Heterogeneous catalysis of Friedel-Crafts alkylation by the fluorapatite alone and doped with metal halides

Ahmed Saber, Abdellatif Smahi, Abderrahim Solhy, Rachid Nazih,
Brahim Elaabar, Mostapha Maizi, Saïd Sebti[*]

*Laboratoire de Chimie Organique Appliquée et Catalyse, Université Hassan II,
Faculté des Sciences Ben M'Sik B.P. 7955, 20702 Casablanca, Morocco*

Abstract

The fluorapatite (FAP) alone or doped with metal halide have been used as the new heterogeneous catalysts for the alkylation of benzene, toluene and *p*-xylene. The comparison of the activities of $ZnCl_2$, $ZnBr_2$, $CuCl_2$, $CuBr_2$ and $NiCl_2$ doped in FAP indicate that the best results were obtained with $ZnCl_2$/FAP and $ZnBr_2$/FAP. A high selectivity of monoalkyl compounds was observed in all cases.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous catalysis; Friedel-Crafts alkylation; Fluorapatite; Zinc bromide; Zinc chloride

1. Introduction

The Friedel-Crafts reaction is one of the most fundamental organic transformations. Recently, several applications of this reaction have been developed using a wide range of catalysts [1–15]. In the last few years, heterogeneous catalysis has been the focus of intensive studies. The use of solid basic and acidic catalysts has attracted attention in different areas of organic synthesis because of their advantages like environmental compatibility, reusability, high selectivity and convenient use and separation of products. Indeed, the use of heterogeneous catalysts allows a simplification of the purification step to a simple filtration, separating the catalyst from the reaction media.
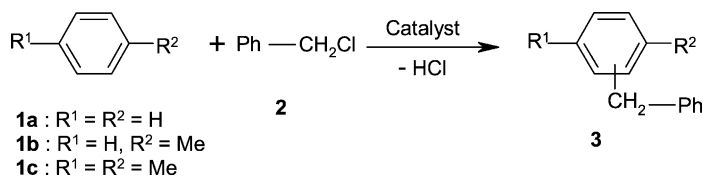
Recently, several heterogeneous catalysts have been used in the Friedel-Crafts reaction such as Fe/montmorillonite [16], Zn/montmorillonite [17], silica and MCM-41 [18], silica and alumina supported polytrifluoromethanesulfosiloxane [19], $MgGa_2O_4$/MgO [20], Fe/zeolite [21], Al/MCM-41 [22], Ga–Mg/hydrotalcite [23], Fe/graphite [24] and Ga/MCM-41 [25].

On the other hand, we have used the natural phosphate (NP) alone or doped as the new heterogeneous catalysts for several reactions such as Knoevenagel condensation [26], nitrile hydration [27], Michael addition [28], epoxidation of alkenes [29], Claisen-Schmidt condensation [30] and flavanones synthesis [31]. NP has been used also as Lewis acid catalyst or support in Friedel-Crafts alkylation [32], 1,3-dipolarcycloaddition [33] and acyclonucleoside synthesis [34]. We have also reported that synthetic hydroxyapatite (HAP) ($Ca_{10}(PO_4)_6(OH)_2$) can promote de Friedel-Crafts reaction [35].
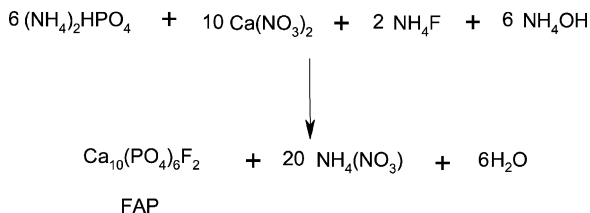
Scheme 1.

In this work, we wish to report the use of the synthetic fluorapatite (FAP) ($Ca_{10}(PO_4)_6F_2$) as an efficient new heterogeneous catalyst and support for Friedel-Crafts benzylation. We have recently used this mineral solid as an excellent catalyst for Knoevenagel condensation free of solvent [36].

The Friedel-Crafts alkylation was carried out using benzene, toluene and *p*-xylene with benzylchloride (Scheme 1). The FAP have been used alone and impregnated with $ZnCl_2$, $ZnBr_2$, $CuCl_2$, $CuBr_2$ and $NiCl_2$.

