Reduction study of Co_3O_4 model catalyst by electron microscopy

D. Potoczna-Petru and L. Kępiński

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław 2, Poland

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Evolution of microstructure and morphology of Co_3O_4 particles in the model systems during reduction in hydrogen was studied by transmission electron microscopy methods. Based on SAED and HRTEM results we found that the degree of reduction of Co_3O_4 strongly depends on the particle size and morphology, which are determined by the pretreatment conditions. Preferential epitaxial growth of CoO and Co phases on Co_3O_4 during reduction was deduced from HRTEM images.

KEY WORDS: Co_3O_4 reduction; model catalyst; nanostructures; TEM; HRTEM

1. Introduction

Cobalt catalysts are important in industrial processes involving hydrogenation (methanation, Fischer–Tropsch synthesis). Commercially the activation of cobalt catalysts in this reaction requires occurrence of metallic cobalt and generally occurs via reduction of an oxide form.

The process of reduction of supported cobalt catalysts in H_2 was investigated by many advanced techniques [1–14]. It was established that the ability of the cobalt catalysts to undergo reduction is greatly affected by support, preparation conditions and metal loading. For reference purposes the reduction of unsupported Co_3O_4 was also investigated by many techniques [1–3,6–15]. Two distinct peaks [2,7,14], a peak with low temperature shoulder [3,6,12] or a single peak [10,11,13], were observed in temperature-programmed reduction (TPR) spectra of unsupported Co_3O_4. From TPR study [3] it appears that the reduction of bulk Co_3O_4 does not start until 573 K and Paryjczak et al. [15] established that the temperature at which Co_3O_4 reduction begins increases from 448 to 503 K with temperature of Co_3O_4 preparation increasing from 573 to 973 K. Generally it is assumed that the reduction of Co_3O_4 proceeds in two steps [2–4,6–8,12]:

$$Co_3O_4 \rightarrow CoO \rightarrow Co$$

In previous papers [1,2,9] it was shown that the particle size is a determining factor in the reduction process of oxidized cobalt catalysts. An increase of the particle–support interaction with decreasing particle size is to be expected and resulting species can be reduced only at elevated temperature [2]. On the other hand, the results of Okamoto et al. [9] suggest that the ability of Co_3O_4 in Co/SiO_2 catalysts to undergo reduction decreases with increasing particle size. The authors assigned two peaks below 600 K in TPR spectra to Co_3O_4 particles with different sizes (7 and 25 nm). For unsupported Co_3O_4 with particle size of 50 and 120 nm TPR peaks at 570 and 590 K, respectively, were reported [9]. Influence of the distribution of particle sizes on the character of the oxidation/reduction process in Co/TiO_2 catalysts was suggested by Martens et al. [4]. The authors proposed also that for large particles metal-assisted reduction may occur.

Existing differences in the literature concerning the reduction of unsupported Co_3O_4 used as the reference system for cobalt catalysts, and lack of detailed microstructure investigations of this process led us to study the influence of the Co_3O_4 particle size on the reduction process by using transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). This paper is a continuation of work in our laboratory on the structure evolution caused by various treatments of real [16] and model catalysts in the form of thin films [17–20]. Particular attention was focused on the microstructure change in the nanoscale and on the process of formation of new phases during successive stages of reduction.

2. Experimental

We prepared model samples containing Co_3O_4 particles with various sizes in a planar form suitable for study by TEM techniques. Thin cobalt films of about 16 nm thick evaporated in an Edward's evaporator onto stainless steel microscope grids covered with an amorphous carbon layer were used as the starting material. Co_3O_4 particles with various mean particle sizes were obtained by heating the films in air at 873, 973, 1073 and 1173 K for 2 h. During such treatment catalytic gasification of an amorphous carbon layer took place. The exothermic effect of oxidation and Co–C interface behaviour have influence on the structure of the Co_3O_4 crystallites formed. As resulted from a previous study [17], during oxidation of Co particles supported on carbon flattening of oxide crystallites took place.

