X-ray Diffraction Studies of Ru:Ag/Alumina Supported Bimetallic System

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Summary: Ru:Ag alumina supported bimetallic system was prepared by co-impregnation method and characterized using X-ray diffraction technique. On the basis of experimental data the intensity lines corresponding in Ag, Al, Ru, RuO with Ag occurring at the surface of Ru, as island were found. The shift in the angle of diffraction and the change in the intensity of the Ru peaks samples indicates the presence of particles greater than 5 nm dispersed randomly on the catalyst surface. At 0.02% Ru:Ag atomic ratios no XRD intensity line of Ag was found indicating that Ag is present on the surface in the form of very small particles. The metal dispersion calculated from the XRD data reveals geometric effect of Ag rather than any Ru-Ag electronic interaction.

Introduction

X-ray diffraction line broadening is widely used for measuring metal particle size. Introductory accounts for the technique in relation to catalysts examination are available in references [1-3]. The simplest method to evaluate XRD profiles is the application of Scherrer equation to obtain average crystallite size [4,5]. Recently more detailed information has been extracted e.g. the distribution of crystallite size, the presence of strain and an indication of crystallite shape.

The crystallite size distribution from X-ray line profile analysis can be complicated by spurious oscillations. A method for the crystallite size distribution by the use of a least squares procedure with a stabilization scheme has been described [6]. One such correction procedure was applied to obtain crystallite size distribution in Platinum dissolved from its alumina support [6]. The contribution of strain in the crystallite to the peak shape was not considered in that case. A comprehensive X-ray study has been made of Platinum on Davison Silica Catalysts prepared by methods devised and studied in detail by Moss *et al.* [7]. The Platinum was strain free or nearly spherical except in catalysts where Platinum particles were of the same size as those of the pores in the silica. The crystallite size distribution were sharper for catalyst prepared by impregnation, as compared to those prepared by ion exchange.

X-ray diffraction can be employed to study alloy formation in bimetallic and multimetallic catalysts. Inferences can be deduced from the position and shape of the diffraction peaks [7].

However limitations apply in studying these type of systems [8]. Inspite of all these limitations It is still a valuable techniques in studying supported catalysts [9-14].

Results and Discussion

Figures 1 to 5 presents the X-ray diffraction pattern of the catalyst system. Due to low Ag loadings and very small particle size less than 5.0 nm which were beyond the detection limit of the instrument, the X-ray intensity line corresponding to 0.02% Ag were not observed.

From the study of figures 1 to 5, it could be concluded that:

1   no systematic decrease in the intensity of Ru with the increase in Ag doping could be observed.

2.   the Ru is present in metallic and in oxide form.

3.   the silver is present in the form of metallic and oxide form having particles bigger than 5.0 nm.

4.   the change in the intensity line of the second and third intense XRD peak for Ru.

5.   a shift in the XRD line intensity with angle of diffraction.

Discussing the results of the study, the trend in the change in intensity lines of Ru with the increase in Ag doping suggest that perhaps Ag is present in different particle sizes and shapes [15]. The shift in the angle of diffraction with Ag doping suggests that some of the Ag particle are present in the close vicinity of Ru not forming Ru-Ag bimetallic.
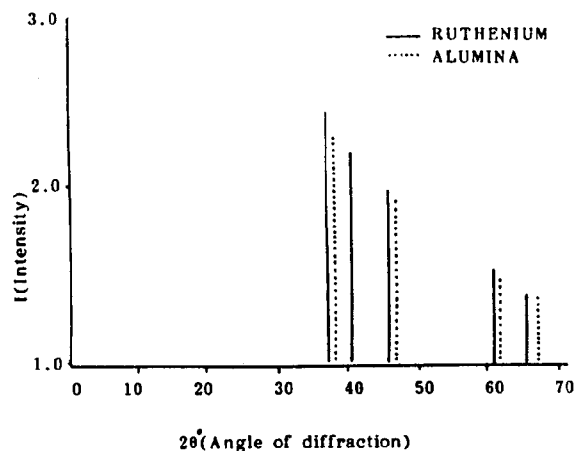
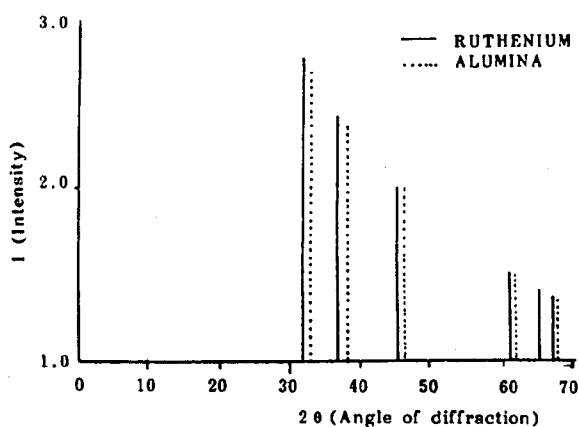Fig.1:   XRD result of 100:00 catalyst sample.