2. Experimental

2.1. Preparation and characterisation of catalysts

The synthesis of FAP was carried out by coprecipitation method (Scheme 2). Two hundred and fifty millilitres of a solution containing 7.92 g of diammonium hydrogen phosphate and 1 g of the NH_4F, maintained at a pH greater than 12, by addition of ammonium hydroxide (15 ml), were dropped under constant stirring into 150 ml of a solution containing 23.6 g of calcium nitrate ($Ca(NO_3)_2\cdot 4H_2O$). The suspension was refluxed for 4 h. Doubly distilled water (DDW) was used to prepare the solutions. The FAP crystallites were filtered, washed with DDW, dried overnight at 80 °C and calcined in air at 700 °C for 30 min before use.

$$6\,(NH_4)_2HPO_4 \;+\; 10\,Ca(NO_3)_2 \;+\; 2\,NH_4F \;+\; 6\,NH_4OH$$

$$Ca_{10}(PO_4)_6F_2 \;+\; 20\,NH_4(NO_3) \;+\; 6H_2O$$

FAP

Scheme 2.

The structure of obtained apatite was confirmed by X-ray diffraction, infrared spectra and chemical analysis. The fluorapatite crystallizes in the hexagonal system with the space group $P6_{3/m}$. The lattice parameters of the prepared FAP are in excellent agreement with standard data: $a = 9.364$ Å and $c = 6.893$ Å. The composition of FAP was determined as calcium 38.29%, phosphorous 17.78% and the molar ratio was Ca/P = 1.66. The surface area of calcined FAP was determined by the BET method from the adsorption–desorption isotherm of nitrogen at its liquid temperature (77 K) and was found to be $S = 15.40\,m^2\,g^{-1}$. The total pore volume was calculated by the BJH method at $P/P_0 = 0.98$ (VT = $0.0576\,cm^3\,g^{-1}$).

The preparation of MCl_2/FAP or MBr_2/FAP (M = Zn, Ni or Cu) was as follows: 10 mmol of MCl_2 or MBr_2 and 10 g of FAP were mixed in 100 ml of water and then evaporated to dryness and dried for 2 h at 150 °C before use.

The XRD patterns of MX_2/FAP are similar to that of FAP as shown in Fig. 1. The modification of the FAP
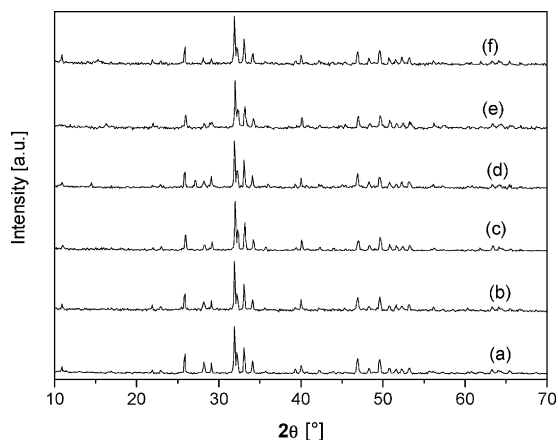

Fig. 1. XRD patterns of: (a) FAP; (b) $ZnBr_2$/FAP; (c) $ZnCl_2$/FAP; (d) $CuBr_2$/FAP; (e) $CuCl_2$/FAP; and (f) $NiCl_2$/FAP.

Table 1
Benzylation of benzene, toluene and *p*-xylene with different prepared catalysts

Substrate	Weight (g)	Time	Conversion[a] (isolated product)[b] (%)	Monoalkyl compound[c] (*ortho/para*)[d] (%)	Dialkyl compound[c] (%)
Benzene	ZnBr$_2$/FAP	70 min	100 (95)	78	17
	ZnCl$_2$/FAP	17 h	98 (95)	77	18
	CuBr$_2$/FAP	48 h	6		
	CuCl$_2$/FAP	48 h	4		
	NiCl$_2$/FAP	48 h	65 (60)	40	20
Toluene	ZnBr$_2$/FAP	1 h	100 (98)	91 (43/57)	7
	ZnCl$_2$/FAP	3 h	100 (97)	90 (45/55)	7
	CuBr$_2$/FAP	24 h	96 (93)	81 (40/60)	12
	CuCl$_2$/FAP	48 h	82 (76)	66 (43/57)	10
	NiCl$_2$/FAP	48 h	18 (16)	14 (41/59)	2
p-Xylene	ZnBr$_2$/FAP	10 min	100 (98)	90	8
	ZnCl$_2$/FAP	15 min	99 (98)	88	10
	CuBr$_2$/FAP	6 h	97 (94)	83	11
	CuCl$_2$/FAP	24 h	100 (96)	84	12
	NiCl$_2$/FAP	24 h	99 (97)	85	12

[a] Conversion of benzylchloride determined by GC.
[b] Yield of isolated products after distillation.
[c] Percentage of isolated products after distillation.
[d] Composition determined by ^{1}H NMR.

