CA5030

EXPERIMENTAL METHODS IN CATALYSIS

ASSIGNMENT-II

SURFACE COMPOSITION ANALYSIS BY XPS OF A TYPICAL CATALYST

SUBMITTED BY

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Generally, we think of a surface as a part of the solid that differs in composition from the average composition of the bulk of the solid. By this definition, the surface comprises not only the top layer of atoms or molecules of a solid but also a transition layer with a non-uniform composition that varies continuously from that of the outer layer to that of the bulk. Spectroscopic surface methods provide both qualitative and quantitative chemical information about the composition of a surface layer of a solid that is a few tenths of nano-meters (a few angstroms) to a few nano-meters (tens of angstroms) thick.

In XPS the solid sample is irradiated with a primary beam made up of photons, and secondary beam of electrons is analysed. The kinetic energy of emitted electrons is recorded. The spectrum thus consists of a plot of the number of emitted electrons, or the power of the electron beam, as a function of the energy (or the frequency or wavelength) of the emitted electrons. XPS provides information about not only the atomic composition of a sample but also the structure and oxidation state of the compounds being examined. Swedish physicist K. Siegbahn, chose to call the technique electron spectroscopy for chemical analysis (ESCA).

One of the photons of a monochromatic X-ray beam of known energy hv displaces an electron e- from a K orbital of energy Eb. The process can be represented as

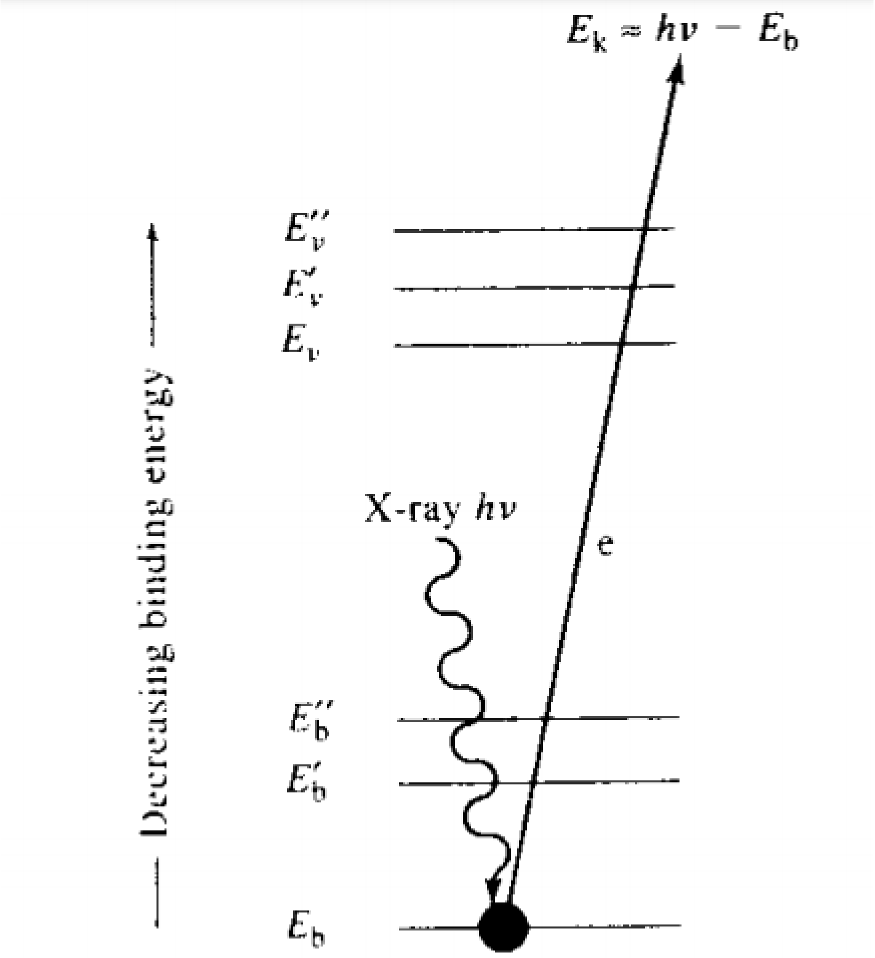
$$A + h\nu \rightarrow A^{+*} + e^{-}$$

where A can be an atom, a molecule, or an ion and A^{+*} is an electronically excited ion with a positive charge one greater than that of A.

