

EFFECTS OF SUPERCRITICAL MEDIA ON CATALYTIC REACTIONS: APPLICATION TO ALIPHATIC ALKYLATION

Maxime MONTILLET¹ (maxime.montillet@ifp.fr), Denis GUILLAUME¹, Nadine ESSAYEM²

¹Institut Français du Pétrole-Lyon BP3 69390 -Vernaison- France

² Institut de Recherche sur la Catalyse, 2 Av Albert Einstein 69626 -Villeurbanne- France

INTRODUCTION

One of the current objectives of modern chemistry is the development of environmentally friendly processes. In the agro alimentary industry, the caffeine extraction process by carbon dioxide in supercritical condition is an example of such new industrial application [1].

Indeed, supercritical fluids possess intermediate properties between those of a liquid (high density) and those of a gas (high diffusivity and low viscosity), that make them excellent extraction agents.

These specific properties of supercritical fluids can be advantageous in the context of heterogeneous catalysed reactions systems, by improving the catalysts stability due to the more effective desorption and extraction of the coke precursors [2,3,4].

The increase of the stability of heterogeneous catalysed reactions systems could allow the evolution of some old processes still based on liquid catalysts, such as the process of aliphatic alkylation towards heterogeneous systems.

The process of light olefins-isobutane alkylation produces paraffinic gasolines with high octane number, respecting the most severe environmental specifications: absence of aromatics, very low sulphur content.

The aliphatic alkylation reaction is catalysed by Brønsted liquid acids. Industrially, HF and H₂SO₄ have been used exclusively for more than 50 years. The development of the alkylation process using a heterogeneous catalyst, under attractive economic conditions, would be a major progress from a point of view of operability, due to the elimination of the corrosive liquid acids, whose treatment involves particular precautions.

The major difficulty encountered during the development of a heterogeneously catalysed alkylation process, is the short catalysts life time (often a few hours). This fast deactivation is due to olefin oligomers formation, which block the catalyst porosity and thus the access to the acid sites. The use of supercritical medium could be an alternative, in order to promote the continuous extraction of oligomers and to lengthen the catalyst life time [5,6,7,8].

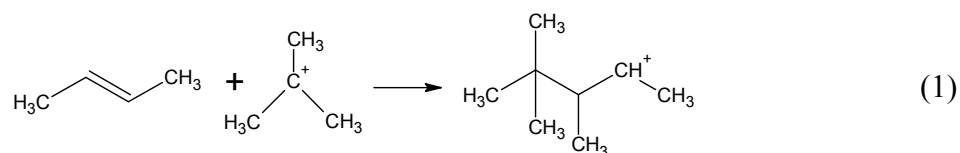
In this study, the reaction system isobutane/propene has been studied under supercritical conditions. A particular attention was paid to the effect of the total pressure in the vicinity of the critical point as regards to the selectivity and the stability of the system.

I Isobutane alkylation process in supercritical conditions

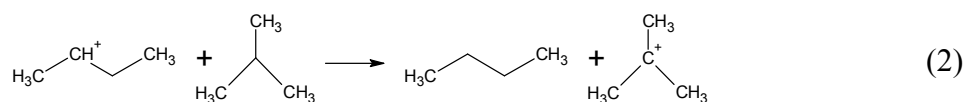
Elementary steps of aliphatic alkylation [9,10,11]

Alkylation

When the butene is the olefin, the alkylation reaction (1) is an electrophilic addition reaction of a ter-butyl carbocation on the butene molecule:



An intermediate iso-octyl carbocation is formed that gives 223 trimethylpentane (223TMP), by hydride transfer with isobutane. This is the primary product of $i\text{C}_4/\text{C}_4^-$ alkylation. The tert-butyl carbocation is formed by hydride transfer between the sec-butyl carbocation (formed by the butene molecule protonation; the initiation step) and an isobutane molecule:



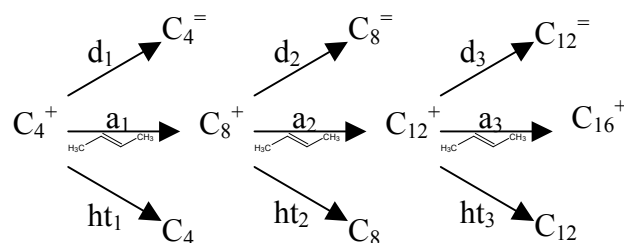
An increase in the tert-butyl carbocation concentration will favour the occurrence of butene addition to this tert-butyl carbenium ion intermediate and hence the alkylation reactions to the expense of the butene di and even trimerisation.