Table 2
Recycling of catalysts in the alkylation of *p*-xylene

Run	Conversion (%) (time)				
	ZnCl$_2$/FAP	ZnBr$_2$/FAP	CuCl$_2$/FAP	CuBr$_2$/FAP	NiCl$_2$/FAP
1	99 (15 min)	100 (10 min)	100 (24 h)	97 (6 h)	99 (24 h)
2	94 (15 min)	99 (10 min)	90 (24 h)	93 (6 h)	96 (24 h)
3	88 (15 min)	90 (10 min)	87 (24 h)	93 (6 h)	90 (24 h)
4	65 (15 min)	79 (10 min)	60 (24 h)	85 (6 h)	70 (24 h)

by MX$_2$ impregnation does not change the crystalline structure of the solid material. The intensity of typical diffraction peaks did not significantly change indicating no disorganisation of the crystalline structure of FAP. It should be noted that no MX$_2$ phases were detected on the doped materials in all cases, indicating that MX$_2$ were highly dispersed in the solid FAP.

2.2. Reaction procedure

The solution of benzylchloride (9 mmol) in benzene, toluene or *p*-xylene (10 ml) was refluxed in the presence of FAP, ZnCl$_2$/FAP, ZnBr$_2$/FAP, CuCl$_2$/FAP, CuBr$_2$/FAP or NiCl$_2$/FAP (0.1 g). The mixture was

stirred. The reaction was monitored by GC. All obtained products were purified by distillation under vacuum and identified by ^{1}H NMR and IR spectroscopy. The results obtained are presented in the figures and grouped in Tables 1 and 2.

3. Results and discussion

3.1. Benzylation of benzene, toluene and p-xylene over fluorapatite

First of all, we have tested the FAP alone as the acidic catalyst in the Friedel-Crafts alkylation. Thus,
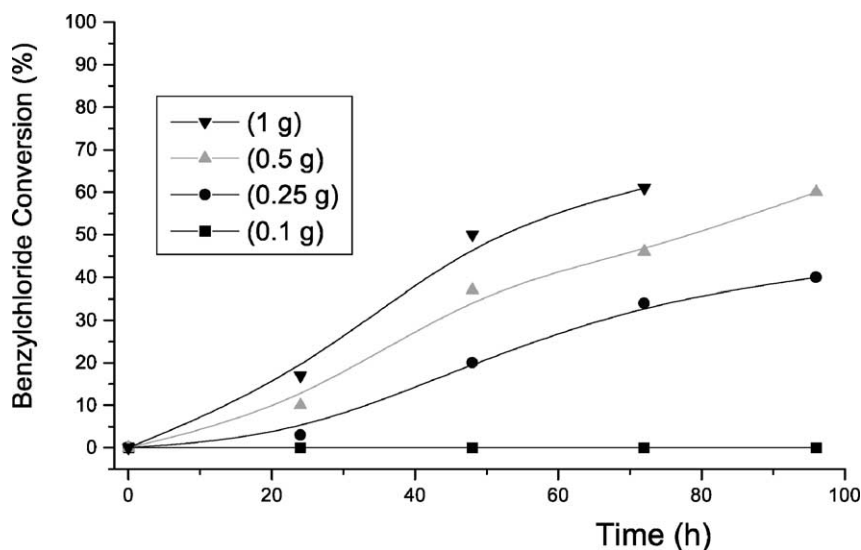
Fig. 2. Weight effect of the FAP in the benzene benzylation.

various amount of FAP have been used to catalyse the benzylation of benzene (Fig. 2), toluene (Fig. 3) and *p*-xylene (Fig. 4) with benzylchloride. The results obtained indicate that the FAP can catalyse these transformations. It is now clear that this solid possesses some acidic properties but it is necessary to use relatively high weight of the catalyst to afford the alkylation in the good yields.