The kinetic energy of the emitted electron E_k is measured in an electron spectrometer. The binding energy of the electron Eb can then be calculated by means of the equation

$$E_b = h\nu - E_k - w$$

In this equation, w is the work function of the spectrometer, a factor that corrects for the electrostatic environment in which the electron is formed and measured. Various methods are available to determine the value of w. The binding energy of an electron is characteristic of the atom and orbital that emits the electron.



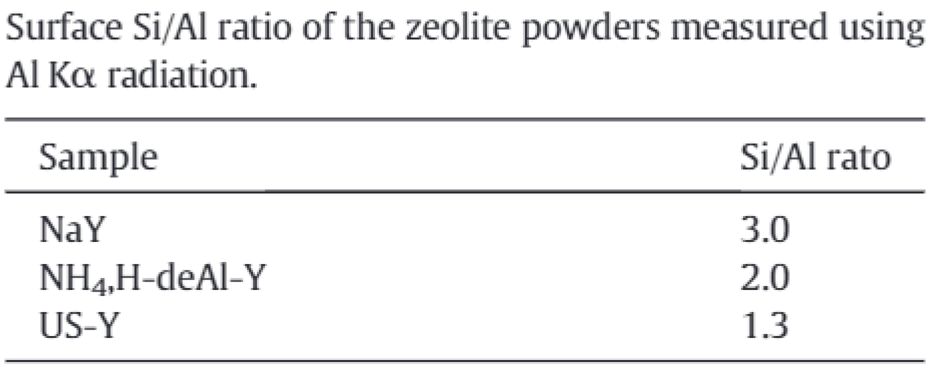
schematic representation of the physical process involved in XPS. Here, the three lower lines labeled Eb, E_b', and E_b'' represent energies of the inner-shell K and L electrons of an atom. The incident beam consists of monoenergetic X-rays. The emitted beam is made up of electrons.

XPS provides qualitative and quantitative information about the elemental composition of matter, particularly of solid surfaces - includes identification of active sites and poisons on catalytic surfaces, determination of surface contaminants on semiconductors, analysis of the composition of human skin, and study of oxide surface layers on metals and alloys.

Application of XPS for surface composition analysis

1) Surface analysis of zeolites

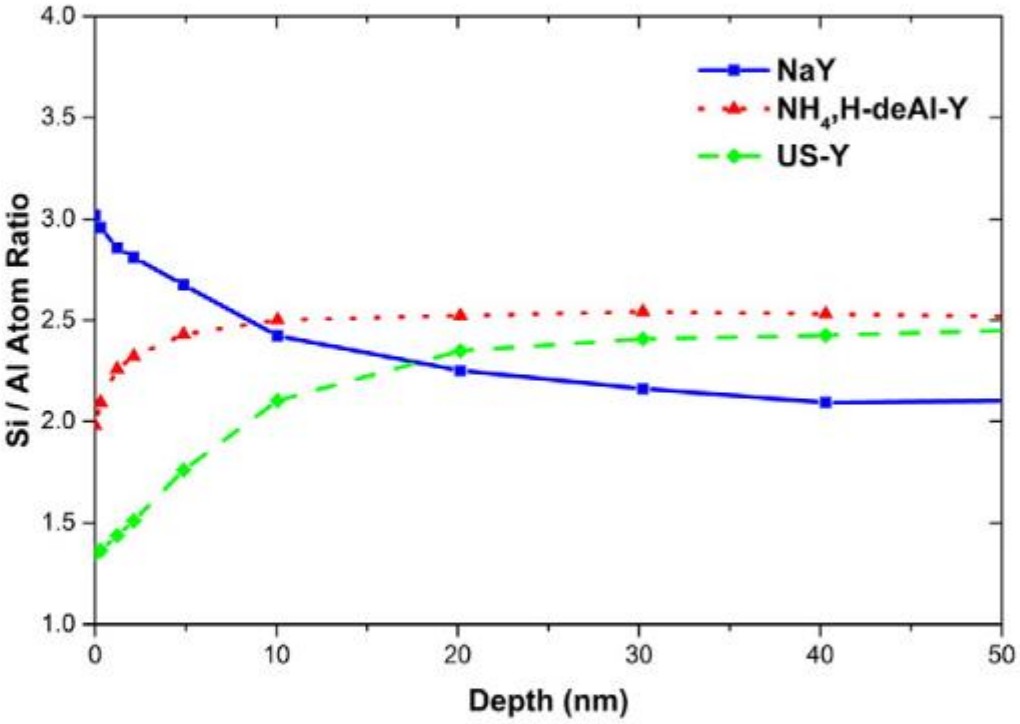
Knowledge of the surface concentration of the Brønsted acid sites in a zeolite is fundamental to understanding the reactivity of this important class of solid acid catalyst, particularly for reactions that may occur at the pore mouth. The acidity/hydrophobicity, and therefore the activity, of an aluminosilicate zeolite are determined by the aluminum content and the location of the Al in the zeolite crystal. A non-destructive depth profile, with increased surface sensitivity, can be obtained by varying the kinetic energy of the photoelectrons in XPS, using the so-called variable kinetic energy XPS. This method has been applied to the study of e.g. a 100 nm Ta layer with native oxide, a Sn doped In_2O_3single crystal and Sn doped In_2O_3 powder, and to the study of catalyst surfaces under reaction conditions.



