Catalysis Letters 60 (1999) 157–159

A novel catalytic method for the alkylation of benzene to diphenylmethane over H-ZSM-5 zeolite catalysts

A.P. Singh * and A.K. Pandey

Catalysis Division, National Chemical Laboratory, Pune 411008, India
E-mail: apsingh@cata.ncl.res.in

Received 26 October 1998; accepted 6 April 1999

Vapour-phase catalytic alkylation of benzene to diphenylmethane in high selectivity (92.5%) at 30.7 wt% conversion of benzene is reported for the first time using dichloromethane (DCM) as an alkylating agent and H-ZSM-5 as the catalyst.

Keywords: alkylation of benzene, preparation of diphenylmethane, H-ZSM-5

1. Introduction

Diphenylmethane is used in the fragrance industry both as a fixative and in scenting soaps [1]. It can serve as a synergist for pyrethrin in pesticides and insecticides [2,3]. Diphenylmethane is recommended as a plasticizer to improve the dyeing properties [4], as a solvent for dyes [5] and as a dye carrier printing with disperse dyes [6]. The addition of diphenylmethane to saturated, linear polyesters improves their thermal stability [7] and its addition to jet fuels increases their stability and lubricating properties [8]. Industrially, diphenylmethane is synthesized by the Friedel–Crafts reaction of benzyl chloride with benzene in the presence of a Lewis acid catalyst, $AlCl_3$ [1,9]. Diphenylmethane is also produced by the reaction of dichloromethane with benzene in the presence of $AlCl_3$ [9,10]. Other known catalysts of this process are elemental aluminium, $FeCl_3$, $SbCl_5$, $ZnCl_2$–HCl, and boron fluoride dihydrate [1]. Apart from these catalysts, when sulphuric acid is used as a catalyst [11] diphenylmethane yield is 83% and with polyposphoric acid [12] yield is over 90%. However, homogeneous systems have their own limitations as these systems pose environmental and difficult operational problems, catalyst recovery from the product and requirement of a stoichiometric amount of the catalyst. In addition, they produce large amounts of undesired products. In view of the above it was of interest to develop a new methodology for the synthesis of diphenylmethane.

Zeolite catalysts, due to their shape selectivity, thermal stability, the easy separation from the products and the possibility of regeneration of deactivated catalyst, have been used widely in the field of petrochemistry [13] and, recently, in the fine organic synthesis [14–16]. However, the potential of zeolite catalysts in the synthesis of diphenylmethane has not yet been exploited. Here, we disclose the first report of diphenylmethane synthesis from benzene and dichloromethane using zeolites as catalysts.

2. Experimental

Zeolite ZSM-5 and Beta were synthesized and changed into protonic forms following the literature procedure [17,18]. H-mordenite was supplied by Laporte Inorganics, Cheshire, UK. Zeolite samples were characterized by AAS (Hitachi 800) for their chemical composition. X-ray powder diffraction (Rigaku, D-max/II-VC model, Cu Kα radiation) for crystallinity and phase purity and scanning electron microscopy (Cambridge Stereoscan 400) for morphology and crystal size. The surface area of the zeolites was measured by the nitrogen BET method using an Omnisorb 100 CX apparatus. Acidity of the zeolites was determined by the temperature-programmed desorption of ammonia [19]. The main characteristics of the zeolite used are summarized in table 1.

The gas-phase alkylation reactions of benzene with DCM were carried out with a fixed-bed glass reactor (1.4 cm I.D.) under atmospheric pressure. The catalyst sample (2.0 g) was utilized in particles with dimensions in the 15–30 mesh range. A mixture of benzene and DCM (2 : 1 molar ratio) was fed into the reactor by a syringe pump. The products were collected in an ice trap and analysed by a gas chromatograph (HP 6890) equipped with a flame ionization detector and a wide bore capillary column (30 m $\times$ 0.52 mm) coated with methylsilicon gum. Reference substances and GC-MS (Shimadzu GC-MS-OP-2000 $\propto$) were used for the identification of the products.

3. Results and discussion

The catalytic activities of various zeolites for the alkylation of benzene are examined under similar reaction conditions at 503 K. The results are listed in table 1. The main

---

[*] To whom correspondence should be addressed.

