Cobalt(III) Complexes of H₂apmp

Bull. Korean Chem. Soc. **1997**, Vol. 18, No. 8 827

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Cobalt(III) Complexes of 1,3-Diaminopropane-N,N'-di-α-(β-methyl)-pentanoic Acid

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Received May 1, 1997

A novel ONNO-type tetradentate ligand, 1,3-diaminopro-pane-N,N'-di-α-(β-methyl)-pentanoic acid (H₂apmp) and its cobalt(III) complexes, [Co(apmp)X₂]$^{n+}$, (X=Cl , NO₂ , H₂O, X₂=CO₃$^{2-}$, en, L-phenylalanine) have been synthesized. During the preparation of the dichloro cobalt(III) complex of apmp, [Co(apmp)Cl₂]⁻, the ligand has coordinated to the cobalt(III) ion in a geometric selectivity to give only the *uns-cis* isomer and, during the substitution reaction between L-phenylalanine and [Co(apmp)Cl₂]⁻, the L-phenylalanine has coordinated to the cobalt(III) ion in a geometric selectivity to give only an *uns-cis*-meridional isomer. It is of interest that this is a rare case of the [Co(ONNO ligand)X₂]$^{n+}$-type complex preparations, which gives only an *uns-cis* isomer with geometric selectivity.

Introduction

A linear flexible tetradentate ligand of the type ONNO in the donor atom array such as edda (ethylenediamine-N,N'-diacetic acid, HOOCCH₂NHCH₂CH₂NHCH₂COOH) can occupy four coordination sites in an octahedral geometry to give three possible geometric isomers: *s-cis* (symmetric *cis*), *uns-cis* (unsymmetric *cis*), and trans (Figure 1). A number of ONNO-type ligands have been prepared, and many studies have been directed toward the stereospecificity of these complexes and the isolation of various isomers.[1-10] The *s-cis* and *uns-cis* geometric isomers have usually been isolated in the preparation of the metal complexes, but no trans isomers have been obtained to date.
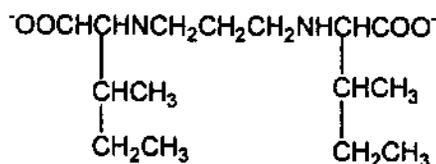
1,3-diaminopropane-di-α-(β-methyl)-pentanoate ligand, apmp

In order to study the relative stabilities of the *s-cis* and *uns-cis* isomers during the preparation process of the metal complexes of an ONNO-type ligand, a novel bulky 1,3-diaminopropane-N,N'-di-α-(β-methyl)-pentanoate (apmp) ligand and the cobalt(III) complexes of this apmp ligand have been prepared.

It is of particular interest to observe what isomers would be formed from the preparation of [Co(apmp)X₂]$^{n+}$-type (X= Cl , H₂O, NO₂ , X₂=CO₃$^{2-}$, en, L-phenylalanine) complexes. It will be shown that only the *uns-cis* geometric isomer is obtained in the preparation of [Co-(apmp)X₂]$^{n+}$ com-

s-cis   uns-cis   trans

Figure 1. The possible geometrical isomers of [Co(edda)X₂]$^{n+}$ complexes.

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plexes, which is a rare case of observing the *uns-cis* isomer only in the preparation of the [Co(ONNO ligand)X₂]ⁿ⁺-type complexes.

Experimental

1,3-Dibromopropane, L-alanine, and L-phenylalanine were purchased from Aldrich Chemical Co. and were used as received. Dowex 50W-X4 cation exchange resin (200-400 mesh, H⁺ form) and Dowex 1-80X anion exchange resin (200-400 mesh, Cl⁻ form) were used after purification.

Electron absorption and infrared spectra were recorded on a Shimadzu UV-240 Double Beam spectrophotometer and a Nicolet Impact 400 FT-IR spectrophotometer, respectively. ¹NMR spectra were measured with a 270 MHz JEOL GSX-270 spectrometer and a Bruker DPX-250 spectrometer. Elemental analyses were performed by Micro-Tech Analytical Lab., located in Skokie, Illinois, USA.