Surface Si/Al ratio of the zeolite powders measured using Al Kα radiation.

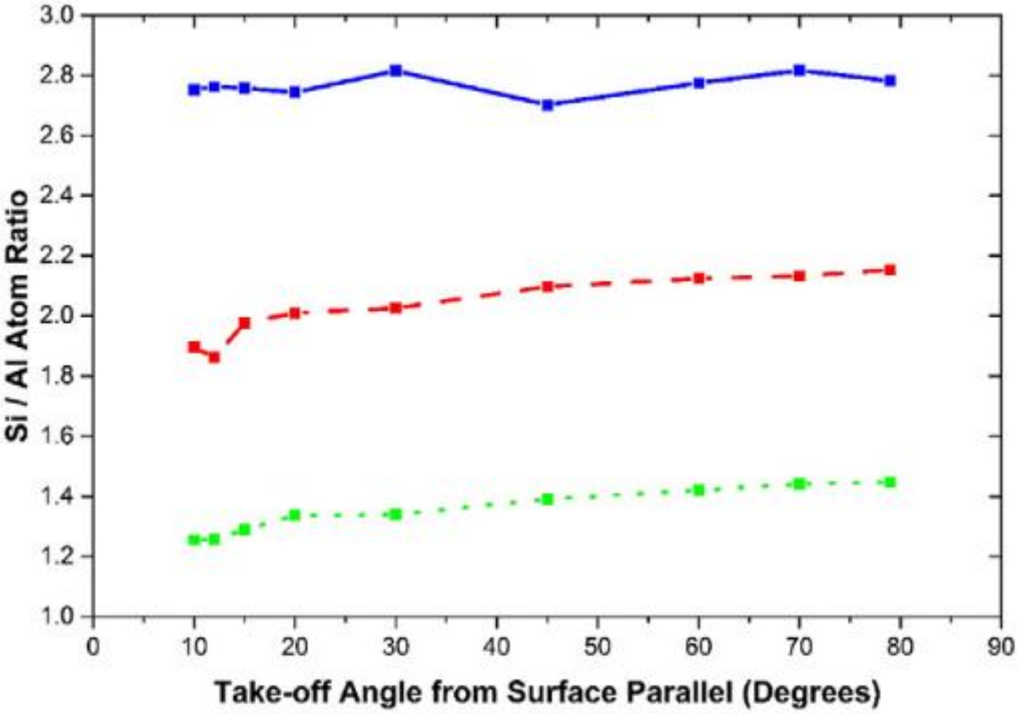
Sample	Si/Al rato
NaY	3.0
NH_4,H-deAl-Y	2.0
US-Y	1.3

The data show that the NaY sample appears to be depleted in Al at surface, the NH4,H-deAl-Y sample is enriched in Al at surface, and the US-Y sample is strongly enriched in Al at surface, compared to the bulk value of 2.6. The Si/Al profile for the NH4H-deAl-Y rapidly reaches its asymptote at close to the bulk value, whereas those for the NaY and US-Y more gradually approach the asymptote. The presence of the sodium in the NaY material may have an effect on the relative removal of the Si or Al in this sample as the Si/Al ratio for this material drops below that of the bulk value.



