

The Catalytic Conversion of *n*-Pentanol to Dialkylether by Some Cation-Exchanged Montmorillonite Catalysts

A. M. HABIB, M. F. ABD-EL-MEGEED, A. SAAFAN and R. M. ISSA
Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

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Abstract. The heterogeneous catalytic conversion of *n*-pentanol to dialkylether was carried out using untreated cation-exchanged montmorillonites and using samples which had been preheated at 300°C in an atmosphere of air, hydrogen or nitrogen. The catalyst has been characterized by applying thermogravimetric analysis, X-ray diffraction and cation exchange capacity tests. Gas-chromatographic analysis of the products showed that the catalytic reactivity of the exchanged montmorillonite is related to the cation radius.

The catalytic conversion of *n*-pentanol by organometallic complexes of either $\text{Al}^{3+}/\text{Fe}^{3+}$ -montmorillonites with benzidine has been doubled compared with the catalytic conversion in the absence of benzidine. This may be attributed to the catalytic effect of benzidinium mono- or di-radical cations that enhance the conversion of *n*-pentanol to alkene.

Key words: Montmorillonite, heterogeneous catalysis, alcohol.

1. Introduction

In purified montmorillonite and related substances, ethanol can displace the primary hydration shell of Ca^{2+} , Cu^{2+} and Al^{3+} [1]. Furthermore, even Na^+ and NH_4^+ can become primarily solvated with ethanol as evidenced by the finding that on successive heating and degassing Na^+ - and NH_4^+ -montmorillonite typically retained ≤ 1 alcohol molecule per cation. Since, even at a relative ethanolic pressure of unity, the basal plane separation does not exceed 1.36 nm it was concluded that intercalated ethanol exists as a monolayer [1].

In similar systems, it has been reported that intercalated aliphatic primary alcohols reacted primarily via an interlamellar nucleophilic displacement of water to give di (alkyl-1-y1) ether in a high yield rather than undergoing intramolecular proton-catalysed dehydration to alkene. On the other hand, the major products of secondary alcohols are alkenes with minor amounts of di-secondary ethers, while benzyl alcohol in Al^{3+} -exchanged montmorillonite gave only polyphenylene methylene. This was confirmed by NMR spectra which indicated the absence of oxygen-function bridges. Coupling occurs via interlamellar protonation and nucleophilic displacement of water at reactive *o*- and *p*-positions of neighbouring rings, and ultimately leads to polymerization [2–4].

In the present paper, the catalytic conversion of *n*-pentanol to di-alkyl ether was studied by montmorillonite exchanged with different cations. The effect of the cation radius and its position in the cavity of the catalyst has also been investigated. The effect of adding benzidine to Al^{3+} and Fe^{3+} exchanged montmorillonite on this reaction was also examined.

2. Experimental

2.1. PURIFICATION OF MONTMORILLONITE AND CATION EXCHANGE MEASUREMENTS

The crude Wyoming montmorillonite from Colorado, U.S.A. was immersed in a cylinder containing de-ionized water. The suspension was allowed to sediment to get rid of all dense components which settled at the bottom of the cylinder. The top fraction of the suspended montmorillonite was collected by decantation into another clean cylinder containing de-ionized water.

The procedure was repeated several times until a very clear suspension of montmorillonite was obtained. The montmorillonite clay was then separated by ultra centrifugation and air dried [6].

The cation exchange capacity (CEC) was evaluated by adding 0.1 M ammonia solution to 0.5 g montmorillonite. After allowing to stand for 48 h, the concentration of the free ammonium ions was determined using a pH-meter with an ammonium selective electrode. The ammonia uptake was then calculated by difference which was found to be *ca.* 75 meq/100 g.

2.2. PREPARATION OF CATION EXCHANGED-MONTMORILLONITES

The cation exchanged montmorillonites were prepared by shaking purified montmorillonite for 24 h in concentrated aqueous solutions of the metal nitrate or bicarbonate. The cation solutions contained three times the expected cation exchange capacity of the catalyst. The product was separated by centrifugation, cleaned by five-fold washing in de-ionised water and finally dried over calcium chloride *in vacuo*.