Preparation of 1,3-Diaminopropane-N,N'-di-α-(β-methyl)-pentanoic acid (H₂apmp). 4.0 g of NaOH dissolved in 20 mL of water was added to a suspened solution of L-isoleucine (13.1 g, 0.1 mol) in 100 mL of water. The solution was heated to 60 °C, and Na₂CO₃ (5.3 g, 0.005 mol) and 1,3-diaminopropane (11.4 g, 0.05 mol) were slowly added to this solution. The solution was stirred at 65 °C for 30 min and the pH of the solution was adjusted to pH 4 using conc. HCl. White precipitates formed were filtered, and washed with water and petroleum ether. Yield: 4.1 g (27%). mp 272-775 °C. Anal. Calcd. for $C_{15}H_{30}N_2O_4$: C, 59.60; H, 9.93; N, 9.27. Found: C, 59.46; H, 9.88; N, 9.30. IR (KBr, 25 °C, cm⁻¹): (CO₂), 1590 (s). ¹H NMR (D₂O+ NaOD, 25 °C, ppm): 3.2 (d, NCH), 2.8 (t, NCH₂), 1.6 (m, 3H), 0.8 (m, 6H).

Preparation of *uns-cis*-Sodium Dichloro(1,3-diaminopropane-N,N'-di-α-(β-methyl)-pentanato) cobaltate(Ⅲ), *uns-cis*-Na[Co(apmp)Cl₂]. 3.2 g (0.01 mol) of apmp was added to 60 mL water. While stirring this suspended solution vigorously with a mechanical stirrer, a little amount of active charcoal and 2.7 g (0.01 mol) of CoCl₂·6H₂O were added. The resultant solution was heated to 60 °C and stirred for 1 h. 4.8 g (0.02 mol) of PbO₂ was slowly added to this solution, and stirring was continued for 10 h. at 60 °C. The reaction mixture was filtered. The Pb²⁺ ions in the filtrate were removed using Na₂SO₄. After filtration, the filtrate was concentrated to 20 mL, which was then stored in a refrigerator for 2 days. The deep green product was collected by filtration, and then washed with ethanol and ether. The filtrate obtained after collecting the deep green product was further concentrated to recover additional products, if any, which was turned out not to contain any other product. Yield: 1.5 g (35%) Anal. Calcd for NaCoC₁₅H₂₈N₂O₄Cl₂H₂O: C, 41.34; H, 6.89; N, 6.43. Found: C, 41.30; H, 6.92; N, 6.39. IR (KBr, 25 °C, cm⁻¹): v(CO₂), 1640 (s). UV-VIS (H₂O, 25 °C, λₘₐₓ nm): 610 (sh), 550, 416. ¹H NMR (D₂O, 25 °C, ppm): 3.4 (dd, NCH), 2.9 (m, NCH₂), 2.2 (m, 2H), 1.8 (m, 3H), 1.0 (m, 6H).

Preparation of *uns-cis*-[Co(apmp)(H₂O)₂]⁺ in situ. 0.5 g (1.1 mmol) of *uns-cis*-Na[Co(apmp)Cl₂] was dissolved in 10 mL of water. The solution was allowed to stand at room temperature for 2 days, during which period the color of the solution was changed from green to violet.

The electronic absorption spectrum was taken at this point. UV-VIS (H₂O, 25 °C, λₘₐₓ nm): 586 (sh), 528, 380.

Preparation of *uns-cis*-Sodium 1,3-Diaminopropane-N,N'-di-α-(β-methyl)-pentanatodinitrocobaltate(Ⅲ), *uns-cis*-Na[Co(apmp)(NO₂)₂]. 0.6 g (1.5 mmol) of *uns-cis*-Na[Co(apmp)Cl₂] was dissolved in 20 mL of water and heated to 60 °C, during which period the color of the solution was changed from green to blue and finally to violet. 0.43 g of NaNO₂ was slowly added to this solution, which was then stirred at 60 °C for 2 h. The solution was concentrated to 10 mL and an excess amount of acetone was added to this solution. The resultant solution was then stored in a refrigerator overnight. Upon filtration, reddish purple crystalline solids were collected, which were washed with acetone. Yield: 0.5 g (68%). Anal. Calcd. for NaCoC₁₅H₂₈N₄O₈: C, 37.97; H, 5.91; N, 11.81. Found: C, 38.14; H, 5.84; N, 11.85. IR (KBr, 25 °C, cm⁻¹): v (CO₂), 1640 (s). UV-VIS (H₂O, 25 °C, λₘₐₓ nm): 482. ¹H NMR (D₂O, 25 °C, ppm): 3.6 (dd, NCH), 3.0 (m, NCH₂), 2.3 (m, 2H), 1.8 (m, 3H), 1.1 (m, 6H).

