

Available online at www.sciencedirect.com



Journal of Catalysis 229 (2005) 470-479

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Michael reaction of β -ketoesters with vinyl ketones by iron(III)-exchanged fluorotetrasilicic mica: catalytic and spectroscopic studies

Ken-ichi Shimizu^{a,*,1}, Masato Miyagi^b, Toshiki Kan-no^a, Tsuyoshi Hatamachi^b, Tatsuya Kodama^b, Yoshie Kitayama^b

^a Graduate School of Science and Technology, Niigata University, Ikarashi-2, Niigata 950-2181, Japan ^b Department of Chemistry & Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi-2, Niigata 950-2181, Japan

Received 6 October 2004; revised 19 November 2004; accepted 24 November 2004

Available online 28 December 2004

Abstract

Michael reaction of β -ketoesters with vinylketones at room temperature under solvent-free condition is investigated with various Fe³⁺ catalysts, including FeCl₃ · 6H₂O supported on various supports (Fe–mica, Fe–mont, Fe–SiO₂, Fe–Al₂O₃, Fe–NaY) and homogeneous catalysts, FeCl₃ · 6H₂O and Fe(NO₃)₃ · 9H₂O. Fe³⁺ -exchanged fluorotetrasilicic mica (Fe–mica) shows highest activity. Fe–mica exhibits almost quantitative yields of Michael adducts, high turnover numbers (TON = 1000), and a low level of Fe leaching. After simple work-up procedures, Fe–mica can be recycled without a loss in activity. The relationship between catalytic activity and the catalyst structure determined by XRD, UV–vis, and Fe *K*-edge XANES/EXAFS is discussed in terms of the effect of clay support on the structure and reactivity of Fe³⁺ species. The Fe³⁺ cation, highly dispersed in the interlayer of clay (mica or mont) or on SiO₂, is more active than the cluster-like Fe³⁺ oxide or hydroxide species in Fe–NaY and Fe–Al₂O₃. UV–vis and XAFS results for the catalysts treated with reactants suggest that, during the reaction, the FeCl₂(O)₄ octahedral species in FeCl₃ · 6H₂O or those on Fe–SiO₂ are converted to the β -diketonato complexes with two β -diketonato ligands, whereas in Fe–mica β -diketonato complexes with one β -diketonato ligand are formed. The formation of β -diketonato ligand to Fe³⁺ as a Lewis acid site. The lower numbers of β -diketonato ligand coordinated with Fe³⁺ in Fe–mica should result in a larger coordination strength for β -diketonato ligand than that in Fe–SiO₂, which was confirmed by acetylacetone-TPD. Thus, the central carbon atom of the β -diketonato ligand in Fe–mica is more reactive toward nucleophilic attack by the coordinated enone, leading to higher activity for the Michael reaction.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Michael reaction; Iron-exchanged clay; XAFS; Lewis acid

1. Introduction

The Michael reaction is among the most useful C–C bond-forming reactions and is widely used in the synthesis of fine chemicals. Although base catalysis of the Michael

reaction is commonly known as a very efficient and highyielding process [1], strongly basic conditions are often a limiting factor since they can lead to a number of side and subsequent reactions such as ester solvolysis. Lewis acids, such as transition metal or lanthanide complexes, have been developed as chemoselective and active catalysts for the Michael reaction under neutral and mild reaction conditions [2–9]. Christoffers reported that FeCl₃ · 6H₂O catalyzes the solventless Michael reaction of β -dicarbonyl compounds with enones at room temperature with excellent yields and

^{*} Corresponding author. Fax: +81 52 789 3193.

E-mail address: kshimizu@apchem.nagoya-u.ac.jp (K.-i. Shimizu).

¹ Present address: Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan.

^{0021-9517/\$ –} see front matter $\,$ © 2004 Elsevier Inc. All rights reserved. doi:10.1016/j.jcat.2004.11.030

selectivity [6,7]. Regarding industrial applications, however, homogeneous catalyst is generally connected with the problems of catalyst-product separation and wasted inorganics that are too difficult to reuse. To overcome these problems, immobilization of Lewis acid catalysts on polymer [10,11] or inorganic supports [12-14] has been attempted. However, the activity of the recycled polymer supported catalyst for the Michael reaction was considerably decreased because of a significant metal leaching [11]. Yb(OTf)₃ supported on silica gel was shown to be a convenient catalyst for the Michael reaction, although the activity of recovered catalyst was considerably reduced because of complexation of Yb(OTf)₃ during the workup procedure [13]. Only Sc-exchanged montmorillonite, recently demonstrated by Kawabata et al. [14], is a successful example of the reusable heterogeneous catalyst for the Michael reaction.

The use of clays as heterogeneous acid catalysts for organic reaction has received considerable attention [14-24]. Ion-exchangeable clay can immobilize metal ions in the interlayer by a strong electrostatic interaction. Water molecules in the interlayer can dissociate under the polarizing effect of the metal cations to produce acidic protons (Brønsted acids). When the coordination of an organic compound to the metal cation is accompanied by expulsion of the interlayer water coordinating to the metal cation, the metal cation in the interlayer is an electron pair accepter and can potentially act as a Lewis acid catalyst. Thus the clay exchanged by a metal cation with high hydration enthalpy, such as Fe^{3+} , can be a solid acid exhibiting both Brønsted and Lewis acidity, depending on the target reaction. Conventionally, the role of Brønsted and Lewis acidity of the clay has been discussed in terms of the relationship between the activity and the acidity characterized by using basic probe molecules such as pyridine [19-22] or amine [23], and several studies proposed Lewis acid catalysis of the cation exchanged clay [19,21]. However, we believe that the role of Lewis (or Brønsted) acidity in each organic reaction should be discussed on the basis of the characterization result, with the reactant as a probe molecule. So far, very few studies have been devoted to elucidating the structure of the metal cation interacting with the reactant molecule, such as carbonyl compounds. In addition, for the Lewis acid catalysis of cation-exchanged clay, a fundamental question arises: Why can the activity of metal cations be enhanced by exchanging them to the clay, though the answer is not clear from the literature.

Fluorotetrasilicic mica [16,25], hereafter referred to as mica, used as a host material in this study, has properties similar to those of swellable clays such as montmorillonite (mont). The interlayer surface of mica, with a F^- ion coordinated to Al^{3+} at the octahedral site present at hexagonal cavities consisting of corner-linked SiO₄ tetrahedra, is less hydrophilic than that of montmorillonite [26], which may be beneficial for the development of a moisture-insensitive catalytic center. Absence of acidity on the surface of its silicate sheet [16] should be also effective in preventing unwanted side reactions.

