

THE USE OF LAYERED CLAYS FOR THE PRODUCTION OF PETROCHEMICALS

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ABSTRACT

Some exchanged Wyoming montmorillonite clays are effective catalysts for the alkylation of benzene with propene or ethylene in the liquid phase. Under these conditions the clay catalysts give equilibrium product distributions. In contrast zeolites are generally poor catalysts and do not give equilibrium product distribution under these mild conditions.

INTRODUCTION

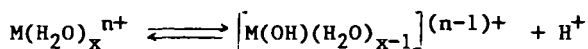
The alkylation of benzene by propene and ethylene is widely practised in the petrochemical industry. Cumene has been manufactured on a large scale for more than 40 years, firstly as a high octane component for aviation gasoline and subsequently as an intermediate for the production of phenol. Ethylbenzene is also manufactured on a large scale as a precursor for the production of styrene.

Acidic catalysts are used in the production of both cumene and ethylbenzene. The former is generally manufactured using a supported phosphoric acid catalyst in a fixed bed reactor with the reactants in the liquid phase although aluminium chloride and sulphuric acid catalysts have also been used (1,2). Ethylbenzene is generally produced using either aluminium chloride as catalyst with the reactants in the liquid phase or with a zeolite catalyst and the reactants in the vapour phase (3,4).

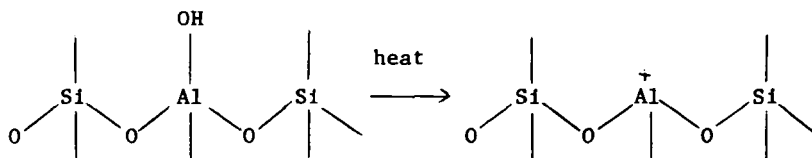
There has recently been considerable interest in the application of layered montmorillonite clays as acidic catalysts so it seemed reasonable to examine these materials for the alkylation of benzene. Montmorillonite clays possess both Lewis and Brønsted acid sites which are responsible for the diverse catalytic activity of these materials eg in ether formation from alcohols and alkenes, olefin hydration, ester formation from carboxylic acids and alkenes and many other reactions (5, 6,7).

The detailed structure of montmorillonite minerals is still the subject of debate although it is generally agreed that they are formed from an octahedrally coordinated alumina sheet sandwiched between two tetrahedrally coordinated silicate sheets. The layers carry an overall negative charge which may arise from isomorphous substitution of Al^{3+} by Fe^{2+} or Mg^{2+} in the octahedral sheet and to a lesser extent of Si^{4+} by Al^{3+} in the tetrahedral sheet. These negative charges on the layers are balanced by hydrated cations, usually Na^+ or Ca^{2+} in the naturally occurring state, which are situated in the interlamellar space and which can be readily ion-exchanged. By suitable choice of cation the acidity and polarisation of coordinated water and other molecules in the interlamellar environment can be varied.

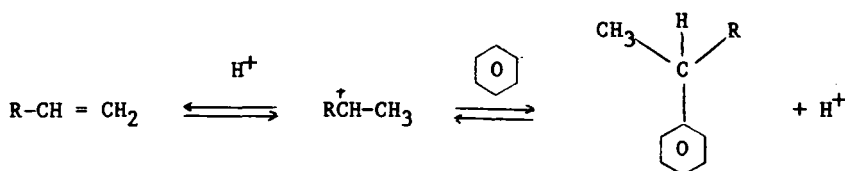
The Bronsted acidity of the cation-exchanged clays can be accounted for by dissociation of coordinated water in the interlamellar space,



and Lewis acidity may arise from dehydroxylation of the framework hydroxyl groups,

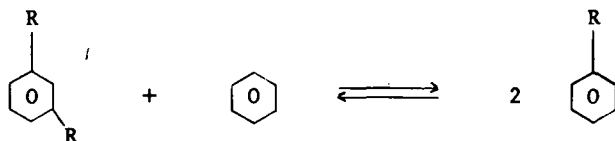


In this paper the performance of montmorillonite clays is compared with zeolite catalysts for the alkylation of benzene with propene and ethylene. The generally accepted mechanism for aromatic alkylation is



where R = alkyl or H.

Further alkylation of the alkylated product can be reduced, if desired, by the use of large benzene:olefin reactant ratios. Alternatively, lower ratios can be used in commercial processes provided the catalyst chosen is also effective for transalkylation reactions such as



since the unwanted polyalkyl-benzenes can be separated and recycled with fresh feed.

EXPERIMENTAL

Catalyst Preparation. Hydrogen and aluminium exchanged Wyoming montmorillonites were prepared by methods described previously (6,7). The zeolite catalysts were either synthesised by known methods or were commercial samples and converted to the hydrogen form by calcination of the ammonium form. The amorphous aluminosilicate (85.5% SiO₂) was obtained from Strem Chemicals Incorporated.