Preparation of *uns-cis*-Sodium Carbonato(1,3-diaminopropane-N,N'-di-α-(β-methyl)-pentanato) cobaltate(Ⅲ), *uns-cis*-Na[Co(apmp)(CO₃)]. This was prepared according to the same method as that used to prepare the *uns-cis*-Na[Co(apmp)(NO₂)₂] using Na₂CO₃ in place of NaNO₂. Yield: 0.3 g (36%). Anal. Calcd. for NaCoC₁₆H₂₈N₂O₇: C, 43.44; H, 6.33; N, 6.33. Found: C, 43.62; H, 6.30; N, 6.38. IR (KBr, 25 °C, cm⁻¹): v (CO₂), 1640 (s). UV-VIS (H₂O, 25 °C, λₘₐₓ nm): 523, 590 (sh). ¹H NMR (D₂O, 25 °C, ppm): 3.6 (dd, NCH), 3.0 (m, NCH₂), 2.5 (m, 2H), 1.6 (m, 3H), 1.0 (m, 6H).

Preparation of *uns-cis*-1,3-Diaminopropane-N,N'-di-α-(β-methyl)-pentanatoethylenediaminecobalt (Ⅲ) perchlorate, *uns-cis*-[Co(apmp)(en)]ClO₄. 1.1 g (2.5 mmol) of *uns-cis*-Na[Co(apmp)Cl₂] was dissolved in 30 mL of water. The solution was heated to 60 °C for 20 min, during which period the color of the solution was changed from green to blue and finally to violet. After adding 0.15 g (2.5 mmol) of ethylenediamine, the solution was stirred for 5 h. at 60 °C. The solution was concentrated to 5 mL, which was admitted to a column packed with Dowex 50W-WX cation exchange resin (200-400 mesh, H⁺ form). One fraction was detected by elution with 0.3 M NaClO₄. The collected solution was concentrated until pink precipitates were formed. The pink solids were washed with acetone and ether. Yield: 0.25 g (19%). Anal. Calcd. for CoC₁₇H₃₆N₄O₈Cl: C, 39.35; H, 6.94; N, 10.80. Found: C, 39.56; H, 7.01; N, 10.77. IR (KBr, 25 °C, cm⁻¹): v (CO₂), 1632 (s). UV-VIS (H₂O, 25 °C, λₘₐₓ nm): 500.

Preparation of uns-cis-mer-1,3-Diaminopropane-N,N'-di-α-(β-methyl)-pentanato-L-phenylalaninato-cobalt(Ⅲ), *uns-cis*-mer-[Co(apmp)(L-phala)]. 1.29 g (3.0 mmol) of *uns-cis*-Na[Co(apmp)Cl₂] was dissolved in 40 mL of water. The solution was heated to 60 °C and stirred for 30 min, 1.32 g (3.0 mmol) of L-phenylalanine was added to the solution and the pH of the solution was adjusted to 8.0 with 1.0 N NaOH. 0.1 g of active carbon was added and the solution was stirred at 60 °C for 5 hrs. The solution was then filtered and the filtrate was concentrated to 5 mL, which was admitted to a column packed with Dowex 50W-X4 cation exchange resin. One fraction was de-

tected by elution with water. The collected fraction was concentrated to isolate the violet *uns-cis*-meridional isomer, which was recrystallized from ethanol and ether, and then vacuum dried. Yield: 0.7 g (45%). Anal. Calcd. for CoC_{24}-$H_{38}N_3O_6$: C, 55.07; H, 7.26; N, 8.03. Found: C, 55.20; H, 7.31; N, 8.10. IR (KBr, 25 °C, cm^{-1}): v (CO_2), 1620 (s). UV-VIS (H_2O, 25 °C, λ_{max} nm): 530, 478.