In this paper, we demonstrate that Fe^{3+} -exchanged mica (Fe-mica) [27] can be a recyclable and highly efficient heterogeneous catalyst for the Michael reaction of β -ketoesters with vinyl ketones. The catalytic behavior and the recycling characteristics of Fe-mica are presented to exemplify the effectiveness of this catalytic system. The structure of various Fe³⁺-containing catalysts is well characterized, and the results are discussed to reveal the nature of the Fe species required for the effective catalysis in the Michael reaction. The local structure of the Fe³⁺ cation coordinated by the reactant molecule (β -ketoesters) is also studied to elucidate the direct interaction of the reactant with Fe³⁺ cation as a Lewis acid site. Comparison of the structure of the Fe species coordinated by the reactant molecule for micasupported and SiO₂-supported or unsupported (FeCl₃ · 6H₂O and $Fe(NO_3)_3 \cdot 9H_2O$) catalysts will help to show why the activity of Fe³⁺ cation is improved by exchanging it to mica.

2. Experimental

2.1. Catalyst preparation and characterization

The following inorganic supports were used: Na–fluorotetrasilicic mica (Na–mica) with an ideal formula of NaMg_{2.5}Si₄O₁₀F₂ (COOP Chemicals Co. Ltd.; Somasif ME-100, surface area = $3 \text{ m}^2 \text{ g}^{-1}$), synthetic Na–montmorillonite (Na–mont) [Kunimine Co. Ltd.; Kunipia F, (Na_{0.13}-Mg_{0.08}Ca_{0.01})(Al_{1.44}Mg_{0.32}Fe³⁺0.09Fe²⁺0.02)(Si_{3.83}Al_{0.17})-O₁₀(OH)₂ · *n*H₂O, surface area = $4 \text{ m}^2 \text{ g}^{-1}$], SiO₂ (JRC-SIO-8, a reference catalyst of the Catalysis Society of Japan, surface area = $303 \text{ m}^2 \text{ g}^{-1}$), Al₂O₃ (JRC-ALO-8, surface area = $148 \text{ m}^2 \text{ g}^{-1}$), and NaY zeolite (JRC-Z-Y 5.6, SiO₂/Al₂O₃ = 5.6, surface area = $870 \text{ m}^2 \text{ g}^{-1}$).

Fe³⁺ catalysts supported on various inorganic supports were prepared as follows. We prepared FeCl₃ \cdot 6H₂O supported on silica gel and Al₂O₃ (Fe–SiO₂ and Fe–Al₂O₃) by mixing the supports with an aqueous solution of FeCl₃ \cdot 6H₂O, followed by complete removal of the solvent at 353 K. We prepared Fe–clay samples and Fe³⁺-exchanged NaY zeolite (Fe–NaY) by exchanging the supports with an aqueous solution of FeCl₃ \cdot 6H₂O at 298 K for 3 h, followed by centrifuging and washing with deionized water, and by drying in vacuo at 298 K. Fe³⁺-exchanged fluorotetrasilicic mica from an aqueous solution of Fe(NO₃)₃ \cdot 9H₂O was also prepared and named Fe–mica-N. ICP analysis showed that Fe contents of Fe–mica, Fe–mica-N, Fe–mont, Fe–SiO₂, Fe– Al₂O₃, and Fe–NaY are 2.3, 1.6, 1.4, 6.1, 4.8, and 2.1 wt%, respectively.

XRD patterns were taken by MX Labo (MAC Science) with Cu-K_{α} radiation (40 kV, 25 mA). Diffuse reflectance spectra of powder samples were obtained with a UV–vis spectrometer (Jasco; V-550) and were analyzed by the Kubelka–Munk method. Fe *K*-edge XAFS was conducted in transmission mode at BL-7C (Photon Factory in High Energy Accelerator Research Organization, Tsukuba, Japan)



with a Si(111) double-crystal monochromator. Ionization chambers filled with N₂ for I_0 (17 cm) and N₂(50%)-Ar(50%) for I (31 cm) were used. The energy was defined by assigning the first inflection point of the Cu foil spectrum to 8980.3 eV. Normalization of XANES and EXAFS analysis were carried out with XAPEC4. The Fourier transforms of k^3 -weighted Fe K-edge EXAFS spectra were typically obtained in the k range of 4–13.5 Å⁻¹. For the curve-fitting analysis of Fe-O and Fe-Cl shells, respectively, parameters extracted from $Fe(NO_3)_3 \cdot 9H_2O$ [28] and $FeCl_3 \cdot 6H_2O$ [29] were used. Temperature-programmed desorption (TPD) of acetylacetone was carried out with TPD equipment (BEL Japan). After adsorption of acetylacetone (10 Torr) to the sample (0.02 g) at 323 K for 1 h, followed by purging of the gaseous and weakly adsorbed acetylacetone in He flow at 373 K for 0.5 h, we performed TPD in the He flow $(60 \text{ cm}^3 \text{ min}^{-1})$ by raising the temperature to 823 K at a rate of 10 K min⁻¹.

2.2. Catalytic test

Various Fe³⁺ catalysts were tested in the model reaction of β -ketoesters **1** (ethyl 2-oxocyclopentanecarboxylate) with methyl vinyl ketone (MVK) **2** (Scheme 1). We carried out the reaction by stirring the reaction mixture containing β -ketoester **1** (5 mmol), MVK (6 mmol), and Fe³⁺ catalysts (0.05 mmol of Fe) at room temperature in air (in the presence of moisture). The solid catalysts were used without any pretreatment. After the mixture was stirred for 20 h, ethyl acetate (5 mL) was added to the reaction mixture, and the solid catalyst was removed by centrifugation. In the kinetic studies with 0.1 mol% catalyst (Fig. 6), progress of the reaction was monitored by GC analysis of aliquots with *n*dodecane as internal standard.

3. Results and discussions

3.1. Structure of as-prepared catalyst

The X-ray diffraction patterns of Fe-mica (Fig. 1) show a typical low-angle reflection (100) at $d_{100} = 1.27$ nm. The basal spacing of Fe-mica is close to that of the original Namica in a hydrated form (1.21 nm), with Na⁺ ions and a single water sheet in the interlayer spacings [30]. From a comparison with the XRD pattern of Na-mica in anhydrous form ($d_{100} = 0.91$ nm), the interlayer spacing of Fe-mica is estimated to be 0.36 nm. These results indicate that the Fe-mica retained the hydrated interlayer structure of Namica, and Fe³⁺ ions should be accommodated in the ditrig-



Fig. 1. XRD patterns of (a) anhydrous Na–mica, (b) hydrous Na–mica, (c) Fe–mica, (d) Fe–mica soaked with β -ketoester 1.

onal holes above and below the central single water sheet in the interlayer spacings [30]. In this form, three water molecules and three lattice oxygens of the silicate are coordinating to the exchanged cation [30]. Note that no lines due to $FeCl_3 \cdot 6H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$ were observed in the XRD pattern of the supported Fe^{3+} catalysts used in this study.

