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(71)

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(72)

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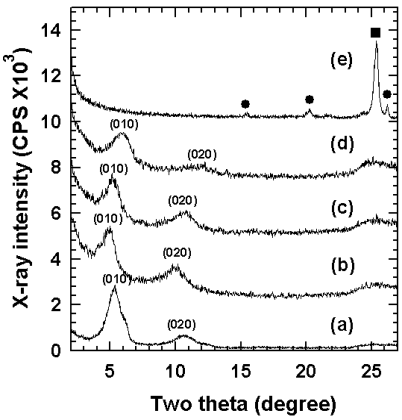
(74)

: 7

(54)

(57)

, $R_2R_3R_4R_5Si$
(R_2 C_1 C_{12} , R_3, R_4 R_5
-OH , C_1 C_6 , C_1 C_6 , R_3,
R_4 R_5 -OH C_1 C_6)
,
, ,
.
- 8



1

$R_2R_3R_4R_5Si$ (R_2 C_1 C_{12} , R_3, R_4 R_5 -OH , C_1 C_6 , C_1 C_6 , R_3, R_4 R_5 -OH C_1 C_6) ,

.

2

1 ,

y 0.67 0.73 $Cs_yTi_{2-y/4}O_4$, $K_2Ti_2O_5$, $K_2Ti_4O_9$, $Na_2Ti_3O_7$, $Cs_2Ti_5O_{12}$, $KTiNbO_5$, $CsTi_2NbO_7$, KTi_3NbO_9 $K_3Ti_5NbO_{14}$ 1 .

3

1 ,

3- ( ) (3-aminopropyl(diethoxy)methylsilane), (3-) ((3-aminopropyl)triethoxysilane) (3-) ((3-aminopropyl)trimethoxysilane) 1 .

4

1 ,

VO^{3-}(metavanadate), $V_2O_7^{4-}$(Pyrovanadate), $V_4O_{12}^{4-}$(Tetravanadate), $V_{10}O_{28}^{6-}$(Decavanadate), MnO_4^-, $Mo_7O_{24}^{6-}$, $MO_8O_{26}^{4-}$, MoO_4^{2-}, $Mo_{19}O_{59}^{4-}$, $W_{12}O_{39}^{6-}$, $W_{12}O_{41}^{10-}$, $W_6O_20(OH)^{5-}$, WO_4^{2-}, HCr_4^-, CrO_4^{2-} $Cr_2O_7^{2-}$ 1 .

5

) pH 6 ,;

) R_1-NH_3^+ (R_1 C_1 C_{18}) ,;

) $R_2R_3R_4R_5Si$ (R_2 C_1 C_{12} , R_3, R_4 R_5 -OH , C_1 C_6 , C_1 C_6 , R_3, R_4 R_5 -OH C_1 C_6) ,;

) .

6

5 ,

VO^{3-}(metavanadate), $V_2O_7^{4-}$(Pyrovanadate), $V_4O_{12}^{4-}$(Tetravanadate), $V_{10}O_{28}^{6-}$(Decavanadate), MnO_4^-, $Mo_7O_{24}^{6-}$, $Mo_8O_{26}^{4-}$, MoO_4^{2-}, $Mo_{19}O_{59}^{4-}$, $W_{12}O_{39}^{6-}$, $W_{12}O_{41}^{10-}$, $W_6O_20(OH)^{5-}$, WO_4^{2-}, HCr_4^-, CrO_4^{2-} $Cr_2O_7^{2-}$

1 .

7

5 ,

3- ( ) (3-aminopropyl(diethoxy)methylsilane), (3-) ((3-aminopropyl)triethoxysilane) (3-) ((3-aminopropyl)trimethoxysilane) 1 .

[0001] , $R_2R_3R_4R_5Si$ (R_2 C_1 C_{12} , R_3, R_4 R_5 -OH , C_1 C_6 , C_1 C_6 , R_3, R_4 R_5 -OH C_1 C_6) , .

[0002] . (clay) .

[0003] pH . clay . pH (V), (Mn), (Mo) .

[0004] .

[0005] . .

[0006] , pH pH (swelling) (dispersion) pH ,

.

[0007] , $R_2R_3R_4R_5Si$ (R_2 C_1 C_{12} , R_3, R_4 R_5 -OH , C_1 C_6 , C_1 C_6 , R_3, R_4 R_5 -OH C_1 C_6)

,

.

