

**Static Secondary Ion Mass Spectrometry (SSSIM)
and X-ray Photoelectron Spectroscopy (XPS)
Studies of Polycrystalline Ag/Ru Supported
Bimetallic Alloy System**

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Summary: Polycrystalline bimetallic Ag/Ru system was prepared by co-impregnation method supported on high surface area alumina support. The system which forms a complicated bimetallic supported alloy was studied using UHV techniques SSIMS and XPS.

On the basis of experimental evidence, the presence of Ru, Ag and Ru Ag bimetallics were found with Ag occurring on the surface of Ru masking the emission of Ru. The electronic interaction between Ag and Ru shifts the Ru electron binding energy towards lower side.

The nature of support have an affect on the Ru electron binding energy and the presence of impurities on the system distort the peak shape of the main metal. Addition of Ag increases the surface area of the system. The data has been discussed in terms of modification of the surface geometry by the addition of Ag which forms bimetallic alloy of different shape and structure.

Introduction

The success of a great number of chemical processes relies heavily upon the selection and effective use of solid state catalysts. For the bimetallic samples, the mutual dispersion of metal elements is also an important parameter, governing the behaviour of the catalysts. Static Secondary Ion Mass Spectrometry (SSIMS) and X-ray Photo Electron Spectroscopy (XPS) can make an important contribution in understanding the behaviour of each metal on the surface of catalyst [1-3].

The present study was conducted to characterize the complicated supported bimetallic system and to study the affect of addition of inactive metal on the surface of active metal using SSIMS and XPS.

Results and Discussion

Catalyst characterization using SSIMS

Ru:Ag/Al₂O₃ system

Table-1 presents the different peaks collected in SSIMS study, Table 1(b) presents the secondary ion yields of the prepared samples using SSIMS. IRu⁺/Al⁺ and IAg⁺/Al⁺ were presented in

Table 1(a): Presenting the SSIMS results.

a.m.u.	Peak
15	CH ₃ ⁺
23	Na ⁺
27	Al ⁺
39	K ⁺
45	AlOH ⁺
61	AlO ₂ H ₂ ⁺
65-80	C _n H _n ⁺
102-105	Ru ⁺
106-108	Ag ⁺

(b) Secondary Ion yields of the prepared samples as obtained in the SSIMS analysis.

Catalyst Samples	¹ Al ⁺ (CPS)	¹ Ru ⁺ (CPS)	¹ Ag ⁺ (CPS)
100:00	60,000	200	-
100:02	42,000	116	700
100:05	78,000	150	150
100:10	128,000	700	134
100:20	110,000	150	118

Table-2. The Ag signal increases with the increase in Ag loadings, the Ru signal was found to decrease with increasing Ag content.

The observed change supports the argument that Ag covers the surface of ruthenium particles and physically blocks the emission of ruthenium. This also leads to the suggestion that silver is preferentially adsorbed on the ruthenium particles.

Similar results were obtained by Lai *et al.* [4], Roberge *et al.* [5] and Dunhill *et al.* [6], while studying Ru:Cu supported catalyst system, with varying amount of Cu by SSIMS.

Table-2: Affect of Ag addition on the Intensity of Ru.

Catalyst Samples	$^{101}\text{Ru}^+/\text{Ag}^+$	$^{107}\text{Ag}^+/\text{Al}^+$
100:00	0.00333	-
100:02	0.00276	0.00196
100:05	0.00234	0.00319
100:10	0.00192	0.00448
100:20	0.00176	0.005

Catalyst characterization using XPS

Table-3 presents the change in Ru electron binding energy and the FWHM. The binding energy changes are determined by computer subtraction from the spectra of all the catalyst taking Ru:Ag/100:00 spectra as a reference and with respect to C_{1s} binding energy at 285 eV [7-9].

Table-3: The effect of Ag addition on the binding energies of $\text{Ru}_{3d_{5/2}}$ and FWHM.

Catalyst Samples	Binding Energy (eV) $\text{Ru}_{3d_{5/2}}$	FWHM
100:00	283.10	0.40
100:02	282.92	0.40
100:05	282.25	0.44
100:10	281.90	0.46
100:20	281.60	0.50

It is suggested that these changes in the system with the addition of Ag are possibly due to:

- (i) the change in particle size with the addition of Ag
- (ii) the electronic interaction between the two metals.