To characterize the Fe^{3+} species in the catalysts, UVvis and XAFS analyses were performed. Fig. 2 shows UVvis diffuse reflectance spectra of Fe-mica, Fe-mica-N, Fe-SiO₂, and FeCl₃ · 6H₂O. The spectrum of Fe–SiO₂, exhibiting a broad LMCT band around 320-340 nm and a shoulder around 440 nm, is similar to that of FeCl₃ · 6H₂O, which consists of FeCl₂(O)₄ distorted octahedron. This suggests that the supported Fe³⁺ species are present on the SiO₂ surface without significantly changing their local structure. In contrast, the position of the LMCT band of Fe-mica is higher in energy than that of FeCl₃ · 6H₂O, and its spectral feature is different from that of FeCl₃ \cdot 6H₂O, indicating that local structure of Fe³⁺ species in Fe-mica is different from that of FeCl₃ · 6H₂O (starting material). The spectrum of Femica-N is very close to that of Fe-mica. The band around 260–280 nm in spectra a and b corresponds to the Fe^{3+} in FeO₆ octahedral complex [31,32]. A weak shoulder around 340 nm suggests the presence of Fe^{3+} in small oligomeric clusters [31,32] as minor species in Fe-clay samples. In the spectra of Fe-Al₂O₃ (spectrum e) and Fe-NaY (not shown). a broad band around 340 nm due to Fe³⁺ in small oligomeric clusters [31,32] and a shoulder at 500 nm due to Fe^{3+} in larger Fe₂O₃-like particles [32] are observed.

X-ray absorption near-edge structures (XANES) are known to be sensitive to the local structure and oxidation state of X-ray absorbing atoms. It is established that the position of the absorption K-edge and that of the pre-edge due to a dipole forbidden $1s \rightarrow 3d$ transition depend on the iron ion valence state; both of them shift to higher energy with an increase in the oxidation number of iron [33–36]. Positions



Fig. 2. Diffuse reflectance UV-vis spectra of (a) Fe-mica, (b) Fe-mica-N, (c) Fe-SiO₂, (d) FeCl₃ · 6H₂O, and (e) Fe-Al₂O₃.



Fig. 3. Fe *K* e-edge XANES spectra of (a) FeSO₂ · 7H₂O, (b) Fe(NO₃)₃ · 9H₂O, (c) FeCl₃ · 6H₂O, (d) Fe–SiO₂, (e) Fe–mica, (f) Fe–mica-N: (A) pre-edge feature, (B) post-edge feature. Dotted lines denote the spectra for the solid samples soaked with β -ketoester 1 (d, e) or 0.1 M solution of FeCl₃ · 6H₂O in β -ketoester 1 (c).

of the pre-edge peak (Fig. 3A) and absorption edge (Fig. 3B) for all of the as-prepared catalysts are almost the same; preedge and edge positions are very close to those for Fe^{3+} compounds, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, but are different from those of the Fe^{2+} compound, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. This indicates that the oxidation number of Fe in the supported catalysts is 3+. The spectrum of Fe–SiO₂, with two maxima at 7130.4 eV and 7136.0 eV, is similar to that of FeCl₃ · 6H₂O, suggesting that the local structure of Fe³⁺ species in Fe–SiO₂ is very close to that of FeCl₃ · 6H₂O.



Fig. 4. Fourier transforms of k^3 -weighted Fe K e-edge EXAFS of (a) Fe(NO₃)₃ · 9H₂O, (b) FeCl₃ · 6H₂O, (c) Fe–SiO₂, (d) Fe–mica, (e) Fe–mica-N, (f) Fe–mont, (g) Fe–Al₂O₃, and (h) Fe–NaY. Dotted lines denote the spectra for the solid samples soaked with β -ketoester **1** (c, d) or 0.1 M solution of FeCl₃ · 6H₂O in β -ketoester **1** (b).

The spectral feature for $Fe(NO_3)_3 \cdot 9H_2O$, in which Fe^{3+} is surrounded by six water molecules, is a fingerprint of FeO₆ octahedra. The spectral feature for Fe-mica and Fe-mica-N, with a peak at 7132.0 eV, is very close to that for Fe(NO_3)_3 \cdot 9H_2O, suggesting that the FeO₆ octahedron is the dominant Fe³⁺ species in Fe-mica and Fe-mica-N.

Fig. 4 shows the Fourier transforms of k^3 -weighted EXAFS for the catalysts and reference compounds. Note that $Fe(NO_3)_3 \cdot 9H_2O$ consists of the FeO_6 octahedra with an Fe–O distance of 0.1986 nm [28], whereas FeCl₃ · 6H₂O consists of the FeCl₂(O)₄ distorted octahedron with an Fe-Cl distance of 0.230 nm and an Fe-O distance of 0.207 nm [29]. A peak centered around 0.169 nm (phase shift uncorrected), observed on the spectra of $Fe(NO_3)_3$. 9H₂O, is assigned to the backscattering from the adjacent O atoms. The EXAFS spectrum of $FeCl_3 \cdot 6H_2O$ has two distinct peaks at 0.160 nm and 0.194 nm, which are due to the backscattering from the adjacent O and Cl atoms, respectively. Peaks around 0.167 nm observed in the spectra of Fe-mica, Fe-mica-N, and Fe-mont suggest that Fe atoms are surrounded by oxygen atoms. For Fe-mica and Fe-mica-N, the inverse Fourier transform of the peak at 0.167 nm (R = 0.13-0.21 nm) in Fig. 4 gives the EXAFS oscillation due to the Fe–O, as shown in Fig. 5 (spectra b, c) with solid lines. Dotted lines in Fig. 5 show the result of a curve-



Fig. 5. Fourier filtered EXAFS function (solid line) and resulting curve fit (dotted line) for the peak around 0.13–0.21 nm in FT of k^3 -weighted EX-AFS (spectra b–e in Fig. 4): (a) Fe–SiO₂, (b) Fe–mica, (c) Fe–mica-N, (d) Fe–SiO₂ soaked with β -ketoester 1, (e) Fe–mica soaked with β -ketoester 1, and (f) 0.1 M FeCl₃ · 6H₂O in β -ketoester 1.

