

Characterization of Lewis acidity of cation-exchanged montmorillonite K-10 clay as effective heterogeneous catalyst for acetylation of alcohol

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Abstract

Catalytic activity of 14 types of metal ion-exchanged montmorillonite K-10 clay (M^{n+} -mont) is tested for the acetylation of cyclohexanol with acetic anhydride at room temperature. The activity increases with an increase in the charge/radius ratio of exchanged cation. The activity of Fe^{3+} -mont is the highest and is higher than those of other Fe^{3+} catalysts, $FeCl_3 \cdot 6H_2O$ and $FeCl_3/SiO_2$, conventional acid catalysts, Al_2O_3 and HZSM5, and homogeneous Lewis acid, $Sc(OTf)_3$. Fe^{3+} -mont exhibits a high turnover numbers (TON = 49,500) and can be recycled without a loss in activity. Acidity of Fe^{3+} -mont, Yb^{3+} -mont and $FeCl_3/SiO_2$ was characterized by IR spectroscopy using three probe molecules: pyridine, acetonitrile and acetone. These catalysts dominantly act as Lewis acid, and the Lewis acid strength changes in the order of Fe^{3+} -mont > Yb^{3+} -mont > $FeCl_3/SiO_2$, as suggested by acetone adsorption microcalorimetry. From the relationship between the activity and the acidic character, factors affecting the catalytic activity for the acetylation are discussed.

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1. Introduction

The acetylation of alcohols is a fundamental process in organic chemistry and provides a cheap and efficient means for protecting OH groups during oxidation, peptide coupling and glycosidation reactions. A variety of procedures follow the transesterification methodology, routinely performed under homogeneous catalysis with acetic acid or acetyl chloride and anhydride in the presence of a convenient basic (amine, DMAP) or acidic (toluene-*p*-sulfonic acid) catalyst [1,2]. Recently, transition metal- or lanthanide complexes-based Lewis acids, such as $Sc(OTf)_3$, $Sn(OTf)_2$, and $Cu(OTf)_2$, have been developed as chemoselective and active catalysts for the acetylation of alcohols with acetic anhydride under mild reaction conditions [3–5]. When industrially applied, however, homogeneous cata-

lysts generally bear the problems of catalyst–product separation and wasted inorganics which are hardly reused. Immobilization of Lewis acid on inorganic supports or use of heterogeneous acid catalysts [6–8] can overcome these problems.

Acidic clays are widely used as catalysts in organic syntheses [7–18]. Their acid-properties and, thus, their catalytic performance depend on the exchanged cations. Water molecules in the hydration sphere of metal cations can dissociate to produce acidic protons (Brønsted acids). When the coordination of an organic compound to the metal cation is accompanied by expulsion of the water coordinating to the metal cation, the metal cation is electron pair accepters and can potentially act as Lewis acid catalyst [11,12,17]. Thus, the clay the proton of which is exchanged for 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 nature of the reactant molecule. The strength of Lewis acid sites can be increased by changing the exchangeable cation, and many workers have reported that Fe^{3+} -exchanged clays exhibit the strongest Lewis acid sites [12–17].

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On the other hand, acid activated clays, montmorillonite K-10 and KSF, have been reported as a remarkable catalyst for acetylation of various alcohols and phenols with acetic anhydride [8]. Knowing the fact that acid activated clays are not stable in the H^+ -exchanged form and their auto-transformation results in the gradual dissolution of metal ions, such as Al^{3+} and Fe^{3+} , from the lattice which take the place of H^+ ions in cation exchange sites [18], one hypothesizes that catalytic activity of K-10 and KSF clays for acetylation reaction could originate from the auto-exchanged cations.

In this study, we show the effect of exchanged cations in montmorillonite K-10 on acid-properties and catalytic performance for acetylation of cyclohexanol with acetic anhydride as a test reaction. For Fe^{3+} -exchanged montmorillonite K-10 (Fe^{3+} -mont) as the most active catalyst, catalytic behavior as well as the recycling characteristics is presented to exemplify the effectiveness of this catalytic system. Using probe molecules sensitive to Lewis acid, acetonitrile [19–22] and acetone [23–25], IR and microcalorimetric experiments are conducted for characterizing acidity of each catalyst, and relationship between the acidity and the catalytic activity is discussed.

2. Experimental

2.1. Catalyst preparation and characterization

Montmorillonite K-10 clay purchased from Aldrich has surface area (S_{BET}) of $220\text{ m}^2\text{ g}^{-1}$ and the following chemical composition (average value): SiO_2 (73.0%), Al_2O_3 (14.0%), Fe_2O_3 (2.7%), CaO (0.2%), MgO (1.1%), Na_2O (0.6%), K_2O (1.9%) [26]. The basal (001) reflection was not observed in the XRD pattern of K-10, which confirms the delamination of the layered structure of the montmorillonite as reported in

the literature [11]. Amorphous silica (JRC-SIO-8, a reference catalyst of the Catalysis Society of Japan, $S_{BET} = 303\text{ m}^2\text{ g}^{-1}$), Al_2O_3 (JRC-ALO-8, surface area = $148\text{ m}^2\text{ g}^{-1}$), and HZSM5 zeolite (JRC-Z5-25H, $SiO_2/Al_2O_3 = 25$) were supplied from the Catalysis Society of Japan. Ion-exchanged K-10 clay samples (M^{n+} -mont) were prepared by treating the support with aqueous solution of metal salts for 3 h at ca. 300 K, followed by centrifuging and washing with deionized water, and by drying in vacuo at 300 K. The metal content in each sample was determined by ICP analysis and listed in Table 1. $FeCl_3 \cdot 6H_2O$ supported on silica gel ($FeCl_3/SiO_2$, $Fe = 0.1\text{ mmol g}^{-1}$) was prepared by mixing the supports with aqueous solution of $FeCl_3 \cdot 6H_2O$, followed by a complete removal of the solvent at 353 K.