Reduction of the samples was performed in a quartz tube furnace in purified H_2 flowing at atmospheric pressure at temperature 573–773 K for 4 h, i.e., under conditions usually used in the reduction of cobalt catalysts. After each stage

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of the thermal treatment the samples were studied with a Philips CM 20 electron microscope. The mean particle size was calculated on the basis of size measurements of about 500 particles.

3. Result and discussion

Figure 1 shows TEM images of the samples heated in air at 873, 973, 1073 and 1173 K for 2 h. The mean size of the particles, identified as pure Co_3O_4 basing on SAED and HRTEM (figure 2), was measured as 5.3, 12.1, 20.3 and 42.4 nm, respectively. Particles with rounded contours formed as the result of heating at 873 K (figure 1(a)), while those heated at higher temperature exhibited polyhedral shape (figure 1(d)). From HRTEM images it appears that the particles are single crystals (figure 2). Treatment of the Co_3O_4 model samples with different particle size in H_2 at temperature 573–773 K resulted in various stages of Co_3O_4 reduction. SAED patterns of the samples reduced at 773 K (figure 3) show that complete reduction of Co_3O_4 to Co occurred for the sample with mean particle size of 5.3 nm while for other samples, besides Co, Co_3O_4 is present, with Co_3O_4 being dominant for the sample with largest (42.4 nm) particles. Phases identified in the samples reduced at 573, 673 and 773 K are summarised in table 1. TEM observations revealed that the reduction caused the morphology change in the particles. For the samples with the smallest particle size which were reduced to metal already af-

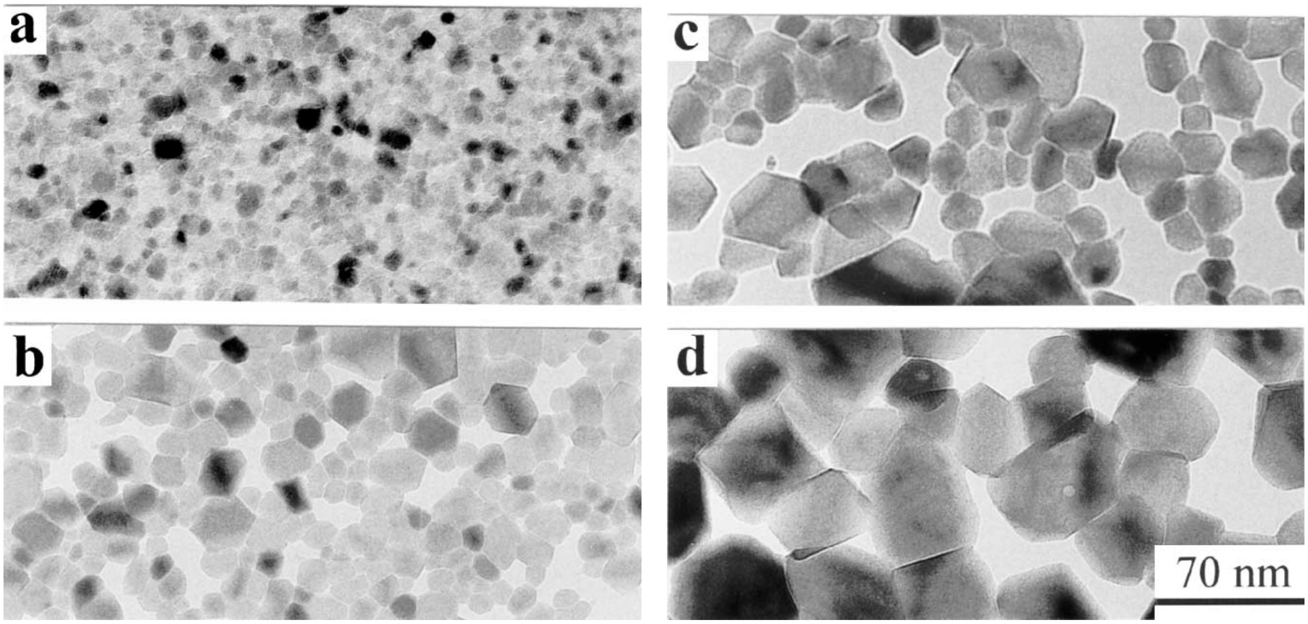

Figure 1. A series of TEM micrographs of Co_3O_4 samples differing in mean particle size: (a) 5.3, (b) 12.1, (c) 20.3 and (d) 42.4 nm.