3.2. Alkylation catalysed by MX$_2$/FAP

In view of the established beneficial effects of the solid supports, we have investigated the use of the FAP impregnated with the metal halides for the alkylation of benzene, toluene and *p*-xylene under mild conditions. These impregnated catalysts have been prepared as indicated before.
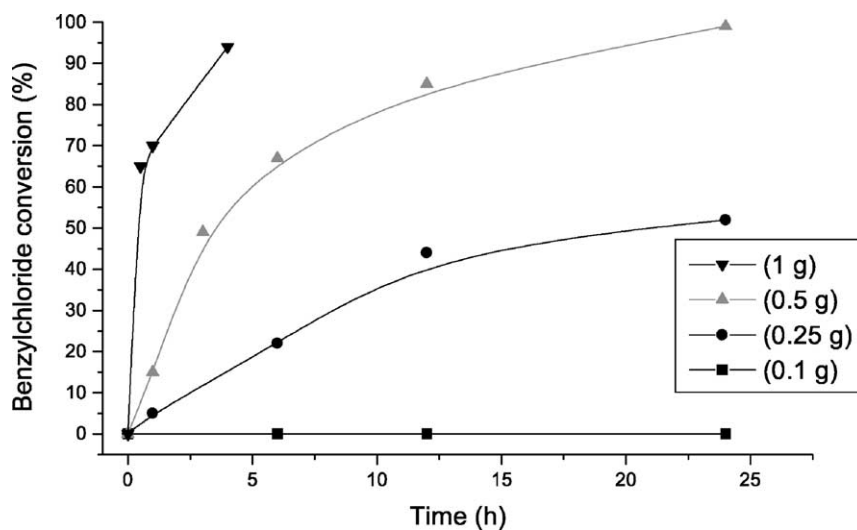

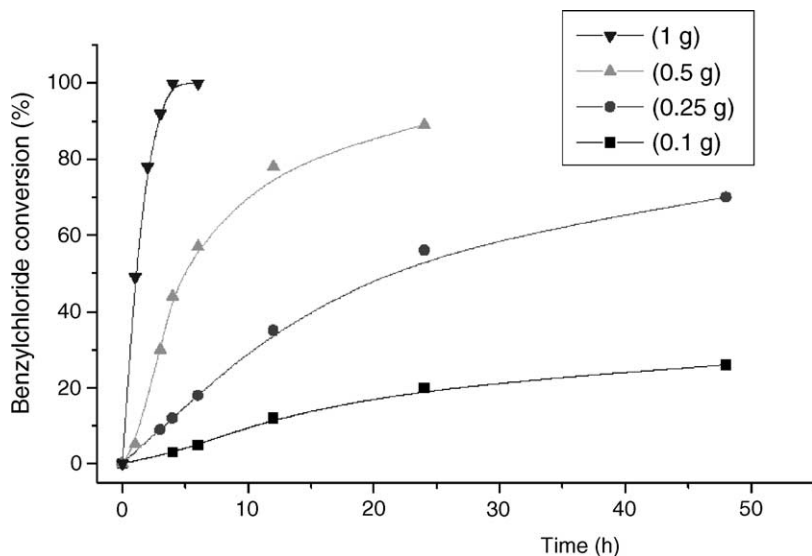Fig. 3. Weight effect of the FAP in the toluene benzylation.

Fig. 4. Weight effect of the FAP in the *p*-xylene benzylation.

Firstly, we have tested the FAP impregnated with $ZnCl_2$ and $ZnBr_2$ as the solid catalysts for the benzylation of benzene (Fig. 5), toluene (Fig. 6) and *p*-xylene (Fig. 7).

In general, the reaction rates of the alkylation of the *p*-xylene and the toluene are higher in comparison

with the benzene alkylation. In the last case, the reaction needs comparatively longer time for completion excepted with $ZnBr_2$/FAP when the total conversion was observed after only 1 h of reaction.

The comparison of the conversion obtained with $ZnCl_2$, $ZnBr_2$, FAP, $ZnCl_2$/FAP and $ZnBr_2$/FAP shows
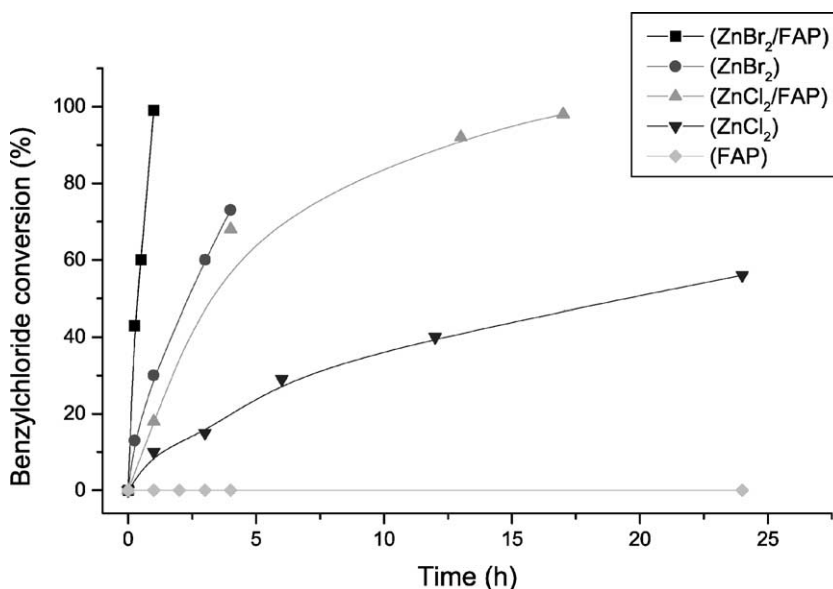

