



ELSEVIER

Journal of Molecular Catalysis A: Chemical 104 (1995) L115–L118



Letter

Conversion of cyclohexanol to dicyclohexyl ether catalyzed by cation-exchanged bentonite clays

Debabrata Chatterjee *, H.M. Mody, K.N. Bhatt

Catalysis and Silicate Group Central Salt & Marine Chemicals Research Institute Bhavnagar-364 002, India

Received 3 May 1995; accepted 30 August 1995

Abstract

Bentonite clays modified by exchanging Al^{3+} , Co^{2+} and its Na^+ form were used in etherification of cyclohexanol to dicyclohexyl ether. Product yields obtained for metal cation exchanged clays followed the order $\text{Al}^{3+} > \text{Co}^{2+} > \text{Na}^+$. Brønsted acidity of the solid catalysts is suggested to play the key role in the studied reaction.

1. Introduction

There has been a renewed interest in the use of clay, earlier known as solid acids, as catalyst in various organic transformations because of the ease of handling and work up, low corrosiveness and low cost [1,2]. Although it is well documented that metal cation-exchanged clays can readily catalyse the ether formation either through combination of primary alcohols to alkenes [3–6] or in the reaction of alcohol themselves [7,8], in this paper we delineate the scope of etherification of cyclohexanol with solid acids which has not been examined so far. The usual method of preparation of dicyclohexyl ether, a very high boiling liquid (B.P. = 236°C) available so far is the hydrogenation of diphenyl ether [9,10]. Interaction of cyclohexanol in presence of *p*-toluenesulfonic acid at high temperature (170°C) also reportedly produced dicyclohexyl ether [11]. In this paper we report a facile method of etherification of cyclohexanol to dicyclohexyl ether with

solid acids. In addition acidic properties and catalytic activities of clays obtained from Kutch district of Gujarat, India, are also evaluated in the present study.

2. Experimental

2.1. Materials

Bentonite clay was procured from Kutch district of Gujarat, India. The crude clay was upgraded by sedimentation process which involves vigorous stirring of clay suspension and allowing the coarser particles to settle. The clay material separated from coarser impurities was dried at 110°C for 12 h. The dried clay sample (designated here as upgraded clay) was used for metal ions exchanged experiments. All other chemicals used were of A.R. grade.

* Corresponding author.

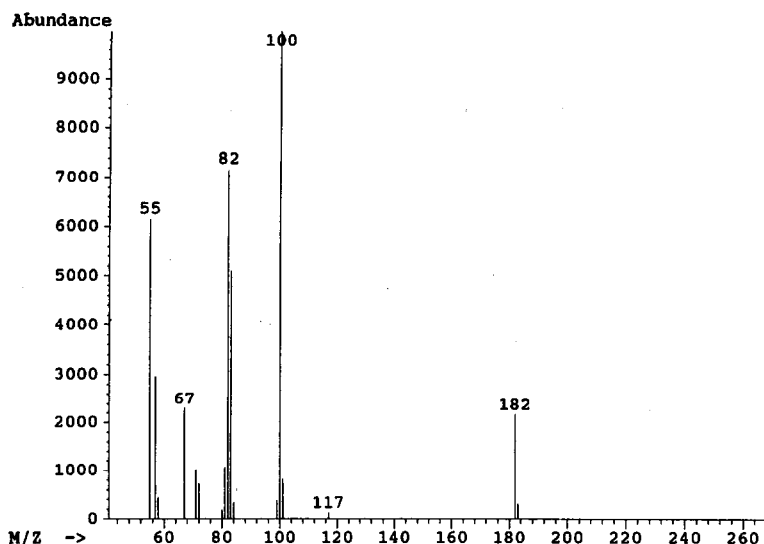


Fig. 1. GC-mass data for dicyclohexyl ether.

2.2. Preparation of metal cation-exchanged clays

Al^{3+} -exchanged clay was prepared by stirring upgraded clay suspension (1%) with the Al^{3+} form of cation-exchange resin for two hours at room temperature. The reaction mixture was then kept overnight for settlement and resin was separated from clay suspension by filtration. Solid Al^{3+} -exchanged clay recovered by slow evaporation was then dried at 110°C .

Co^{2+} -exchanged bentonite was prepared by stirring H^+ form of bentonite (obtained by passing Na-bentonite through H^+ -exchange resin) in aqueous CoCl_2 solution (13 mM) for four hours at room temperature. Solid Co^{2+} -exchanged clay was separated by filtration and repeatedly washed with double distilled water and dried at 110°C .

Aluminium pillared clay (APC) was prepared by following the procedure reported earlier [12].

2.3. Instrumentation

Surface areas [BET, (single point) N_2 adsorption at 77 K] of the clay samples prepared were measured by using a Flow Sorb II 2300 Micromeritics, USA, apparatus. Product identification and analysis were carried out by gas chromatographic technique. A Shimadzu GC-9A gas chromato-

graph and Hewlett-Packard 5890 series II gas chromatograph equipped with a mass-selective detector (5971 series) were used for this purpose.

2.4. Catalysis study

In a typical catalytic experiment 25 ml of net cyclohexanol was refluxed for 3 h in presence of clay samples prepared. After that the reaction mixture was filtered and the filtrate was subjected to GC and GC-mass analysis (Fig. 1) for product identification. Catalyst clay samples separated by filtration was activated again at 110°C and reused for another set of experiments.