[0008] , y 0.67 0.73 $Cs_yTi_{2-y/4}O_4$, $K_2Ti_2O_5$, $K_2Ti_4O_9$, $Na_2Ti_3O_7$, $Cs_2Ti_5O_{12}$, $KTiNbO_5$, $CsTi_2NbO_7$, KTi_3NbO_9 $K_3Ti_5NbO_{14}$ 1

.

[0009] , 3- ( ) (3-aminopropyl(diethoxy)methylsilane), (3-) ((3-aminopropyl)triethoxysilane) (3-) ((3-aminopropyl)trimethoxysilane) 1

.

[0010] , VO^{3-}(metavanadate), $V_2O_7^{4-}$(Pyrovanadate), $V_4O_{12}^{4-}$(Tetravanadate), $V_{10}O_{28}^{6-}$(Decavanadate), MnO_4^-, $Mo_7O_{24}^{6-}$, $MO_8O_{26}^{4-}$,MoO_4^{2-}, $Mo_{19}O_{59}^{4-}$, $W_{12}O_{39}^{6-}$, $W_{12}O_{41}^{10-}$, $W_6O_20(OH)^{5-}$, WO_4^{2-}, HCr_4^-, CrO_4^{2-} $Cr_2O_7^{2-}$ 1 .

[0011] ,) pH 6 ,;) R_1-NH_3^+ (R_1 C_1 C_{18}) ,;) $R_2R_3R_4R_5Si$ (R_2 C_1 C_{12} , R_3, R_4 R_5 -OH , C_1 C_6 , C_1 C_6 , R_3, R_4 R_5 -OH C_1 C_6) ,;)

.

[0012] , VO^{3-}(metavanadate), $V_2O_7^{4-}$(Pyrovanadate), $V_4O_{12}^{4-}$(Tetravanadate), $V_{10}O_{28}^{6-}$(Decavanadate), MnO_4^-, $Mo_7O_{24}^{6-}$, $MO_8O_{26}^{4-}$, MoO_4^{2-}, $Mo_{19}O_{59}^{4-}$, $W_{12}O_{39}^{6-}$, $W_{12}O_{41}^{10-}$, $W_6O_20(OH)^{5-}$, WO_4^{2-}, HCr_4^-, CrO_4^{2-} $Cr_2O_7^{2-}$ 1 .

[0013] , 3- ( ) (3-aminopropyl(diethoxy)methylsilane), (3-) ((3-aminopropyl)triethoxysilane) (3-) ((3-aminopropyl)trimethoxysilane) 1

.

[0014] ,

.

[0015] pH
pH (swelling) (dispersion)
. (building block)
bottom-up .

[0016] .

[0017] $R_2R_3R_4R_5Si$ (R_2 C_1 C_{12}
, R_3, R_4 R_5 -OH , C_1 C_6
, C_1 C_6 , R_3, R_4 R_5 -OH C_1
C_6)
, .

[0018] , " " " "
, " " " "
.

[0019] , . ,
. ,
.
FeOOH 2 . TiO_6
Cs .
,
1 nm .
(nanosheet)
(flocculation) . pH < 7
pH ≤
7
. pH
.

[0020]) pH 6
,;)
R_1-NH_3^+ (R_1 C_1 C_{18}
)
,;) $R_2R_3R_4R_5Si$ (R_2 C_1 C_{12}
, R_3, R_4 R_5 -OH , C_1 C_6 ,
C_1 C_6 , R_3, R_4 R_5 -OH C_1 C_6
)
,;)
.

[0021] $R_2R_3R_4R_5Si$ (R_2
C_1 C_{12} , R_3, R_4 R_5 -OH , C_1 C_6
, C_1 C_6 , R_3, R_4 R_5

-OH C_1 C_6), . R_2

, R_3, R_4 R_5 -OH

. 5 1

^{29}Si MAS (NMR spectrum) , 5 ,

.

[0022] ,

, VO^{3-}(metavanadate), $V_2O_7^{4-}$(Pyrovanadate), $V_4O_{12}^{4-}$(Tetravanadate), $V_{10}O_{28}^{6-}$

(Decavanadate), MnO_4^-, $Mo_7O_{24}^{6-}$, $MO_8O_{26}^{4-}$, MoO_4^{2-}, $Mo_{19}O_{59}^{4-}$, $W_{12}O_{39}^{6-}$, $W_{12}O_{41}^{10-}$, $W_6O_20(OH)^{5-}$, WO_4^{2-}, HCr_4^-, CrO_4^{2-}

$Cr_2O_7^{2-}$ 1 .