Fig. 5. Benzene benzylation with FAP, $ZnCl_2$, $ZnBr_2$, $ZnCl_2$/FAP and $ZnBr_2$/FAP.
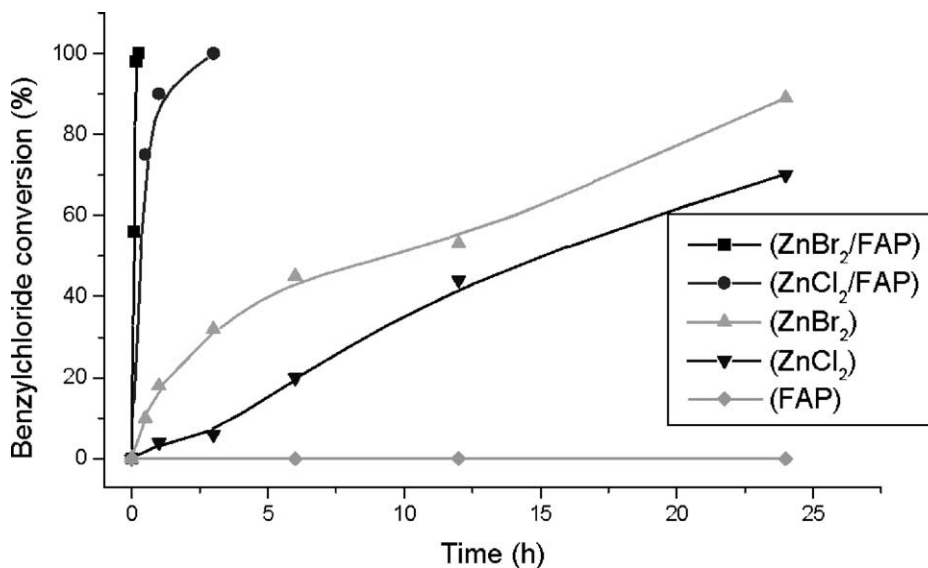
Fig. 6. Toluene benzylation with FAP, ZnCl$_2$, ZnBr$_2$, ZnCl$_2$/FAP and ZnBr$_2$/FAP.

clearly the positive effect of the impregnating process. Thus, in all cases the activity of the impregnated catalyst was higher than that of the metal halide alone. No reaction was observed without heating or when the catalyst was omitted from the reaction mixture. The results obtained with ZnBr$_2$ and ZnBr$_2$/FAP are higher than those obtained with ZnCl$_2$ and ZnCl$_2$/FAP, respectively, in all cases.

The *p*-xylene and the toluene are more reactive than the benzene. This behaviour can be due to donating effect of methyl group in addition with reaction temperature corresponding to the refluxing temperature of the aromatic compounds (135, 108 and 80 °C, respectively). In the case of *p*-xylene the relatively highly steric effect is in opposition with the electronic effect.
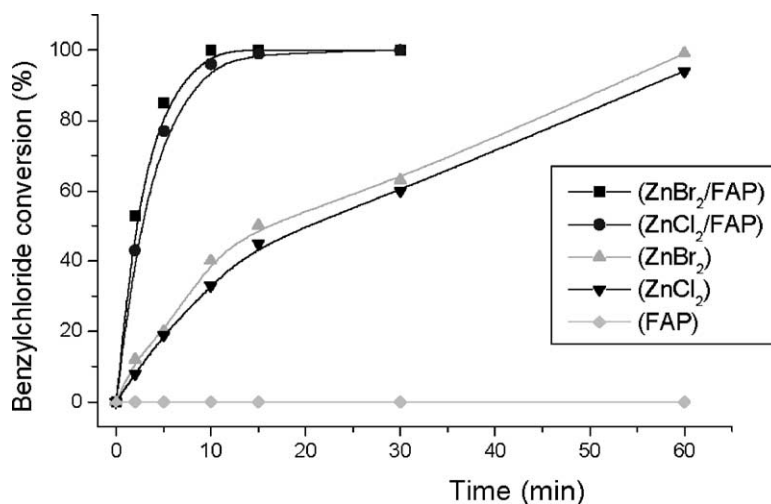

Fig. 7. *p*-Xylene benzylation with FAP, ZnCl$_2$, ZnBr$_2$, ZnCl$_2$/FAP and ZnBr$_2$/FAP.