Results and Discussion

The reaction between L-isoleucine and 1,3-dibromopropane in basic aqueous solution results in 1,3-diamino-propane-N,N'-di-α-(β-methyl)-pentanoic acid (H_2apmp). The H_2apmp compound was characterized by elemental analysis and spectroscopic methods. The apmp ligand can act as a tetradentate chelation ligand with two nitrogen and two oxygen donor atoms. The infrared spectrum of the H_2apmp compound shows a strong carbonyl stretching band at 1590 cm^{-1}. From the ^{1}H NMR spectrum the α-methylene protons are shown at 3.2 ppm as a doublet, the metylene protons in the propanediamine backbone at 2.8 ppm as a triplet, and the methyl protons attached to the β-carbon and the other terminal methyl protons at 0.8 ppm as a combination of doublets and triplets, respectively. The elemental analysis data are quite accurate for this H_2apmp compound.

The reaction of $CoCl_2$ with H_2apmp at 60 °C in aqueous solution using PbO_2 as an oxidant has yielded only one deep green solid dichlorocobalt(III) complex of apmp to give the *uns-cis*-[Co(apmp)Cl₂]$^-$ complex. The elemental analysis data are quite accurate for this complex. The infrared spectrum of this complex shows an anti-symmetric CO_2 vibration at 1640 cm^{-1}, which is of higher energy that that of H_2apmp, indicating the bond formation between metal and ligand carboxylate oxygen donor atoms. As the carboxylate oxygen coordinates to the metal, the frequency of the carboxylate stretching vibration increases due to the formation of a pseudo-ester type bond.[11] The electronic absorption spectrum of [Co(apmp)Cl₂]$^-$ (Figure 2) is related to [Co(edda)X₂]$^{n+}$ species[7,12,13] (X=Cl , Br , OH , H_2O, X₂= CO_3^{2-}), which are *cis*-CoN_4O_2 systems.[1,2] Fortunately, in

these *cis*-CoN_4O_2 systems, the electronic absorption spectrum can unambiguously distinguish whether this complex has an *s-cis* or *uns-cis* geometry. Since the *uns-cis* isomer shows a higher $^1T_{1g}$ splitting than the *s-cis* isomer, the electronic absorption band of the *uns-cis* isomer usually has a very broad and non-sysmmetrical spectrum with a shoulder in the longer wavelength side, while that of the *s-cis* isomer shows a more symmetrical Gaussian shape.[1,2,7,12,15] The electronic absorption spectrum of the [Co(apmp)Cl₂]$^-$ complex (Figure 2) shows a broad non-sysmmetrical first band (λ_{max}=550 nm) with a shoulder (λ_{max}=610 nm), which is assigned to the transition $^1A_{1g}$ to $^1A_{2g}+^1E_g$, and which clearly indicates that the [Co(apmp)Cl₂]$^-$ complex has the *uns-cis* geometric configuration. The second band with max at 416 nm is assigned to the transition $^1A_{1g}$ to $^1B_{2g}+^1E_g$.[2,15] The ^{1}H NMR spectrum of the *uns-cis*-[Co(apmp)Cl₂]$^-$ complex shows the α-methylene protons as two doublets at near 3.5 ppm and the methylene protons in the propanediamine backbone as two triplets at near 2.9 ppm. Such ^{1}H NMR spectrum shows essentially twice as many peaks as would be found in the *s-cis* isomer as well as a much more complicated nature than the *s-cis* isomer.

The *uns-cis*-[Co(apmp)(H_2O)₂]$^+$ complex ion has been formed *via* the slow aquation of the *uns-cis*-[Co(apmp)Cl₂]$^-$ in water solution at room temperature. Like the *uns-cis*-[Co(apmp)Cl₂] , the electronic absorption spectrum of this *uns-cis*-[Co(apmp)(H_2O)₂]$^+$ complex shows a broad non-symmetrical first band (λ_{max}=528 nm) with a shoulder (λ_{max}=586 nm) as expected for an *uns-cis* geometry.