Secondary reactions

In aliphatic alkylation, mainly three types of secondary reactions can be distinguished: oligomerisation, cracking and self-alkylation.

a) Oligomerisation reactions

The oligomerization rate increases with the degree of olefins ramification. The oligomerization affects the octane number and is involved in the catalyst deactivation process.

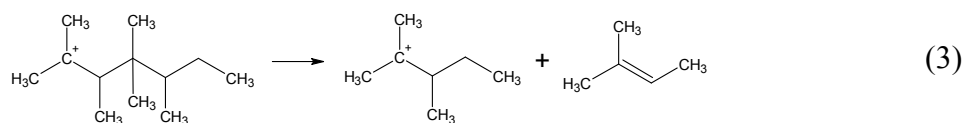


d: deprotonation. a: olefin addition. ht : hydride transfer

The olefin oligomerization dominates the overall reaction scheme when the rate of addition of a butene molecule on the sec-butyl cation is higher than the rate of hydride transfer between the isobutane molecule and the sec-butyl cation (2).

b) Cracking reactions

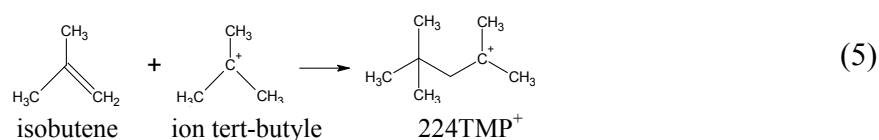
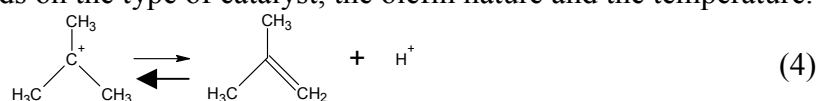
Cracking follows the oligomerization. The multibranched carbocations will be cracked by β -scission, giving back a carbocation and olefins.



Part of C_8 isomers is produced by reactions of oligomerization-cracking or by alkylation multiple-cracking. This is one of the ways to form dimethylhexane isomers.

c) The Self alkylation reaction

The self-alkylation reaction is strongly penalizing because it involves an over-consumption of isobutane. This reaction depends on the type of catalyst, the olefin nature and the temperature.



Why replace butene by propene?

Previous studies have shown that chemical effects observed when switching towards a supercritical medium (products selectivity; occurrence of the secondary reactions) were not easily appreciable by using butene. Indeed, in the case of isobutane alkylation with butene, it is difficult to discriminate between products resulting from principal reaction and secondary reactions. According to the reaction mechanisms presented above, in terms of primary products, alkylation produces trimethylpentanes, dimerisation produces dimethylhexanes and the self alkylation produces also trimethylpentanes. The reactions of skeletal isomerization make it extremely delicate to identify the origin of the C₈ cut products and to deduce the selectivity of the three reactions.

The use of propene to alkylate isobutane seems to be more recommended to understand the chemical effects of the phase shift. The reaction mechanisms will be of the same nature as those described previously. The isobutane/propene alkylation, the propene dimerisation and the iC₄ self alkylation will produce respectively: C₇, C₆ and C₈. That is why the analysis of the products distribution will be richer in information.

II Effect of the pressure on the physicochemical properties of the reagents in a supercritical medium

The physicochemical properties in a supercritical medium are intermediate between those in a liquid and a gas: high density (liquid), strong diffusivity and low viscosity (gas) [12]. These properties are adjustable by tuning the pressure [13,14]. Calculations obtained with the ProII software of SIMSCI made it possible to determine the evolution of the density of the isobutane-propene mixture with the pressure (Figure 1). It appears that a slight increase in pressure leads to a significant increase of the density in the vicinity of the critical point; showing an inflection point.