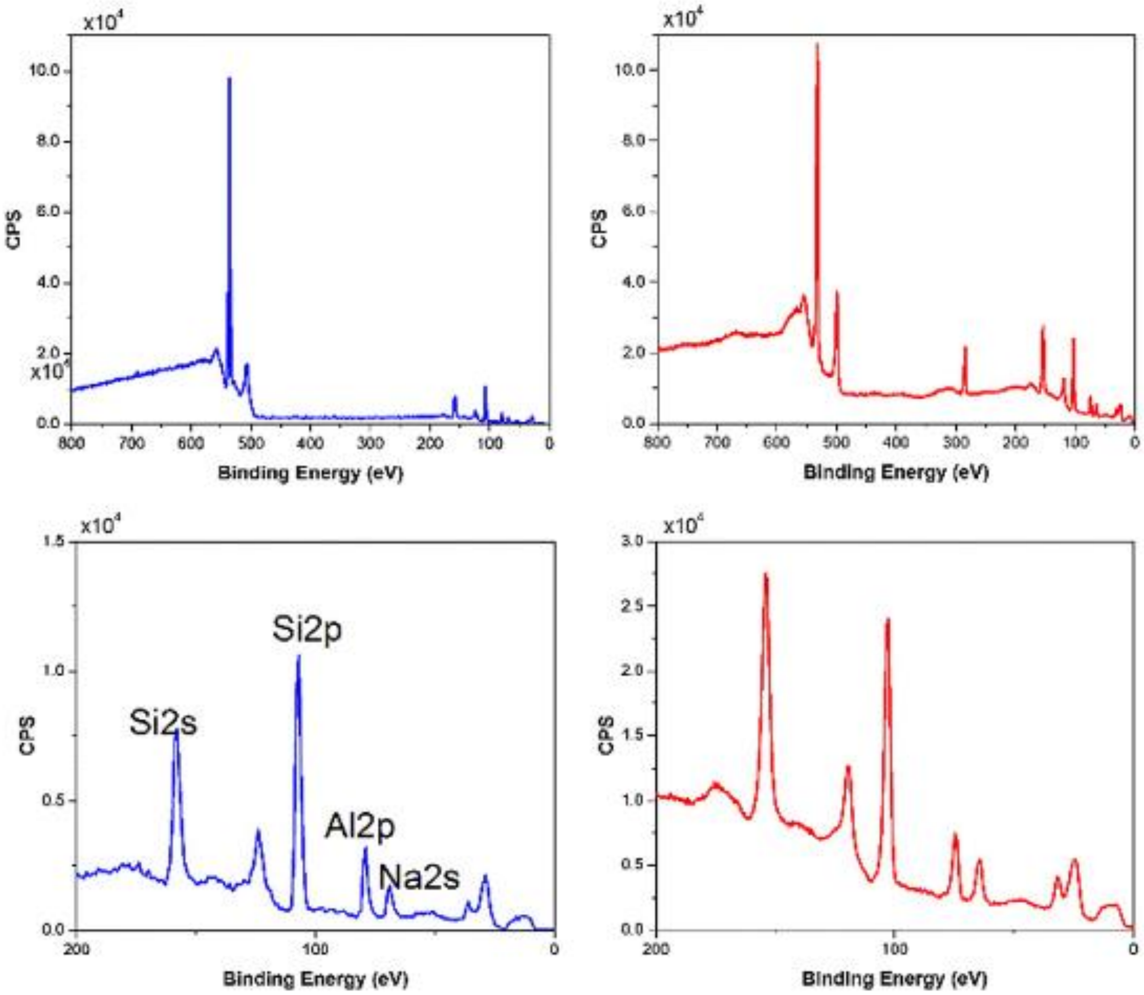
The depth scale is approximate and was calibrated using a thin silica film on silicon.

In the laboratory instrument used in this study the angle between the x-ray and the analyzer is fixed at 45°. In the laboratory instrument used in this study the angle between the x-ray and the analyzer is fixed at 45°. The data shown were obtained by rotating the sample with respect to the analyser and thus this also changes the angle of the incident x-ray beam. Nevertheless, the data are consistent with the Si/Al ratio of theNH4, H-deAl-Y and US-Y decreasing towards grazing exit (low take-off angle, more surface sensitive), while that from the NaY appears to be insensitive to the angle.

