

Notes

Generation of Metal Nanoparticles on Montmorillonite K 10 and Their Characterization

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Introduction

Montmorillonite K 10 is a commercial acid activated clay which is useful as a solid Bronsted acid.¹ It is mesoporous in nature with laminar structure retained to a significant degree^{2,3} and exhibits high surface area. Such clays can be utilized as effective supports for various transition metal salts and ions.^{4,5} These supported reagents have been widely used in various organic reactions as solid acid catalysts and are gaining much importance from the environmental point of view.^{1,6} Metal salts and/or metal ions supported on montmorillonite K 10, for example, zinc chloride (clayzic), copper chloride (claycue), iron nitrate (clayfen), and so forth, and metal ions such as Zn²⁺, Cu²⁺, and so forth are used as solid acid catalysts in various organic reactions, namely Friedel Crafts, Diels–Alder, and so forth.^{1,4–11}

An important class of solid catalysts is metals. They are used for a number of processes such as hydrogenation of double or triple bonds in hydrocarbons, dehydrogenation of hydrocarbons, and oxidation of hydrocarbons into different value added products. Platinum metals act efficiently as catalysts for pollution control, like detoxication of exhaust gases from automobiles. In most cases, metal catalysts are prepared in the form of very fine small (1–100 nm) metal particles and are supported on different types of high surface area acidic oxide supports such as SiO₂, Al₂O₃, and so forth.¹² Such supported composites

are likely to act as bifunctional catalysts (metal + acid functions).¹³

Attempts are being made to generate metal clusters (size 4–5 Å) or metal nanoparticles in the interlayer spacing of montmorillonite.^{14–16} Recently we have successfully generated intercalated metal clusters (size 3–4 Å), and their thermal behaviors have been studied.¹⁷

Development of nanoparticles of metals on montmorillonite K 10 has not been reported so far. The present work reports the in situ generation of Ni and Co nanoparticles on montmorillonite K 10. Such metal nanoparticles supported on montmorillonite K 10 have been characterized by transmission electron microscopy (TEM) substantiated by X-ray diffraction (XRD), thermal analysis, and infrared (IR) spectroscopy.

Experimental Section

Montmorillonite K 10 (hereafter mont K 10) was obtained from M/S Aldrich. Deposition of metal acetate hydrates M(CH₃COO)₂·xH₂O (where M = Ni, Co) on mont K 10 was carried out by evaporating a 2% suspension of support in methanolic solutions of metal acetate to dryness in order to obtain a composite having a salt loading of 4.2 m mol g⁻¹ of support.^{3,7}

1 g of metal acetate loaded mont K 10 [M(CH₃COO)₂–mont K 10] was suspended in 100 mL of ethylene glycol in a double necked round-bottom flask and refluxed at 195 °C for 6 h in a nitrogen environment to form an in situ solid product of metal nanoparticles deposited on mont K 10 (M⁰–mont K 10). The product was recovered, washed with methanol till it was free from ethylene glycol, and then dried under nitrogen at about 50 °C for 3 h.

Equipment and Methods. Specimens for TEM were prepared by dispersing powdered samples in isopropyl alcohol, placing them on a copper grid, and allowing them to dry. Sample grids were examined by TEM using the smallest condenser aperture using a JEOL model JEM 100 C XII (100 kv) electron microscope. XRD patterns of powdered samples were taken in the range 2θ = 2–60° at the rate 6°/min (X-ray diffractometer JEOL, JDX-11 p 3A, Japan) using Cu Kα radiation. The TG, DTG, and DTA measurements were done with the thermal analyzer (TA Instruments, Model STD 2960 simultaneous DTA–TGA) with about 14 mg of sample in a platinum crucible at the heating rate 10 °C min⁻¹ in air as well as nitrogen atmosphere. FTIR spectra were obtained from KBr (analytical grade and dried at 110 °C) pressed disks of about 12 mm diameter and 1 mm thickness prepared by applying about 8 × 10³ bar pressure for 10 min on finely ground particles containing about 3 mg of material and 97 mg of KBr in the range 400–4000 cm⁻¹ using a Perkin-Elmer infrared spectrophotometer, Model 580 B.