The variations of the diffusion coefficient were estimated by using the model suggested by He and Yu [15], valid in supercritical medium. The diffusion coefficient decreases with the pressure, but remains higher in the supercritical phase than in liquid phase in the range of pressures studied. An increase in pressure could help the products desorption from the catalyst surface (due to the medium high density) but will reduce the transport properties (lower diffusion coefficient). Hence, the choice of the pressure will be a compromise between the solvent capacity and the mass transfer, in order to extract the products from the catalyst surface.

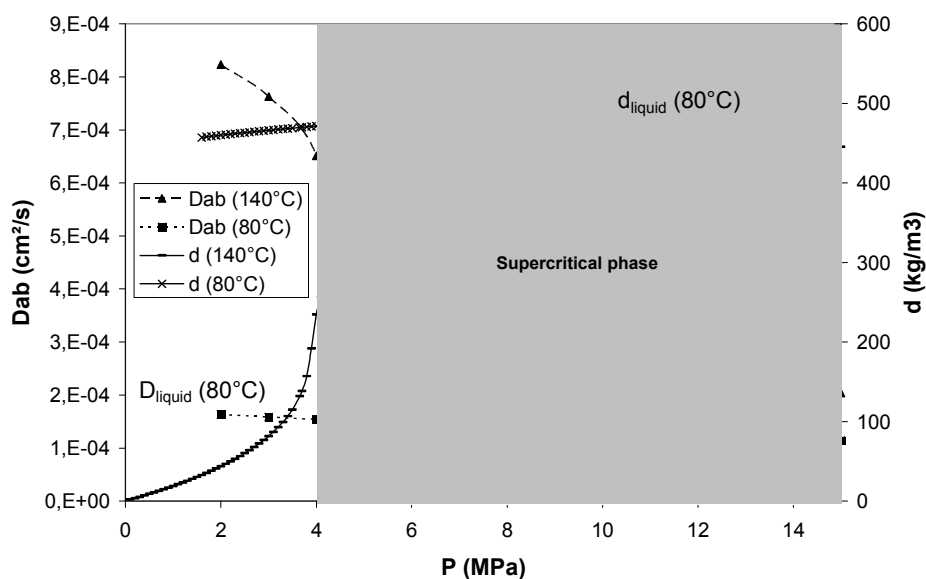


Figure 1: Evolution of the density and diffusivity of the isobutane-propene mixture (Isobutane/propene=100 mol/mol) with the pressure for $T=140^{\circ}\text{C}$ ($\sim T_c$) and $T=80^{\circ}\text{C}$ (liquid phase)

Experimentation

The catalyst chosen for this study is a Beta Zeolite, known to catalyze the reactions of alkylation in the range of operating conditions used in this study (temperature/pressure). A fixed bed continuous reactor with of 15 cm^3 was used. The reaction of alkylation was carried out by using a large isobutane excess compared to the olefin (propene): $iC_4/\text{olefin}=100$ mol/mol, at a temperature close to the critical temperature of the reaction mixture (140°C) and for a pressure range varying from 4 to 15MPa. The reactor is fed by a HPLC pump which assure the desired olefin space velocity, expressed as the ratio of the olefin mass flow to the weight of catalyst per hour (whsv of $0,4\text{h}^{-1}$). The reaction effluents were analysed by two on-line gas chromatographs equipped with FID detectors. To operate in supercritical phase, the operating conditions were estimated with the Peng-Robinson equations of state.

III Résultats and discussion

The results obtained from this study showed an increase of the catalyst lifetime when the reaction is conducted under supercritical conditions. Figure 2 illustrates the evolution of the olefin conversion with time on stream for various types of phases: liquid phase (80°C , 4 MPa), at the critical point (140°C , 4 MPa) and under supercritical high pressure media (140°C , 6, 8, 10 and 15 MPa). One can observe that the catalyst deactivation is reduced under supercritical conditions (whatever the pressure) compared to the liquid phase.

