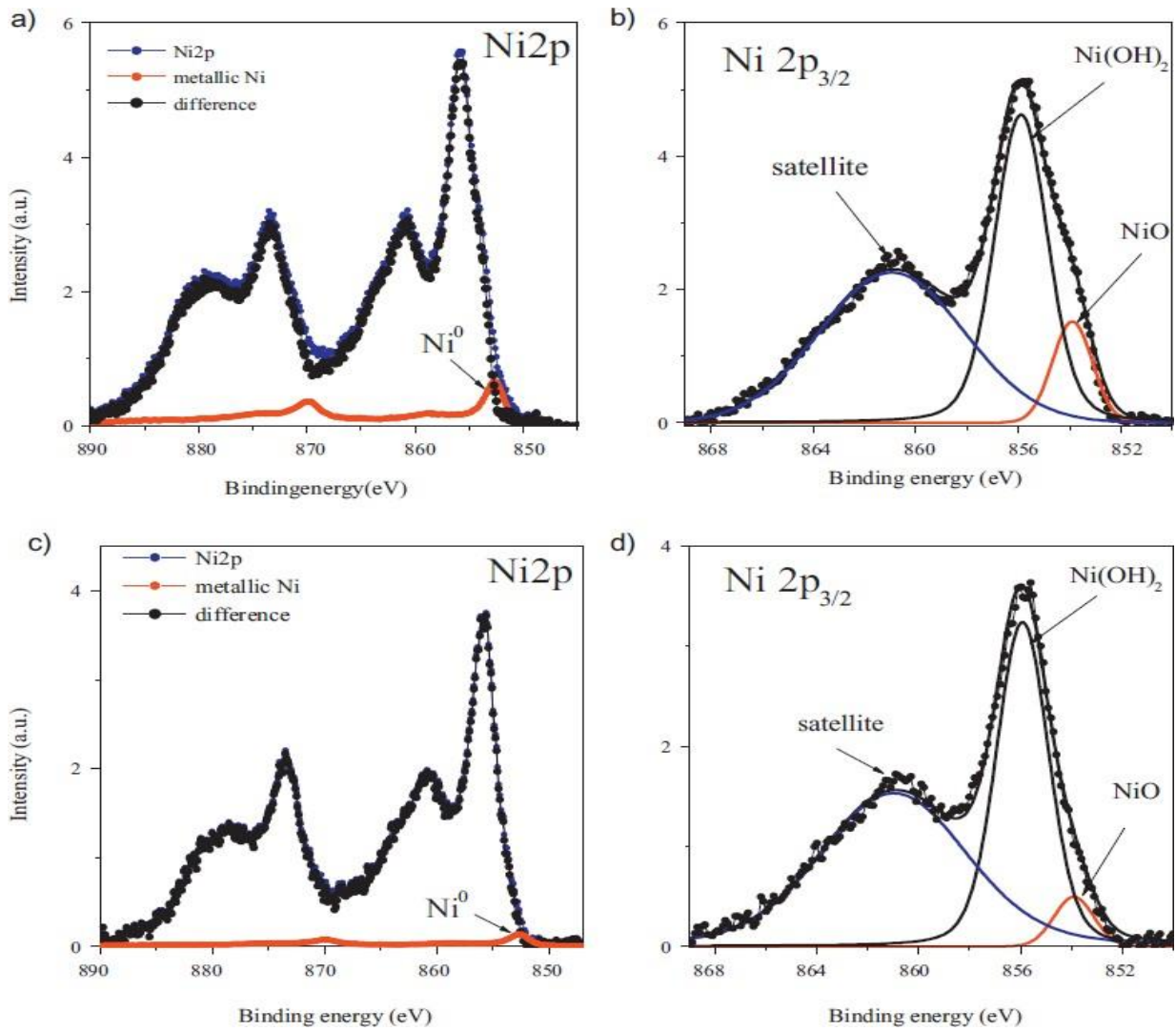
Fig. 4. (a and c) Ni 2p spectra taken for Ni and Ag-Ni NPs, respectively after Shirley background subtraction and the corresponding difference spectra after substrate the metallic Ni contribution. (b and d) Ni 2p3/2 spectra after subtraction the metallic contribution for Ni and Ag-Ni NPs, respectively and its deconvolution.

XPS indicates that the surface of Ag NPs is not oxidized, while Ni NPs are clearly oxidized to nickel oxide and hydroxide. Absorptions at 384 and 600 nm in Ni optical spectrum are consistent with the presence of nickel in oxidized state;

however the presence of metallic Ni 2p signal in Ni XPS spectrum indicates that a metallic nickel core is still present. In the case of bimetallic Ag-Ni NPs, the XPS results are consistent with the presence of metallic silver core surrounded by NiO + Ni(OH)2 shell. XPS spectra also show the presence of Ag2O at the interface between the Ag metallic core and the oxidized nickel shell. XRD patterns of Ag-Ni and Ag NPs show the typical FCC structure of metallic silver, confirming the presence of Ag metallic core in Ag-Ni NPs.