[0023] , R_1-NH_3^+

. ,

. ,

. R_1-NH_3^+

R_1 C_1 C_{18} ,

R_1 C_6 C_{12} .

[0024] .

[0025] (1)

[0026] (Cs_2CO_3) (TiO_2) , 1

750 24 y 0.67 0.73 $Cs_yTi_{2-y/4}\square_{x/4}O_4$

(□ vacancy).

800 24 . ,

(orthorhombic) (lepidocrocite) $Cs_yTi_{2-y/4}\square_{x/4}O_4$

. $Cs_yTi_{2-y/4}\square_{x/4}O_4$ 1 M HCl (H^+) $H_yTi_{2-y/4}\square_{x/4}O_4 \cdot zH_2O$

. , $Cs_yTi_{2-y/4}\square_{x/4}O_4$ 1 g 1M 100 . , 3

5 .

60 . X $Cs_yTi_{2-y/4}\square_{x/4}O_4$ Cs (H^+) $H_yTi_{2-y/4}\square_{x/4}O_4 \cdot zH_2O$

$Cs_{0.67}Ti_{1.83}\square_{0.17}O_4$ $H_{0.67}Ti_{1.83}\square_{0.17}O_4 \cdot H_2O$

.

[0027] $H_{0.67}Ti_{1.83}\square_{0.17}O_4 \cdot H_2O$

(octylamine) . H^+ 2 5

.

100 10 . . 3

.

60 .

[0028]

. (3-) ((3-aminopropyl)triethoxysilane, APS) . (toluene) 50 $H_{0.67}Ti_{1.83}\square_{0.17}O_4 \cdot H_2O$ 0.5 g APS 11 60 50 .

.

[0029] .

. (decavavadate) $V_{10}O_{28}^{6-}$ (ammonium metavanadate, NH_4VO_3) pH = 4 $V_{10}O_{28}^{6-}$. APS pH = 4 . (ultra sonicator) 15 . V Si 3 5 $V_{10}O_{28}^{6-}$. 3 . 5:5 . 50 .

[0030] (2)

[0031] $K_2Ti_2O_5$ 1 .

[0032] (3)

[0033] 3- ( ) (3-aminopropyl(diethoxy)methylsilane) 1 .

[0034] (4)

[0035] 3- ( ) (3-aminopropyl(diethoxy)methylsilane) 1 .

[0036] (5-7)

[0037] (CrO_4^{2-}), (MnO_4^-) ($Mo_7O_{24}^{6-}$) 1 .

[0038] 1 1 (a) $Cs_{0.67}Ti_{1.83}\square_{0.17}O_4$ 1M HCl (b) $H_{0.67}Ti_{1.83}\square_{0.17}O_4 \cdot H_2O$ (c) $(CH_3(CH_2)_7NH_2)_xH_{0.67}$-$Ti_{1.83}\square_{0.17}O_4 \cdot yH_2O$, APS $(APS)_x$-$Ti_{1.83}\square_{0.17}O_4 \cdot yH_2O$ X-ray . $Cs_{0.67}Ti_{1.83}\square_{0.17}O_4$ body-centered orthorhombic (unit cell) . 1M HCl $H_{0.67}Ti_{1.83}\square_{0.17}O_4 \cdot H_2O$ (020) $Cs_{0.67}Ti_{1.83}\square_{0.17}O_4$. Cs^+ H_3O^+ (020) (020) . (octylamine, $CH_3(CH_2)_7NH_2$) . 1c . 1c (0k0)

. (010) 19.90 . (octylamine)
11.25 7.6 gallery height 12.30
octylamine . (ICP-
AES) (TG) $(CH_3(CH_2)_7NH_2)_{0.61}H_{0.67}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 1.5H_2O$. APS X-ray 1d
. $(CH_3(CH_2)_7NH_2)_{0.61}H_{0.67}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 1.5H_2O$ (010)
. (010) 16.61 APS 7.5 gallery height
9.01 . $(CH_3(CH_2)_7NH_2)_{0.61}H_{0.67}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 1.5H_2O$ ICP-AES
$(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 0.8H_2O$.