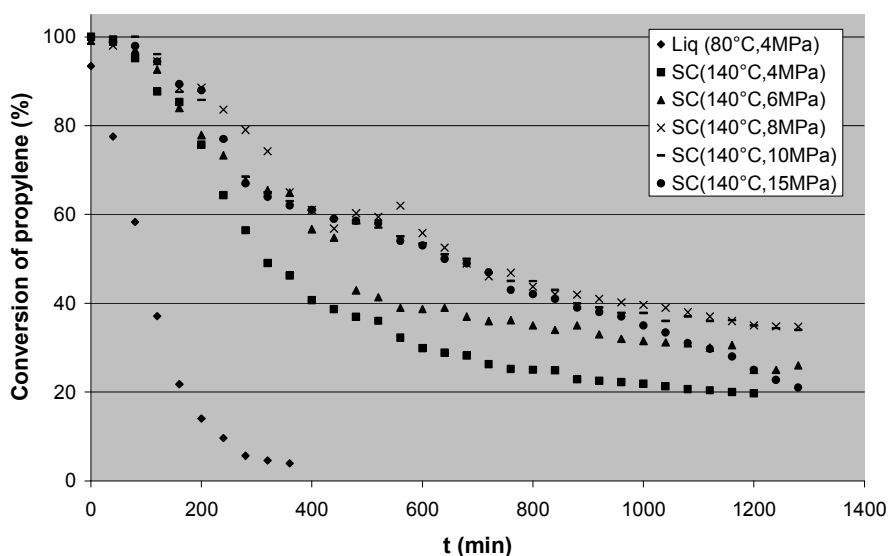


Figure 2: Evolution of the olefin conversion with the age of the catalyst. Alkylation of isobutane by propene: $iC_4/C_3 = 100$ mol/mol, $whsv = 0,4h^{-1}$, tests carried out in liquid phase (80°C, 4 MPa) and supercritical phases (140°C, 4, 6, 8, 10 and 15 MPa).

The increase in pressure under supercritical conditions is accompanied by an increase of the catalyst stability. Under high pressure (6-15MPa) the propene conversion remains higher than 60% after 6 hours of reaction, compared to 45% at 4MPa (critical point) and 5% in liquid phase (80°C, 4 MPa).

The fact that only isobutane and propene were used (no solvent was added in the reaction system) makes the results exploitation more delicate, since the experimental results in liquid phase were obtained at a lower temperature. However, the study of the total pressure effect at iso-temperature is possible. The main objectives of this work were to understand the influence of medium characteristics (density...) on the couple selectivity/stability in supercritical media.

Pressure effect: from 4 to 8 Mpa

The table 1 presents the selectivities obtained under various operating conditions. The analysis of the products distribution shows that the increase in pressure from 4 to 8 MPa is favourable for the alkylation. The concentration of C_7 (alkylation products) increases to the expense of the production of heavy products (C_9^+). The concentration of C_8 isomers, products of the iC_4 self alkylation reaction, decreases slightly with the pressure although the selectivity of the trimethylpentane of the C_8 cut increases significantly (table 1).

	Liquid	SC (4MPa)	SC (6MPa)	SC (8MPa)	SC (10MPa)	SC (15MPa)
Light product/ C_5^+	17,4	13,3	9,3	8,1	7,1	7,0
C_6/C_5^+	10,0	4,9	7,4	7,4	8,1	7,9
C_7/C_5^+	52,4	37,1	55,9	56,9	51,0	48,4
C_8/C_5^+	18,0	19,2	17,0	17,2	20,4	21,4
C_9^+/C_5^+	2,1	25,5	10,4	10,3	13,3	15,2
DMP/ C_7	96,9	95,7	95,9	97,1	96,5	96,4
TMP/ C_8	66,8	32,9	37,5	40,1	37,8	35,9
DMH/ C_8	16,2	42,5	38,5	39,7	38,6	39,1