Fig.2:   XRD results of 100:02 catalyst sample.
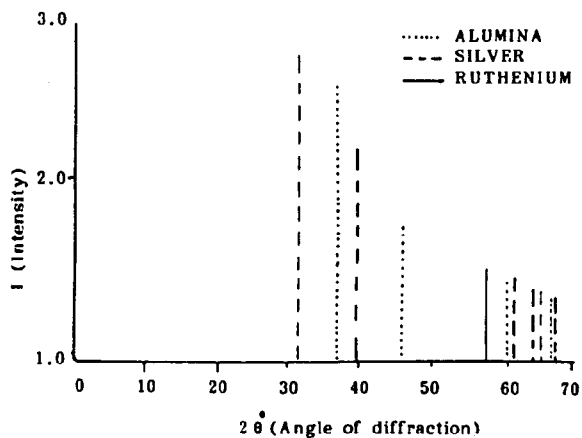

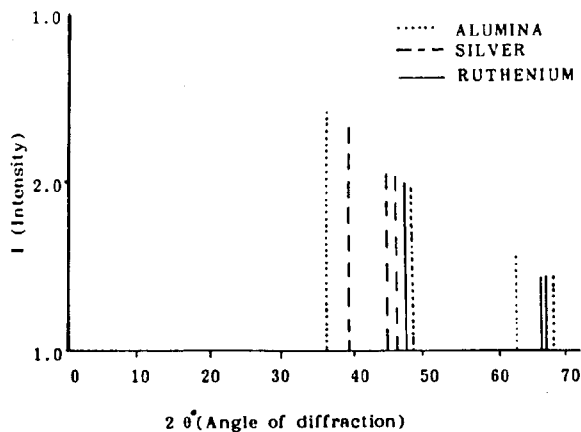Fig.3:   XRD results of 100:05 catalyst sample

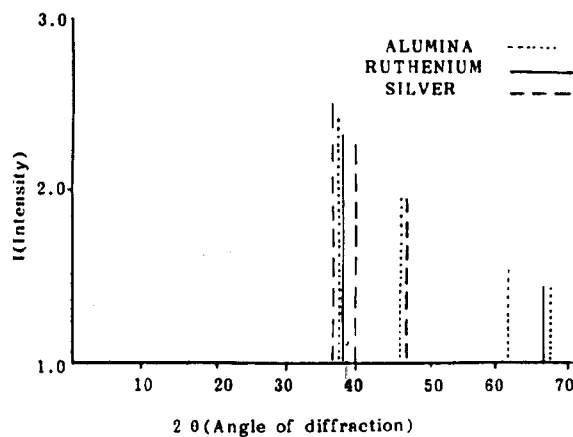Fig.4:   XRD results of 100:10 catalyst sample.

Fig.5:   XRD results of 100:20 catalyst sample.

This also reflects the sensitivity of this technique in studying these type of system. Only particles greater than 5.0 nm and above could be detected by this technique. The change is intensity lines of different samples of Ru further demonstrate this effect that there are particles of different diameter are present. On 100.02 catalyst sample particles below 5.0 nm which is beyond the detection limit of XRD [16] are present. Wolf et al. [12] observed similar change in intensity lines with the increase in tungsten loadings and they attributed it to the change in crystallite shape with the addition of tungsten. This suggestion further supports the findings that the change could be the effect of some type of surface changes induced by the addition of Ag. Moss et al. [17] observed in their XRD study on a 10% Pd/SiO₂ catalyst that the

Table-1: Measured characteristics of the catalysts samples.