[0039] 2 . (a) $(CH_3(CH_2)_7NH_2)_{0.61}H_{0.67}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 1.5H_2O$
(b) $(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 0.8H_2O$. (i)
, (ii) . (iii)
. (a) (b)
. Si Ti
. C, H, N
$(CH_3(CH_2)_7NH_2)_{0.61}H_{0.67}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 1.5H_2O$ C 24.6%(mass), N 3.4%(mass)
$(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 0.8H_2O$ C 16.0%(mass), N
5.3%(mass) .
. C octylamine
C .
.

[0040] (FT-IR)
. 3 (a) (b) $(CH_3(CH_2)_7NH_2)_{0.61}H_{0.67}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 1.5H_2O$ $(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 0.8H_2O$
. 2600 3300 cm^{-1} peak (amine salt) RNH_3^+
2900cm^{-1} C-C bond . 1630 cm^{-1}
N-H vibration . 980 1180 cm^{-1}
. 3a 3b
SiO-C vibration . Si-O-Ti
950cm^{-1} .

[0041] 4 3 FT-IR . 4
. APS
.

[0042] Si ^{29}Si MAS NMR . 5
Si chemical shift .
. NMR (1), (2) .
bidentate > tridentate > monodentate .
APS .
. 6 $2 \le pH \le 4$ 30
45 mV .
. pH ,
$V_{10}O_{28}^{6-}$ pH < 6
.
(swelling) (dispersion) . pH = 4 (swelling)

(dispersion) 7 . 7a $(CH_3(CH_2)_7NH_2)_{0.61}H_{0.67}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 1.5H_2O$ pH = 4 .

. 7c 7d pH = 13 4 . pH = 13 . pH = 4 (H_3O^+) (flocculation) . 7b pH = 4 , pH = 13 . 7b 7c .

[0043] . 8 X- . 8a $(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 0.8H_2O$ 8b $V_{10}O_{28}^{6-}$ VO_x-$(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot yH_2O$-RT . 8b $V_{10}O_{28}^{6-}$ 8a (010) . $V_{10}O_{28}^{6-}$ 1 nm (010) . . X . 8c 8d 300 400 . 8b . . $V_{10}O_{28}^{6-}$ VO_x $V_{10}O_{28}^{6-}$. 500 (010) two theta 15° V_2O_5(●) TiO_2 anatase(■) . TiO_2 TiO_2 V_2O_5 . 2b 500 (iii) TiO_2 .

[0044] 9 APS (a) (b) . $V_{10}O_{28}^{6-}$. ICP-AES Ti : Si : V 1 : 0.52 : 0.29 . VO_x-$(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot yH_2O$-RT 400 (transmission electron microscopy) . 10a 10b 400 . 10 1.80 nm 1.50 nm . 8 X (010) . . . TEM X 11 Ti, Si, V . EDS Ti : Si : V 1 : 0.46 : 0.35 . ICP-AES .

[0045] TEM-EDS Ti, Si, V mapping . 12 12a 12b, c, d Ti, Si, V . , V .

[0046] Ti K- V-K x-ray (XANES) .

[0047] 13 1 (a) $Cs_{0.67}Ti_{1.83}\square_{0.17}O_4$,(b) $H_{0.67}Ti_{1.83}\square_{0.17}O_4 \cdot H_2O$, (c) $(CH_3(CH_2)_7NH_2)_{0.61}H_{0.67}$-$Ti_{1.83}\square$

$_{0.17}O_4 \cdot 1.5H_2O$, (d) $(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 0.8H_2O$ (e) anatase TiO_2 (f) rutile TiO_2 XANES . $Cs_{0.67}Ti_{1.83}\square_{0.17}O_4$ anatase rutile TiO_2 . 1a lepidocrocite . 13b, c, d 13a . TiO_2 4+ . 14 $V_{10}O_{28}^{6-}$ Ti-K XANES .

[0048] 14a $(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot 0.8H_2O$ VO_x-$(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot yH_2O$-RT 300 , 400 $Ti_{1.83}\square_{0.17}O_4$. 500 (14e) anatase TiO_2(14g) . 2b(iii) 8e TiO_2(anatase TiO_2) . 700 (14f) rutile TiO_2(14h) anatase rutile .

[0049] V XANES 15 . 15a (i),(ii),(iii) V_2O_3, V_2O_4, V_2O_5 (iv), (v), (vi), (vii), (viii) VO_x-$(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot yH_2O$-RT 300 , 400 , 500 , 700 . V_2O_5 5+ . 15b Pre-edge . V_2O_3(open circles), V_2O_4(open triangles), V_2O_5(open squares) , VO_x-$(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot yH_2O$-RT (solid lines), 300 (dashed lines), 400 (dot-dashed lines), 500 (dot-dot-dashed lines) 700 (close diamonds) . 15a V_2O_5 .