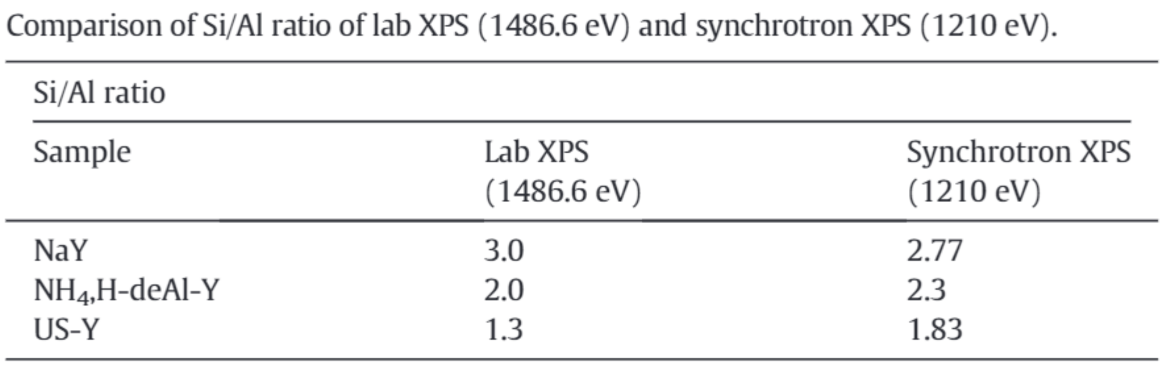


Using 1486.6 eV (AlKα) as the incident x-ray energy the resultingSi2p photoelectron has a kinetic energy of ~1386 eV, so the measured XPS signal will originate from 38–114 Å (1–3λ). One can then legitimately ask if such a measurement can be called “surface” analysis. For a material only comprising low atomic number elements like these aluminosilicates zeolites the laboratory XPS is not truly “surface” sensitive, especially when the photoelectron being measured has a low binding energy, as is the case of for the Si2p and Al2p photoelectron lines that are commonly used to characterize the surface composition of zeolites.

Figure below shows comparative XPS data from the lab instrument (photon energy of 1486.6 eV) and the synchrotron (using a photon energy of 1210 eV) from the sample NaY. As can be seen in the figure, the data quality obtained at the beam line is comparable to that obtained using the laboratory instrument.



Comparison of lab XPS (right) with synchrotron XPS (left) for the NaY sample. Survey scans (top), and Si2p and Al2p regions (bottom).



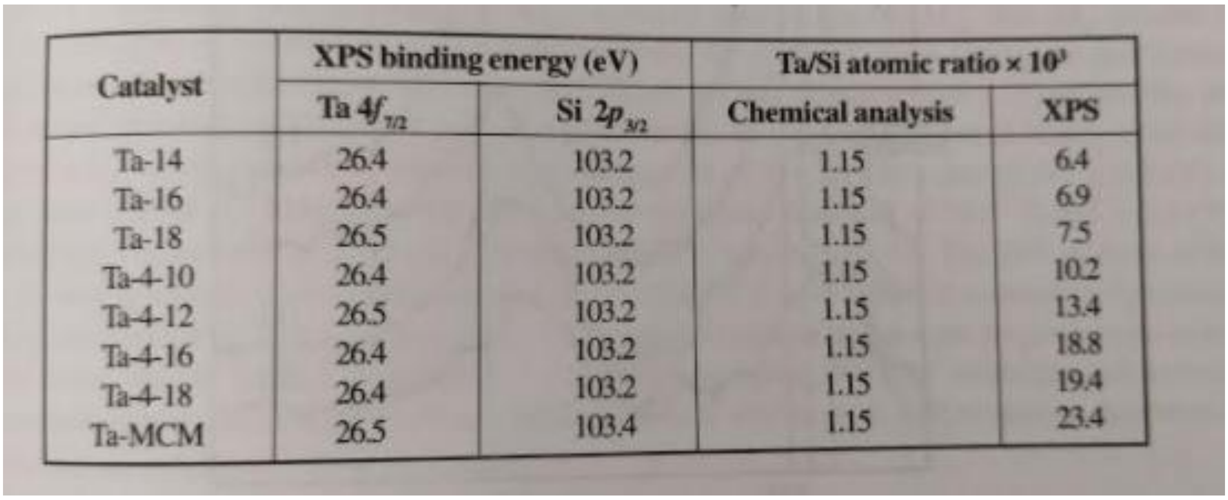
Comparison of Si/Al ratio of lab XPS (1486.6 eV) and synchrotron XPS (1210 eV).

Si/Al ratio		
Sample	Lab XPS (1486.6 eV)	Synchrotron XPS (1210 eV)
NaY	3.0	2.77
NH_4,H-deAl-Y	2.0	2.3
US-Y	1.3	1.83

2) Correlation between the atomic ratios and the activities

A highly dispersed Ta in a mesoporous like matrix was used for the liquid phase sulphonation of 4,6-dimethyl-2-thiomethylpyrimidine to the corresponding sulfoxide. Ta_2O_5-SiO_2 catalysts were prepared by a sol-gel method using tetraethyl orthosilicate (TEOS) and tantalum (V) ethoxide as the sources of silicon and tantalum respectively.