On the other hand, it has been known that the catalytic activity of metal halides can be modified by the presence of protic acid in the homogeneous Friedel-Crafts reaction. In our case, the by-product HCl formed during the reaction is probably immediately adsorbed on the solid catalyst or reacted with them. Thus, no free protic acid was present in the reaction mixture.

Furthermore, the metal halide effect was also examined. Thus, we have tested $CuCl_2$, $CuBr_2$ and $NiCl_2$ alone and supported on FAP. The conversion of the benzylchloride in the benzene alkylation with $CuCl_2$, $CuBr_2$, $CuCl_2$/FAP and $CuBr_2$/FAP are 5, 4, 4 and 6%, respectively, after 48 h of the reaction time. In contrast, when we use $NiCl_2$ and $NiCl_2$/FAP for this alkylation, the conversions observed are 15 and 65%, respectively, after 48 h.

In this condition, impregnating FAP with $CuCl_2$ or $CuBr_2$ does not affect their activity in the benzene alkylation. So impregnating the FAP with $NiCl_2$ provokes enhancement of both activities.

The same results were observed in the benzylation of the toluene. Thus, the reaction was also unaffected by impregnating the FAP with $CuCl_2$ (Fig. 8), although the conversion obtained was 65% after 24 h for both $CuCl_2$ and $CuCl_2$/FAP. In contrast, $CuBr_2$/FAP greatly accelerate the rate of the reaction, and the conversions obtained were 70 and 90% comparatively to 53 and 78% using $ZnBr_2$ alone for 12 and 24 h, respectively.

With $NiCl_2$ and $NiCl_2$/FAP, the conversions observed in the benzylation of toluene after 24 h of reaction were 69 and 7%, respectively. These results are in contradiction with those obtained with the benzene.

In the alkylation of p-xylene with the benzylchloride catalysed by $CuCl_2$, $CuBr_2$ and $NiCl_2$ alone and impregnated on the FAP (Fig. 9), it clearly shows the positive effect of impregnating the FAP with $CuBr_2$. For example, the conversions of the benzylchloride were 5, 52 and 97% using FAP, $CuBr_2$ and $CuBr_2$/FAP, respectively, after 6 h of reaction time. In contrast, it appears that the effect observed with $CuCl_2$/FAP is somewhat low compared with the effect of both $CuCl_2$ and FAP. For example, using FAP, $CuCl_2$ and $CuCl_2$/FAP the conversions are 5, 41 and 62% after 6 h of reaction and 20, 82 and 100% after 24 h of reaction, respectively.

In the catalysis of the benzylation of the p-xylene with $NiCl_2$, FAP and $NiCl_2$/FAP, the conversions observed with the doped material seem to be due to the separate effect of $NiCl_2$ and FAP. Thus, after 24 h of reaction the conversions were 85, 20 and 99% with $NiCl_2$, FAP and $NiCl_2$/FAP.

The comparison of the results obtained in the benzylation of benzene, toluene and p-xylene using impregnated catalysts is regrouped in Table 1. The yields of the isolated products are also reported.

Among these catalysts, satisfactory results have been obtained with $ZnCl_2$ and $ZnBr_2$ supported on the FAP. The selectivity of the monoalkylation was
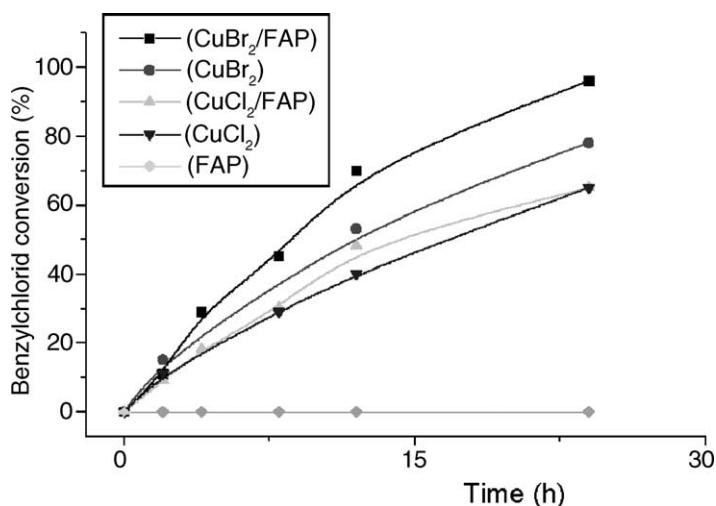