2.3. HEAT TREATMENT

A weighed amount (2–3 g) of the cation exchanged montmorillonite (cation catalyst) was heated to 300°C at a rate of 4°C/min in static air or in a dried stream of the selected gas (H₂ or N₂). The catalyst was maintained at the high temperature limit for three hours. After cooling, each sample was analysed by thermogravimetry to estimate the amount of residual water. X-ray diffraction was applied to detect the interlamellar spacing *d*(001).

2.4. REACTION CONDITIONS AND PRODUCT ANALYSIS

n-Pentanol (5 cm³) and catalyst (0.5 g) were heated at 175°C in a 20 cm³ sealed stainless steel vessel. The reaction was stopped after a standard period of 3 h by plunging the vessel into cold water for 10 min.

The products were analysed by gas chromatography, the selectivity to ether formation was calculated from the relation [4].

$$\% \text{ selec.} = \frac{\text{concn. of ether to all component}}{\text{tot. conversion of } n\text{-pentanol}} \times 100$$

Table I. The catalytic reactivity of *n*-pentanol using different metal cation/Montmorillonite catalyst

Catalyst	Pre-treatment	Time (h)	Temp. (°C)	<i>d</i> (001) (Å)	W. loss (%)	Catalytic reactivities	
						Conv. (%)	Select. (%)
Li ⁺ -Mont.	None	–	25	13.6 ± 0.4	12.5	24.5	36.7
K ⁺ -Mont.	None	–	25	12.1 ± 0.1	7.0	18.2	37.8
Cs ⁺ -Mont.	None	–	25	12.6 ± 0.1	6.0	24.6	37.0
Li ⁺ -Mont.	N ₂	3	300	9.8 ± 0.1	–	32.2	49.3
K ⁺ -Mont.	N ₂	3	300	10.1 ± 0.1	–	25.6	37.3
Cs ⁺ -Mont.	N ₂	3	300	11.8 ± 0.1	–	29.4	39.8
Mg ²⁺ -Mont.	None	–	25	15.2 ± 0.1	14.5	30.1	39.1
Ca ²⁺ -Mont.	None	–	25	15.2 ± 0.1	13.0	25.4	37.0
Ba ²⁺ -Mont.	None	–	25	12.6 ± 0.1	10.5	19.7	34.2
Mg ²⁺ -Mont.	N ₂	3	300	9.8 ± 0.1	–	33.9	48.1
Ca ²⁺ -Mont.	N ₂	3	300	9.8 ± 0.1	–	28.3	38.6
Ba ²⁺ -Mont.	N ₂	2	300	11.8 ± 0.1	–	26.4	36.8
Ni ²⁺ -Mont.	None	–	25	15.2 ± 0.1	14.5	25.7	45.8
Cu ²⁺ -Mont.	None	–	25	12.1	12.0	25.6	50.2
Ni ²⁺ -Mont.	N ₂	3	300	9.8	–	30.3	55.9
Cu ²⁺ -Mont.	N ₂	3	300	9.8	–	35.4	70.3
Cu ²⁺ -Mont.	H ₂	3	150	–	–	23.8	57.1
	H ₂	3	250	–	–	22.4	58.9
	H ₂	3	300	–	–	20.0	62.0
Cu ²⁺ -Mont.	Air	3	150	–	–	38.0	70.3
	Air	3	250	–	–	33.1	68.4
	Air	3	300	–	–	38.4	71.1

Table II. Catalytic reactivity of *n*-pentanol using Ag⁺-, Pt²⁺- and Pd²⁺ montmorillonite catalyst

Catalyst	Pre-treatment	Time (h)	Temp. (°C)	Catalytic reactivities	
				Conv. (%)	Select. (%)
Ag ⁺ -Mont.	None	–	25	32.2	51.9
Pt ²⁺ -Mont.	None	–	25	16.7	56.3
Pd ²⁺ -Mont.	None	–	25	49.5	68.5
Ag ⁺ -Mont.	N ₂	3	300	38.1	63.3
Pt ²⁺ -Mont.	N ₂	3	300	16.9	56.8
Pd ²⁺ -Mont.	N ₂	3	300	51.2	73.0