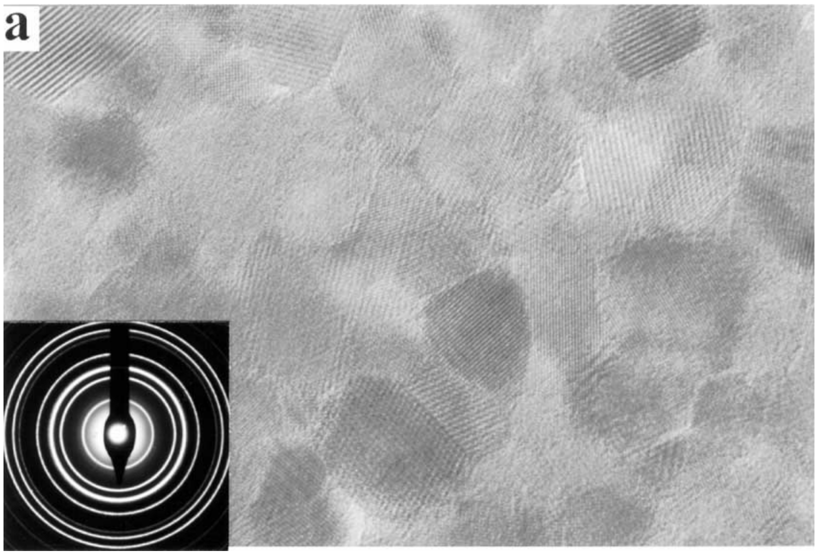

Figure 2. HRTEM images and SAED patterns (insets) of Co_3O_4 samples with mean particle size: (a) 5.3 and (b) 42.4 nm.

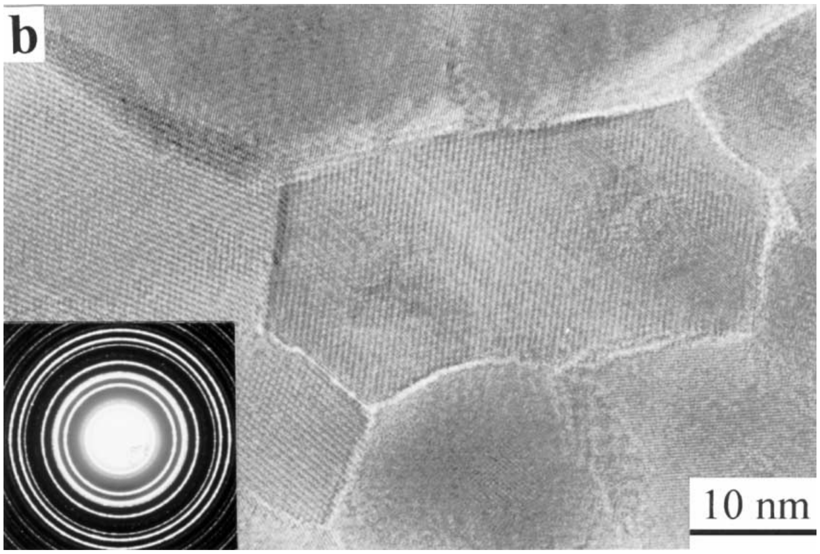

Figure 2. (Continued.)