FTIR measurement of adsorbed base molecules on various solid acids was performed with JASCO FT/IR-620. The sample was pressed into ca. 0.03 g of self-supporting wafers and mounted into a quartz IR cell with CaF_2 windows, and the sample was evacuated under vacuum at 423 K for 1 h. A base molecule, pyridine (15 Torr), CD_3CN (10 Torr) or acetone (30 Torr), was dosed on the evacuated samples from the gas phase through a vacuum manifold directly connected to the cell, followed by evacuation at a fixed temperature for 0.5 h. Then, a difference spectrum was recorded at room temperature. CD_3CN was used instead of CH_3CN to avoid the well-known spectroscopic complication due to Fermi resonance between the $\nu(CN)$ vibration and the combination mode $\delta(CH_3) + \nu(CC)$ [19–22].

Microcalorimetric measurement of acetone adsorption was performed at 323 K using a calorimeter (Tokyo Rikou Co., HAC-450G) connected to a volumetric glass line (308 K) with on-line injection system for pulsing acetone gas. Before the adsorption experiments the sample (0.1 g) was pretreated under vacuum for 1 h at 423 K.

Table 1
Properties and acylation rates of M^{n+} -mont catalysts

Cations	Metal source ^a	Loading ^b (mmol g ⁻¹)	Exchange level ^c (%)	e/r ^d	EN ^e	Rate ^f (mmol h ⁻¹ g ⁻¹)	TOF ^g (h ⁻¹)	Leaching ^h (%)
Hf^{4+}	$HfCl_4$	0.093	106	4.7	11.7	380	4100	1.8
Al^{3+}	$AlCl_3 \cdot 6H_2O$	0.082	70	4.4	10.5	120	1400	0
Fe^{3+}	$FeCl_3 \cdot 6H_2O$	0.103	88	4.3	12.6	580	5600	1.5
Ce^{4+}	$Ce(NH_4)_2(NO_3)_6$	0.107	122	3.7	9.9	65	610	0
Yb^{3+}	$YbCl_3 \cdot 6H_2O$	0.103	88	3.5	8.4	200	1900	0
Sc^{3+}	$ScCl_3 \cdot 6H_2O$	0.094	81	3.4	9.1	170	1800	0
Y^{3+}	$YCl_3 \cdot 6H_2O$	0.110	94	2.9	8.4	122	1100	0
Mn^{2+}	$MnCl_2 \cdot 4H_2O$	0.087	50	2.8	7.5	6	70	0
La^{3+}	$LaCl_3 \cdot 7H_2O$	0.126	108	2.6	7.7	28	220	1.5
Co^{2+}	$CoCl_2 \cdot 6H_2O$	0.110	63	2.5	9.0	19	170	0
Ni^{2+}	$NiCl_2 \cdot 6H_2O$	0.091	52	2.4	9.0	10	100	1.1
Zn^{2+}	$ZnCl_2$	0.153	87	2.3	8.0	50	330	0.2
Pb^{2+}	$PbCl_2$	0.142	81	1.5	9.0	22	160	0.1
Na^+	$NaCl$	0.350	100	0.9	2.7	3	8	-

^a Metal source for cation exchange of montmorillonite K-10.

^b Metal loading determined by ICP.

^c Cation exchange level estimated by adopting the CEC of K-10 clay as 0.35 mmol g^{-1} [11].

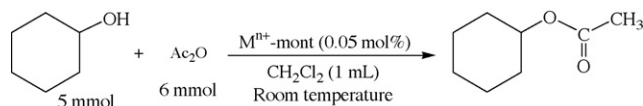
^d The ratio of charge and ionic radius (e/r).

^e Electronegativity of cation [30].

^f Initial rate for the acetylation of cyclohexanol (5 mmol) with acetic anhydride (6 mmol) at room temperature in CH_2Cl_2 (1 cm^3) with 0.05 mol% ($M^{n+} = 0.0025\text{ mmol}$) of M^{n+} -mont catalyst.

^g Turnover frequency estimated from the initial rate and metal loading.

^h Percentage of the metal cation leached from M^{n+} -mont catalysts to the solution after acylation reaction.



Scheme 1.

2.2. Catalytic test

The acetylation of cyclohexanol with acetic anhydride (Scheme 1) was carried out by stirring the reaction mixture containing cyclohexanol (5 mmol), acetic anhydride (6 mmol), CH_2Cl_2 (1 cm^3) and catalysts (typically, 0.05 mol% of metal cation with respect to cyclohexanol) at room temperature in air (in the presence of moisture). The solid catalysts were used without any pretreatment. Progress of the reaction was monitored by GC analysis of aliquots using *n*-decane as internal standard.

3. Results and discussion

3.1. Catalytic tests on acetylation

For the acetylation of cyclohexanol with acetic anhydride was tested by montmorillonite K-10 the proton of which is exchanged for 14 types of metal cations listed in Table 1. Each catalyst showed a high yield of acetylation product (above 92%) and cyclohexanol conversion (100%) after 24 h except for Mn^{2+} (74% yield) and Na^+ (5% yield) catalysts (results not shown). No by-products, such as cyclohexene, were observed by GC analysis. The inactive nature of Na^+ -mont means that the catalytically active sites in M^{n+} -mont catalysts must be the exchanged cations. Fig. 1A shows the time course of the acetylation reaction with selected M^{n+} -mont catalysts. The results show that the reaction rates depend strongly on the type of metal cation and changes in the order $\text{Fe}^{3+} > \text{Yb}^{3+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Na}^+$. The rate per gram of catalyst and the intrinsic rate per metal center, i.e. turnover frequency (TOF) are summarized in Table 1. After each experiment, the percentage of metal cations leached out from the solid catalyst to the solution was determined by ICP analysis of