 Table 1

 Curve-fitting analysis of Fe K-edge EXAFS for as-prepared samples

| Catalysts | Shell | CN ^a | $R^{\mathbf{b}}(\mathbf{\mathring{A}})$ | $\sigma^{2\mathfrak{c}}(\mathrm{\AA}^{2})$ | $\Delta E_0 \; (\mathrm{eV})$ | $R_{\rm f}^{\rm d}$ (%) |
|---------------------|-------|-----------------|---|--|-------------------------------|-------------------------|
| Fe-mica | 0 | 4.2 | 2.00 | 0.0003 | 0 | 4.9 |
| Fe-mica-N | 0 | 3.8 | 2.01 | 0.0008 | 0 | 9.7 |
| Fe-SiO ₂ | 0 | 2.8 | 1.97 | -0.0321 | -7 | 7.1 |
| | Cl | 3.0 | 2.20 | -0.0016 | -7 | |

^a Coordination number.

^b Bond distance.

^c Debye–Waller factor.

^d Residual factor.

fitting analysis that used Fe-O shell parameters extracted from $Fe(NO_3)_3 \cdot 9H_2O$. A simulated spectrum fitted well with the experimental one. As shown in Table 1, the curvefitting analysis for Fe-mica and Fe-mica-N showed that the peak at 0.167 nm is assigned to an Fe-O bond with a coordination number of about 4 and a bond distance of about 0.20 nm. This indicates that Fe³⁺ species are coordinated with the interlayer water and/or the surface anionic oxygen in the silicate layer. The peak position for the first shell of $Fe-SiO_2$ (0.182 nm) is higher than that for the Fe-O shell of $Fe(NO_3)_3 \cdot 9H_2O$ (Fig. 4), suggesting the presence of a larger atom, a Cl atom, at a larger distance than Fe-O. For the peak at 0.182 nm in Fe-SiO₂, the analysis was unsuccessful with a Fe-O shell, and the optimum fitting result gives 2.8 Fe-O bonds of 0.201 nm and 3.0 Fe-Cl bonds of 0.220 nm. Combined with the UV-vis and XANES results suggesting that the local structure of Fe³⁺ species on Fe–SiO₂ is close to that of $FeCl_3 \cdot 6H_2O$ consisting of $FeCl_2(O)_4$ octahedron,

a most probable model for Fe^{3+} species on $Fe-SiO_2$ is the $FeCl_2(O)_4$ distorted octahedron.

In the spectra of Fe–NaY and Fe–Al₂O₃, a large peak at 0.272 nm assignable to the Fe atom in oxide or hydroxide particles is clearly observed. On the other hand, very small peaks around 0.27–0.30 nm are observed in the spectra of Fe–mica, Fe–mica-N, Fe–mont, and Fe–SiO₂, indicating that the amount of the cluster-like Fe³⁺ oxide or hydroxide species in these samples is quite small.

Summarizing the above characterization results, we can provide consistent pictures of the catalyst structure as follows. XAFS and UV-vis results for Fe-clay samples indicate that intercalated Fe^{3+} species are highly dispersed FeO_6 octahedron, where O refers to the oxygen atom of interlayer water or the anionic oxygen of the silicate layer (species 4 in Scheme 2). The d_{100} value of Fe-mica, suggesting that the Fe³⁺ cation in the interlayer is coordinated by the interlayer water and the silicate oxygen atoms [30], supports the above structural model. In Fe–SiO₂, the starting salt, FeCl₃ \cdot 6H₂O, is highly dispersed on Fe–SiO₂ without significantly changing its structure, and the local structure can be described as $FeCl_2(O)_4$ octahedron, where O refers to the oxygen atom of H₂O or the support oxygen (species 8 in Scheme 3). Fe-NaY and Fe-Al₂O₃ mainly consist of small Fe³⁺ oxide or hydroxide particles.

3.2. Structure–activity relationship

The Michael reaction of β -ketoester **1** (ethyl 2-oxocyclopentanecarboxylate) with methyl vinyl ketone (MVK) 2 was tested with various Fe³⁺ catalysts (Table 2). Fe-clay catalysts (Fe-mica, Fe-mica-N, and Fe-mont) gave high yields comparable to that of $FeCl_3 \cdot 6H_2O$ (a homogeneous catalyst); full conversion of 1 and almost quantitative yield of the product **3** were observed. Although Fe–SiO₂ gave a high yield, a large amount of supported Fe (33%) was leached from the solid. This indicates that the activity of Fe–SiO₂ is partially due to homogeneous catalysis of the leached Fe³⁺ in solution. With Fe-Al₂O₃ and Fe-NaY, poor yields and significant Fe^{3+} leaching were observed. Fig. 6 shows the time course of the Michael reaction by Fe-mica, Fe-mica-N, Fe-mont, FeSiO₂, FeCl₃ · 6H₂O, and Fe(NO₃)₃ · 9H₂O with low catalyst concentration (0.1 mol%). Under these conditions, a clear difference in the activity was observed, and the initial rate increased in the order of Fe-mica > Fe-mica- $N = FeCl_3 \cdot 6H_2O > Fe-mont > Fe-SiO_2 > Fe(NO_3)_3 \cdot$ 9H2O. Fe-mica was the most effective of the catalysts tested, and the reaction proceeded smoothly to give a quantitative yield after 6 h.

From the above results and the structural information on the catalysts, the nature of the Fe species required for this reaction can be described as follows. Highly dispersed Fe^{3+} complexes in Fe–clay and Fe–SiO₂ exhibit much higher activity than Fe³⁺ oxide or hydroxide species present in Fe– NaY and Fe–Al₂O₃ as major Fe species. The FeCl₃(O)₃ complex on Fe–SiO₂ is easily dissolved in the liquid phase,

Table 2 Michael reaction of β -ketoester 1 with MVK 2^a

| Catalysts | Fe content (wt%) | Yield ^b (%) | Fe leaching (%) |
|-----------------------------------|------------------|---|-----------------|
| Fe-mica | 2.3 | 97, 99 ^c , 99 ^c , 99 ^c | 0.19 |
| Fe-mica-N | 1.6 | 91 | 0.21 |
| Fe-mont | 1.4 | 93, 99 [°] , 99 [°] , 99 [°] | 0.52 |
| Fe-SiO ₂ | 6.1 | 99 | 33 |
| Fe-Al ₂ O ₃ | 4.8 | 13 ^d | 16 |
| Fe–NaY | 2.1 | 23 ^d | 8.3 |
| $FeCl_3 \cdot 6H_2O$ | - | 99 | _ |
| $Fe(NO_3)_3 \cdot 9H_2O$ | - | 99 | _ |
| | | | |

^a Reaction conditions: β -ketoester **1** (5.0 mmol), MVK (6.0 mmol), Fe³⁺ catalyst (0.05 mmol, 1 mol%), no solvent, at room temperature for 20 h. ^b Isolated yields.