The absorption spectra of [Co(apmp)CO_3]$^-$ and [Co(apmp) (NO₂)₂] (Figure 3), which have been prepared from the reaction of *uns-cis*-[Co(apmp)Cl₂]$^-$ with CO_3^{2-} and NO_2 , respectively, also show the broad non-symmetrical bands in the visible region, indicating the fact that these complexes also have the *uns-cis* geometry. The ^{1}H NMR spectral data of the *uns-cis*-[Co(apmp)(NO₂)₂] are particularly helpful in showing whether this complex has an *uns-cis* or *s-cis* geometry. The ^{1}H NMR spectrum of the *uns-cis*-[Co(apmp) (NO₂)₂] shows the α-methylene protons as two doublets at
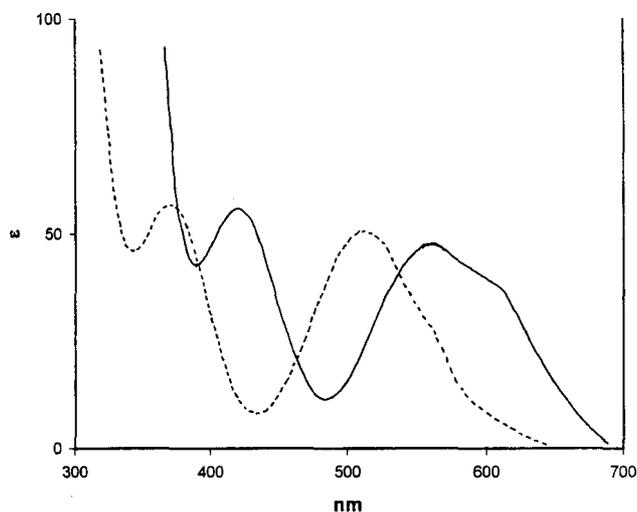
Figure 2. Electronic absorption spectra of *uns-cis*-[Co(apmp)Cl₂] (—) and *uns-cis*-[Co(apmp)(H_2O)₂]$^+$ (---).
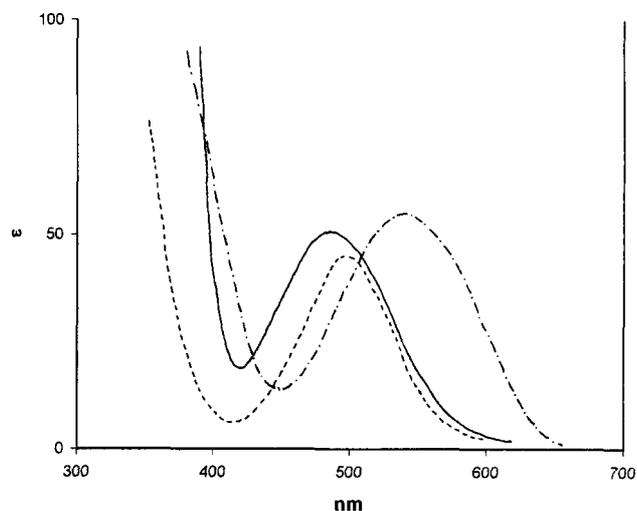
Figure 3. Electronic absorption spectra of *uns-cis*-H[Co(apmp) (NO₂)₂] (—), *uns-cis*-H[Co(apmp)(CO₃)] (-·-·-) and *uns-cis*-[Co (apmp)(en)]ClO₄] (---).

uns-cis-facial   uns-cis-meridional
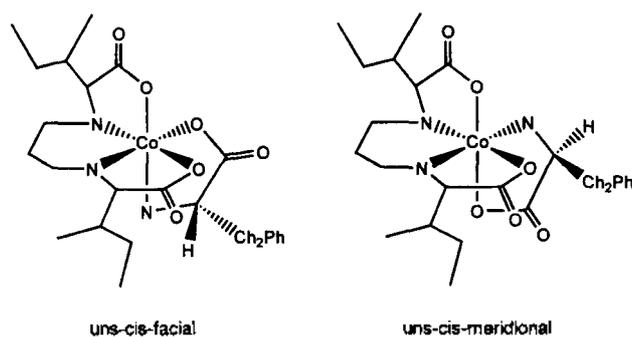
Figure 4. The *uns-cis*-facial and *uns-cis*-meridional structures of the *uns-cis*-[Co(apmp)(L-pala)] complex.