Apparatus. Alkylation experiments with both ethylene and propene were carried out in stainless steel autoclaves in the normal manner. The autoclaves were heated to the reaction temperature, held for 2.5 hours, and allowed to cool overnight. Continuous experiments were carried out with a premixed feed under pressure in a small continuous unit whose schematic flow diagram has been described previously (6).

Analysis. All reaction products were analysed by capillary gas chromatography using calibration factors derived from authentic standards.

RESULTS AND DISCUSSION

Cumene. The performance of Wyoming montmorillonite clay catalysts is compared with that of a range of zeolite and other catalysts for the alkylation of benzene with propene in Table 1. In these batch reactions the H⁺ and Al³⁺ exchanged Wyoming montmorillonite clays gave complete conversion of propene at 150°C with the former giving virtually the same product over the temperature range 125° to 230°C. In contrast none of the other catalysts examined gave more than 65% propene conversion at 150°C. The best result was obtained with the commercial amorphous aluminosilicate and the worst with the large pore size zeolite-Y.

TABLE 1

FORMATION OF CUMENE FROM BENZENE AND PROPENE

Catalyst	Reaction Temp °C	Propene Conversion %	Product Distribution		
			Benzene (Mole%)	Cumene (Mole%)	DIPB ^a (Mole%)
H ⁺ -Montmorillonite	125	100	84.4	14.7	0.9
H ⁺ -Montmorillonite	150	100	84.3	14.7	1.0
H ⁺ -Montmorillonite	230	100	84.3	14.7	1.0
Al ³⁺ -Montmorillonite	150	100	85.6	13.9	0.6
H-Y Zeolite	150	5	99.3	0.7	tr
H-Mordenite	150	20	97.8	2.0	0.2
H-MFI	150	25	96.7	3.3	tr
Aluminosilicate	150	65	90.5	8.9	0.6

Reactants:- Benzene 120g, Propene 10g, Catalyst 5g, C₆:C₃ = 6:1

a) DIPB = di-isopropylbenzene

In a second series of experiments the catalysts were compared for the reaction of benzene, propene and meta-di-isopropylbenzene (DIPB) in order to determine how much, if any, of the DIPB was transalkylated to give additional cumene (Table 2). Only H⁺-Montmorillonite gave any significant conversion of DIPB under these conditions. The best result with the remaining catalysts was obtained with zeolite-Y whilst the

TABLE 2

FORMATION OF CUMENE FROM BENZENE, PROPENE AND DIPB^a

Catalyst	Temp °C	DIPB (Prod) DIPB (React)	Product Distribution		
			Benzene (Mole%)	Cumene (Mole%)	DIPB ^a (Mole%)
H ⁺ -Montmorillonite	230	0.6	72.6	24.7	2.7
H-Y Zeolite	230	0.9	93.9	2.1	4.0
H-MFI	230	1.3	90.2	5.6	4.1
H-MFI	270	1.1	85.3	9.7	4.9
Aluminosilicate	230	1.1	83.5	11.7	4.8

Reactants:- Benzene 120g, Propene 12g, meta-DIPB 12g, Catalyst 5g

a) DIPB = di-isopropylbenzene

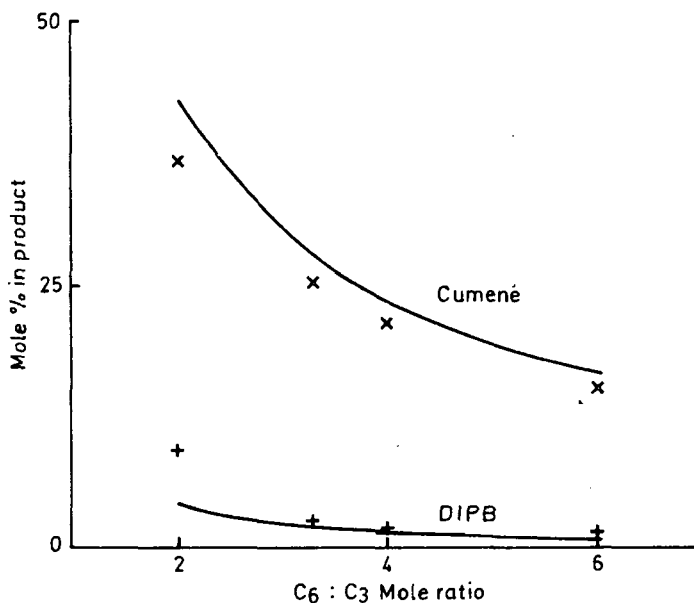


Figure 1. Calculated thermodynamic (solid lines) and experimental (plotted points) product distributions for the formation of cumene.