^c Yields in the first, second, third and fourth repeated reuses of the same catalyst.

^d Yields determined by ¹H NMR using internal standard method.

and leached Fe species act as homogeneous catalysts with moderate activity. Fe³⁺ species intercalated to the fluorote-trasilicic mica have higher activity than corresponding Fe³⁺ salts and SiO₂-supported one. An explanation of this phenomena will be given later.

3.3. Catalytic performance of Fe-mica

As shown in Table 2, Fe-mica gave full conversion of 1 and almost quantitative yield of the product 3. As reported by Christoffers for FeCl₃ \cdot 6H₂O catalyst [6,7], no side products were detected by TLC, GC, or ¹H NMR analyses. It should be noted that, for Fe-clay catalysts, evaporation of supernatant after the centrifugation gave directly a Michael adduct 3. ICP analysis of supernatant after the reaction (Table 2) shows that metal leaching of clay-supported catalysts was significantly low. A possible contribution of homogeneous catalysis was excluded by the following experiment. When the Fe-mica catalyst was removed at an early stage of the reaction (t = 30 min, 40% yield), the reaction did not proceed further, confirming that the observed catalysis of Fe-mica is truly heterogeneous in nature [37]. After the first run, reusability of the Fe-mica and Fe-mont catalysts was tested. The catalyst can easily be separated from the reaction mixture by a simple centrifugation and can be recycled at least three times while retaining almost quantitative yield without any reactivation treatment. As shown in Fig. 6, Femica shows high durability; turnover numbers (TON, moles of products/moles of Fe) as high as 1000 are achieved.

Several examples of Fe-mica-catalyzed Michael reactions are summarized in Table 3. Fe-mica was generally very effective in the reaction of various Michael donors with methyl vinyl ketone or ethyl vinyl ketone. After the reaction mixture was stirred for 20 h at room temperature, Michael adducts were obtained in high yields with only 1 mol% of the catalyst and without solvent. Ester hydrolysis as a side reaction was negligible, even for methyl ester (entry 2) in the presence of moisture. Use of ethyl 3-oxobutanate as a Michael donor resulted in a moderate yield (41%). No



Fig. 6. Plot of GC yield versus time for the Michael reaction of β -ketoester **1** with MVK at room temperature by various catalysts; (\bigcirc) Fe-mica, (\diamondsuit) Fe-mica-N, (\triangle) Fe-mont, (\Box) Fe-SiO₂, (\bullet) FeCl₃ · 6H₂O, (\blacklozenge) Fe(NO₃)₃ · 9H₂O. Conditions: β -ketoester **1** (25 mmol), MVK (30 mmol), the catalyst amount (0.1 mol%).

Michael adduct was obtained for the reaction of diethyl malonate with MVK by Fe–mica (3 mol%). When acrylonitrile, ethyl acrylate, 2-cyclopenten-1-one, 2-cyclohexen-1-one, or 4-phenyl-3-buten-2-one was used for the reaction with β ketoester **1** by Fe–mica (3 mol%), the Michael reaction did not proceed.

3.4. Characterization of the catalyst interacted with β -ketoester

Homogeneous transition-metal catalysis of the Michael reaction of β -dicarbonyl compounds has been studied by many authors. It was proposed, for homogeneous Ni^{2+} [4], Co^{2+} [5], and Fe³⁺ [6,7] catalysts, that under reaction conditions β -diketonato species 5 (Scheme 2) are first formed, though very few authors have focused on detailed spectroscopic evidence for the reaction mechanism. On the basis of the result that Fe(acac)₃ does not catalyze the Michael reaction, Christoffers proposed for the FeCl₃ · 6H₂O-catalyzed Michael reaction that the enone 2 coordinates at a vacant coordination site of 5 to form species 6, and, subsequently, the central carbon atom of the β -diketonato ligand is alkylated by the coordinated enone, resulting in the formation of the Michael adduct (Scheme 2) [6,7]. On the basis of the IR result of the β -diketonato complex, Kawabata et al. [14] also proposed a similar reaction mechanism for the Sc-exchanged montmorillonite-catalyzed Michael reaction. In this study, to investigate the structure of the Fe³⁺ species interacting with the reactant, 0.5 g of the catalyst powder (Fe-mica, Fe-mica-N, or Fe–SiO₂) was soaked in 1.0 g of β -ketoester 1 for 10 min, and the filtered catalyst was washed with CH₂Cl₂ and dried in vacuo at 298 K, and the obtained powder was characterized by XRD, UV-vis, and XAFS as shown below. In situ UV-vis and XAFS studies for the homogeneous catalysts (FeCl₃ · 6H₂O and Fe(NO₃)₃ · 9H₂O) interacting

Table 3 Fe-mica catalyzed Michael reactions^a



^a Conditions are the same as in Table 1.

^b Isolated yields.

^c Yields determined by ¹H NMR using internal standard method.



Scheme 3.

with the β -ketoester **1** are also examined. Comparison of the spectroscopic results for the clay-supported (Fe-mica or Fe-mica-N) and SiO₂-supported or unsupported catalysts will give some explanation of why the Lewis acidity of metal cation is improved by their immobilization on the exchange-able clay. A significant effect of the local structure of the Fe



Fig. 7. UV-vis spectra of 1 mM CH₂Cl₂ solution of (a) Fe(NO₃)₃ · 9H₂O and (b) FeCl₃ · 6H₂O in the presence of β -ketoester **1** (10 mM) and (c) FeCl₃ · 6H₂O in the presence of β -ketoester **1** (10 mM) and MVK (10 mM).



Fig. 8. UV-vis spectra of (a) the soaked with β -ketoester 1: (a) Fe-mica, (b) Fe-mica-N, (c) Fe-SiO₂ and (d) Fe-mont. Dotted line (e) denotes the spectrum for the Fe-mica soaked with β -ketoester 1 and MVK.

site in the working state on the Lewis acidity will be also demonstrated.