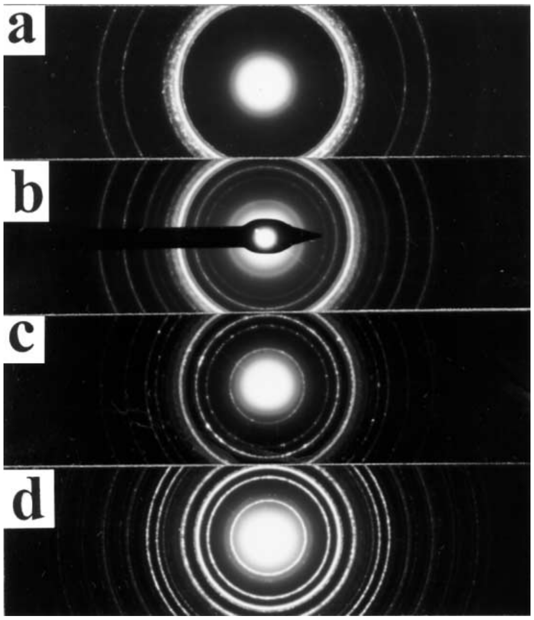

Figure 3. A series of SAED patterns of samples after reduction (H_2, 4 h) at 773 K with mean particle size: (a) 5.3, (b) 12.1, (c) 20.3 and (d) 42.4 nm. Identified phases are given in last column of table 1.

Table 1
Phases identified in the Co_3O_4 model samples after reduction in H_2 at various temperatures for 4 h.

Sample	D (nm)	Phases identified		
		$T = 573$ K	$T = 673$ K	$T = 773$ K
1	5.3	Co	Co	Co
2	12.1	Co_3O_4 CoO Co	Co_3O_4 Co	Co Co_3O_4
3	20.3	Co_3O_4 Co CoO	Co_3O_4 Small amount Co Trace CoO	Co_3O_4 Co
4	42.4	Co_3O_4	Co_3O_4	Co_3O_4 Trace Co

ter heating in H_2 at 573 K the morphology of the particles changed only slightly following successive reduction treatment. However, in the sample with mean particle size of 12.1 nm, the Co_3O_4 particles were not reduced completely after treatment at 573–773 K, as appeared from SAED data (table 1). The changes of morphology of the samples with mean particle size of 12.1 nm and 42.4 nm reduced at increasing temperature are presented in figures 4 and 5, respectively. It is evident that the morphology of the samples differs drastically. The sluggishness of the reduction kinetics in the samples oxidised at higher temperature allows for a better observation of the sequence of reduction stages (figure 5). Irregular areas with weaker contrast were formed in the particles reduced at 573 K (figure 5(a)). These areas increased in size and became more regular after reduction at 673 and 773 K (figures 5 (b) and (c)) and contained particles with higher contrast.

Details of the elementary steps of Co_3O_4 reduction were obtained from HRTEM study. Figure 6 shows HRTEM image and fast Fourier transform (FFT) pattern of Co_3O_4 after reduction at 673 K. Coexisting phases of Co, CoO and Co_3O_4 can be seen as well as their mutual crystallographic orientation. In region A wide lattice fringes, 0.47 nm, corresponding to Co_3O_4(111) are identified. Two kinds of nearly parallel lattice fringes with spacing 0.20 and 0.24 nm, occur in region B which could correspond to Co(111) and CoO(111) planes. Finally, in region C parallel 0.49 and 0.24 nm fringes occur. We postulate that the 4.9 nm fringes are actually Moiré fringes originating from overlapping of parallel CoO(111) (0.24 nm) and Co_3O_4(111) (0.47 nm) fringes. It means that the CoO phase grows on Co_3O_4 in a preferred orientation, such that the [111] directions of both crystals are parallel. Figure 7 shows an example of a large Co_3O_4 crystallite in [110] orientation (see FFT pattern A) that is partly reduced to metallic Co following reduction at