near 3.8 ppm and the methylene protons in the propanediamine backbone as two triplets at near 2.9 ppm, while the protons attached to the β-carbon and the other terminal ethyl protons as essentially a combination of two doublets and two triplets, respectively. As is the case for the *uns-cis*-[Co(apmp)Cl₂] complex, the ¹H NMR spectral data of the *uns-cis*-[Co(apmp)(NO₂)₂]⁻ complex shows essentially twice as many peaks as would be found in the *s-cis* isomer as well as more complicated nature than the *s-cis* isomer. Therefore, it is evident that the dichloro, carbonato, and dinitro cobalt(III) complexes of apmp prepared in this work have the *uns-cis* geometric configuration.

The fact that only the *uns-cis* isomer has been obtained in this work is a rare case in the preparation series of the [Co(edda)X₂]ⁿ⁺ type complexes. Because of the tetrahedral nature of the four bond around the nitrogen, the chelate rings in the *uns-cis* isomer are strained and distorted from the plane containing the nitrogen atoms, and, as a result, the *s-cis* isomer is usually favourable more than the *uns-cis* isomer.[4,12] Such preference for the *uns-cis* isomer shown by the apmp ligand can, however, be understood considering the fact that, since the apmp ligand possesses two sterically bulky isobutyl groups, there will be insurmountable nonbonded interactions between the middle chelate ring and the isobutyl groups on the α-carbon, if the complex takes the *s-cis* geometry, while such non-bonded interactions will be reduced in half in the *uns-cis* geometry.

The observation in this work that the dichloro cobalt(III) complex of apmp takes the *uns-cis* geometry is further substantiated *via* the reaction between this dichloro complex and L-phenylalanine (L-pala) which has yielded only the *uns-s-cis*-meridional isomer (Figure 4). If the complex takes an *uns-cis*-facial structure according to a study using molecular models, the non-bonded interactions between the phenylalanine chelate ring and the outside N-O chelate ring coplanar with the middle chelate ring should be great, while such nonbonded interactions will be greatly lessened in the *uns-cis*-meridional isomer (Figure 4). Therefore, it can be seen that the meridional isomer is the only isomer which the complex can take. Figure 5 shows the electronic absorption spectrum of the *uns-cis*-mer-isomer prepared in this work. The loss of symmetry from the facial geometry (holohedrized cubic symmetry) to the meridional geometry (holohedrized rhombic symmetry) is expected to cause a splitting or at least a broadening of the first band absorption.[16,17] Thus, the visible absorption peaks of the facial isomers are
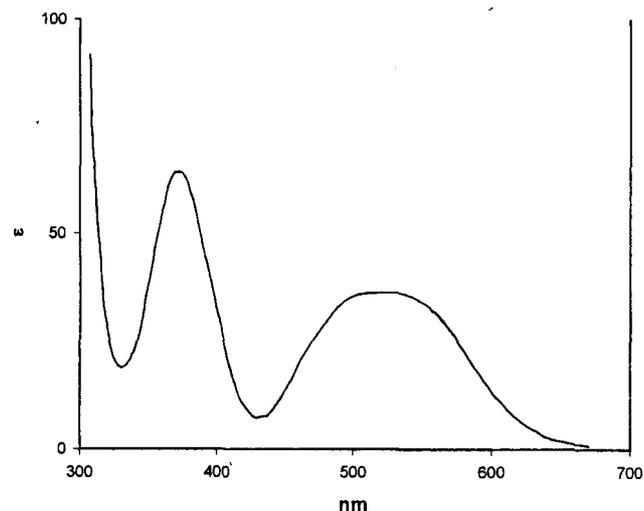
Figure 5. Electronic absorption spectrum of *uns-cis*-mer-[Co(apmp)(L-pala)].

generally sharp and symmetrical in nature, while those of the meridional isomers are broadened.[17-19] The absorption spectrum of the *uns-cis*-mer-[Co(apmp)(L-pala)] (Figure 5) shows a very broadened band in the visible region, which is broadened by the uns-cis geometry as well as the meridional geometry. It is quite interesting to observe in this work that the apmp ligand has shown a remarkable "geometric selectivity" for the *uns-cis* geometry in its coordination to form a dichloro cobalt(III) complex and that the L-phenylalanine has also shown such selectivity in its substitution reaction with the [Co(apmp)Cl₂]⁻ complex.