The Fe-containing catalysts with low activity for the Michael reaction, Fe–Al₂O₃ and Fe–NaY, did not change its color (yellow) during the reaction. The color of Fe–clay catalysts changed from light yellow to blue or green during the Michael reaction and after the sample was soaked in β -ketoester **1**, suggesting a significant change in the Fe³⁺ species. A color change was also observed for Fe–SiO₂, FeCl₃ · 6H₂O, and Fe(NO₃)₃ · 9H₂O; the color of the solid or solution during the reaction was deep purple. The color change is reflected in UV–vis spectra. In the UV–vis spectra for homogeneous catalysts (Fig. 7), a new band centered around 530–550 nm appeared when β -ketoester **1** or a mix-

ture of β -ketoester **1** and MVK was added to a 1 mM solution of Fe³⁺ salts in CH₂Cl₂. For heterogeneous catalysts (Fig. 8), diffuse reflectance UV-vis spectra showed a new band centered around 550-700 nm after Fe-mica, Fe-mica-N, or FeSiO₂ was soaked in β -ketoester 1. In general, LMCT bands can be found in the visible region, for complexes with lone-pair electrons on anionic ligands and metal atoms in high oxidation states [38]. The band around 500-700 nm in Figs. 7 and 8 is mainly due to the charge transfer from the oxygen atom of β -diketonato ligands to Fe³⁺ typically observed for β -diketonato Fe³⁺ complexes [39], suggesting the formation of β -diketonato Fe³⁺ complexes in each catalyst. The position of the band for Fe-SiO₂ (550 nm) was close to those for homogeneous catalysts, whereas the band for Fe-mica-N and Fe-mica appeared in a lower energy region (650-700 nm). The same band appeared when Fe-mica was soaked with a mixture of β -ketoester 1 and MVK (not shown), indicating that Fe³⁺ species in the catalyst are present as β -diketonato Fe³⁺ complex during the reaction. Previously, Handa et al. [39] reported a spectroscopic study of the formation of acetylacetonato Fe³⁺ complexes in acetonitrile. Using a spectroscopic titration technique, they assigned the UV-vis bands centered around 590, 500, and 430 nm to Fe(acac)²⁺, Fe(acac)₂⁺, and Fe(acac)₃, respectively, indicating that the band shifts to higher energy with increasing numbers of β -diketonato ligands. Taking into account this result and a similarity in the nature of acetylacetone and β -ketoester 1, we assign the band around 530– 550 nm (for Fe–SiO₂ and homogeneous catalysts) and the band around 650-700 nm (for Fe-mica and Fe-mica-N) to β -diketonato complexes with two and one β -diketonato ligands, respectively. In the UV-vis spectrum of Fe-mont once treated in β -ketoester 1, a new band around 570 nm appeared (spectrum d in Fig. 8). This could indicate the higher coordination number of β -diketonato ligands to Fe³⁺ cation in

The structural model for β -diketonato complexes derived from UV-vis is further supported by XAFS. Fe K-edge XANES and EXAFS of the above samples are included in Figs. 3 and 4, respectively. The spectra for a 0.1 M solution of FeCl₃ · 6H₂O in β -ketoester **1** are also included in the figures. For FeCl₃ · 6H₂O, Fe-SiO₂, and Fe-mica samples, the position of the pre-edge peak did not essentially change after the reaction, and their position is higher in energy than that of Fe^{2+} compound, $FeSO_4 \cdot 7H_2O$ (Fig. 3A). This indicates that the Fe species in β -diketonato complex are present as Fe³⁺. However, as shown in Fig. 3B, the edge positions of XANES spectra for FeCl₃ · 6H₂O, Fe-SiO₂, and Fe-mica decreased by 2.0, 1.8, and 2.0 eV, respectively, after the samples were treated with the β -ketoester, though these edge positions are about 2-3 eV higher that of the Fe²⁺ compound, FeSO₄ · 7H₂O. These results suggest that the oxidation number of the Fe species in the catalyst is slightly lowered from 3+ after the formation of β -diketonato complex. We propose that Fe species in β -diketonato complex are present as slightly electron-rich Fe³⁺ species, as a re-

Fe-mont than that in Fe-mica.

sult of the electron donation from the β -diketonato ligand to Fe³⁺ as a Lewis acid center. It is known that the pre-edge peak is sensitive to a symmetry of metal species; the pre-edge intensity increases with an increase in a distortion from the perfect octahedral symmetry [36]. In the spectrum of Fe-mica, the pre-edge feature of as-prepared catalyst is almost the same as that of β -diketonato complex, indicating that the symmetry of Fe³⁺ species does not change after the coordination of the β -diketonato ligand. In contrast, the pre-edge peak intensity of Fe–SiO₂ and FeCl₃ · 6H₂O increased after the coordination of the β -diketonato ligand to Fe³⁺, which suggests an increase in Jahn–Teller distortion of Fe³⁺ after the formation of β -diketonato complexes.

Fe K-edge EXAFS spectra of Fe–SiO₂ and FeCl₃ \cdot 6H₂O significantly changed after the formation of β -diketonato complexes, indicating significant changes in the local structure around Fe species. For FeCl3 · 6H2O, the peak at 0.160 nm due to the oxygen atom of the coordinating H₂O ligand almost disappeared, and the intensity of the peak at 0.194 nm increased. For Fe–SiO₂ the intensity of the peak at 0.184 nm increased. In contrast, the Fourier transform of EXAFS for Fe-mica did not markedly change after the formation of β -diketonato complexes. For the EXAFS spectra of the above samples after the samples were treated with the β -ketoester, the curve-fitting within the range of R = 0.13 - 0.21 nm was performed to obtain the structural parameters listed in Table 4. For Fe–SiO₂ and FeCl₃ \cdot 6H₂O, the analysis was unsuccessful with a Fe-O shell. Taking into account the fact that Cl⁻ is coordinated to Fe³⁺ ions in the as-prepared Fe–SiO₂ and FeCl₃ \cdot 6H₂O, the curve-fitting was performed with Fe-O and Fe-Cl. The optimum fitting result for Fe-SiO₂ gives 6.5 Fe-O bonds of 0.197 nm and 1.6 Fe-Cl bonds of 0.219 nm and 4.0 Fe-O bonds of 0.198 nm and 2.4 Fe-Cl bonds of 0.222 nm for FeCl₃ · 6H₂O (Table 4). Summarizing the above characterization results, structural models of the β -diketonato complexes in each catalyst are illustrated in Schemes 2 and 3. The UV-vis result suggests that, after the addition of β -ketoester to Fe³⁺, Fe species in Fe–SiO₂ and FeCl₃ \cdot 6H₂O are converted to the β -diketonato complexes with two β -diketonato ligands. Therefore, Fe–O bonds with a 0.197-0.198-nm length in these samples can be assigned to the oxygen atoms of the β -diketonato ligands. About two Fe–Cl bonds with longer bond lengths than those of Fe-O bonds (Table 3) can be assigned to Cl atoms in the *trans* position (species 9 in Scheme 3). The optimum curvefitting result for Fe-mica (Fig. 5) gives 2.3 Fe-O bonds of 0.195 nm and 2.7 Fe–O bonds of 0.199 nm. Combined with the UV-vis result suggesting that the β -diketonato complex in Fe–mica have one β -diketonato ligand, the structural model is proposed as species 5 in Scheme 2. We assign the Fe–O bond of 0.199 nm to the oxygen atoms of the β diketonato ligand, and the Fe-O bonds of 0.195 nm to the oxygen atoms of interlayer water and/or the surface anionic oxygen in the silicate layer.