Results and Discussion

The transmission electron micrographs of Ni⁰–mont K 10 (composite **I**) and Co⁰–mont K 10 (composite **II**) are shown in Figure 1. Most of the nanoparticles of metals

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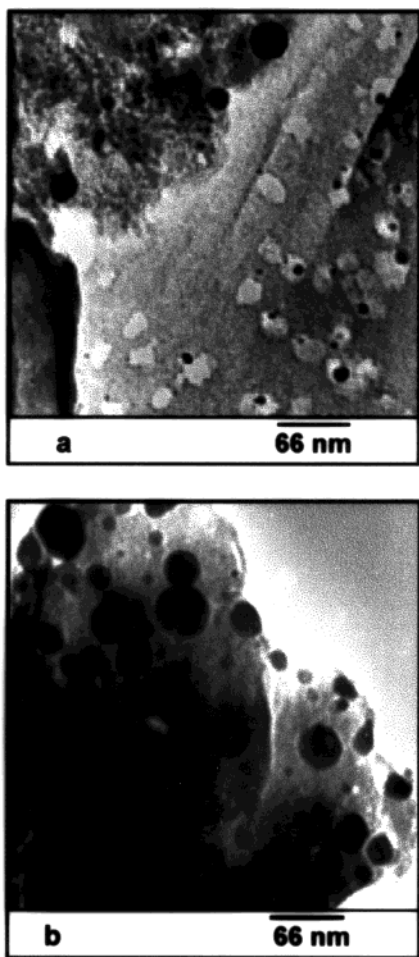


Figure 1. TEM images of (a) Ni⁰-mont K 10 and (b) Co⁰-mont K 10.

are round. The metal particles of composite **I** are up to 26 nm in size (Figure 1a) and are comparatively smaller than those of composite **II**, where the maximum size of the particles is limited to 40 nm (Figure 1b). It appears from Figure 1 that a wide range of particle size distribution occurred in both the cases and the metal nanoparticles are widely sprayed over the mont K 10 matrix.

The powder X-ray diffraction pattern of composite **I** shows peaks at 2.03 Å (111 reflection) and 1.76 Å (200 reflection), indicating the presence of Ni metal having a

face centered cubic structure¹⁸ on the clay matrix. Similarly, in the case of composite **II** the peaks at 2.05 Å (111 reflection) and 1.78 Å (200 reflection) show the presence of Co metal having a face centered cubic structure¹⁹ on the clay matrix. Such face centered cubic metal particles supported on high surface area mont K 10 are expected to show efficient catalytic properties.¹³

Thermal studies reveal that, in air atmosphere, oxidation of Ni⁰ in composite **I** and Co⁰ in composite **II** occurs in the temperature ranges 500–650 °C and 130–500 °C, respectively. On the other hand, under nitrogen atmosphere the metal nanoparticles in composites **I** and **II** are stable at least up to 700–800 °C. IR spectra of composites **I** and **II** show all the characteristic bands of mont K 10, and the disappearance of the acetate bands confirms complete reduction of metal acetate to metal.

Conclusions

Ni⁰-mont K 10 (composite **I**) and Co⁰-mont K 10 (composite **II**) are synthesized in situ by polyol reduction of nickel acetate and cobalt acetate impregnated mont K 10 having a salt loading of 4.2 mmol g⁻¹ of support. The TEM study reveals that nanoparticles of metal in composite **I** are up to 26 nm in size whereas the maximum particle size of the metal in composite **II** is about 40 nm. The XRD study shows face centered cubic structure of both the metals in composites **I** and **II**. From thermal studies, it is observed that, in air atmosphere, oxidation of Ni⁰ in composite **I** and Co⁰ in composite **II** occurs in the temperature ranges 500–650 °C and 130–500 °C, respectively, while under nitrogen atmosphere the metal nanoparticles of the composites are stable at least up to 700–800 °C. Such nanometal-clay composites may find application as bifunctional catalysts (metal + acid functions).

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