MH/C ₈	3,4	13,9	11,1	7,6	8,2	9,2
C ₈ ⁼ /C ₈	13,6	10,7	12,9	12,6	15,4	15,8
RON	84,3	78,0	83,5	84,1	83,7	83,5
MON	82,6	76,7	81,8	82,5	82,2	81,9
Alkylation Selectivity	57,0	51,7	61,3	58,1	56,6	54,0
Oligomerisation Selectivity	21,0	27,3	23,4	27,1	27,0	27,9
Self alkylation Selectivity	22,0	21,0	15,3	14,8	16,4	18,1

Table 1: Products distribution, Research octane number (RON) and reactions selectivities at olefin conversion of 80%. Isobutane alkylation by propene: $iC_4/C_3 = 100$ mol/mol, $whsv = 0,4h^{-1}$.

In order to reach supercritical conditions, higher temperatures up to 140°C are necessary. Under these conditions, cracking reactions are promoted and the quality of the alkylate is affected. The Research octane number (RON) decreases from 82 in liquid phase (80°C, 4 Mpa) to 78 (table 1) in supercritical phase (140°C, 4 MPa). However, an increase of the pressure leads to a higher C₇ content as well as to a higher octane number.

The isomers distribution within the C₇ cut is equivalent in liquid and supercritical phase. The proportion of dimethylpentanes (produced directly from the isobutane alkylation by propene) is approximately 97%. The concentration of trimethylpentanes in the C₈ cut decreases with the temperature; the temperature increase favours the isomerization of tribranched C₈ into dibranched C₈ (even monobranched). However, one can note that an increase of pressure, at the same temperature, results to an increase of the trimethylpentane concentration in the C₈ cut.

The increase of pressure in the vicinity of the critical point, is accompanied by a significant variation of the medium properties, and in particular of the density. The density of the medium is equal to 200 kg/m³ at 4 Mpa, 350 kg/m³ at 6 Mpa and 410 kg/m³ at 8 MPa (Figure 1). The expected "physical effect" of a supercritical fluid of high density which is the acceleration of the products extraction, seems to be reinforced by a "chemical effect": an isobutane supercritical medium with a high density may improve the bimolecular reactions as which involve iC_4 molecules.

In particular, the reaction between adsorbed iso-heptyl carbocations and isobutane molecules (hydride transfer) leads to the desorption of the desired products (dimethylpentanes). The intermediate species formed are probably "evacuated" more rapidly from the catalyst surface in iC_4 supercritical phase of high density. The residence time of the intermediate iso-heptyls cations is thus reduced, limiting the secondary reactions (oligomerization, polyalkylation, cracking).

Pressure effect: from 8 to 15 Mpa

Figures 3 and 4 show the distribution of C₇, C₈ and C₉⁺ and the respective contributions of each reaction (alkylation, self-alkylation and oligomerisation). It seems that the rate of the alkylation is maximum near 8 MPa, where the concentration of C₇ is maximum. Under higher pressure, the rates of the oligomerization and self-alkylation increase.

Near 7-8 MPa, it seems that the conditions are optimal for the alkylation reaction. The concentration of C₇, the rate of alkylation and the research octane number are maximum. Previously, it was noted that the density of the reaction medium was an important process parameter. However, other parameters may have a great influence otherwise the supercritical medium would not have interest, since the maximum density is obtained in liquid phase.

Beyond 8 MPa, the density increases slightly (410 kg/m³ under 8 MPa and 435 kg/m³ under 15 MPa), whereas the diffusion coefficient continues to decrease of more than 20% between 8 and 15 MPa (2.61×10^{-4} cm²/s under 8 MPa and 2.04×10^{-4} cm²/s under 15 MPa). This

reduction of the diffusion coefficient may explain the decrease of the yield of the alkylation reaction beyond 8 MPa.

The pressure favours the alkylation reaction and the mechanisms of catalyst regeneration (desorption, hydride transfer), however if the pressure is too high there is no positive apparent effect of the density whereas the diffusion coefficient (which is related to the mass transfer throughout the pores) continues to decrease. The transport of the products becomes more difficult then and the performances of the catalyst decreases. These phenomena explain certainly the decrease of catalyst lifetime at 15 MPa (figure 1).