the filtrate after the reaction in Table 1. The results show that excellent to moderate resistivity of M^{n+} -mont catalysts against metal leaching (0–1.8% leaching). Together with a significant influence of metal cation on the reaction rate, it is shown that the acetylation activity of M^{n+} -mont catalysts originates from metal cations supported on the clay. Rate per gram of catalyst and the intrinsic rate per metal center (TOF) were plotted as a function of the ratio of charge and ionic radius [27–29], e/r , and the electronegativity of cations [30] in Fig. 2. Although there are some deviations from the curves, there are general tendencies for TOF and the reaction rate per gram of catalyst to increase with increase in the e/r value and the electronegativity of cations. The ratio e/r is an approximate measure for the Lewis acidity of metal cations [28,29], and the electronegativity of cation has been used as a parameter of electron-withdrawing ability of metal cation. Hence, it is suggested that higher Lewis acidity results in a higher reaction rate. To investigate the effect of clay support, the catalytic activity of Fe^{3+} -mont was compared with those of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (a homogeneous catalyst), $\text{FeCl}_3/\text{SiO}_2$ and conventional acids (Table 2). With conventional Brønsted acid (HZSM5 zeolite) and Lewis acid (Al_2O_3) no or only low yields (7%) were obtained. Among Fe catalysts, the yield and rate per Fe (TOF) depended strongly on the support and increased in the order of Fe^{3+} -mont \gg $\text{FeCl}_3/\text{SiO}_2 > \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Reusability of the Fe^{3+} -mont catalyst was tested. After the first run, the catalyst can be easily separated from the reaction mixture by a simple centrifugation and can be recycled at least four times with almost quantitative yields kept without any reactivation-treatment. The initial rate did not markedly decrease in the catalyst recycle tests (TOF = 5600 and 4300 h^{-1} for cycles 1 and 5, respectively). It is noteworthy that the heterogeneous catalyst, Fe^{3+} -mont, showed higher TOF than $\text{Sc}(\text{OTf})_3$, one of the most effective homogeneous catalyst for this reaction [3]. Fig. 1B shows the time course of the acetylation of cyclohexanol over Fe^{3+} -mont with a low catalyst concentration ($\text{Fe} = 0.002$ mol%). A complete conversion of cyclohexanol, 99% yield of the product (99% selectivity), and a high TON (49,500) were attained, indicating the high activity and durability of Fe^{3+} -mont.

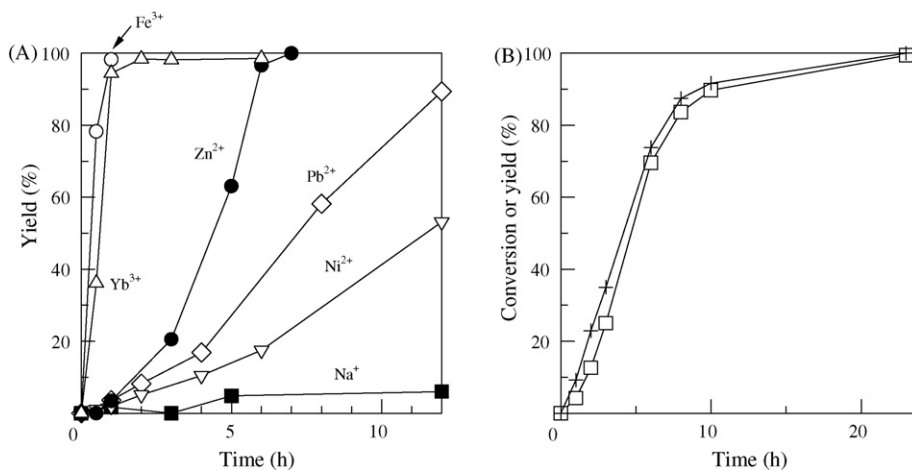


Fig. 1. (A) Plot of GC yield vs. time for acetylation of cyclohexanol with acetic anhydride by M^{n+} -mont catalysts. Conditions are shown in Table 1. (B) Cyclohexanol conversion (+) and yield of acetylation products (□) for acetylation of cyclohexanol (50 mmol) with acetic anhydride (60 mmol) in CH_2Cl_2 (10 cm^3) at room temperature by Fe^{3+} -mont ($\text{Fe} = 0.002$ mol%).