As expected, the binding energies corresponding to Ta $4f_{7/2}$ level exhibit typical values for Ta^{5+} for Ta-n and Ta-MCM catalysts. A significant difference between the bulk and surface Ta/Si atomic ratios was found with materials showing surface enrichment of tantalum in all cases.



Catalyst	XPS binding energy (eV)		Ta/Si atomic ratio × 10^3	
	Ta $4f_{7/2}$	Si $2p_{3/2}$	Chemical analysis	XPS
Ta-14	26.4	103.2	1.15	6.4
Ta-16	26.4	103.2	1.15	6.9
Ta-18	26.5	103.2	1.15	7.5
Ta-4-10	26.4	103.2	1.15	10.2
Ta-4-12	26.5	103.2	1.15	13.4
Ta-4-16	26.4	103.2	1.15	18.8
Ta-4-18	26.4	103.2	1.15	19.4
Ta-MCM	26.5	103.4	1.15	23.4

XPS binding energies of $4f_{7/2}$ and Si $2f_{3/2}$ levels and comparative XPS and chemical Ta/Si atomic ratios ICP-AES

3) Surface oxidation

The oxidation of metallic surface by oxygen is illustrated by considering nickel as example. At low oxygen exposure, emission from a level characteristic of adsorbed oxygen is observed at 5eV below the Fermi energy, in addition to the emission from the metallic d orbitals of Ni within 3eV of the Fermi energy. Further exposure results in the spectrum losing its metallic character and becoming insulator like – in other words the density of states at the Fermi level has nearly vanished. By comparison with the spectrum of bulk NiO one can identify the levels for oxidized Ni near 2eV and 5eV with contributions of the d-electrons of oxidized nickel and with surface oxide p bands. Thus the spectra show that oxidized Ni is similar to bulk NiO.

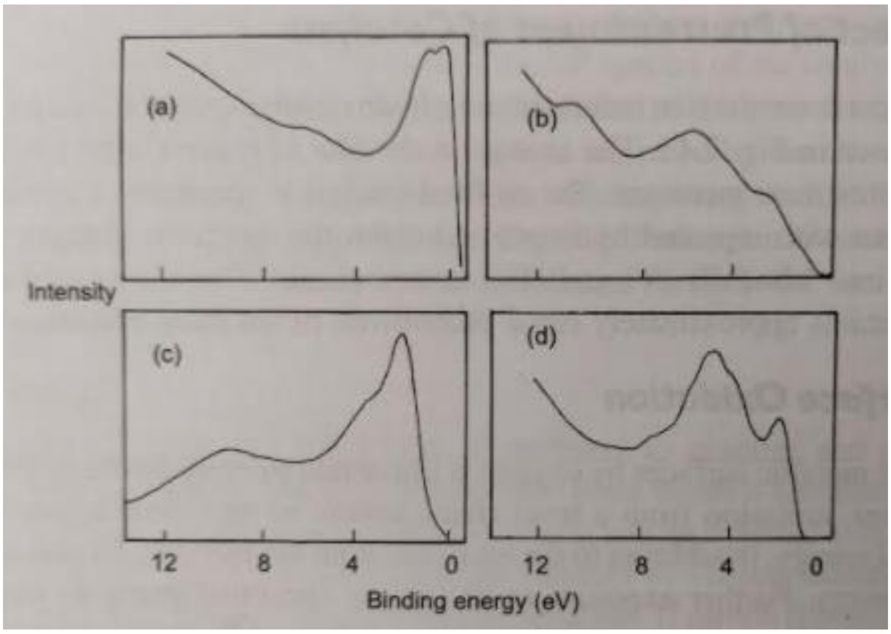
The XPS spectra are given below

(a) UPS spectra for clean Ni and for Ni with a half monolayer of chemisorbed oxygen.

(b) spectrum of surface oxide formed by oxygen exposure

(c) Ni^{2+} 3d state emission and oxide p-band emission

(d) XPS for bulk NiO showing the Ni^{2+} 3d state emission.