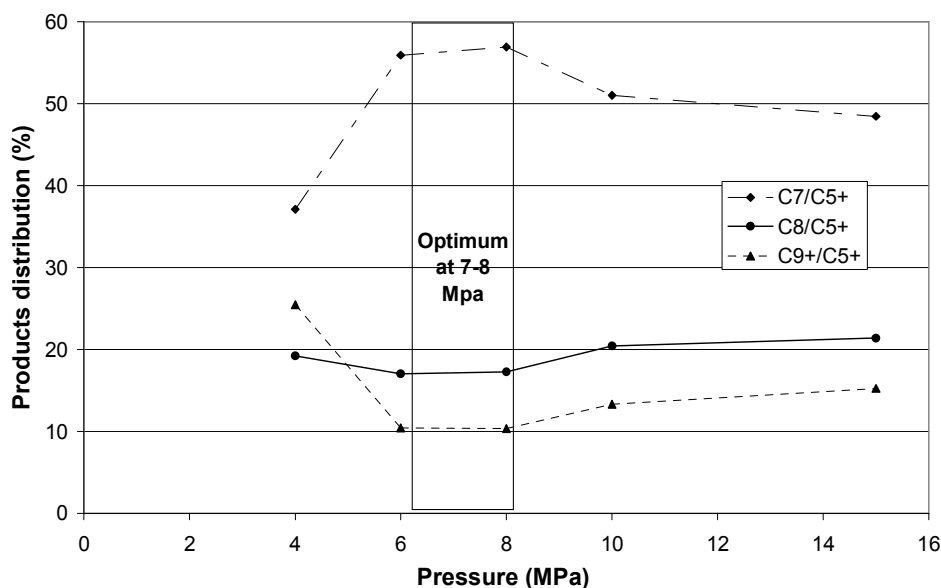


Figure 3: Pressure effect on the products distribution (C_7 , C_8 and C_9^+). Alkylation of isobutane by propene: $iC_4/C_3 = 100$ mol/mol, $whsv = 0,4h^{-1}$ tests carried out in supercritical phase ($140^\circ C$, 4, 6, 8, 10 and 15 MPa).

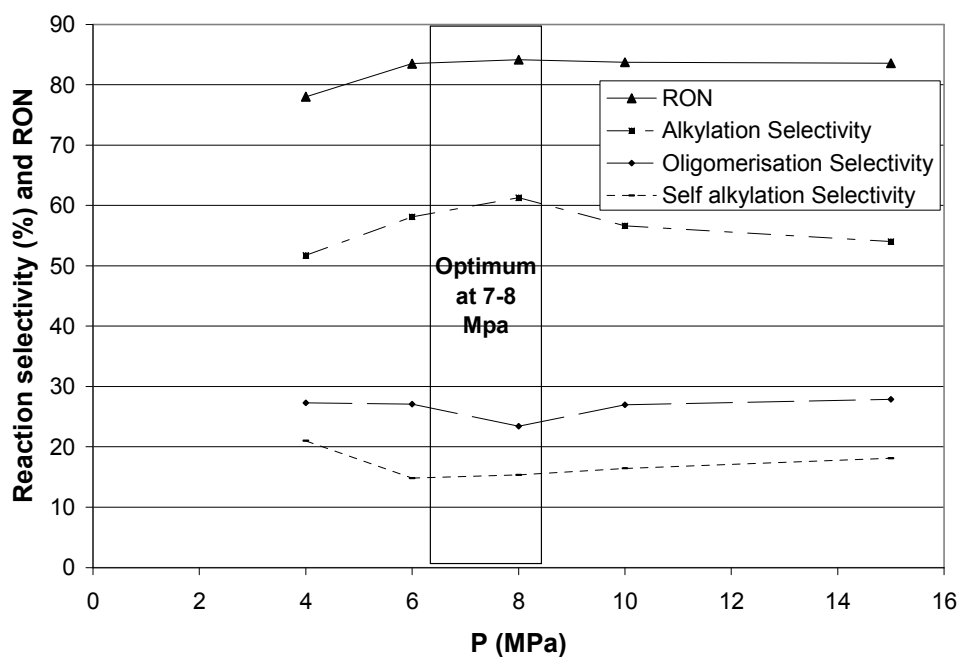


Figure 4: Pressure effect on the reaction rates and RON. Alkylation of isobutane by propene: $iC_4/C_3 = 100$ mol/mol, $whsv = 0,4h^{-1}$ tests carried out in supercritical phase ($140^\circ C$, 4, 6, 8, 10 and 15 MPa).