Table 1
Alkylation of benzene to diphenylmethane.[a]

Catalyst	SiO_2/Al_2O_3 ratio	NH_3 desorbed at different temperature (mmol/g)					NH_3 chemisorbed at 303 K (mmol/g)	React. temp. (K)	Alkylating agent	Conv. of benzene	TOF[b] ($\times 10^{-3}$ mol s^{-1} mol^{-1} Al)	Product distribution[c] (wt%)		
		303–353 K	353–433 K	433–513 K	513–653 K	653–773 K						DPM	$C_6H_5CH_3$	Others
H-β[d]	26.0	0.14	0.24	0.05	0.16	0.16	0.75	503	CH_2Cl_2	4.5	0.09	25.1	68.1	6.8
H-mordenite[e]	22.0	0.20	0.17	0.15	0.12	0.07	0.71	503	CH_2Cl_2	1.7	0.03	25.4	25.4	49.2
H-ZSM-5[f]	41.0	0.55	0.16	0.05	0.26	0.21	1.23	463	CH_2Cl_2	8.8	0.26	97.9	0.8	1.3
H-ZSM-5[f]	41.0	–	–	–	–	–	–	483	CH_2Cl_2	16.1	0.47	96.0	1.4	2.6
H-ZSM-5[f]	41.0	–	–	–	–	–	–	503	CH_2Cl_2	30.7	0.90	92.5	3.7	3.8
H-ZSM-5[f]	41.0	–	–	–	–	–	–	523	CH_2Cl_2	31.8	0.93	82.0	7.2	10.8
H-ZSM-5[f]	41.0	–	–	–	–	–	–	503	1,3,5-trioxane	7.30	0.21	60.2	14.6	25.2

[a] Reaction conditions: catalyst weight = 2.0 g; benzene/CH_2Cl_2 (molar ratio) = 2 : 1; feed ratio = 2 ml/h.

[b] Turnover rates are expressed as turnover frequencies (TOF, mole of benzene converted per second per mole of aluminium).

[c] DPM = diphenylmethane ($C_6H_5CH_2C_6H_5$); $C_6H_5CH_3$ = toluene; others = benzyl chloride and heavier products.

[d] H-beta: degree of H^+ exchange >98.7%; crystal size = 0.5 μm; surface area = 745 m^2/g.

[e] H-mordenite: degree of H^+ exchange >98%; crystal size = 1.0 μm; surface area = 552 m^2/g.

[f] H-ZSM-5: degree of H^+ exchange >98%; crystal size = 0.4 μm; surface area = 413 m^2/g.

product of the reaction is diphenylmethane (DPM). Small amounts of toluene, benzyl chloride and heavier products (others) are also detected.

Among the zeolite catalysts screened, H-ZSM-5 is found to be a more active and selective catalyst in the conversion of benzene and formation of DPM. In addition, the turnover rate of benzene conversion (TOF) is found to be higher (0.90×10^{-3} mol s^{-1} mol^{-1} Al) at 503 K over H-ZSM-5 than that of H-beta (0.09×10^{-3} mol s^{-1} mol^{-1} Al) and H-mordenite (0.03×10^{-3} mol s^{-1} mol^{-1} Al), whereas H-Y and amorphous SiO_2–Al_2O_3 were not able to catalyse the reaction. Presumably, the higher activity of H-ZSM-5 may be attributed to its smaller crystal size and stronger Brønsted acid sites compared to the H-beta and H-mordenite zeolites [19] (table 1). The higher selectivity for DPM over H-ZSM-5 may be explained on the basis of its small openning (0.51 × 0.55 and 0.54 × 0.56 nm) compared to the H-beta (0.55 × 0.70 nm) and H-mordenite (0.65 × 0.7 nm). The conversion of benzene under identical reaction conditions (503 K) over H-beta, H-mordenite and H-ZSM-5 are found to be 4.5, 1.7 and 30.7 wt%, respectively. The corresponding selectivities for diphenylmethane are 25.1, 25.4 and 92.5%, respectively (table 1). The mechanism for the formation of diphenylmethane is not ascertained yet. However, it is assumed that the formation of diphenylmethane in the alkylation of benzene with CH_2Cl_2 takes place by a secondary pathway [9,10]. Presumably, the mechanism involves the polarization of CH_2Cl_2 into an electrophile (CH_2^+Cl) by the acidic catalyst, which attacks the benzene ring and leads to the formation of benzyl chloride [9,10]. Further, heterolytic dissociation of benzyl chloride into a benzyl cation ($C_6H_5CH_2^+$), and reaction of the benzyl cation with benzene results mainly in the formation of diphenylmethane [9,10], a fact which suggests that the formation of diphenylmethane occurs by a polar rather than a homolytic process.