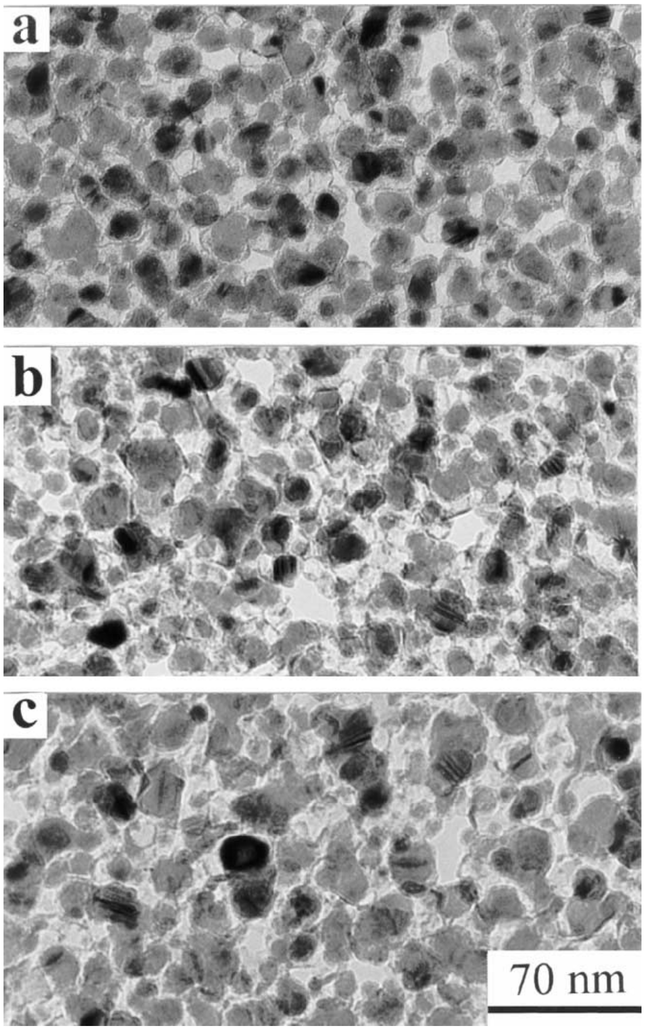

Figure 4. A series of TEM micrographs of Co_3O_4 sample with mean particle size of 12.1 nm after reduction (H_2, 4 h) at: (a) 573, (b) 673 and (c) 773 K.

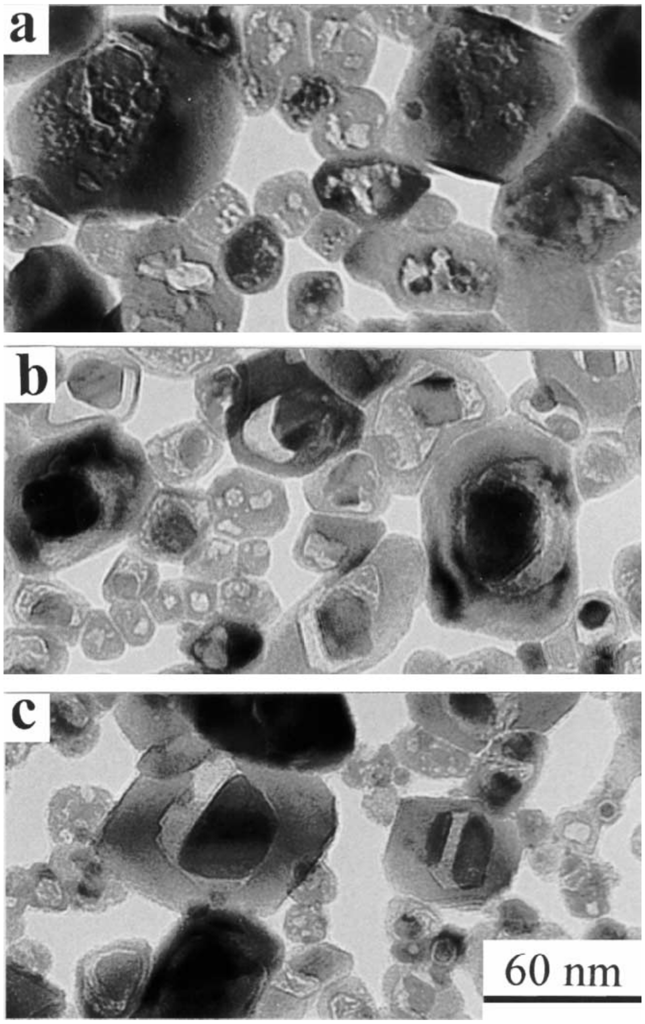

Figure 5. A series of TEM micrographs of Co_3O_4 sample with mean particle size of 42.4 nm after reduction (H_2, 4 h) at: (a) 573, (b) 673 and (c) 773 K.

773 K. The formed Co crystallite contains many stacking faults what results in a complex FFT pattern (B). It is seen from figures 6 and 7 that due to the nearly twofold volume contraction upon reduction to Co, empty spaces (voids) are formed in the Co_3O_4 crystallites.

