

Transmission Electron Microscopy (TEM) Study of Polycrystalline Ru:Ag/Alumina Supported Catalyst System.

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Transmission Electron Microscopy (TEM) was used to characterize bimetallic Ru/Ag Catalyst samples dispersed on a high surface area Alumina support. The addition of Ag increases the metal dispersion but no consistent trend is observed. Ag forms crystallites of various shape and sizes, some of them are present in the close vicinity of Ru but not forming Ru:Ag bimetallics. A part of Ag crystallites cover the Ru surface hence blocking Ru emission. These irregular shaped crystallites are possibly responsible for the increase in metal dispersion. Particles below 2.5 nm were Ag particles, between 2.5 to 5.0 nm were Ru:Ag mixed crystallites and above that were Ru particles. The data has been discussed in terms of geometric effect caused by the addition of Ag.

Introduction

Transmission Electron Microscopy (TEM) is a valuable characterization tool for studying heterogeneous catalysts. In the case of supported metal catalysts it is possible to use a TEM to probe the nature of dispersed phase (particle size, composition) and its structural relationship with the support¹⁻¹⁰. Energy dispersive x-ray data in conjunction with microprobe analysis has enabled the metal composition of the particles to be examined⁵. The present study was conducted to characterise the supported Ru:Ag/Al₂O₃ catalysts system and to observe the effect of Ag addition on the particle shape and dispersion of the active metal.

Experimental

Catalysts Preparation

Catalyst samples were prepared by coimpregnation method using RuCl₃ and AlO₃ dispersed on the high surface area aluminum oxide supports varying the atomic ratios of Ag/Ru from the sample without Ag(100:00) and with 0.02 (100:02), 0.05 (100:05), 0.10 (100:10) and 0.20 (100:20) % Ag. Catalyst preparation procedures are described in detail elsewhere¹³.

Sample Preparation for TEM Analysis

Samples required for TEM analysis were first reduced for 30 minutes in flowing hydrogen at 770 K to remove any carbon deposits which may interfere with the image contrast and with EDAX analysis. The samples were then carefully splintered into very small crystallites in an agate mortar. The crystallites were dispersed in acetone. A drop of suspension was transferred to a porous carbon film supported on a metal grid and acetone removed by evaporation. The grid was checked for specimen quality under an optical microscope before analysis in the electron microscope (EM 420 Phillips). Samples were examined in a TEM at an accelerating voltage of 400 KeV.

TEM Analysis

Representative electron micrographs of the catalysts are shown in figures 1-4. The electron micrographs were enlarged 2.5 times and the diameter of the metal particles was measured using TGA -10 particle size analyser. The particle size determination was done by randomly measuring the size of approximately 200-500 particles on the TEM micrographs. Only particles with a diameter of 1.5 nm and above are included. The metal dispersion was calculated, assuming the particle shape to be spherical¹¹ and the methods described in references 12 and 24.

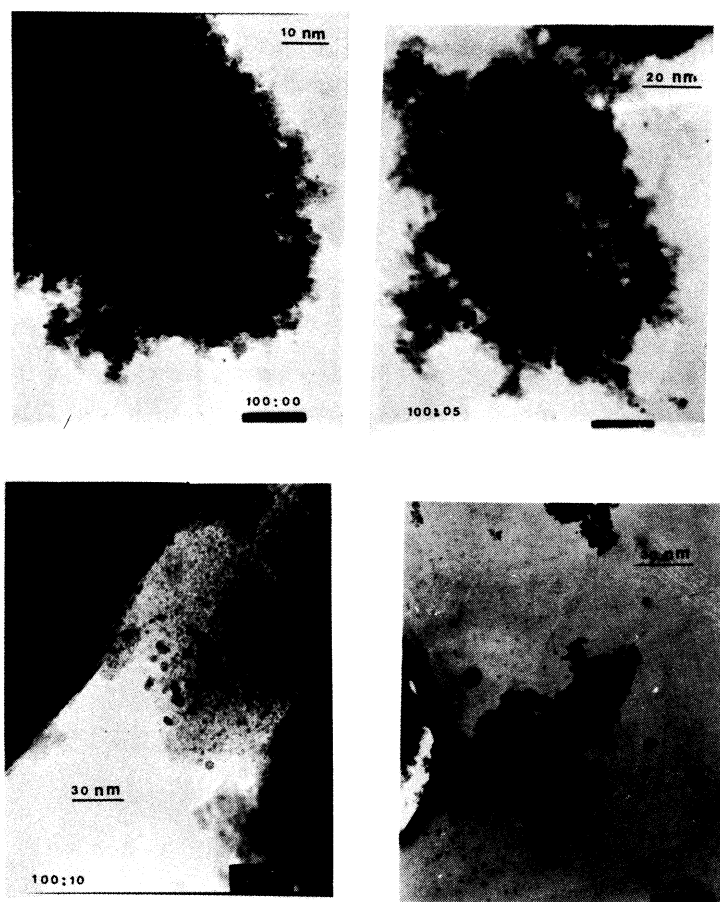


Figure 1-4. Representative TEM micrographs of the system.

Discussion

TEM micrograph of the alumina support indicates that the support is γ -alumina. The polycrystalline nature of the support confirms that the structure of the support is heterogeneous, Figure 5¹³.

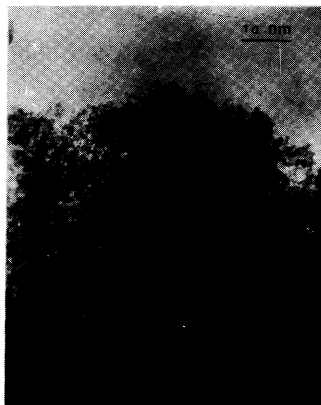


Figure 5. The TEM micrograph of the alumina support.

