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ACI 7851

PERPUSTAKAAN UNIVERSITI MALAYA

INVC. 17/12/00

**SYNTHESIS OF ALKYLANILINES AND
ALKYLHETEROCYCLES
OVER ION-EXCHANGED ZEOLITES**

A DISSERTATION

**SUBMITTED TO THE UNIVERSITY OF MALAYA
IN FULFILMENT OF THE
DEGREE
OF
MASTER OF PHILOSOPHY**

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**INSTITUTE OF POSTGRADUATE STUDIES
AND RESEARCH**

May 1999

Perpustakaan Universiti Malaya



A508765760

Djmikrofiskan pada... 24. 11. 2001
No. Mikrofis... 15110
Jumlah Mikrofis... 2

HAMSI AH BT MOHAMAD ZAHARI
UNIT REPROGRAFI
PERPUSTAKAAN UTAMA
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Appendix : Publication entitled " Studies on the alkylation of aniline with *n*-propanol and isopropanol on ion-exchanged zeolites."

ABSTRACT

Alkylated anilines and alkylated aromatics are industrially important intermediates in the synthesis of dyes, antioxidants and pharmaceuticals.

In this study, cation-exchanged Y- and ZSM-5 zeolites were synthesised and characterised, and their potential in catalysing the vapour- phase alkylation of aniline, thiophene, pyrrole and pyridine by *n*-propanol and/or isopropanol was investigated at atmospheric pressure and in the temperature range 350-450°C.

In the case of aniline, the N-alkylated product was dominantly obtained with either alcohol (55-70 %), but a greater selectivity for C-alkylated products, in particular *ortho*- isopropylaniline over its *para*- isomer, was observed with isopropanol. The selectivity for the N-alkylated product tended to decrease with an increase in the flow rate. Under comparable conditions of temperature and flow rates, Ce-Y zeolite proved to be the more active among the catalysts studied. With this catalyst, the alkylation with *n*-propanol proceeded to 83% aniline conversion at 450°C and 5mL/hr flow rate; with isopropanol the conversion yield under identical conditions was 63%. For both the Y- and ZSM-5 zeolites, aniline conversion yields increased in the order Ce > H > Na, attesting to the importance of acidic sites on the catalyst for the success of the alkylation reaction.

A SN₂ pathway has been proposed to account for the C-alkylated products obtained in the reaction with *n*-propanol. With isopropanol a SN₁ mechanism, involving the isopropylcarbonium ion, has been proposed. An alternate source

of the carbonium ion was identified in propene whose formation via the dehydration of the alcohol was observed to be more pronounced for isopropanol. The deactivation of the catalyst in aniline alkylation with isopropanol was also investigated using Na- and Ce-Y zeolites. Blockage of the zeolite pores and coverage of its surface by carbonaceous materials ('coke'), with consequent loss of surface area were identified as the principal causes of the catalyst deactivation. Greater coke deposition was observed in the Ce-Y zeolite relative to the Na-Y zeolite. It was additionally observed that increasing deactivation of the zeolite tended to disfavour C-alkylated products, thereby leading to an increase the N-alkylated aniline content in the product mixture. The deactivated catalysts could, however, be regenerated by heating at 500⁰C for 8hr, and showed activity closely comparable to their original states.

Isopropylation of pyridine and other heterocycles was attempted over H-Y zeolite using similar conditions as noted for the aniline alkylation. Pyridine registered a poor conversion yield of 13% at 500⁰C. A mixture of products characterised by GC-MS, was obtained with 2- and 3-isopropylpyridines being relatively the more dominant. Identified among the products was 2-2'-bipyridyl and 2-4'-bipyridyls, whose origin was traced to the molecular transformation that the heterocycle undergoes when contacted in the neat with the hot zeolite. Although improved conversion yields (39.4- 46.1 %) were obtained with thiophene and pyrrole, the products of the alkylation of

these also included thermal transformation products. Thus thiophene yielded benzothiophene and bithiophene, and pyrrole yielded indole and carbazole.

Acknowledgements

I wish to express my gratitude and appreciation to my supervisors, Prof. V.G. Kumar Das and Dr. R.B.C. Pillai, for their encouragement and enthusiastic guidance throughout my candidature.

It is a pleasure to thank the Dean, Institute of Postgraduate Studies and Research, and the Head, Department of Chemistry, University Malaya, for the use of facilities in the department in carrying out the research. I would like to convey my appreciation to the Zeolite Research Group of Indian Institute of Technology, Madras, for kindly supplying the ZSM-5 zeolite used in the investigation and for extending to me the facilities to carry out surface area measurements on some of the synthesised zeolites.