The XRD pattern of Fe-mica soaked in β -ketoester **1** is included in Fig. 1. The basal spacing of Na-mica did

Table 4 Curve-fitting analysis of Fe *K*-edge EXAFS for the catalysts soaked with β -ketoester **1**

| Catalysts | Shell | CN ^a | <i>R</i> ^b (Å) | $\sigma^2 c (Å^2)$ | $\Delta E_0 (\mathrm{eV})$ | $R_{\rm f}^{\rm d}$ (%) |
|----------------------|-------|-----------------|---------------------------|--------------------|----------------------------|-------------------------|
| Fe-mica | 0 | 2.3 | 1.95 | 0.015 | 0 | 11.6 |
| | 0 | 2.7 | 1.99 | 0.030 | | |
| Fe-SiO ₂ | 0 | 6.5 | 1.97 | 0.0285 | -7 | 13.7 |
| | Cl | 1.6 | 2.19 | -0.0013 | | |
| $FeCl_3 \cdot 6H_2O$ | 0 | 4.0 | 1.98 | -0.0215 | 0 | 8.0 |
| | Cl | 2.4 | 2.22 | -0.0011 | | |

^a Coordination number.

^b Bond distance.

^c Debye–Waller factor.

^d Residual factor.

not change with the addition of β -ketoester 1 (result not shown), whereas the basal spacing of Fe-mica was increased to 1.75 ± 0.05 nm, corresponding to the expansion of the interlayer distance to 0.84 ± 0.05 nm. Similar interlayer distances $(0.84\pm0.1 \text{ nm})$ were also observed when the Fe-mica was soaked with the mixture of β -ketoester 1 and MVK or when Fe-mica-N or Fe-mont was soaked with β -ketoester 1 (results not shown). It is clear that the interlayer space of Fe-clay is expanded during the Michael reaction via a formation of β -diketonato complex, as indicated by the above spectroscopic results. Hence, Fe³⁺ sites in the interlayer are available as Lewis acid site, although the surface area of Fe-mica is very low (3 m² g⁻¹). During the reaction, the β diketonato complex is present in the interlayer space, where the cationic complex is immobilized by an electrostatic interaction with the anionic interlayer surface of the clay. This feature is responsible for the low level of Fe³⁺ leaching (Table 2), whereas in the case of Fe-SiO₂, interaction between the SiO₂ surface and β -diketonato complexes is weak, resulting in a high level of Fe^{3+} leaching (Table 2).

Handa et al. [39] investigated resonance Raman spectra for an acetonitrile solution of $Fe(acac)^{2+}$, $Fe(acac)_{2+}^{+}$, and Fe(acac)₃ with a 514.5-nm Ar⁺ ion laser. They reported that the order of ν (Fe–O) was Fe(acac)²⁺ > Fe(acac)₂⁺ > Fe(acac)₃ and that of ν (C–O) was Fe(acac)²⁺ < Fe(acac)₂⁺ < Fe(acac)₃. These results indicate that the coordination strength of acac⁻ to Fe becomes weaker, because the Lewis acidity of the metal decreases as the number of coordinated acac⁻ increases. From the structural model of species 5 and 9, one speculates that the coordination strength of β -diketonato ligands to Fe changes in the following order: Fe–mica > Fe–SiO₂ = FeCl₃ \cdot 6H₂O. Strong evidence to support this hypothesis is obtained with a temperatureprogrammed desorption (TPD) experiment with acetylacetone. Fig. 9 shows TPD profiles of acetylacetone for Femica and Fe-SiO₂. The TPD profile for Fe-SiO₂ shows a peak at 210 °C, a shoulder at 260 °C, and a very small shoulder at 350 °C. The TPD profile for Fe-mica shows peaks at 183, 306, and 350 °C. Clearly, the TPD profile for Femica has a peak at higher desorption temperature than that for Fe–SiO₂, indicating the larger coordination strength of β -diketonato ligands in Fe-mica. This implies the higher



Fig. 9. TPD curves of the mass signal due to acetylacetone (m/z = 43) for (a) Fe–mica and (b) Fe–SiO₂. The samples were pre-exposed to acetylacetone (10 Torr) at 323 K for 1 h, followed by purging in He flow at 373 K for 0.5 h.

Lewis acidity (higher electrophilicity) of Fe³⁺ cation in Fe-mica. During the Michael reaction of β -ketoesters with vinylketone, most of the Fe³⁺ are present as β -diketonato complexes. The higher Lewis acidity of Fe³⁺ species in Fe-mica than those in Fe–SiO₂ or FeCl₃ · 6H₂O causes higher electrophilicity of the central carbon atom of the β diketonato ligand, which has higher reactivity toward nucleophilic attack by the coordinated enone (Scheme 2). Thus, the higher activity of Fe–mica for the formation of the Michael adduct is achieved. From the UV–vis results in Figs. 7 and 8, the activity orders Fe–mica > Fe–mont and Fe–mica-N > Fe(NO₃)₃ · 9H₂O (Fig. 6) can be understood in the same manner as above: the lower numbers of β -diketonato ligand coordinated to Fe³⁺ in Fe–mica or Fe– mica-N result in the higher Lewis acidity of Fe³⁺ species.

Interestingly, Fe-mica acts as a Lewis acid catalyst with high TON without removal of adsorbed water before the reaction (Fig. 6), though the Lewis acidity of metal cations is believed to be decreased by water molecules. This can be explained as follows. A drastic change in the UV-vis spectrum of Fe-mica after the introduction of β -ketoester 1 (from Fig. 2 to Fig. 8) indicates that ligands of Fe³⁺ cations, including water molecules, were exchanged to the β -diketonato ligand. Hence Fe-mica shows Lewis acid catalysis during the Michael reaction, even though water was coordinated to the Fe³⁺ cations before the reaction.