Table III. Catalytic reactivity of *n*-pentanol using Fe³⁺ and Al³⁺-Montmorillonite catalyst

Catalyst	Temp. (°C)	Catalytic reactivities	
		Conv. (%)	Select. (%)
Fe ³⁺ -Mont. [4]	25	13.4	65.6
Al ³⁺ -Mont. [4]	25	25.9	70.65
Fe ³⁺ /Mont.-benz.	25	28.7	53.7
Al ³⁺ /Mont.-benz.	25	46.0	64.1

geometry of the reactant with respect to the surface of the catalyst should also be taken into account.

The reactivity of Cu^{2+} -montmorillonite is greater in the presence of a stream of dried air compared to a stream of hydrogen. This may be due to the reduction of Cu^{2+} to Cu^+ by hydrogen. This lowers the catalytic conversion and selectivity to give dialkyl ether.

The catalytic conversion reaction by alkaline earth metal ions coincides with the decrease in the ionic radius since there is a more symmetrical distribution of these cations in the interlamellar spacings. The Pd^{2+} ion has a catalytic reactivity three times higher than Pt^{2+} and 50% higher than Ag^+ ($\text{Pd}^{2+} > \text{Ag}^+ > \text{Pt}^{2+}$).

A general reaction scheme is proposed based on the observation that water is retained in interlamellar spaces upon heat-treatment at temperatures below $\approx 160^\circ\text{C}$, which is sufficient to inhibit the interlamellar dehydration reaction of the alcohol, but enhances the relatively slow proton catalysed alkene formation reaction. This accounts for the lower overall conversion and the lower selectivity of catalysts preheated below 160°C to ether formation. For catalysts preheated at high temperature ($\approx 250^\circ\text{C}$), the overall *n*-pentanol conversion is enhanced. This is explained on the basis that the protonation of the residual water molecules around the central metal ions is increased in addition to restricted diffusion caused by shrinking of the interlamellar spacing.

The Al^{3+} ion evidently catalyses the protonation reaction more efficiently than does Fe^{3+} ion. The reactivity of these cations increased by about 100% in the presence of benzidine which can form complexes with these cations of the general form $[\text{Al}(\text{Benz})_n]^{3+}$, $[\text{Fe}(\text{Benz})_n]^{3+}$ etc. Al^{3+} -complexes exhibit higher covalence compared with Fe^{3+} -complexes and this eventually affects their relative stabilities and catalytic efficiency. Steric factors prohibit the trapping of these complexes in the hexagonal cavity of the catalyst and exhibit symmetrical distribution which results in an increased protonation action of residual water molecules. On the other hand, benzidine species can exist in the oxidised form giving mono-radical cations $[\text{H}_2\dot{\text{N}}-\text{Ph}-\text{Ph}-\dot{\text{N}}\text{H}_2]^+$ of blue colour and the di-radical cation $[\text{H}_2\dot{\text{N}}-\text{Ph}-\text{Ph}-\dot{\text{N}}\text{H}_2]^{2+}$ of yellow colour between the silicate sheet structure of the catalyst, depending on the degree of dryness resulting in increased positive charge [5, 6]. These factors increase the acidic strength of the catalyst and consequently increase the selectivity towards alkene generation while the conversion to ether formation decreases.

It has been reported that the reactivity of cations depends strongly on the Brønsted acid strength of montmorillonite [7]. The acid strength was calculated from the degree of transformation of triphenylmethanol (Ph_3COH) into its carbonium ion (Ph_3C^+) on the clay surfaces. The acidity was explained in terms of enhanced dissociation of residual water molecules which depends on the polarizing power of the cation occupying the exchange sites. This depends on the charge density of the cation and more generally on the electric field conditions in the interlamellar spacing [7].

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