The majority of particles in the Ag rich samples, in the range of 1.5-2.5 nm were found to be silver on EDAX analysis. Particles in the range of 2.5-5.0 nm gave signal for Ru and Ag indicating the presence of Ru and Ag in the close vicinity. It could also be concluded from the study that the number of Ru, Ag crystallite increases from lowest to the highest Ag loadings. Figure 6 presents the diffraction pattern of (100:20) sample. The appearance of additional rings in the pattern support the suggestion that Ru, Ag do not form bimetallics but are present close to each other. The addition of Ag to the catalyst system increases the dispersion of metal particles (table 2) but no definite trend is observed. It is proposed that the addition of Ag produces irregular shaped particles (Figure 7) which may have led to an increase in the surface area of the active metal but in some cases blocks the emission of Ru hence decreasing the metal dispersion. Vannice et al²⁵ studied the supported bimetallic system. They postulated that the addition of inactive metal produces structural promotion in the catalyst system due to electronic effect resulting in the change in the system. Studying figures 1-4 it could be suggested that the role of Ag in the present system is geometrical. This would be consistent with the idea that one metal component is chemisorbed on the surface of the other producing the surface site responsible for the change¹⁴⁻¹⁹. A number of other authors have postulated this type of argument for the nonlinearity in the increase in metal dispersion²⁰⁻²³.

By assuming spherical crystallites the specific metal surface area, defined as the surface area per gram of metal calculated by the procedures described in reference²⁴ and presented in table 2.

Table 1. Specific metal surface area/gram of metal calculated from TEM data

Catalyst	Al ₂ O ₃
-(m ² g ⁻¹)-	
100:00	78
100:02	80
100:05	76
100:10	82
100:20	74

The addition of Ag have no appreciable effect on the specific metal surface area calculated from the TEM data. This suggest that the addition of Ag on the surface does not produce any new surface instead

it forms isolated Ag islands which randomly blocks Ru surface.

Table 2 presents the catalyst dispersion and the particle size distribution on the to supports estimated by TEM, this table also supports the argument presented in Table 1. The data presented in table 2 clearly demonstrate the effect of addition of Ag on the surface of the catalyst system. This also suggest that the role of Ag is merely blocking the Ru surface sites coupled with the formation of Ru, Ag crystallites in the close vicinity of the surface¹³.

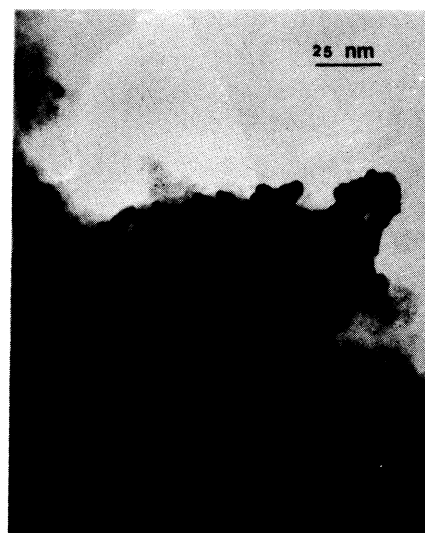
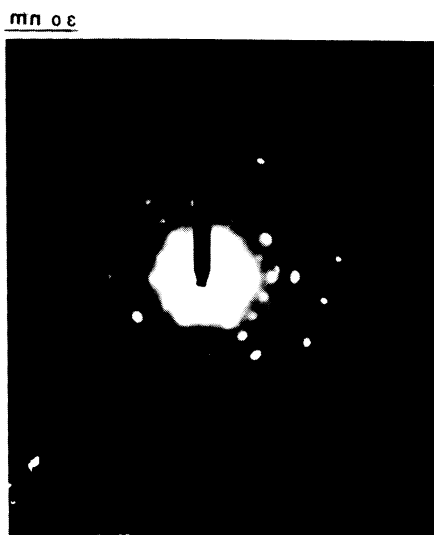


Figure 6. Diffraction pattern of 100:20 catalyst sample.

Figure 7. TEM micrographs of 100:20 catalyst sample showing the effect of Ag addition on the particle shape.

Table 2. Average catalyst size and dispersion calculated from TEM micrographs

Catal. Desig.	Catal. Support.	No. of counted particles (no)	Surface Number-Diameter (nm)	Vol. Aup. Diameter (nm)	Metal Diameter (nm)	Disp. %
100:00	Al ₂ O ₃	410	4.00	6.11	6.19	23.77
100:02		265	4.08	6.00	6.91	20.15
100:05		309	3.12	5.60	6.87	26.78
100:10		316	3.72	5.70	6.02	19.75
100:20		232	3.65	5.14	6.31	22.18

Studying table 2 it could also be seen that the volume no. average particle diameter for the system is 6.35 nm. Assuming that ruthenium crystallites are composed of spheres of volume $(6.35)^3 \text{ nm}^3$ and knowing the amount of ruthenium added to 1.0 gm of catalyst, it is possible to calculate the number of cubes present and hence the surface area of ruthenium exposed. From a ruthenium metallic density of $1.24 \times 10^7 \text{ gm}^{-3}$ ^{11,12}, the total area of the ruthenium exposed per gram of the catalyst was calculated to be 0.66 m^2 .

Conclusions

Electron microscopy studies of the catalyst system demonstrated several important features.

1. Ru, Ag crystallites were identified in the size range 2.5-5.0 nm.

2. Particles less than 2.5 nm were monometallic Ag
3. Particles larger than 5.0 nm were monometallic Ru.
4. The addition of Ag have no definite effect on the dispersion and metal surface area of the system.
5. The role of Ag in the present study is merely geometrical, partially blocking Ru, rather than surface modification.

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