[0050] VO_x-$(APS)_{0.96}$-$Ti_{1.83}\square_{0.17}O_4 \cdot yH_2O$ V Cr, Mn, Mo . 16 .

[0051] . , . .

[0052] 1 1 X- (powder X-ray diffraction)

[0053] 2 1 (thermogravimetric analysis)

[0054] 3 1 - (FT-IR spectroscopy)

[0055] 4 1 - (FT-IR spectroscopy)

[0056] 5 1 ^{29}Si MAS (NMR spectrum)

[0057] 6 1 pH (zeta potential)

[0058] 7 1 pH = 4

[0059] 8 1 X- (powder X-ray diffraction)

[0060] 9 1

[0061] 10 1 400 (transmission electron microscopy)

[0062] 11 1 X-ray (energy dispersive x-ray spectroscopy)

[0063] 12 1 X-ray (energy dispersive spectroscopy) (mapping)

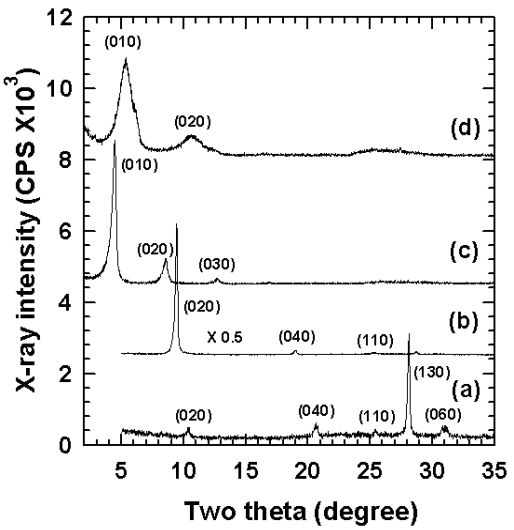
[0064] 13 1 XANES(X-ray absorption near edge structure)

[0065] 14 1 XANES(X-ray absorption near edge structure)

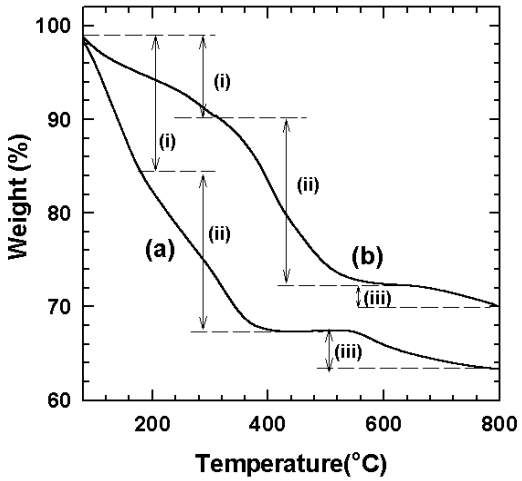
[0066] 15 1 XANES(X-ray absorption near edge structure)

[0067] 16 1, 5 7 , , ,

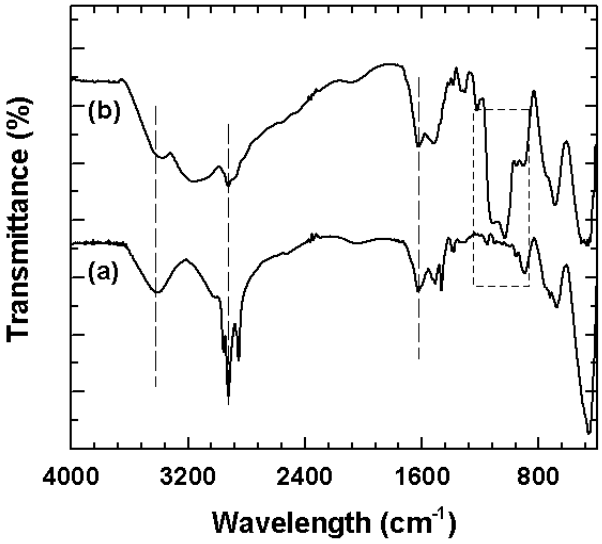
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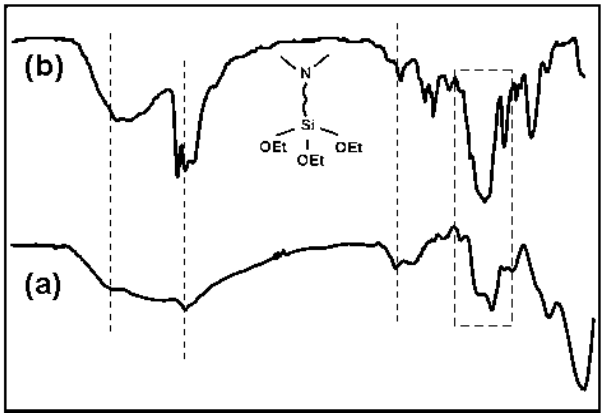
2


