Content

CONTENT

A Intro	A INTRODUCTION	
B Prior	Art	3
1 Us	es of amines	3
2 Me	ethods of synthesis	3
3 Th	e dehydroamination	5
4 Th	e amination as a nucleophilic substitution	7
4.1	Phosphates as catalysts	7
4.1.1	Structural properties of phosphates	7
4.1.2	Preparation	8
4 1.3	Catalyst characterisation	8
4.1.3.1	Surface area	9
4.1.3.2	Pore size distribution and pore volume	9
4.1.3.3	Surface acidity by butylamine titration	10
4.1 4	Reactions catalysed by phosphate catalysts	10
4.1.4 1	Dehydration of alcohols	10
4.1.4 2	Condensation reactions	11
4.1.5	Conclusion on the phosphates	12
4.2	Zeolites	13
4 2.1	Synthesis of methylamines	13
4.2.2	Reactions of higher alcohols with ammonia over zeolites	15
4.2.3	Computer modelling	15
5 An	nines of the present work	10
5.1	Dimethylethylamine	16
5.2	Cyclohexylamine	19
5.3	1-octatylamine	20



Content II

C RE	SULTS	AND DISCUSSION	23
C.1 A	MINA	TION OF METHANOL TO DIMETHYLETHYLAMINE	23
1	Study	of the reaction parameters on zirconium phosphate CZP100	23
1.1		Influence of the temperature	23
1.2		Influence of the carrier gas	24
1.3		Influence of the molar ratio methanol:ethylamine	26
1 4		Influence of a copper impregnation	27
1.5		Influence of the contact time	29
1.6		Optimisation of the reaction parameters	29
1.6.1		Influence of the contact time at 350 °C with a molar ratio	
		MeOH.EtNH ₂ of 5:1	30
1.6.2		Study of the side reactions	31
1.6.2.1		Reaction with methanol and ethylmethylamine	31
1.6.2 2	;	Reaction with methanol and dimethylethylamine	32
1.6.3		Influence of the contact time at 300 °C with a molar ratio	
		MeOH:EtNH ₂ of 5:1	33
1.7		Conclusion of the study of the reaction parameters on zirconium	
		phosphate CZP100	34
2	Study	of other zirconium phosphates	35
3	Study	of boron phosphate	39
3.1		Influence of the temperature	39
3.2		Comparison of boron phosphate and zirconium phosphate CZP100	40
3.3		Optimisation of the reaction parameters on boron phosphate	40
3.4		Conclusion of the study on boron phosphate	43
4	Study	of aluminium phosphates	43
5	Study	of other phosphates	46
5.1		Study of cerium phosphate	46
5.2		Study of iron phosphate	47
5.3		Study of strontium phosphate	48
6	Conc	usion of the amination of methanol on phosphate catalysts	49

Content I

C.2 Amination of cyclohexanol to cyclohexylamine		51
l An	nination in the liquid phase	51
1.1	Amination in a batch reactor without pressure	51
1.2	Amination in a batch reactor with pressure	51
2 An	nination in the gas phase	52
2.1	Reductive amination for the synthesis of cyclohexylamine	52
2.1.1	Study in the presence of copper chromite G22	52
2.1.1.1	Influence of the temperature	52
2.1.1.2	Influence of hydrogen as carrier gas	53
2.1.1.3	Influence of the molar ratio ammonia:hydrogen	54
2.1.1.4	Influence of the time on stream	55
2.1.2	Study of nickel catalysts	57
2.1.3	Mechanism of the reductive amination	58
2.2	Nucleophilic substitution for the synthesis of cyclohexylamine	59
2.2.1	Dehydration of cyclohexanol to cyclohexene	59
2.2.2	Study of the reaction on zirconium phosphate CZP100	60
2.2.2.1	Influence of the temperature	60
2.2.2.2	Influence of the molar ratio ammonia:cyclohexanol	62
2.2.2.3	Influence of the presence of hydrogen as carrier gas	63
2.2.2.4	Conclusion of amination of cyclohexanol on zirconium phosphate	
	CZP100	65
2.2.3	Screening of phosphate catalysts	65
3 Conclu	sion	68
С.3 Амі	NATION OF 1-OCTANOL TO 1-OCTYLAMINE	69
1 Re	ductive amination for the synthesis of 1-octylamine	69
1.1	Case of copper chromite G22	69
1.1.1	Influence of the temperature on copper chromite G22	69
1.1.2	Influence of a potassium impregnation on copper chromite G22	70
1.1.3	Influence of hydrogen as carrier gas on copper chromite G22	71
1.1.4	Conclusion of the study on conner chromite G22	72

ontent IV

1.2	The use of nickel oxide catalysts	73
2	Nucleophilic substitution for the synthesis of 1-octylamine	74
2.1	Dehydration of 1-octanol to 1-octene	74
2.2	Screening of phosphate catalysts	75
2.2,1	Influence of the temperature	76
2.2.2	Influence of hydrogen as carrier gas on zirconium phosphate CZP100	77
2.2.3	Influence of the contact time in the presence of zirconium phosphate	
	CZP100	78
2.2.4	Influence of a copper impregnation on zirconium phosphate CZP100	79
2.3	Conclusion of the study over phosphate catalysts	79
3	Amination of 1-octanol on zeolites	80
3.1	Screening of three zeolites having MFI structure	80
3.2	Study in the presence of Al-MFI	81
3.3	Conclusion of the study on zeolites	83
4	Conclusion	83
D GENERAL CONCLUSION 84		84
E Ex	PERIMENTAL PROCEDURE	87
1	Apparatus	87
1.1	Introduction of the gas phase	87
1.2	Introduction of the liquid phase	87
1.3	The tubular reactor	87
1.4	The collecting system	88
2	Analytic	88
2.1	Gas chromatography	88
2.2	Determination of conversion and selectivity	90
2.3	Determination of the contact time	90
2.4	The pH measurement for determination of acidity	91
3	The catalysts	91
3.1	The phosphates	91
3.1.1	Preparation of the phosphates	91

Content			
3.1.2	Determination of acid strength of the phosphates	94	
3.1.2.1	Conversion of acetonylacetone	94	
3.1.2.2	Conversion of isopropanol	97	
3.1.3	BET surface area of the phosphate catalysts	98	
3.1.4	Conclusion about the phosphate catalysts	99	
3 2	The nickel oxides	100	
3.3	Zeolites	100	
3 4	The reactants	100	
F REFER	RENCES	102	