3. Results and discussion

The composition and physico-chemical properties of natural bentonite clays are summarised in Table 1. The cation exchange capacity of the clay estimated by ammonium acetate method was 100 meq/100 g. The surface areas (BET) of different cation-exchanged clays activated at a constant temperature (110°C) fall in the range $80\text{--}100\text{ m}^2\text{ g}^{-1}$. The results for the etherification of cyclohexanol with several cation-exchanged clays are summarised in Table 2. As seen in Table 2, Al^{3+} -exchanged bentonite is the most active cat-

Table 1
Chemical components of bentonite clay obtained from Kutch district of Gujarat, India

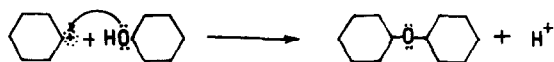
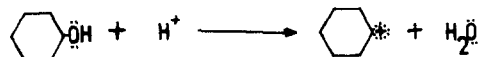
SiO ₂	55.37%
Al ₂ O ₃	17.81%
Fe ₂ O ₃	11.50%
TiO ₂	1.64%
CaO	0.75%
MgO	2.34%
SO ₃	0.89%
Na ₂ O	3.00%
K ₂ O	0.06%
Loss on ignition	6.77%

Table 2
Catalytic activity of metal cation exchanged bentonite clays for etherification of cyclohexanol to dicyclohexyl ether ^a

Sample	% conversion of cyclohexanol to dicyclohexyl ether
Na ⁺ -bentonite	0.1
Co ²⁺ -exchanged bentonite	5.4
Al ³⁺ -exchanged bentonite	15.0
APC (aluminium pillared clay) ^b	5.8

^a See experimental for reaction conditions.

^b Dried at 200°C.



Scheme 1.

alyst for the etherification reaction studied here. Co²⁺-exchanged clay also shows some reactivity, but Na⁺-bentonite is found almost unreactive for this specific reaction. The results (Table 2) are expectedly in line when Brønsted acidity of the clay is concerned. The Brønsted acidity of cation-exchanged clays stems from the hydration sphere [13] of the exchangeable cations which polarise the coordinated water molecules including their dissociation. This dissociation is favoured (i.e. higher Brønsted acidity) when the charge on the exchanged cation is higher.

Another factor which governs the Brønsted acidity of cation-exchanged clays is the activation

temperature. At high temperature clay dehydrates and consequently it loses Brønsted acidity, but gains Lewis acidity as the exchanged metal cations become coordinatively unsaturated. The last entry in Table 2 indicates the lower percentage conversion (5.8) in comparison to first entry. The clay sample used in last entry was activated at 200°C. It is worth to note here that according to an earlier report [14] higher Brønsted acid may be achieved at higher temperature. This is because of synergistic interaction between Lewis acid site (formed at higher temperature) and weak neighbouring Brønsted acid site. However, we did not observe this effect in our case, though the surface area of APC was high (280 m² g⁻¹). On the basis of above observation we propose a working mechanism for the conversion of cyclohexane to dicyclohexyl ether in Scheme 1.

In conclusion, this work affords a facile method of preparation of dicyclohexyl ether where catalyst can be separated by simple filtration method for further use after activation. Finally the clays procured from Kutch district of Gujarat, India, are now recognised to be competent for this catalytic process.

References

- [1] M. Iwamoto, H. Yahiro, Y. Mine and S. Kagawa, *Chem. Lett.* (1989) 213.
- [2] Y. Li and J.N. Armor, *Appl. Catal. B*, 1 (1992) L21.
- [3] J.M. Adams, D.E. Clement and S.H. Graham, *Clays Clay Miner.*, 31 (1983) 129.
- [4] J.A. Adams, J.A. Ballantine, S.H. Graham, R.J. Laub, J.H. Purnell, P.I. Reid, W.Y.M. Shaman and J.M. Thomas, *J. Catal.*, 58 (1979) 238.
- [5] J.A. Ballantine, M. Davies, I. Patel, J.H. Purnell, M. Rayanakorn, K.J. Williams and J.M. Thomas, *J. Mol. Catal.*, 26 (1984), 34.
- [6] J. Adams, A. Byline and S.H. Graham, *J. Catal.*, 75 (1982) 190.
- [7] A.M. Habib, M.F. Ald-El-Megeed, A. Saafan and R.M. Issa, *J. Inclusion Phenomena*, 4 (1986) 185.
- [8] A.M. Habib, A. Saafan, A.K. Abou-Seif and M.A. Salem, *Colloids Surf.*, 29 (1988) 33.
- [9] W. Ipatiev and O. Phillipow, *Berichte*, 41 (1908) 1001.
- [10] S. Nishimura, H. Tagachi, *Bull. Chem. Soc. Jpn.*, 36 (1963) 353.
- [11] A. Lacourt, *Bull. Soc. Chim. Belg.*, 36 (1937) 346.

- [12] H.M. Mody, P.M. Oza and V.P. Pandya, *Appl. Clay Sci.*, 8 (1993), 53.
- [13] J.M. Adams, T.V. Clapp and D.E. Clement, *Clay Miner.*, 18 (1983) 411.
- [14] B.K.G. Theng, in H. van Olphan and F. Veniale (Eds.), *Clay-Activated Organic Reactions, Development in Sedimentology*, 35th International Clay Conference, 1981, Elsevier, Amsterdam, p. 197.