TABLE 3

CONTINUOUS PRODUCTION OF CUMENE

Catalyst	H ⁺ -Montmorillonite
Temperature (°C)	190
Pressure (bar)	30
LHSV (h ⁻¹)	2.1
Feed (Mole %)	
benzene	82
Propylene	15
DIPB	2.1
C ₆ :C ₃	5:1
Product (Mole %)	
Benzene	79 ± 1
Cumene	18 ± 1
DIPB	2.3 ± .25

others gave a net production of DIPB. Thus, with the exception of the H^+ -Montmorillonite catalysed reaction, the initial DIPB behaves as an inert diluent in these systems.

The reaction product distribution with the Wyoming montmorillonite catalyst in both sets of experiments is close to the calculated thermodynamic equilibrium. In Figure 1 the calculated and experimentally observed product distributions are plotted for a wide range of initial benzene and C_3 -alkyl fragment compositions. The experimental points were obtained from reactions using various combinations of propene, benzene and DIPB as the initial reactants and the calculated equilibrium compositions show little variation with temperature over the range 120° to $230^\circ C$ which is in agreement with the experimental results in Table 1.

The performance of the H^+ - Montmorillonite was also examined in the continuous production of cumene using a feed comprising benzene, propene, and DIPB. The product composition shown in Table 3 remained constant over a test period of 50 hours on stream at constant temperature and LHSV. The product composition was also close to the calculated thermodynamic value shown in Figure 1 illustrating that equilibrium is also achieved in continuous reactions with this catalyst and a relatively short contact time.

Ethylbenzene. The performance of Wyoming montmorillonite clay catalysts is compared with the H-MFI zeolite for the alkylation of benzene with ethylene in Table 4. In these batch reactions at $230^\circ C$ where benzene is in the liquid phase both the H^+ and Al^{3+} Wyoming montmorillonite catalysts gave complete conversion of ethylene compared to only 20% with H-MFI.

As in the earlier experiments with propene only the Wyoming montmorillonite clay catalysts give product distributions which are close to the calculated thermodynamic equilibrium composition. Thus, at a $C_6:C_2$ ratio of 2.5 :1, the experimentally observed product distribution is ethylbenzene 28.4% and diethylbenzene 5.5% compared to 32.4% and 3.8% respectively for the calculated thermodynamic equilibrium.

Reaction mechanism and catalytic activity. There would seem to be no reason to suggest that the generally accepted mechanism for the acid catalysed addition of an olefin to an aromatic ring should not be extended to reactions catalysed by Wyoming montmorillonite clay, zeolite, or aluminosilicate catalysts. All of these catalysts have acidic sites capable of supplying the necessary proton for formation of the carbonium ion intermediate.

TABLE 4
FORMATION OF ETHYLBENZENE

Catalyst	Temp °C	Ethylene Conv ⁿ %	Product Distribution		
			Benzene (Mole%)	Ethyl- benzene (Mole%)	DEB ^a (Mole%)
H ⁺ -Montmorillonite ^b	230	100	65.1	28.4	6.4
Al ³⁺ -Montmorillonite ^b	230	100	66.1	28.4	5.5
H-MFI ^b	230	20	92.6	6.3	tr
H ⁺ -Montmorillonite ^c	250	100	89.6	9.8	0.6

- a) DEB = diethylbenzene
b) Reactants:- Benzene 120g, Ethylene to 40bar, Catalyst 5g
c) Reactants:- Benzene 120g, Ethylene to 40bar, DEB 12g, Catalyst 5g

It is proposed that the substantial difference in catalytic activity between the clay and zeolite catalysts is due to the ready accessibility of the acidic sites to the reactants in the former case. In liquid phase reactions diffusional constraints for reactants or products will be greatest for catalysts with rigid microporous structures such as zeolites. The expanding layer structure of the Wyoming montmorillonite clay catalysts allows access to the interlamellar acidic sites with few diffusional constraints and hence these have greater activity. Similarly the acidic sites on the amorphous aluminosilicate are more accessible than those in the zeolite structure.

It is known that zeolite catalysts such as MFI are effective for the vapour-phase alkylation and transalkylation of benzene and ethylene at 425°C (4). Under these conditions the diffusional constraints would probably be much less significant but collapse of the interlamellar space in Wyoming montmorillonite would decrease the activity.

CONCLUSION

It is concluded that Wyoming montmorillonite clays are effective catalysts for the alkylation of benzene with propene or ethylene in liquid phase reactions to give cumene and ethylbenzene respectively. Under these conditions, these catalysts are also effective for transalkylation

reactions thereby allowing recycle of unwanted polyalkylated products to extinction in commercial processes. They are also more effective than zeolite catalysts in these liquid phase reactions.

ACKNOWLEDGEMENTS

We thank the British Petroleum Company plc for permission to publish this paper.

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