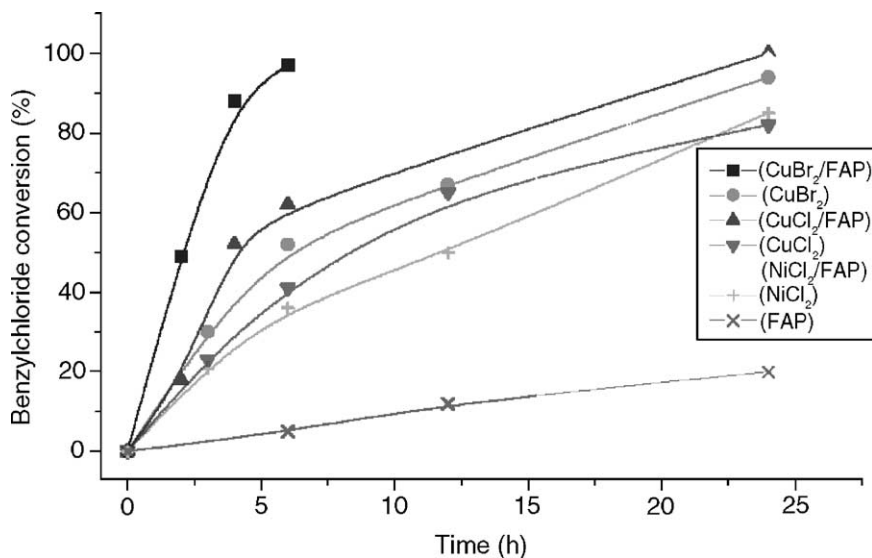Fig. 8. Toluene benzylation with FAP, $CuCl_2$, $CuBr_2$, $CuCl_2$/FAP and $CuBr_2$/FAP.

Fig. 9. *p*-Xylene benzylation with FAP, CuCl₂, CuBr₂, NiCl₂, CuCl₂/FAP, CuBr₂/FAP and NiCl₂/FAP.

observed in all cases studied. For the toluene benzylation, the ratio of *ortho*/*para* determined after isolating the products was in the range of 45/55 to 40/60.

Because recyclability is an important aspect of the process on environmental and economic ground, we have investigated the reusability of our catalysts in the benzylation of the *p*-xylene. After the reaction time, the catalyst was isolated by filtration, washed with the solvent/substrate used in the reaction (benzene, toluene or *p*-xylene) and dried at 150 °C in vacuum before reuse. For all cases (Table 2), the conversion of the benzylchloride decreases slowly. These results demonstrating that the impregnated materials can be easily recycled with a low cost of the activity. To compare the recycled catalyst to initial one, we have analysed ZnCl₂/FAP isolated after the first and second cycle and the Zn composition was determined by atomic absorption as 93 and 90% of weight report, respectively, compared to the Zn weight used in the initial catalyst ZnCl₂/FAP. This result indicate clearly that very low lixiviation of Zn^{2+} was observed in the process of isolating the catalyst after the reaction. The same behaviour was observed with NiCl₂/FAP and only 7% of the metal was lost after the first cycle.

In summary, we have developed a novel method for the alkylation of aromatic ring using the FAP alone and doped with metal halide as heterogeneous catalysts.

The comparison of the catalytic activity of the ZnCl₂, ZnBr₂, CuCl₂, CuBr₂ and NiCl₂ alone and doped on the FAP indicate that ZnCl₂/FAP and ZnBr₂/FAP are the new and efficient heterogeneous catalysts for the Friedel-Crafts alkylation performed with relatively high selectivity in the monoalkyl products.