100
90
80
70
60
Weight (%)
200
400
600
800
Temperature(°C)
(i)
(i)
(ii)
(ii)
(a)
(b)
(iii)
(iii)

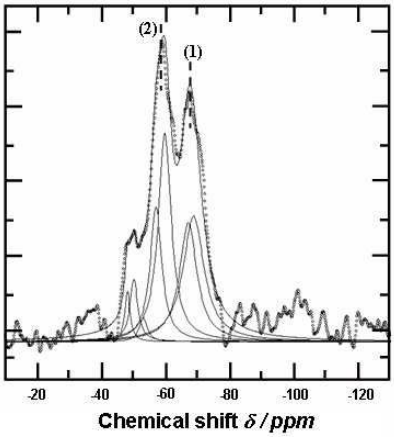
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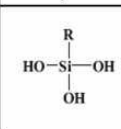
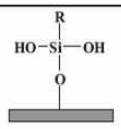
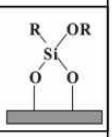
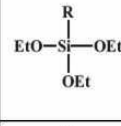
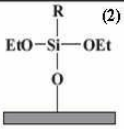
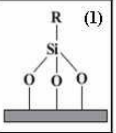

Transmittance (%)
(b)
(a)
4000
3200
2400
1600
800
Wavelength (cm-1)

4

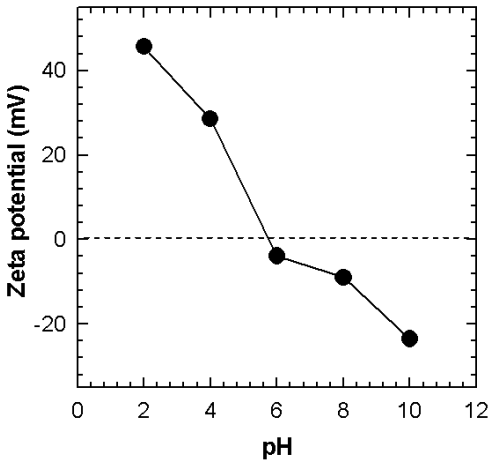


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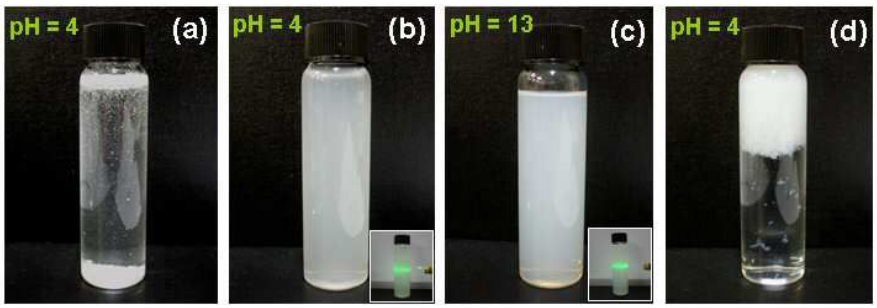


	T^0	T^1	T^2
Oxane bond type			
Chemical shift [ppm]	-31	-43	-59
	T^0	T^1	T^3
Oxane bond type			
Chemical shift [ppm]	-37	-53	-67