CONCLUSION

In this study a relatively simple reaction system (isobutane + propene), without the addition of a co-solvent, has permitted to understand the influence, under supercritical conditions, of certain parameters like the density and the diffusion coefficient.

The experimental data have confirmed the positive contribution of the supercritical medium for the alkylation reaction: the main result is an increase of the catalyst stability.

In the vicinity of the critical point, a pressure increase improves the selectivities and the catalyst stability up to 8 MPa.

Under higher pressures, the decrease of the diffusion coefficients leads to lower catalyst performances.

Under iC_4 supercritical conditions, combination of high density and a rather strong diffusivity coefficient can control the product distribution and catalyst lifetime.

References

- [1] E.J.Beckman et al., "Green chemical processing using CO_2 ", *Ind.Eng.Chem.Res* 42, 2003, 1598-1602.
- [2] D. M.Ginosar et B. Subramaniam, "Olefinic oligomer and cosolvent effects on the coking and activity of a reforming catalyst in supercritical reaction mixtures", *J.Catal.* 152, 1995, 31-41.
- [3] J.-D. Grunwaldt, R. Wandeler et A. Baiker, "Supercritical fluids in catalysis : opportunities of in situ spectroscopic studies and monitoring phase behaviour", *Catal. Rev.* 145, 2003, 1-96.
- [4] B. Subramaniam, "Enhancing the stability of porous catalysts with supercritical reaction media", *Appl. Catal. A : General* 212, 2000, 199-213.
- [5] P-Y Gayraud, « Alkylation isobutane-butènes en présence de zircone sulfatée et d'hétéropolyacides en phase liquide et supercritique », thèse de doctorat (IRC Lyon), 2000.
- [6] A. Husain, "Isoparaffin-olefin alkylation with MCM microporous material", brevet WO 94/03415, 1994.
- [7] B. Subramaniam, Final report : "Coking and activity of solid acid alkylation catalysts in supercritical reaction media", *Ind.Eng.Chem.Res*, 37,1998, 1243-1250.
- [8] A. L. Mota Salinas, D. Kong, , Y.B. Tâarit, N. Essayem « Continuous iC_4/C_4^- alkylation under iC_4 Supercritical conditions over $K_{2.5}H_{0.5}PW_{12}O_{40}$ and H-Beta solid acids » *Ind. Eng. Chem. Res.* 43 (20) 2004 6355-6362
- [9] A.Feller, "Reaction mechanism and deactivation pathways in zeolithe catalysed : Isobuatne/2-butene alkylation", thèse de doctorat (Universität München), 2003.
- [10] G.Ertl, H.Knözinger et J.Weitkamp, "Alkylation of isobutane with alkenes on solid catalysts", *Handbook of heterogeneous catalysis*, vol4, 1997.
- [11] L. F. Albright, "Alkylation of isobutane with C_3 - C_5 olefins to produce high-quality gasolines: physicochemical sequence of events", *Ind.Eng.Chem.Res* 42, 2003, , 4283-4289.
- [12] A. Baiker, "Supercritical fluids in heterogeneous catalysis", *Chem. Rev.* 99, 1999, 453-473.
- [13] J. R. Hyde, P. Licence, D. Carter et M. Poliakoff, "Continuous catalytic reactions in supercritical fluids", *Appl. Catal. A : General* 222, 2001, 119-131.
- [14] S. C. Tucker, "Solvent density inhomogeneities in supercritical fluids", *Chem.Rev.* 99, 1999, 391-418.
- [15] B. E. Poling, J.M. Prausnitz, J. P. O'Connell, "The Properties of Gases and Liquids", 5th Ed, Mc Graw Hill, 2000, 11-18.