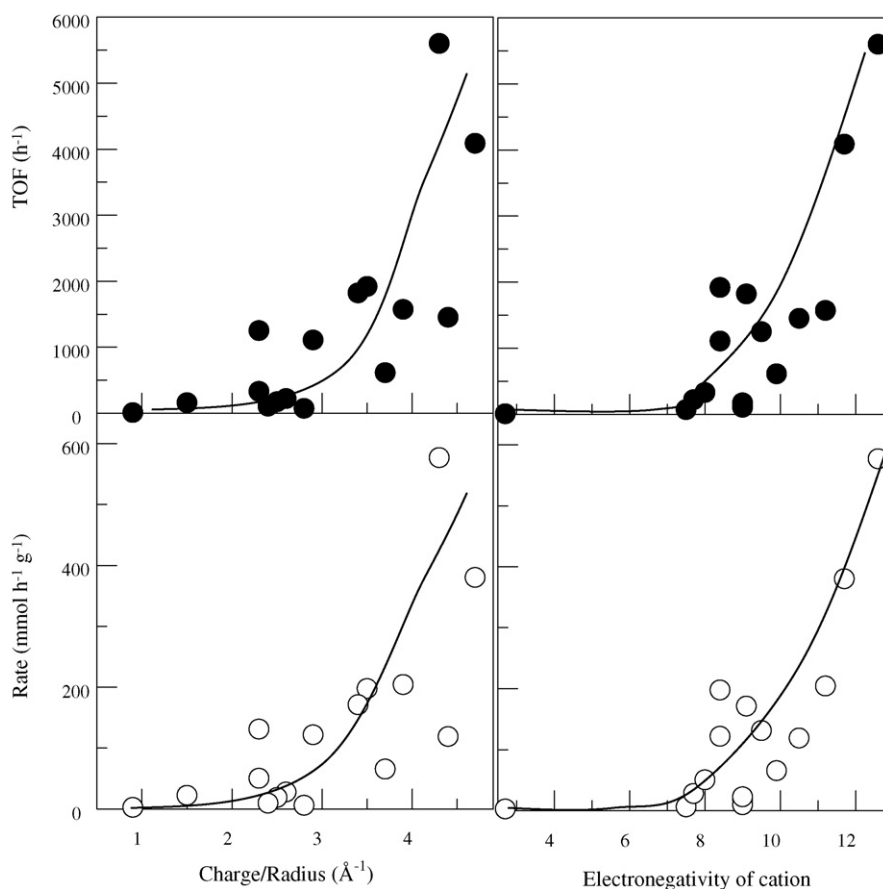


Fig. 2. Rate per gram of catalyst and the intrinsic rate per metal center (TOF) as a function of the ratio of charge and ionic radius (e/r) of the cation or electronegativity of the cation [30] in M^{n+} -mont.

3.2. IR spectra of adsorbed pyridine

IR spectra of pyridine adsorbed on various catalysts in the ring-stretching region are shown in Fig. 3. Samples were first evacuated at 423 K for 0.5 h. All spectra of adsorbed species are background subtracted and are obtained after contact with

pyridine vapor (15 Torr) at 300 K for 0.5 h and successive evacuation at 473 K for 0.5 h. According to the literature of pyridine adsorption on montmorillonite K-10 clay [11,14,15] and metal oxides [19,21,22,31], the bands are assigned in the following

Table 2
Acetylation of cyclohexanol with acetic anhydride^a

Entry	Catalysts	Yield (%)	Rate ^b (mol h ⁻¹ g ⁻¹)	TOF ^c (h ⁻¹)
1	Fe ³⁺ -mont	98, 98 ^d , 96 ^d , 95 ^d , 99 ^d	580	5600
2	FeCl ₃ /SiO ₂	21	80	71
3	FeCl ₃ /6H ₂ O ^e	3	–	10
4	Al ₂ O ₃ ^f	0	0	–
5	H-ZSM-5 ^f	7	0.6	–
6	Sc(OTf) ₃ ^{e,g}	91	–	910

^a Reaction was performed with cyclohexanol (5 mmol), acetic anhydride (6 mmol), CH₂Cl₂ (1 cm³) at room temperature with 0.05 mol% of Fe catalysts. Reaction time was 6 h except for Fe³⁺-mont ($t=1$ h) and Sc(OTf)₃ ($t=2$ h).

^b Initial rate for the acetylation.

^c Turnover frequency estimated from the initial rate and metal loading.

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

^e CH₃CN (1 cm³) was used as solvent.

^f Amount of the catalyst was 0.03 g.

^g Amount of the catalyst was 0.05 mol%.

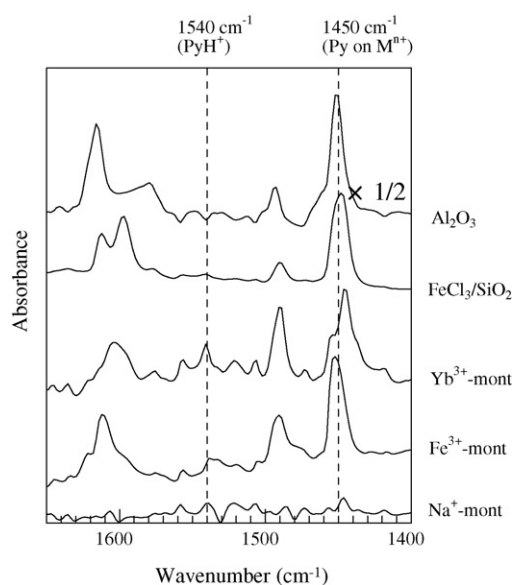


Fig. 3. IR spectra of pyridine adsorbed on various catalysts after outgassing at 473 K. Samples were pre-evacuated at 423 K prior to pyridine adsorption at 300 K.

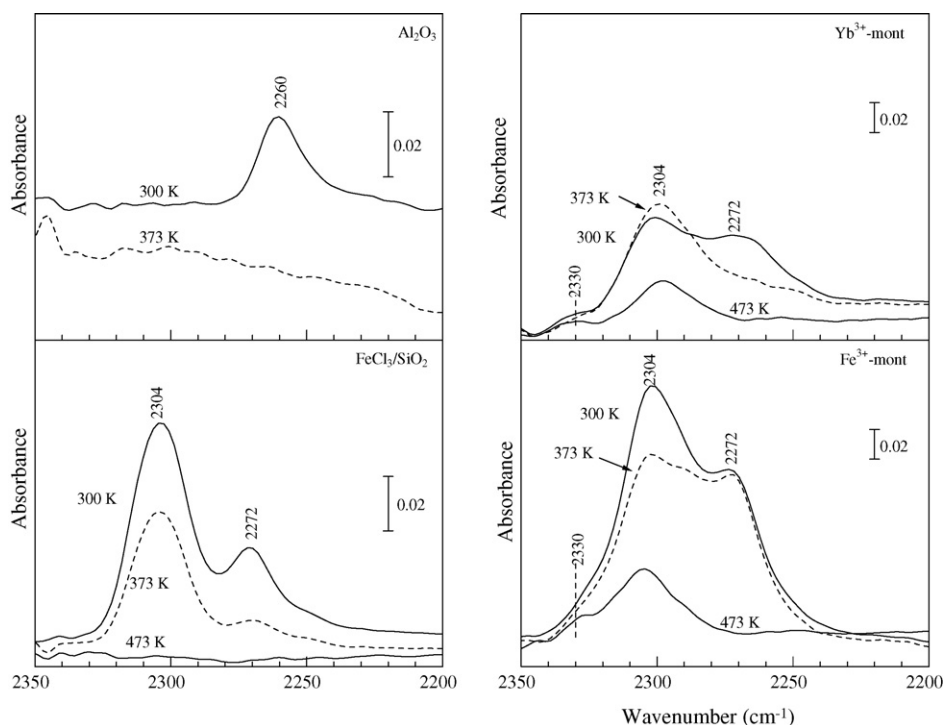


Fig. 4. IR spectra of CD_3CN adsorbed on various catalysts after outgassing at each temperature. Samples were pre-evacuated at 423 K prior to CD_3CN adsorption at 300 K.