Acknowledgements

References

[1] I. Shiina, M. Suzuki, K. Yokoyama, Tetrahedron Lett. 43 (2002) 6395.
[2] I. Shiina, M. Suzuki, Tetrahedron Lett. 43 (2002) 6391.
[3] M. Shi, S.C. Cui, J. Fluorine Chem. 116 (2002) 143.
[4] M.C. McMills, D.L. Wright, R.M. Weekly, Synth. Commun. 32 (2002) 2417.
[5] X. Peng, J. Wang, J. Cui, R. Zhang, Y. Yan, Synth. Commun. 32 (2002) 2361.
[6] G.D. Yadav, S. Sengupta, Org. Process. Res. Dev. 6 (2002) 256.

[7] J. Kaur, K. Griffin, B. Harrison, I.V. Kozhevnikov, J. Catal. 208 (2002) 448.

[8] W. Zhuang, K.A. Jorgensen, Chem. Commun. (2002) 1336.

[9] I. Komoto, J. Matsuo, S. Kobayashi, Top. Catal. 19 (2002) 43.

[10] G.D. Yadav, B. Kundu, Can. J. Chem. Eng. 79 (2001) 805.

[11] N.A. Paras, D.W.C. MacMillan, J. Am. Chem. Soc. 123 (2001) 4370.

[12] S. Kobayashi, I. Komoto, J. Matsuo, Adv. Synth. Catal. 343 (2001) 71.

[13] P. Wasserscheid, M. Sesing, W. Korth, Green Chem. 4 (2002) 134.

[14] J. Ross, J. Xiao, Green Chem. 4 (2002) 129.

[15] K.S. Yeung, M.E. Farkas, Z. Qiu, Z. Yang, Tetrahedron Lett. 43 (2002) 5793.

[16] B.M. Choudary, B.P. Rao, N.S. Chowdari, M.L. Kantam, Catal. Commun. 3 (2002) 363.

[17] V.R. Choudhary, K. Mantri, Catal. Lett. 81 (2002) 163.

[18] A. Corma, H. Garcia, A. Moussaif, M.J. Sabater, R. Zniber, A. Redouane, Chem. Commun. (2002) 1058.

[19] D.Q. Zhou, C.M. Wang, J.H. Yang, M.Y. Huang, Y.Y. Jiang, Polym. Adv. Technol. 13 (2002) 169.

[20] V.R. Choudhary, S.K. Jana, V.S. Narkhede, Catal. Commun. 2 (2001) 331.

[21] A.M.F. Bidart, A.P.S. Borges, L. Nogueira, E.R. Lachter, C.J.A. Mota, Catal. Lett. 75 (2001) 155.

[22] H. Hamdan, A.B. Kim, M.N.M. Muhid, Stud. Surf. Sci. Catal. 135 (2001) 282.

[23] V.R. Choudhary, S.K. Jana, A.B. Mandale, Catal. Lett. 74 (2001) 95.

[24] M. Nagai, T. Yoda, S. Omi, M. Kodomari, J. Catal. 201 (2001) 105.

[25] K. Okumura, K. Nishigaki, M. Niwa, Microporous Mesoporous Mater. 44–45 (2001) 509.

[26] S. Sebti, A. Smahi, A. Solhy, Tetrahedron Lett. 43 (2002) 1813.

[27] S. Sebti, A. Rhihil, A. Saber, N. Hanafi, Tetrahedron Lett. 37 (1996) 6555.

[28] S. Sebti, H. Boukhal, N. Hanafi, S. Boulaajaj, Tetrahedron Lett. 40 (1999) 6027.

[29] J.M. Fraile, J.I. Garcia, J.A. Mayoral, S. Sebti, R. Tahir, Green Chem. 3 (2001) 271.

[30] S. Sebti, A. Solhy, R. Tahir, S. Boulaajaj, J.A. Mayoral, J.M. Fraile, A. Kossir, H. Oumimoun, Tetrahedron Lett. 42 (2001) 7953.

[31] D.J. Macquarrie, R. Nazih, S. Sebti, Green Chem. 4 (2002) 56.

[32] S. Sebti, A. Rhihil, A. Saber, Chem. Lett. 8 (1996) 721.

[33] H.B. Lazrek, A. Rochdi, Y. Kabbaj, M. Taourirte, S. Sebti, Synth. Commun. 29 (1999) 1057.

[34] A. Alahiane, A. Rochdi, M. Taourirte, N. Redwane, S. Sebti, H.B. Lazrek, Tertrahedron Lett. 42 (2001) 3579.

[35] S. Sebti, R. Tahir, R. Nazih, S. Boulaajaj, Appl. Catal. A 218 (2001) 25.

[36] S. Sebti, R. Nazih, R. Tahir, L. Salhi, S. Saber, Appl. Catal. A 197 (2000) L187.