Catalyst Samples	Surface Area m^2g^{-1}	Ru loadings %(w/w)	Ag loadings % (w/w)	Ru/Ag atomic ratios (%)	100*Ru (Ru + Ag)[a]
		on alumina support			
100:00	134	1.02	0.00	0.00	100
100:02	141	0.98	0.019	1.93	98
100:05	143	0.91	0.051	5.60	95
100:10	148	0.96	0.094	9.76	91
100:20	152	0.90	0.192	21.33	83

a = Atomic Adsorption Spectroscopy

change in the observed spectra could be due to the formation of a Pd-Si phase. In the present study any type of phase transformation was not observed. It is suspected that perhaps this transformation occurs at a higher temperature than the one used in this study. It is also suggested that this difference in the XRD spectra which is observed in this study could be due to the influence of combination of different parameters apart from the presence of Ru, RuO, Ag, AgO and Al.

Table-2 summarizes the crystallite size calculated from the XRD data. These calculations are based on the X-ray line broadening using Scherrer equation [18]. Studying Table-2, no consistent trend in crystallite size could be observed with the addition of Ag. It is further proposed that Ag is present in the form of crystallits, some of Ag particles covers the Ru surface and some are present in the close vicinity of Ru, not producing any electronic interaction. The Ag particles present on the surface or Ru exerts the geometric effect, consequently blocking the emission of Ru.

Table-2: Crystallite size calculated from XRD data.

Catalyst samples	Crystal size (nm). Alumina Supported
100:00	13.76
100:02	10.21
100:05	21.88
100:10	18.40
100:20	17.90

Table-3 presents the dispersion calculated from XRD data [19]. The results of this study gave further support to the argument that addition of Ag introduces no definite trend in metal dispersion [21]. It has been well documented in the literature that addition of an inactive metal on the active metal not only increases the surface area of the

metal but also induces surface modification which finally results in the different catalytic behaviour [21]. But not such modification was observed in the study.

Table-3: Dispersion calculated from XRD data.

Catalyst Samples	Dispersion (%)
100:00	23.49
100:02	26.00
100:05	21.66
100:10	19.16
100:20	20.5

Experimental

Catalysts preparation

The Ruthenium-Silver series of catalysts supported on alumina were prepared by the method suggested in reference [21] using co-impregnation method. Ruthenium trichloride trihydrate and Silver Chloride (Analar Grade) were used for catalysts preparation. Five catalyst samples were prepared. One catalyst sample contains only Ru. Four catalysts contained Ru and Ag in the atomic ratios 0.02, 0.05, 0.10 and 0.20. To ensure high metallic dispersion loading of only 1% w/w of Ru was used. The atomic ratios of each catalyst was checked by Atomic Adsorption Spectroscopy. The B.E.T. surface area of each sample was measured and the results are summarized in Table-1.

Sample mounting and handling

All catalyst sample were analyzed using a Phillips PW 1830 powder diffractometer using Nickel filtered Copper K Alpha radiation with generator settings of 49 keV and 20 mA.

About 0.5 gm of the powder sample is pressed into the glass window backed by a glass slide and smoothed to an even packing. After carefully mounting the sample into the diffraction chamber, the sample was scanned from the Bragg angle $2\theta = 16°$ to $2\theta = 70°$. The peak identification was accomplished through comparison of measured spectra with ASTM powder diffraction data file.

Conclusion

The conclusion of this study could be summarized as follows:

1. The Ruthenium is present in metallic and oxide form.

2. The Silver is present in the form of very small particles on 100:02 sample, which is beyond the detection limit of the technique.

3. The discontinuity and the shift in the XRD line intensity is perhaps due to the presence of Ru, RuO and Ag, AgO.

4. The change in the intensity of Ru peaks indicates the presence of different particle sizes and shapes.

5. The mixed trend observed in the crystallite size (Table-2) is possibly due to presence of Ag islands around Ru metal, exerting a geometric effect.

6. No Ru:Ag electronic interaction was observed in the study.

7. It could be generalized from the present study that the role of Ag is mainly geometric rather than any electronic and surface modification.

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