way. Pyridinium ion (PyH^+) produced by the reaction of pyridine with Brønsted acid site shows bands near 1537 and 1637 cm^{-1} . Coordinatively bound pyridine on Lewis acid site shows bands at 1450 and 1610 cm^{-1} . Physisorbed or hydrogen-bonded pyridine shows bands at 1440 and 1597 cm^{-1} . The band around 1490 cm^{-1} is common to vibrations due to PyH^+ and coordinatively bound pyridine. Bands assignable to coordinatively bound pyridine were observed for Fe^{3+} -mont (1450 and 1610 cm^{-1}), Yb^{3+} -mont (1445 and 1602 cm^{-1}) and $\text{FeCl}_3/\text{SiO}_2$ (1450 and 1618 cm^{-1}). These bands are stable to outgassing at 473 K. This indicates that these bands are not assignable to hydrogen-bonded pyridine on metal oxides, which is known to be unstable to outgassing at temperature as low as 370 K [30]. The above assignment is also supported by comparison with IR experiments of pyridine dosed on Al_2O_3 (a solid characterized by strong Lewis acid sites), where bands at 1610 and 1450 cm^{-1} were observed. In the spectra of Fe^{3+} -mont, Yb^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$, the intensity of the band due to PyH^+ (1540 cm^{-1}) was very weak. From these results, it is found that acid sites of Fe^{3+} -mont, Yb^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$ are predominantly Lewis acidic in nature. This means that the metal cation acts as electron pair accepters and can potentially act as Lewis acid catalyst.

3.3. IR spectra of adsorbed CD_3CN

Fig. 4 shows IR spectra in the CN stretching region obtained after acetonitrile- d_3 (CD_3CN) adsorption on various catalysts pre-evacuated at 423 K for 0.5 h. All spectra were obtained after contact with CD_3CN vapor (10 Torr) at 300 K for 0.5 h and successive evacuation at a certain temperature for 0.5 h. Acetonitrile is sensitive to Lewis acid strength; electron withdrawal from the

nitrogen lone pair upon coordination leads to an increase in the $\nu(\text{CN})$ frequency [21]. Based on the previous band assignments for CD_3CN adsorbed on Al_2O_3 and zeolites [19–21], bands at 2315 – 2340 , 2300 , 2273 and 2250 cm^{-1} are attributed to interaction of the nitrile group with Al^{3+} Lewis acid sites, strong Brønsted acid sites on zeolite, SiOH groups, and the asymmetric stretching vibration of physisorbed CD_3CN , respectively. Bonino et al. [22] reported IR study of CD_3CN adsorbed on TS-1 catalyst and assigned the band at 2302 cm^{-1} to a direct interaction of CN with Ti(IV) which acts as a medium-strength Lewis site. As shown in Fig. 4, bands at 2304 and 2272 cm^{-1} were observed in the spectra for Fe^{3+} -mont, Yb^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$. For Fe^{3+} -mont and Yb^{3+} -mont, an additional shoulder band was observed at 2330 cm^{-1} . Taking into account the result of pyridine adsorption IR (Fig. 3), which indicate that these three solids are Lewis acidic in nature, the bands at 2304 and 2330 cm^{-1} can be attributed to interaction of the CN group with Lewis acid sites with medium and strong acid strength, respectively. The band at 2272 cm^{-1} is assigned to interaction of the CN group with SiOH groups. Outgassing the samples at higher temperature causes an intensity decrease in the bands due to CD_3CN coordinated to M^{n+} (2330 , 2304 cm^{-1}) and SiOH groups (2272 cm^{-1}). The band intensity at 2304 cm^{-1} is plotted as a function of outgassing temperature in Fig. 5. After outgassing at 473 K, the band at 2304 cm^{-1} completely disappeared for $\text{FeCl}_3/\text{SiO}_2$, whereas this band was still observed for M^{n+} -mont, indicating the high Lewis acid strength of M^{n+} -mont compared to $\text{FeCl}_3/\text{SiO}_2$. From desorption experiments of Fe^{3+} -mont and Yb^{3+} -mont at increasing temperatures, it clearly appears that coordinated species characterized by the band at 2330 cm^{-1} were more strongly adsorbed than those correspond-

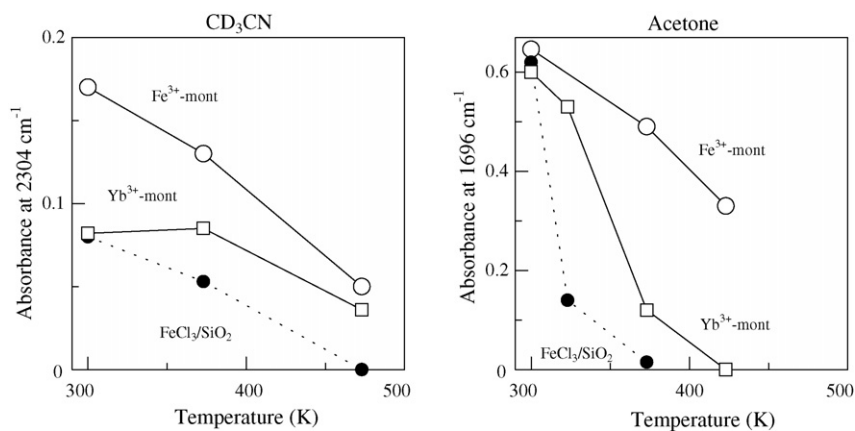


Fig. 5. Band intensity for CD_3CN adsorbed on Lewis acid site at 2304 cm^{-1} (from Fig. 4) and that for acetone coordinated to Lewis acid sites at 1696 cm^{-1} (from Fig. 7) as a function of outgassing temperature.

