Characterization of an Ultrafine Ni–Ru Alloy Powder and of Alumina-dispersed Bimetallic Particles Derived from the Molecular Cluster $(C_5H_5)NiRu_3H_3(CO)_9$

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The tetrahedral heterobimetallic cluster $(C_5H_5)NiRu_3H_3(CO)_9$ produces a finely divided Ni–Ru alloy powder by chemically induced decomposition in tetrahydrofuran and an alumina-supported bimetallic catalyst, active in ammonia synthesis, by thermal treatment under flowing dihydrogen.

It is now generally recognized that mixed-metal clusters may serve as precursors to dispersed bimetallic crystallites, often exhibiting improved catalytic activity when compared with the monometallic counterparts.[1] Several recent reports have dealt with investigations on bimetallic catalysts prepared from certain bimetallic carbonyl clusters; combinations studied have been: Fe–Os,[2] Fe–Ru,[2,3] Fe–Co,[2,4] Fe–Pd,[5] Ni–Os[6] and Fe–Rh,[7] and, in some instances, microanalytical evidence for the presence of bimetallic particles has been provided.[2,3,5]

Finely divided powders of metals or alloys are of great

Table 1 Ammonia production rates[a]

Catalyst precursor	Temp./°C	Productivity[b]
2 ($NiOs_3$)	360	0.35
	400	0.69
	450	1.71
1 ($NiRu_3$)	375	3.13
	400	4.56
	450	2.26
3 (Ru_3)	350	6.93
	400	7.14
	450	2.57

[a] Feed: 100 ml min^{-1} of an N_2–H_2 (3:1) mixture at standard temperature and pressure. 2% metal for each catalyst. [b] mg of NH_3 (g cat.)$^{-1}$ h^{-1}.

interest both in fundamental research[8] and in industrial powder technology.[9] These nanometre-scale materials often exhibit particular properties unobserved in molecular atomic species or in the bulk solid state. Recently nanometre-scale iron particles have been prepared by metal clustering in cold pentane[10] and finely divided alloy powders have been obtained by reducing metal salts in organic phases.[11]

We report the preparation and the characterization of a bimetallic alloy powder obtained by chemically induced decomposition of the molecular cluster $(C_5H_5)NiRu_3H_3(CO)_9$ **1**,[12] containing a tetrahedral framework of metal atoms, which has previously been studied as a heterogeneous catalyst precursor for hydrogenation.[13] This paper also deals with the use of the same cluster to prepare an alumina-supported Ni–Ru bimetallic catalyst active in ammonia synthesis.

Complex **1**, treated in tetrahydrofuran with alcoholic KOH, at room temperature, firstly undergoes deprotonation of the bridging hydride ligands (IR monitoring), then decomposes in a few hours, giving a black, finely divided, conductive, metallic powder, insoluble in mineral acids. It was separated by centrifugation, washed several times with water, ethanol and ether, and dried *in vacuo*. X-Ray diffraction analysis showed that it is amorphous and elemental analysis revealed the presence of carbon (6%) and hydrogen (1%).

The powder was characterized by transmission electron microscopy (TEM). Bright field images were recorded on a Philips CM 30 microscope (LaB_6 filament, 300 keV), equipped with an energy-dispersive EDAX PV 9900 X-ray spectrometer (EDX). The powder consists of ultrafine spheroidal particles ranging in diameter from 2 to 5 nm. A large number of individual metal particles have been analysed in the nanoprobe mode, with a spot size of 6.5 nm; care was taken that the analyses encompassed only one particle. Only ruthenium and nickel were detected in these aggregates, the observed Ru/Ni atomic ratio (3.4 : 2.5) being the same, within experimental error, as that of the starting cluster **1**. Traces of potassium, as a possible contaminant, were occasionally observed over large areas of the product. This material represents, to our knowledge, the first example of a nanoscale bimetallic powder prepared, by chemical decomposition, from a mixed metal cluster. Particle sizes are comparable with those obtained with other techniques, such as laser breakdown vapour deposition.[14]

Furthermore, cluster **1** was supported on γ-alumina (modified with 30 wt% K as KOH and treated as in ref. 15), by evaporating to dryness its chloroform solution. The IR spectrum of the material obtained (total metal content 2 wt%) gave practically the same bands, in the carbonyl stretching region, as the pure solid **1** (KBr disc), consisting of four strong bands at 2001, 2016, 2059 and 2090 cm^{-1} and suggesting a simple physisorption of the cluster on the support. Following the encouraging results obtained by using ruthenium compounds as catalyst precursors in ammonia synthesis,[15,16] we have started to study the effectiveness of the product of decomposition of supported **1** in this process: it was placed in a tubular microreactor, gradually decomposed under H_2 and fed with an N_2–H_2 mixture, as described in ref. 15. The isostructural cluster $(C_5H_5)NiOs_3H_3(CO)_9$ **2** and $Ru_3(CO)_{12}$ **3** were also processed in the same manner as **1**, for comparison. The observed ammonia productivities are reported in Table 1.

The data in Table 1 show that **1** produces a more effective catalyst in ammonia synthesis than its osmium homologue. However, the catalyst derived from the homometallic cluster **3** is the most active, probably because the presence of nickel causes dihydrogen to be absorbed strongly, which could inhibit ammonia synthesis, in spite of the excess of dinitrogen in the feed mixture. In the case of the two ruthenium catalysts, the activities decrease at 450 °C, indicating the attainment of reagent equilibrium conversion below this temperature.

After the catalytic process, the Ni–Ru catalyst was subjected to TEM investigations, under the same conditions as described above. The catalyst consists of amorphous metal particles dispersed on γ-alumina, most of them exhibiting spherical or possibly icosahedral shape. Also in this case EDX analysis showed the bimetallic nature of these dispersed metal particles, the Ru–Ni atomic ratio being practically the same as in the starting material. The size of these particles was in the diameter range 3–6 nm, a result which is comparable with those previously observed for bimetallic particles.[2,3,5]

This work has been supported by CNR, Progetto Finalizzato Chimica Fine II. Preliminary TEM studies were carried out at Centro Strumenti, University of Modena and at Istituto MASPEC, CNR, Parma; we thank Dr. G. Salviati (MASPEC) for skilled assistance.

Received, 22nd June 1990; Com. 0/02816I

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