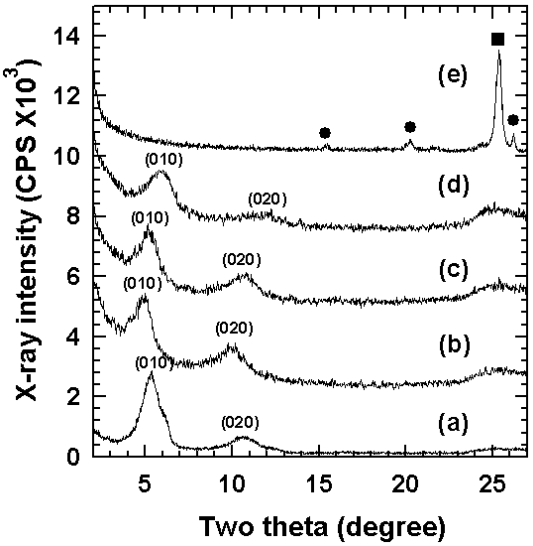
6



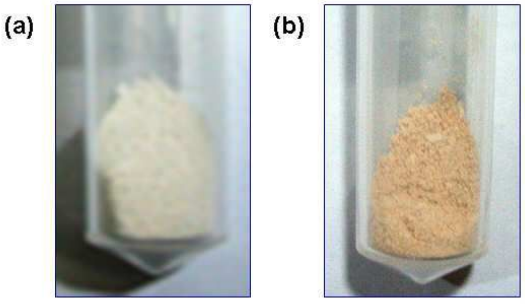
7


pH = 4
(a)
pH = 4
(b)
pH = 13
(c)
pH = 4
(d)

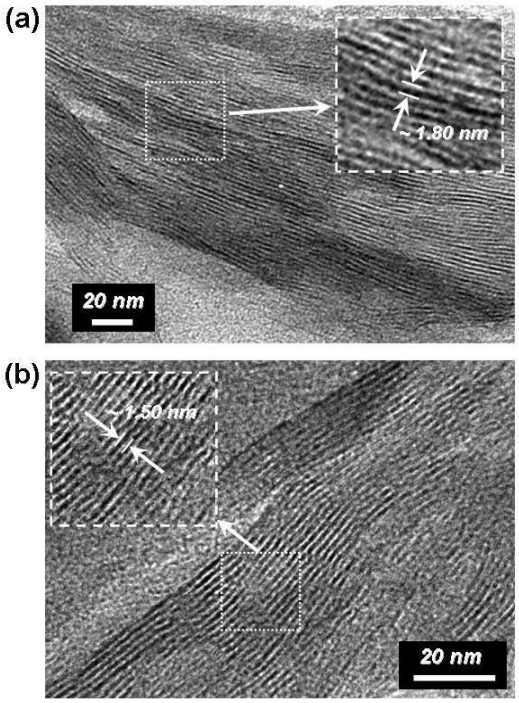
8


X-ray intensity (CPS X10^3)
Two theta (degree)
(e)
(d)
(c)
(b)
(a)
(010)
(020)

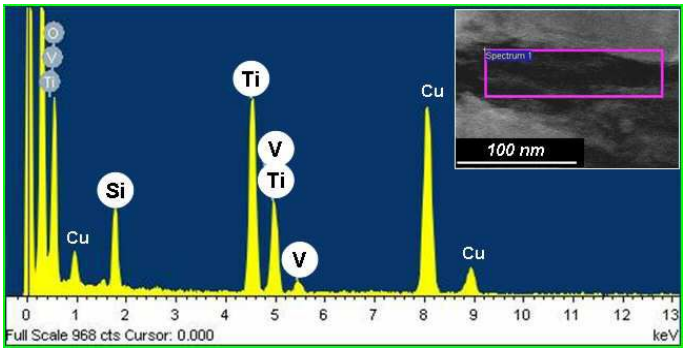
9


(a)
(b)