ing to the band at 2304 cm^{-1} , since the intensity of the latter preferentially decreased with temperature. This supports the above band assignment: CD_3CN species with higher wavenumber (2330 cm^{-1}) is coordinated to Lewis acid sites with higher acid strength than those coordinated to medium-strength Lewis sites (2304 cm^{-1}). The higher thermal stability of coordinated species on Fe^{3+} -mont than those on $\text{FeCl}_3/\text{SiO}_2$ as well as the presence of coordinated species with higher wavenumber (2330 cm^{-1}) indicate that Lewis acid strength of Fe^{3+} on the clay is higher than that on SiO_2 .

Fig. 6 (solid line) shows the spectrum obtained after CD_3CN adsorption on Fe^{3+} -mont pre-evacuated at 300 K for 0.5 h. A band due to CD_3CN coordinated to medium-strength Lewis acid site (2304 cm^{-1}) and a shoulder band due to CD_3CN on strong Lewis acid site (2330 cm^{-1}) were observed, and the band intensity was not lower than that for Fe^{3+} -mont pre-evacuated at 423 K (dashed line). In parallel, a negative band at 1625 cm^{-1} due to adsorbed water was observed. These results indicate that water molecule coordinated to Fe^{3+} Lewis acid sites was replaced by CD_3CN , and Fe^{3+} species on the clay potentially act as Lewis acid catalyst even in the presence of water in the

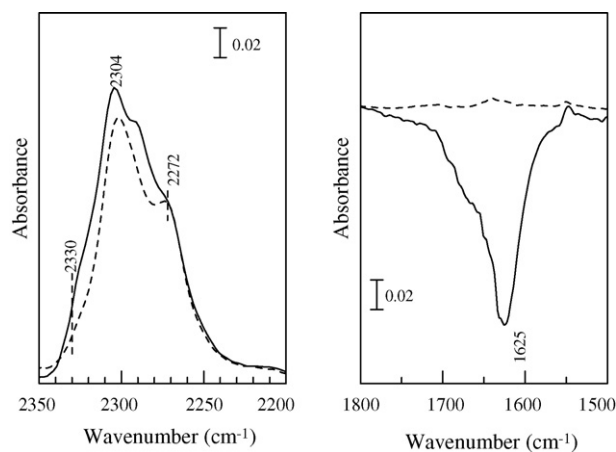


Fig. 6. IR spectra of CD_3CN adsorbed on Fe^{3+} -mont after outgassing at 300 K. The sample was pre-evacuated at 300 K (solid line) or 423 K (dashed line) prior to CD_3CN adsorption at 300 K.

first coordination sphere. Several authors reported that CD_3CN adsorption on Al_2O_3 dehydrated at high temperature (typically above 873 K) resulted in the formation of CD_3CN bonded to coordinatively unsaturated Al^{3+} Lewis sites ($2315\text{--}2340\text{ cm}^{-1}$) [20,21]. The IR spectrum measured after CD_3CN adsorption on Al_2O_3 , which was pre-evacuated at 423 K , showed a band at 2262 cm^{-1} due to H-bonded species (Fig. 4). Outgassing at 373 K led to desorption of all the H-bonded species. Taking into account the results in Fig. 3, it is shown that the surface of Al_2O_3 partially dehydrated at low temperature (423 K) has Lewis acidity toward strong base, pyridine, but does not have Lewis acidity toward weak base, CD_3CN . On the other hand, the hydrated metal cation in Fe^{3+} -mont shows Lewis acidity toward weak base, CD_3CN , because coordination of CD_3CN to the metal cation is accompanied by expulsion of the water coordinating to the metal cation.

3.4. Acetone adsorption experiments

Fig. 7 presents IR spectra of Fe^{3+} -mont, Yb^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$ taken after their exposure to acetone (30 Torr) for 0.5 h and successive evacuation at certain temperature for 0.5 h. Previous IR studies of acetone adsorption on metal oxides [23–25] have established that at room temperature acetone molecule is irreversibly adsorbed on coordinatively unsaturated M^{n+} Lewis acid sites ($(\text{CH}_3)_2\text{C}=\text{O} \rightarrow \text{M}^{n+}$), which shows $\nu(\text{C}=\text{O})$ bands around $1678\text{--}1702\text{ cm}^{-1}$. It is also known that physisorbed acetone shows a $\nu(\text{C}=\text{O})$ band at $1710\text{--}1715\text{ cm}^{-1}$ [23–25]. In the spectrum of Fe^{3+} -mont, bands at 1696 cm^{-1} with shoulder bands at 1712 , 1702 and 1682 cm^{-1} were observed. A band at 1696 cm^{-1} was also observed for $\text{FeCl}_3/\text{SiO}_2$. Thus, a band at 1696 cm^{-1} and shoulder bands at 1702 and 1682 cm^{-1} are assigned to acetone coordinated to Lewis acid sites. A shoulder band at 1712 cm^{-1} is assigned to physisorbed acetone. For all samples evacuated at 300 K, $\nu(\text{C}=\text{O})$ band around 1607 cm^{-1} assignable to mesityl oxide on Lewis acid site [23,24] was negligible, confirming that coordinated acetone does not undergo aldolcondensation-type reaction. The spectrum of acetone adsorbed on Yb^{3+} -mont showed basically the same feature as that on Fe^{3+} -mont. Desorption experiments at increasing tem-