The conversion of benzene decreases with the progress of the reaction (reaction conditions: table 1, catalyst = H-ZSM-5, reaction temperature = 463 K). A marginal increase in the selectivity for DPM is noticed with the reaction time.

Table 1 also illustrates the conversion of benzene, turnover rates of benzene and selectivity for DPM as a function of reaction temperature. The turnover rate of benzene conversion (TOF) is increased from 0.26 to 0.93×10^{-3} mol s^{-1} mol^{-1} Al, when the reaction temperature is raised from 463 to 523 K. The corresponding selectivity for DPM decreased from 97.9 to 82.0%, respectively. The results show that higher temperature favours the formation of toluene and heavier products. The apparent activation energy over H-ZSM-5 is found to be 57.3 kJ/mol.

1,3,5-trioxane is also used as an alkylating agent instead of CH_2Cl_2, but the zeolite H-ZSM-5 is not found active and selective under the reaction conditions (table 1).

4. Conclusions

In summary, zeolite H-ZSM-5 catalyzes the alkylation of benzene with CH_2Cl_2 efficiently which leads to the formation of diphenylmethane in high selectivity. A higher yield of diphenylmethane is obtained by raising the reaction temperature.

Acknowledgement

We thank P. Ratnasamy and A.V. Ramaswamy for helpful discussion and encouragement. AKP thanks CSIR, New Delhi, for a fellowship.

References

[1] U. Beck and A.G. Bayer, in: *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A 13, eds. W. Gerhartz, Y.S. Yamamoto and F.T. Campbell (Weinheim, New York, 1985) p. 260.

[2] A.D. Harford and H.W. Vernon, US Patent 2 897 112 (1956).

[3] A. Douglas and H.W. Vernon, DE-AS 1 094 035 (1957).

[4] N.K. Moshinskaya, V.S. Olifer and L.I. Zhuoiev, SU 137 993 (1960).

[5] E. Siggel, US Patent 2 710 849 (1952).

[6] W. Braun, E. Hartwig and R. Krallmann, BASF DAS 1 142 338 (1960).

[7] M.I. Stewart and O.K. Carlson, US Patent 3 539 640 (1967).

[8] A.M. Leas, US Patent 3 529 944 (1967).

[9] M. Grayson et al., eds., *Kirk-Othmer*, *Encyclopedia of Chemical Technology*, Vol. 5 (Wiley, New York, 1979) pp. 686, 830; Vol. 11 (Wiley, New York, 1980) p. 275.

[10] Y. Lavaux and M. Lombard, Bull. Soc. Chim. Fr. (1910) 7913.

[11] K. Ichikawa and H. Shingu, Kogyo Kagaku Zasshi 54 (1951) 183; Chem. Abstr. 47 (1953) 8662b;
J.G. Matveev, D.A. Drapkina and R.L. Globus, Tr. IREA 21 (1956) 83; Chem. Abstr. 52 (1958) 15474e.

[12] S. Murohashi, Nagaoka Koggo Koto Senmon Gakko Kenkyu Kiyo 9 (1973) 103; Chem. Abstr. 80 (1974) 132917r.

[13] D.W. Breck, *Zeolite Molecular Sieves* (Wiley, New York, 1974);
A. Dyer, *An Introduction to Zeolite Molecular Sieves* (Wiley, Chichester, 1988).

[14] W. Hölderich, M. Hesse and F. Naumann, Angew. Chem. Int. Ed. Engl. 27 (1988) 226.

[15] P.B. Venuto, Micropor. Mater. 2 (1994) 297.

[16] P. Ratnasamy, A.P. Singh and S. Sharma, Appl. Catal. 25 (1996) 135.

[17] R.J. Argauer and G.R. Landolt, US Patent 3 702 886 (1972).

[18] M.A. Camblor and P.J. Perez, Zeolites 6 (1986) 307.

[19] A.P. Singh, D. Bhattacharaya and S. Sharma, J. Mol. Catal. 102 (1995) 139.