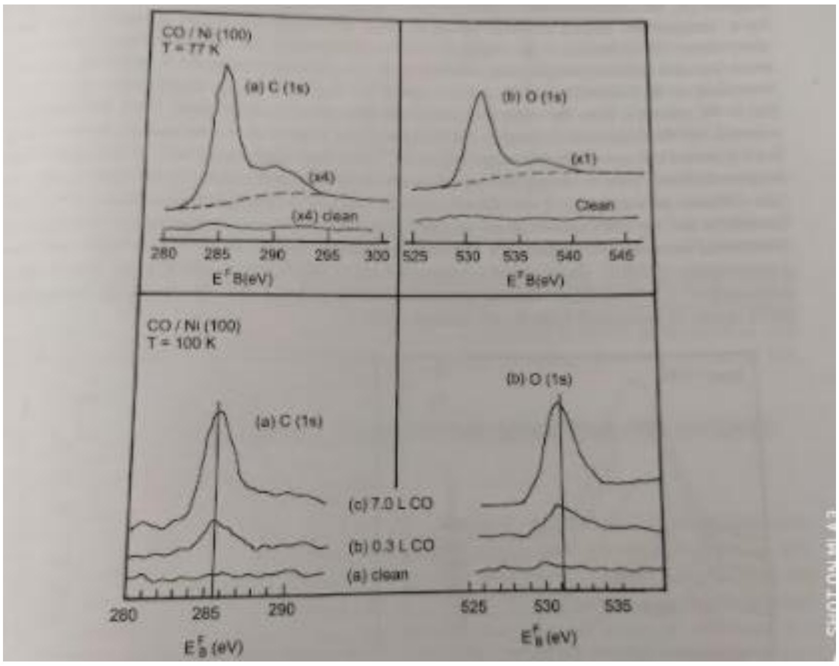
4) Study of adsorption phenomena

The X-ray photoelectron spectra obtained for the adsorbed CO on Ni (100) at 77K are shown in in the figure below

(a) Spectrum in fig(a)corresponds to the 2σ(C 1s level region)

(b) Fig(b) corresponds to 1σO(1s)

In both cases in addition to the main emission at 286eV and 532eV respectively, shoulders appear at 291eV and 537eV with respect to Fermi level. The separation between the shoulder and main peak is almost 6eV in both cases. The corresponding spectra obtained for CO adsorbed on Ni(100) at 100K are shown in the figure namely 0,3L and 7L of CO. the position of the peaks are at 285.4eV and 531.1eV at 0,3L exposure, while they are at 285.5eV and 531.2eV at 7L exposure. The shift in the binding energy with coverage is very small.



X-ray photoelectron spectra of adsorbed CO on Ni (100)

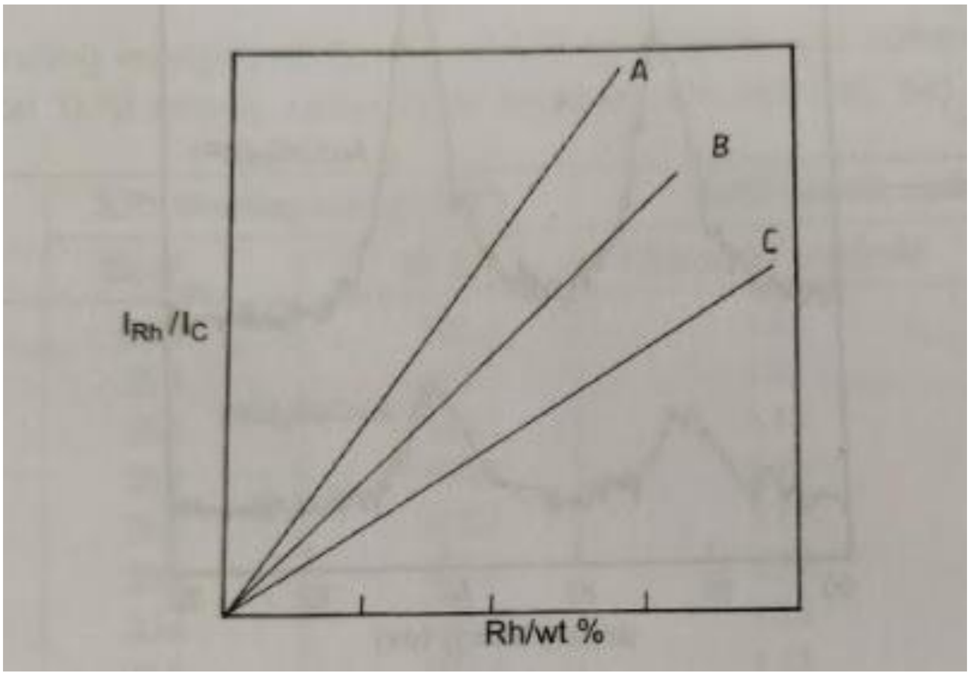
(a)after adsorption at 77K, (b)after adsorption at 100K

The position of the peaks due to 2σ or 1σ emissions are 286eV and 531eV referenced to E_F. these positions are approximately 2eV higher than those observed for atomic adsorption of C and O on these surfaces. In addition to these main peaks, peaks appear around 290eV, which is considered to be due to shake-up process. The satellite structure obtained in the core level excitations for adsorbed CO is usually considered in terms of screened and unscreened states. These situations are based on the assumptions that the 2π level of CO is pulled down below the Fermi level of the adsorbent. Another possibility is that the satellite peak at 6eV with respect to the main core level emission peak is due to simultaneous excitations of the 5σ or 2π levels occurring together with the ejection of the photoelectrons.