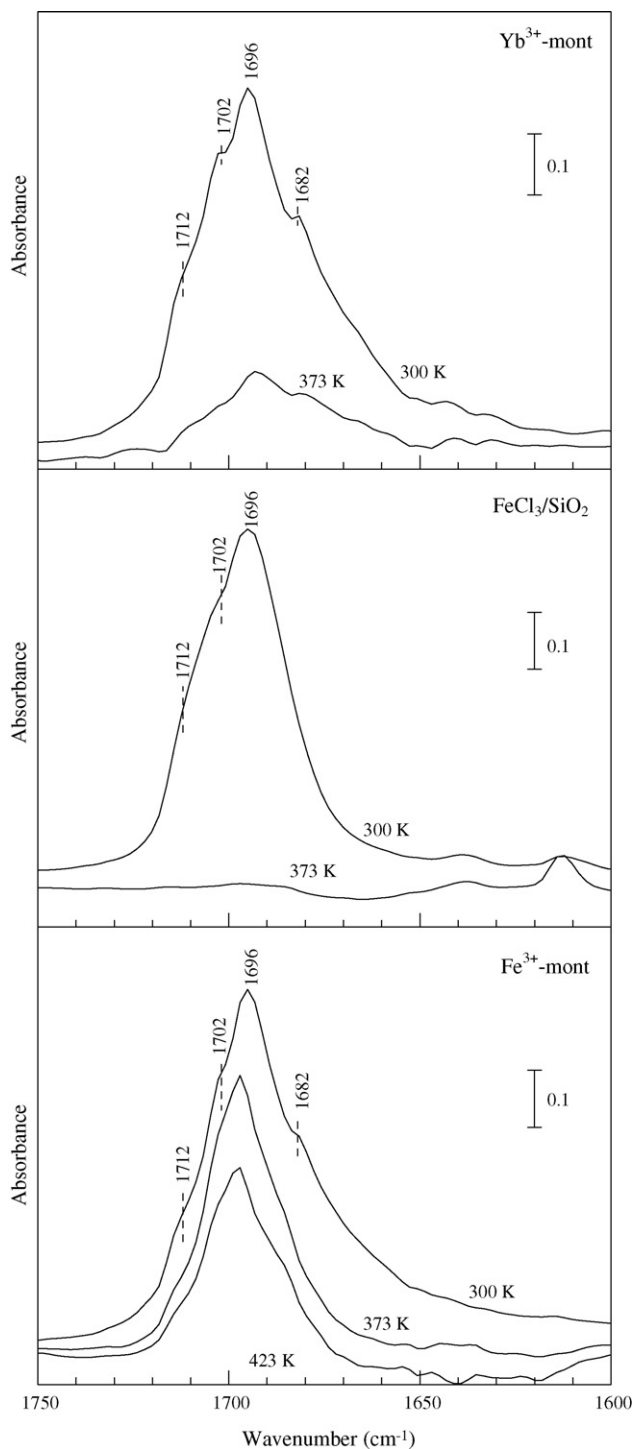


Fig. 7. IR spectra of acetone adsorbed on various catalysts after outgassing at each temperature. Samples were pre-evacuated at 423 K prior to acetone adsorption at 300 K.

peratures were performed to investigate the stability of adsorbed acetone. The band intensity at 1696 cm^{-1} is plotted as a function of outgassing temperature in Fig. 5. For $\text{FeCl}_3/\text{SiO}_2$, the band completely disappeared after outgassing at 373 K, and for Yb^{3+} -mont the band disappeared at 473 K. However, it was still observed for Fe^{3+} -mont even after evacuation at 473 K. This indicates that acetone coordinated on Fe^{3+} -mont are more

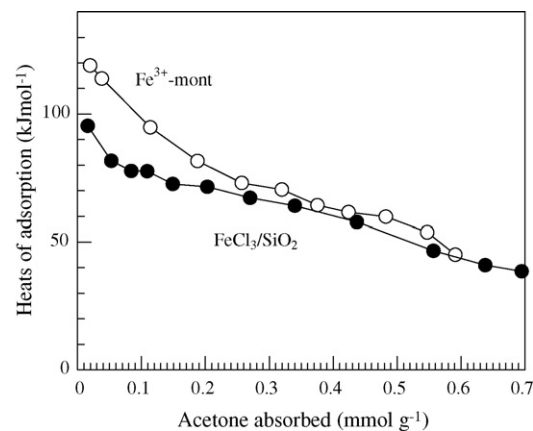


Fig. 8. Differential heat of adsorption of acetone on Fe^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$ at 323 K. Samples were pre-evacuated at 423 K prior to acetone adsorption.

strongly adsorbed than Yb^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$ because of the higher Lewis acid strength of Fe^{3+} -mont. From acetone adsorption IR results, it is shown that Fe^{3+} -mont, Yb^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$ are predominantly Lewis acidic toward a weak base acetone, and the Lewis acid strength changes in the order of Fe^{3+} -mont > Yb^{3+} -mont > $\text{FeCl}_3/\text{SiO}_2$. This is in agreement with that obtained using CD_3CN as a probe molecule.

We have carried out an acetone adsorption microcalorimetric experiment at 323 K to obtain more reliable information on Lewis acid strength of Fe^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$. Fig. 8 compares the curves of the differential heat of acetone adsorption on Fe^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$. Li and Shen reported that acetone adsorption on Lewis acid sites on Al_2O_3 , pre-evacuated at 673 K, produced initial heats of 115 kJ mol^{-1} assignable to acetone adsorption on strong Lewis acid site of Al_2O_3 [32]. Fe^{3+} -mont showed the initial heat of adsorption of 119 kJ mol^{-1} and a gradual drop in the heat. This indicates that Fe^{3+} -mont has strong Lewis acid sites, and Lewis acid sites in Fe^{3+} -mont are not homogeneous in terms of the acid strength, which is in good agreement with the presence of the $\nu(\text{C}=\text{O})$ bands at several wavenumbers for Fe^{3+} -mont (Fig. 7). $\text{FeCl}_3/\text{SiO}_2$ showed lower initial heat of adsorption (95 kJ mol^{-1}). This indicates that Lewis acid strength of Fe^{3+} -mont is higher than that of $\text{FeCl}_3/\text{SiO}_2$, which is in good agreement with IR experiments for CD_3CN and acetone adsorption (Fig. 5).

