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Acidity Comparison between Ion-Exchanged Clay Montmorillonites by Using Silylation of Alcohol

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Abstract: Acidities of various ion-exchanged clay montmorillonites in organic media are compared by use of the reaction of a primary alcohol with allyltrimethylsilane. The order of catalytic activities of the montmorillonites coincide with a sequence of hydration enthalpy of exchanged cations in the clays.

Acidic clay montmorillonites are useful solid acid catalysts in liquid-phase organic reactions.[1] Acidic characters of montmorillonites are dependent on the sort of exchanged cations staying in interlamellar spaces. We have demonstrated that aluminium,[2a] iron,[2b] and tin[2c] ion-exchanged montmorillonites (M-Mont)[3] are strongly acidic and efficient for several acid-catalyzed organic reactions. Application of commercially available acidic clay K10[4] in organic synthesis was also frequently found in recent literatures.[5] It is difficult to compare acidities of the strongly acidic montmorillonites with the Hammett indicator method as shown in Table 1, but the evaluation of acidities in organic media among the cation-exchanged clays is demanded in light of more practical use of the clays in organic synthesis. In this communication the reaction of a primary alcohol with allyltrimethylsilane was selected as a probe to tell a relative acidity order of acidic ion-exchanged montmorillonites, because the reaction proceeds quantitatively, producing a silylated alcohol and gaseous propene which are not poisonous to the catalyst, and in homogeneous acid-catalyzed precedents (use of p-toluenesulfonic acid and triflic acid) the silylation works more quickly as the catalyst applied is more acidic.[6]

$$C_{10}H_{21}OH \; + \; CH_2{=}CHCH_2SiMe_3 \; \xrightarrow{\text{Clay}} \; C_{10}H_{21}OSiMe_3 \; + \; CH_2{=}CHCH_3 \uparrow$$

The catalytic activities of various cation-exchanged montmorillonites were compared using the same mass of catalyst. In a 20-ml round-bottom flask a clay (0.05 g) was activated under 0.5 Torr at 120°C for 3 h. Under argon a CH_2Cl_2 (5 ml) solution of 1-decanol (1 mmol) and allyltrimethylsilane (2 mmol) was introduced, and the suspended mixture was stirred (700 rpm) at 30°C. The silylation was monitored by GC at regular intervals.

Table 1 shows the time taken for completion of the silylation on clay catalysts. The origin of acidic nature on a clay is a proton dissociated from the water which coordinates with an interlamellar exchangeable cation:[7]

$$M^{n+}(H_2O) \longrightarrow M^{(n-1)+}(OH) \; + \; H^+$$

Therefore the acidity of a clay should be related to electron negativity[8] or hydration enthalpy of an exchanged cation. The catalytic activities of clays in Table 1 well coincide with the sequence of hydration enthalpy ($-\Delta H_h$=kJ/g-ion) of cations: Sn^{4+} (7754) > Fe^{3+} (5464) > Al^{3+} (4768) > Cu^{2+} (2772) > Ni^{2+} (2168) ~ Zn^{2+}

Table 1. Silylation of 1-Decanol

Clay	S. A.[a] (m^2/g)	Acid strength (H_0)	Completion time (min)
Sn-Mont	280	$-8.2 \geq H_0$	10
Fe-Mont	26	---[b]	35
K10	223	$-8.2 \geq H_0$	45
Al-Mont	26	$-8.2 \geq H_0$	50
H-Mont	27	$-8.2 \geq H_0$	70
Cu-Mont	39	---[b]	100
Zn-Mont	41	$-5.6 \geq H_0 > -8.2$	360
Ni-Mont	19	$-5.6 \geq H_0 > -8.2$	380

a) Specific surface area. b) It is hard to judge a color change of an indicator because the clay is colored.

(2118). Except for Sn-Mont and K10, the cation-exchanged montmorillonites have specific surface areas between 20 and 40 m^2/g. Sn-Mont was found more acidic than Fe- and Al-Mont in the conjugate addition of cyanide to 2-cyclohexenone because Sn-Mont can isomerize a 1,2-adduct to a 1,4-adduct more exclusively and rapidly.[2c] Therefore the highest activity of Sn-Mont in the silylation is ascribed primarily to the intrinsic high acidity, not to the high surface area. Based on these experimental results, the acidity order of the ion-exchanged montmorillonites in CH_2Cl_2 can be estimated to be Sn-Mont > Fe-Mont > Al-Mont > H-Mont > Cu-Mont > Zn-Mont ~ Ni-Mont. It should be noted that Sn-Mont is a very acidic clay with high specific surface area, and more acidic than commercial K10.

From a viewpoint of organic synthesis, the present acid clay-catalyzed process becomes a useful method for the formation of a trimethylsilyl ether from various primary alcohols. However, in the case of secondary and tertiary alcohols, elimination reactions concur owing to high acidity of the catalyst.

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