XPS Study on the Deactivation and Reactivation of B-MFI Catalysts:

A weakly acidic borosilicate of MFI-type (B-MFI) was utilized as a catalyst for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam in a vapour phase process. XPS and SIMS depth profiling techniques were applied to study the fresh catalyst as well as the deactivation and the reactivation phenomena on and below the catalyst surface. Figure 1 depicts the SIMS depth profiles of the B-MFI catalysts investigated at various activity levels. The in-depth variations of the secondary ion intensities of boron, silicon, carbon, and oxygen are compared for a fresh, a deactivated, and a regenerated B-MFI catalyst. For the fresh catalyst no significant changes of the Si and B signals as a function of depth occur, whereas the deactivated specimen shows lower intensities of Si and B in the surface regions due to the deposition of carbon. The carbon is indicated by increased relative intensities of C^+, CH^+, CH^+, CH_2^+, CH_3^+. The corresponding XPS data showed that the C 1s signals appeared at binding energies between 284.8–285.1 eV which is an indication for aliphatic carbon (20, 21) and not for coke-like deposits or carbons of enhanced aromaticity or sp2-character.
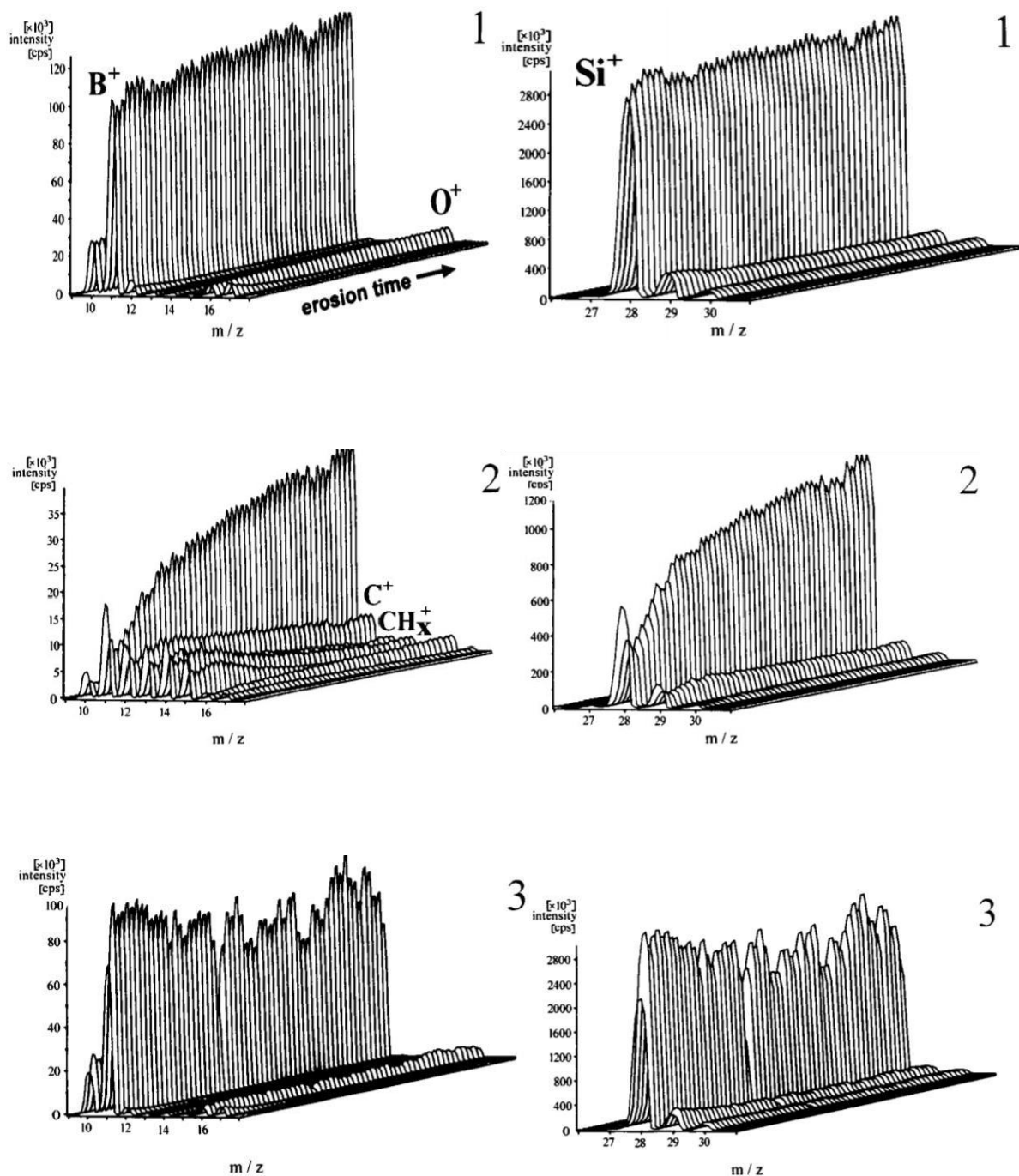
FIG. 1. SIMS depth profiles of B-MFI catalysts: left, B+ (10, 11), C+, CH+ x (12, 13, 14), and O+/OH+ (16, 17)-region; right, Si+-signal region. (1), fresh catalyst; (2), used catalyst after deactivation, residual activity 30%; (3), used catalyst after oxidative regeneration.

The concentrations of the elements as determined by means of XPS in a separate set of XPS depth profiling experiments are given in Table 1. With respect to preferential sputtering effects the XPS data obtained after surface erosion are given for a qualitative comparison of the active, deactivated, and reactivated

TABLE 1

Results of a Quantitative Evaluation of XPS-Spectra as Measured Before (Surface) and After (Subsurface) Ar^+-Ion Bombardment of B-MFI Catalysts of Different Catalytic Activity

Surface	Original	30% activity	After regeneration
O	59	44	59
N	—	1.3	—
C	1.0	16	5.7
B	1.9	traces	1.6
Si	37	39	34
Subsurface			
O	58	52	60
N	—	0.8	—
C	0.7	5.2	—
B	1.8	0.4	3.0
Si	39	42	37

Note. Relative sensitivity factors: O 1s: 0.61, N 1s: 0.36, C 1s: 0.20, B 1s: 0.101, Si 2p: 0.195.

material, respectively. The results of the quantitative evaluations are given in percentage of area.

References

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