3.5. Relationship between Lewis acidity and catalytic activity

From IR results of pyridine adsorption, it is found that acid sites of Fe^{3+} -mont, Yb^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$ are predominantly Lewis acidic in nature. The metal cation acts as electron pair acceptor and can potentially act as Lewis acid catalyst. This conclusion was supported by IR results for adsorption of CD_3CN and acetone. As shown in Table 2, HZSM5, a typical Brønsted acid catalyst, gave a lower yield of acetylation products than Fe^{3+} -mont and $\text{FeCl}_3/\text{SiO}_2$ (Lewis acids), indicating that Lewis acid site is responsible for the higher activity for acetylation of cyclohexanol. Relative Lewis acid strength of these catalysts is estimated from the stability of adsorbed CD_3CN and acetone at

elevated temperatures under evacuation (Fig. 5), being found to increase in the order of $\text{Fe}^{3+}\text{-mont} > \text{Yb}^{3+}\text{-mont} > \text{FeCl}_3/\text{SiO}_2$. This is further supported by the result of acetone adsorption microcalorimetry. Catalytic test of $M^{n+}\text{-mont}$ for the acetylation of cyclohexanol with acetic anhydride showed that the activity increased with the charge/radius ratio of exchanged cation (Fig. 3). Taking into account the result that $M^{n+}\text{-mont}$ showed low level of leaching (Table 1) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in the reaction mixture (homogeneous catalyst) showed low catalytic activity, it is clear that the acetylation activity of $M^{n+}\text{-mont}$ catalysts originates from metal cations supported on the clay, and the metal cation with higher Lewis acidity gives higher reaction rates. Although we do not have any proof of the mechanism, we assume that the reaction is initiated by coordination of Ac_2O or cyclohexanol to the metal cation (Lewis acid) site. The metal cations with higher Lewis acid strength polarize carbon oxygen bond in the coordinated species, which should result in the higher catalytic activity.

For the Lewis acid catalysis of the cation exchanged clay a fundamental question arises: why the activity of metal cations can be enhanced by loading them onto the clay, though the answer is not clarified in the literature. $\text{Fe}^{3+}\text{-mont}$ was more active than $\text{FeCl}_3/\text{SiO}_2$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ under the same reaction conditions (Table 2). The higher Lewis acid strength of $\text{Fe}^{3+}\text{-mont}$ than $\text{FeCl}_3/\text{SiO}_2$, as evidenced by microcalorimetric and IR experiments of acetone adsorption, should be responsible for the higher activity of the former catalyst. On the silicate sheet of clay, the negative charge can be dispersed over many oxygen atoms. The lower partial charge of the clay anion sheet than Cl^- ion may lead to higher exchangeability of the Fe^{3+} cation in the clay and consequently to the higher Lewis acid strength.

The catalytic and characterization results in this study demonstrate clear difference between the clay exchanged Lewis acid, $\text{Fe}^{3+}\text{-mont}$, and a conventional solid Lewis acid, Al_2O_3 . IR result for CD_3CN adsorption on the hydrated $\text{Fe}^{3+}\text{-mont}$ (Fig. 5) showed that water molecules coordinated to Fe^{3+} sites were replaced by CD_3CN . This implies that the Fe^{3+} cation on the clay act as Lewis acid site even in the presence of water in the first coordination sphere. On the other hand, Al_2O_3 partially dehydrated at low temperature (423 K) acts as Lewis acid toward strong base, pyridine, but does not act as Lewis acid toward weak base, CD_3CN . As shown in Table 2, the acetylation reaction was not catalyzed by Al_2O_3 . From a comparison of these catalytic results with the acidic character, it is proposed that Ac_2O or cyclohexanol as a weak base can coordinate to the Fe^{3+} cation on the hydrated $\text{Fe}^{3+}\text{-mont}$, while the weak base cannot compete with stronger base such as OH^- and water, which is strongly coordinated to an Al^{3+} cation on hydrated Al_2O_3 .

4. Conclusion

Among 14 types of metal ion-exchanged montmorillonite K-10 clay ($M^{n+}\text{-mont}$), $\text{Fe}^{3+}\text{-mont}$ is most effective for the acetylation of cyclohexanol with acetic anhydride at room temperature. $\text{Fe}^{3+}\text{-mont}$ provides a clean and convenient alternative for the acetylation reaction, because the reaction proceeds smoothly in the presence of moisture, producing acetylation

products in high yields using the heterogeneous catalyst with reusable and a non-polluting nature that offers easy handling and ready work-up. From the relationship between the activity and the acidic character of $\text{Fe}^{3+}\text{-mont}$ and reference catalysts, the following conclusion is reached. Lewis acid catalysts are more suitable for acetylation than typical Brønsted acid, HZSM5 zeolite. The order of Lewis acid strength, $\text{Fe}^{3+}\text{-mont} > \text{Yb}^{3+}\text{-mont} > \text{FeCl}_3/\text{SiO}_2$, is consistent with the order of catalytic activity, indicating that Lewis acid strength is an important factor affecting the activity. Unlike conventional heterogeneous Lewis acid, Al_2O_3 , the Fe^{3+} cation in $\text{Fe}^{3+}\text{-mont}$ act as Lewis acid for weak base, CD_3CN , even in the presence of water in the first coordination sphere, which should account for the moisture-tolerant and highly effective Lewis acid catalysis of $\text{Fe}^{3+}\text{-mont}$.

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