4. Conclusion

We have succeeded in developing Fe³⁺-exchanged fluorotetrasilicic mica as a highly effective heterogeneous catalyst for the Michael reactions of β -ketoester with vinyl ketones. This novel catalyst provides a clean and convenient alternative for the Michael reaction in view of the following advantages. The reaction proceeds smoothly and selectively in the presence of moisture under solvent-fee conditions, producing Michael adducts in high yield at room temperature. The catalyst is a stable, reusable, and nonpolluting solid that offers easy handling and ready workup.

From the structure-activity relationship, Fe³⁺ cations highly dispersed in clays (mica or mont) or on SiO₂ show much higher activity than the cluster-like Fe³⁺ oxide or hydroxide species in Fe-NaY and Fe-Al₂O₃. During the reaction, the FeCl₂(O)₄ octahedral complex in FeCl₃ \cdot 6H₂O or on Fe–SiO₂ is converted to the β -diketonato complexes with two β -diketonato ligands, whereas in Fe-mica, β -diketonato complexes with one β -diketonato ligand are formed in the interlayer space. The formation of these β -diketonato complexes results in a slight lowering of Fe oxidation number from 3+, as a result of the electron donation from the β -diketonato ligand to Fe³⁺. The lower numbers of β diketonato ligand coordinated to Fe³⁺ in Fe-mica results in the higher Lewis acidity of the Fe³⁺ site toward β diketonato ligand, which should be responsible for the high activity of Fe-mica. In addition, immobilization of Fe³⁺ by an electrostatic interaction with the anionic interlayer surface of the clay is effective for preventing Fe^{3+} leaching.

Acknowledgment

The X-ray absorption experiments were performed under the approval of the Photon Factory Program Advisory Committee (proposal no. 2003G-274).

References

- [1] E.D. Bergman, D. Ginshburg, R. Pappo, Org. React. 10 (1959) 179.
- [2] T. Saegusa, Y. Ito, S. Tomita, H. Kinoshita, Bull. Chem. Soc. Jpn. 45 (1972) 496.
- [3] K. Irie, K. Miyazu, K. Watanabe, Chem. Lett. (1980) 353.
- [4] J.H. Nelson, P.N. Howells, G.C. DeLullo, G.L. Landen, R.A. Henry, J. Org. Chem. 45 (1980) 1246.
- [5] H. Brunner, B. Hammer, Angew. Chem. Int. Ed. 32 (1984) 312.
- [6] J. Christoffers, Chem. Commun. (1997) 943.
- [7] J. Christoffers, Eur. J. Org. Chem. (1998) 1259.
- [8] E. Keller, B.L. Feringa, Tetrahedron Lett. 37 (1996) 1879.
- [9] Y. Mori, K. Kakumoto, K. Manabe, S. Kobayashi, Tetrahedron Lett. 41 (2000) 3107.
- [10] C.P. Feri, T.H. Chan, Synthesis (1982) 467.

- [11] P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. A 103 (1995) 23.
- [12] P. Laszlo, M.-T. Montaufier, S.L. Randrimahefa, Tetrahedron Lett. 31 (1990) 4867.
- [13] H. Kotsuki, K. Arimura, Tetrahedron Lett. 38 (1997) 7583.
- [14] T. Kawabata, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 125 (2003) 10486.
- [15] Y. Izumi, M. Onaka, Adv. Catal. 38 (1992) 244.
- [16] Y. Morikawa, Adv. Catal. 39 (1993) 302.
- [17] J.H. Clark, D.J. Macquarrie, Chem. Soc. Rev. (1996) 303.
- [18] B.M. Choudary, N.S. Chowdari, M.L. Kantam, Tetrahedron 56 (2000) 7291.
- [19] J.H. Clark, S.R. Cullen, S.J. Barlow, T.W. Bastock, J. Chem. Soc., Perkin Trans. 2 (1994) 1117.
- [20] L. Jankovic, P. Komadel, J. Catal. 218 (2003) 227.
- [21] D.R. Brown, C.N. Rhodes, Catal. Lett. 45 (2001) 35.
- [22] T. Cseri, S. Bekassy, F. Figueras, S. Rizner, J. Mol. Catal. A 98 (1995) 101.
- [23] C. Breen, J. Forsyth, J. Yarwood, T. Hughes, Phys. Chem. Chem. Phys. 2 (2000) 3887.
- [24] J. Tateiwa, T. Nishimura, H. Horiuchi, S. Uemura, J. Chem. Soc., Perkin Trans. 1 (1994) 3367.
- [25] H. Tateyama, S. Nishimura, K. Tsunematsu, K. Jinnai, Y. Adachi, M. Kimura, Clays Clay Minerals 40 (1992) 180.
- [26] C. Ooka, H. Yoshida, K. Suzuki, T. Hattori, Micropor. Mesopor. Mater. 67 (2004) 143.
- [27] K. Shimizu, M. Miyagi, T. Kan-no, T. Kodama, Y. Kitayama, Tetrahedron Lett. 44 (2003) 7421.
- [28] N.J. Hair, J.K. Beattie, Inorg. Chem. 16 (1977) 245.
- [29] M.D. Lind, J. Chem. Phys. 47 (1967) 990.
- [30] R.E. Grim, in: Clay Mineralogy, second ed., McGraw–Hill, New York, 1968, p. 104.
- [31] S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola, G. Vlaic, J. Catal. 158 (1998) 486.
- [32] M.S. Kumar, M. Schwidder, W. Grunert, A. Bruckner, J. Catal. 227 (2004) 384.
- [33] C.A. Linkous, W.E. O'Grady, D. Sayers, C.Y. Yang, Inorg. Chem. 25 (1986) 3761.
- [34] T.E. Westre, P. Kennepohl, J.G. Dewitt, B. Hedmann, K.O. Hodgson, E.I. Solomon, J. Am. Chem. Soc. 119 (1997) 6297.
- [35] E. Hensen, Q. Zhu, P. Liu, K. Chao, R. van Santen, J. Catal. 226 (2004) 466.
- [36] A.L. Roe, D.J. Schneider, R.J. Mayer, J.W. Pyrz, J. Widom, L. Que Jr., J. Am. Chem. Soc. 106 (1984) 1676.
- [37] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485.
- [38] F.A. Cotton, G. Wilkinson, P.L. Gaus, in: Basic Inorganic Chemistry, third ed., Wiley, New York, 1995, Chapt. 23.
- [39] M. Handa, H. Miyamoto, T. Suzuki, K. Sawada, Y. Yukawa, Inorg. Chim. Acta 203 (1992) 61.