In this study we established that the degree of reduction of Co_3O_4 depends strongly on the conditions of its preparation (figure 3, table 1). The particles obtained at 873 K were reduced easily to Co at 573 K while those obtained at 1173 K were not reduced even at 773 K (table 1). We suppose that two effects may be responsible for this: diffusion limitation occurring with increasing particle size and differences in the microstructure of the particles. The effect of microstructure of Co_3O_4 particles on the process of their reduction in H_2 may be interpreted in terms of the nucleation model [21,22]. According to this model, the kinetics of reduction involves an induction period. Furstenau et al. [23] by LEED, AES and XPS study of reduction of single crystal NiO(111) in H_2 postulated that the induction period preceding the reduction is controlled by the surface defect concentration. The effect of pretreatment conditions on duration of induction time in the reduction of cobalt molybdate was established by Haber [24]. Study of reduction of NiO (111) [23] evidenced that the reduction of the oxide proceeds through the formation of metal nuclei on the surface which subsequently form three-dimensional metal particles. Formation of three-dimensional Co particles following reduction of Co_3O_4 was also observed in our samples by SAED (table 1, figure 3) and HRTEM (figures 6 and 7) studies. The presented images (figures 5 and 6) show a rather peculiar morphology of the partly reduced crystallites. In most cases it appears that the reduction begins in the center of the particle, leaving the edges intact. Having no clear explanation for that we suppose that this behaviour may be caused by the special structure (a kind of texture) of Co crystallites formed by oxidation of planar Co films. On the other hand, we cannot exclude a role in the initiation of surface reduction of undetected surface impurity or defect of very low concentration. For samples containing particles with smaller, 12.1 nm mean size (figures 1(b) and 4) the induction time for reduction may be much shorter and the reduction process is much more advanced after 4 h time (figure 3, table 1). The morphology of

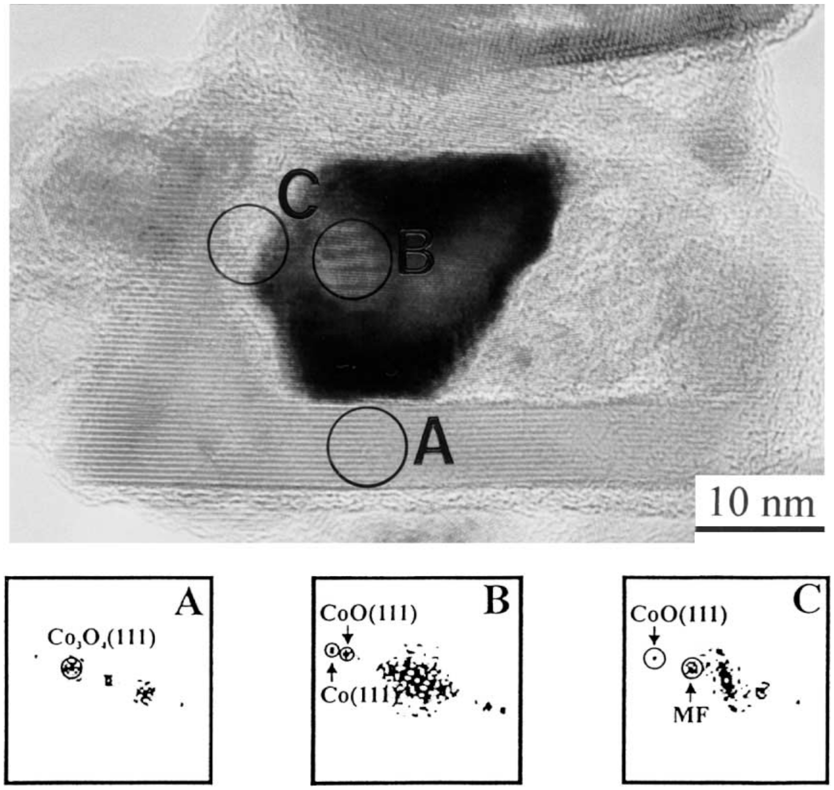

Figure 6. HRTEM image and FFT analysis of Co_3O_4 sample (20.3 nm mean particle size) after reduction (H_2, 4 h) at 673 K. Coexisting phases of Co, CoO, Co_3O_4 can be identified.