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Effect of Core Morphology on the Decomposition of CCl₄ over the Surface of Core/Shell Structured Fe₂O₃/MgO Composite Metal Oxides

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Received May 1, 1997

Core/shell structured composite metal oxides of Fe₂O₃/MgO were prepared by thermal decomposition of Fe(acac)₃ adsorbed on the surface of MgO cores. The morphology of the composites conformed to that of the MgO used as the cores. Broad powder X-ray diffraction peaks shifted toward larger d, large BET surface area (~350 m²/g), and the size of crystalline domains in nano range (4 nm), all corroborate to the nanocrystallinity of the Fe₂O₃/MgO composite which was prepared by using nanocrystalline MgO as the core. By use of microcrystalline MgO as the core, microcrystalline Fe₂O₃/MgO composite was prepared, and it had small BET surface area of less than 35 m²/g. AFM measurements on nanocrystalline Fe₂O₃/MgO showed a collection of spherical aggregates (~80 nm dia) with a very rough surface. On the contrary, microcrystalline Fe₂O₃/MgO was a collection of plate-like flat crystallites with a smooth surface. The nitrogen adsorption-desorption behavior indicated that microcrystalline Fe₂O₃/MgO was nonporous, whereas nanocrystalline Fe₂O₃/MgO was mesoporous. Bimodal distribution of the pore size became unimodal as the layer of Fe₂O₃ was applied to nanocrystalline MgO. The macropores in a wide distribution which the nanocrystalline MgO had were absent in the nanocrystalline Fe₂O₃/MgO. The decomposition of CCl₄ was largily enhanced by the overlayer of Fe₂O₃ on nanocrystalline MgO making the reaction between nanocrystalline Fe₂O₃/MgO and CCl₄ be nearly stoichiometric. The reaction products were environmentally benign MgCl₂ and CO₂. Such an enhancement was not attainable with the microcrystalline samples. Even for the nanocrystalline MgO, the enhancement was not attained, if not with the Fe₂O₃ layer. Without the layer of Fe₂O₃, it was observed that the nanocrystalline domain of the MgO transformed into microcrystalline one as the decomposition of CCl₄ proceeded on its surface. It appeared that the layer of Fe₂O₃ on the particles of nanocrystalline Fe₂O₃/MgO blocked the transformation of the nanocrystalline domain into microcrystalline one. Therefore, in order to attain stoichiometric reaction between CCl₄ and Fe₂O₃/MgO core/shell structured composite metal oxide, the morphology of the core MgO has to be nanocrystalline, and also the nanocrystalline domains has to be sustained until the core was exhausted into MgCl₂.

Introduction

Nanophase materials have attracted scientist's interest, at first by stimulating a pure scientific curiosity, and lately because of unconventional applicability they may have. It has been well known that materials exhibit unexpected physical and chemical properties as the size of their particles get small down to a few nanometer range.[1-7] The properties observed for such nanophase materials have been shown to be quite different from the ones observed for their bulky counterparts, and this difference can be related to the fact that the fraction of the moieties exposed to the surface can no longer be negligible. Therefore, it has been proposed that

the surface chemistry on the nanophase materials should be prominently different from the one on the bulk, and ample experimental observations have shown that it is the case.[8-10]

For the study of the surface chemistry on metal oxides, MgO used to be a choice for the material, and both experimental and theoretical data on the material have been accumulated. Having a simple rock salt crystal structure, theoretical consideration is especially simple, and recent studies on modelling of oxide surface produced many results which are applicable to surface chemistry experimentally observed on MgO.[11-14] Perfect cubic shaped crystal of MgO has (100) crystalline facets exposed on its surface. Among the facets other than (100), the (111) facet is worth noticing. Experimental observations which were supported by ample theoretical considerations indicated that the (111) surface of

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