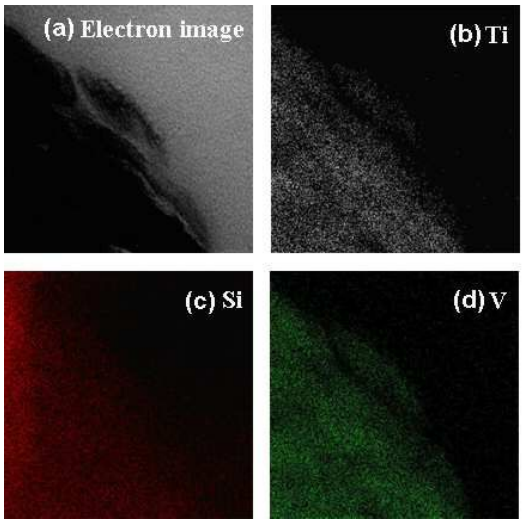
10


(a)
~1.80 nm
20 nm
(b)
~1.50 nm
20 nm

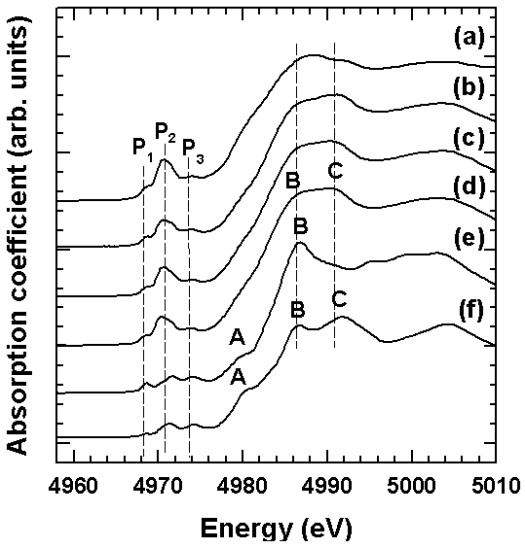
11


O
V
Ti
Ti
Cu
Si
V
Ti
V
Cu
Cu
Spectrum 1
100 nm
0 1 2 3 4 5 6 7 8 9 10 11 12 13
Full Scale 968 cts Cursor: 0.000
keV

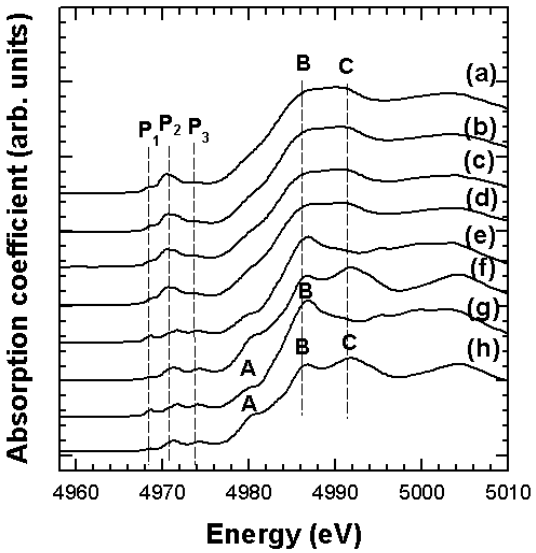
12


(a) Electron image
(b) Ti
(c) Si
(d) V

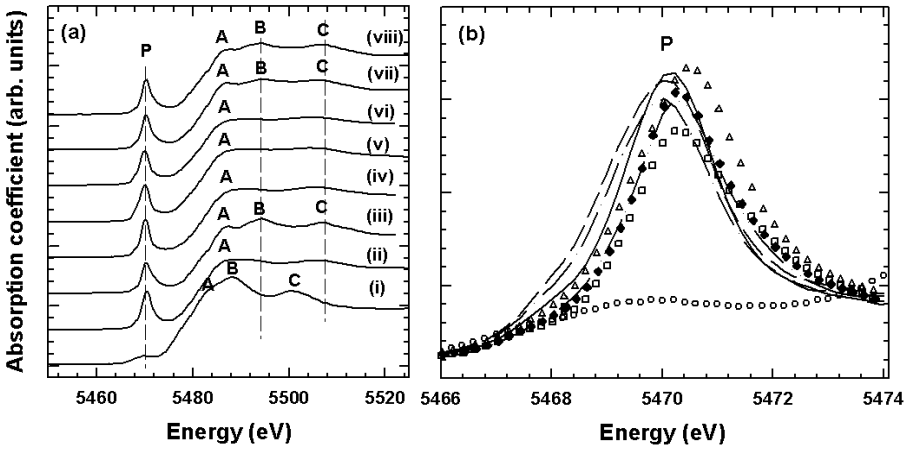
13


Absorption coefficient (arb. units)
Energy (eV)
4960
4970
4980
4990
5000
5010
(a)
(b)
(c)
(d)
(e)
(f)
P1
P2
P3
A
A
B
B
B
C
C

14


Absorption coefficient (arb. units)
Energy (eV)
4960
4970
4980
4990
5000
5010
P1 P2 P3
A
B
C
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)

15


Absorption coefficient (arb. units)
(a)
(b)
P
A
B
C
(viii)
(vii)
(vi)
(v)
(iv)
(iii)
(ii)
(i)
5460
5480
5500
5520
5466
5468
5470
5472
5474
Energy (eV)
Energy (eV)

16


APS
V
Cr
Mn
Mo