5) Intensity ratio as probe of catalyst structure

Since ESCA is a tool for the surface characterization, the intensities of the observed electron lines reflect surface structure of the supported metals and oxides. Information on the depth of metal and penetration into pores of the carbon supports of different physical properties was obtained from ESCA measurements on Rh/C catalysts by Brinen and Schmidtt.

Intensity ratios vary directly with metal loading for three catalyst supports A,B and C. However intensity ratios are different for carbon supports and cannot be explained on the basis of surface area alone, since large surface area carbon B(850m^2/g) has intensity ratio(I_{Rh}/I_C) intermediate between carbon A(10m^2/g) and carbon C(560m^2/g). the difference can be attributed to the pore structure, since surface area of carbon A is low, Rh on impregnation can form 5-6 atomic layers on the support and a large fraction of Rh is accessible to ESCA. Carbon B is microporous and Rh is preferentially deposited in the outer portion of the pores during catalyst preparation and is expected to be non-uniform. The effect is less important for carbon C since Rh particles are easily coated on the large pores and the intensity variation s uniform throughout the support and may also represent high dispersion. These results suggest that understanding of the physical structure of the support is required for the proper interpretation of the ESCA spectra of metals loaded on porous supports. In the case of reactions such as hydrogenation of benzene, which is a facile reaction, the activity is directly dependent on the accessible metal surface and hence a direct correlation between the catalytic activity and intensity ratio($I_{m/}I_s$) is possible.

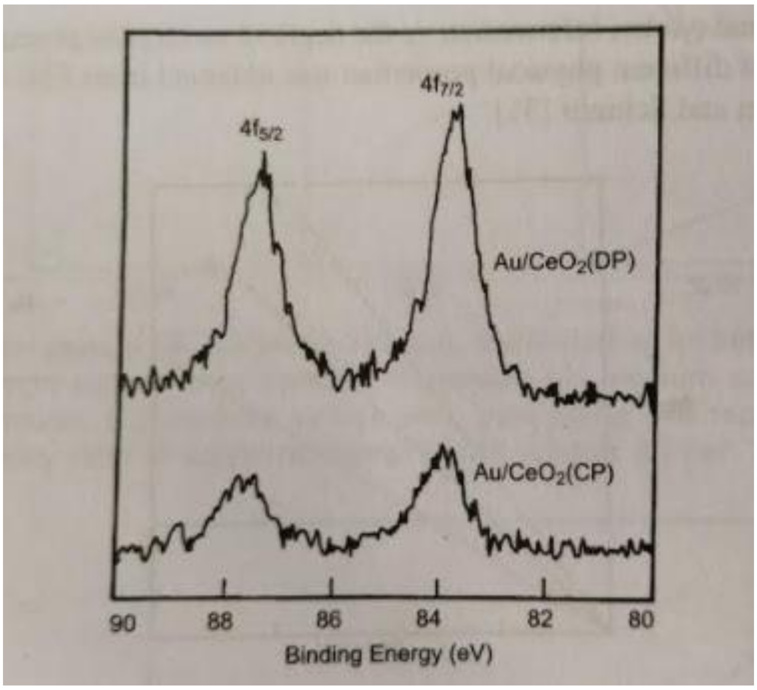


Variation of I_{Rh}/I_C for various loadings of rhodium on three different carbons. Carbon A=10m^2/g; carbon B=850m^2/g with average pore radius 11A^o; carbon C= 560m^2/g with average pore radius 53A^o.

6) Effect of Preparation methods

Au supported on CeO_2 is a good catalytic system for the oxidation of the volatile organic compounds. When two different methods such as deposition precipitation(DP) and precipitation deposition(PD) are used for the preparation of Au/CeO_2, both showed different activities.

It can be seen that the metallic gold on ceria support is more if precipitation method is deposition precipitation so the Au/CeO_2 will exhibit better catalytic activity since higher amount of active species is present on the surface.



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