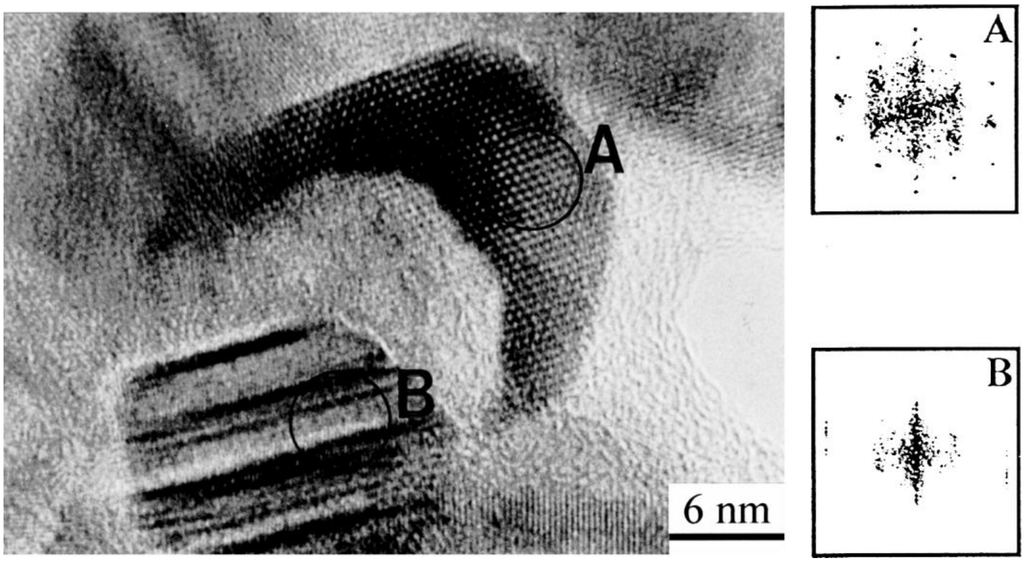

Figure 7. HRTEM image of Co_3O_4 sample (20.3 nm mean particle size) after reduction (H_2, 4 h) at 773 K. Co_3O_4 and Co can be identified.

the reduced samples (figure 4) is thus determined mostly by Co phase.

It can be expected that the Co_3O_4 particles with rounded shape obtained at lower temperature (873 K) have more structural defects than the well crystallized polyhedral ones obtained at higher temperature (figures 1 and 2). The defects present at the surface of the former particles facilitate the reduction. This interpretation is consistent with the finding of Paryjczak et al. [15] that increasing pretreatment temperature of Co_3O_4 in the range 573–973 K caused increasing temperature (448–503 K) in which the reduction began.

We conclude from SAED (table 1) and HRTEM (figure 6) that in early stages of reduction, lower cobalt oxide (CoO) was formed and this result is consistent with the previous literature data [2–4,6–8,12]. The growth of CoO occurred in an epitaxial manner on Co_3O_4 with CoO(111) planes parallel to Co_3O_4(111) planes. In the next stage the CoO was reduced to Co and again epitaxial growth with Co(111) parallel to CoO(111) was observed (figure 6). From analysis of SAED data (table 1, figure 3) it results that the relative amount of CoO decreases with increasing reduction temperature and in samples reduced at 773 K only Co_3O_4 and Co were established. We suppose that this phenomenon is caused by an autocatalytic effect of growing Co nuclei on reduction of Co_3O_4. Activated H_2 formed upon adsorption on metallic Co participates first of all in the reduction of CoO to Co due to spatial proximity of these phases. Autocatalytic reduction of CoO was reported in previous papers [4,24]. Haber [24] established that the addition of CoO to cobalt molybdate completely eliminates the induction period owing to the metallic cobalt formed in the first minutes of the reduction at 773 K.

Summarizing we can state that electron microscopy techniques have proved to be a useful tool for investigating the microstructure and phase evolution during reduction of Co_3O_4.

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