The electronic structure of small metal clusters has been an active area of research for both the theoretician and the experimentalist [10-11] particularly in heterogeneous catalyst [12]. In 1973 Ross *et al.* [13] presented binding energies of Pt/SiO₂ catalyst and indicated an apparent chemical shifts of +1.5 eV (to higher binding energy) of photoelectrons as compared to Pt foil. On a conductive carbon support this shift was only 0.4 eV. The shift in Pt/C might indicate a net electron transfer from Pt to the support, however most of the shift in Pt/SiO₂ was according to Ross *et al.* produced by practically uncompensated

charging. Verdine *et al.* [14] reported for atomically dispersed Pt⁰ and Pd⁰ in Y-zeolite a shift of +1.3 eV for Pt 4f and +1.4 eV for Pd 3d levels and they ascribed them due to the combined effect of electronic interaction between the two metals and the different particles geometry. Pederson and Lunford [15] observed for Ruthenium system in Y-zeolite in analogy with Verdine *et al.* a shift of 0.9 eV. Bileon *et al.* [16] observed a shift of +0.6 eV in binding energies for Pt 4f electrons in reduced Pt/SiO₂ system. Escard *et al.* [17] reported that XPS energy shifts of Ru on Alumina supported system are greater than those on silica supported system and they suggested that the changes are due to formation of Schottky barrier as proposed by Solymosi [18]. Katrib *et al.* [19] found similar trend with Ir supported system. The general experimental results of these many studies are now well established. The core level binding energies (E_B) generally decreases with increasing particle size. The present study add further support to these many studies.

Studying Table-3 it could be concluded that with the increase in Ag loadings the B.E. of $\text{Ru}_{3d_{5/2}}$ decreases. The change in B.E. (Δ B.E. = 1.5 eV) in going from pure ruthenium to Ag/Ru atomic ratios of 100:20 suggests that apart from geometric effect of Ag, electronic effect of silver is also contributing in the observed change. Hence it could be added here that combination of Ru:Ag is also producing a new surface site through electronic interaction and hence contributing to the observed change. This is also confirming the SSIMS findings where a similar trend was observed.

The FWHM (Table-3) for alumina support reflect the affect of different parameters (like impurities on the supported system) prevailing in the real catalyst samples [20]. Rhodine *et al.* [21] while studying the highly dispersed catalyst system on silica and alumina supports observed the distortion in the peak shape of the alumina/silica supported system and they attributed it to presence of impurities which modifies the surface geometry.

Experimental

The polycrystalline bimetallic system was prepared from RuCl₃ and AgCl₂ by co-impregnation method described previously [22]. The composition of the prepared samples were

determined by Atomic Absorption Spectroscopy. The samples are designated as RM/ x:y where x:y is the ruthenium:silver ratio in the sample.

The surface concentration of ruthenium and silver were determined with Secondary Ion Mass Spectroscopy SIMS in its static mode. The positive secondary ions generated on bombardment of the surface of the catalyst with an argon ion beam were analyzed using a VG 12-12 quadrupole mass spectrometer. The incident argon ions had an energy of 2KeV, a current of 1 nA/Cm² was used.

XPS spectra were recorded in an ESCA-III Instrument, using MgK α radiation. Targets were prepared from powder samples. Prior to the analysis the samples were sputtered with an argon ion current of 20 μ A for 5 minutes to remove hydrocarbons adsorbed on the catalysts surface. The low atomic concentration of 1B metal and the overlap of contamination C1s peak on the strongest Ru3d_{3/2} signal complicate the interpretation of the spectra. Peaks used for quantitative analysis were Ru3d_{5/2} and the Al_{2p}.

Conclusions

The following conclusions could be made from the SSIMS and XPS studies.

- (i) Ag is present on the surface of Ru, blocking the emission of Ru.
- (ii) Ag interact with Ru forming Ru:Ag bimetallic complex producing a new surface site.
- (iii) The shift in Ru electron binding energies and change in FWHM of the Ru peaks reflects the presence of combined affect of particle size and electronic interaction produced by Ru:Ag interaction.
- (iv) The study also very clearly presents the reliability of two different UHV techniques in studying these types of systems.
- (v) The informations obtained from this study could be combined with other spectroscopic techniques like IR, EELS, TPD, to have a very clear and reliable characterization of the complicated solid systems.

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