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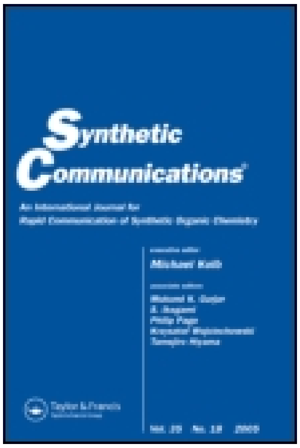

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Fe^{3+}-Montmorillonite as Effective, Recyclable Catalyst for Paal-Knorr Pyrrole Synthesis Under Mild Conditions

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Abstract: Fe^{3+}-montmorillonite clay catalyst was used for the first time for pyrroles preparation by Paal–Knorr condensation. The features of this catalytic system are improved yields, mild conditions, a simple procedure, and high catalytic efficiency. The catalyst could be easily recycled and reused for three times without visible losing of activity.

Keywords: Catalysis, diketones, heterocycles, solid support

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INTRODUCTION

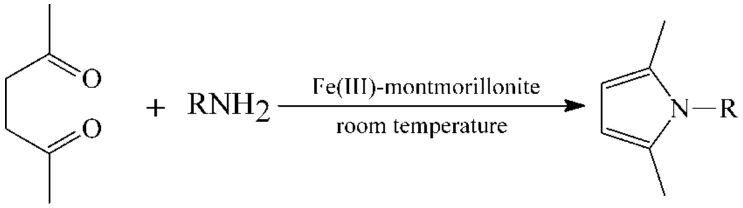
In recent years, the use of clay, particularly montmorillonites, has received considerable attention in chemical synthesis.[1] Clay catalysts act as both Brønsted and Lewis acids in their natural ion-exchanged forms.[2] They are inexpensive, noncorrosive, and recyclable. Thus, the montmorillonite-catalyzed procedures have many advantages, such as environmental compatibility and ease of handling. Various catalysts prepared by exchanged transition metal cations on montmorillonite have been used in many typical acid-catalyzed reactions, such as Friedel–Crafts reactions,[3] Beckmann rearrangement,[4] esterification,[5] and nitration.[6]

Recently, Paal–Knorr condensation has experienced a rekindled interest in the synthetic chemistry for preparation of pyrrole, pyrazoles, and their derivatives, as naturally occurring organic compounds and intermediates for pharmaceuticals. Various acidic materials, such as zeolite,[7] *p*-TSA,[8] Al_2O_3,[9] montmorillonite (K10,[9a] KSF[10]), layered zirconium phosphate, and zirconium sulfophenyl phosphonate,[11] and the microwave technology[12] have been used to promote these condensations. Although some of these processes offer distinct advantages over conventional methods, they suffer from certain drawbacks, such as hazardous organic solvents, high cost, long reaction time, and large amounts of solid catalysts. We previously reported ionic liquids promoted Paal–Knorr condensation between amines and 2,5-hexandione,[13] but the expensive cost of ionic liquids makes this methodology far from practical. In continuation of our work on the synthesis of pyrroles, we report Fe^{3+}-montmorillonite catalyzed Paal–Knorr condensation under mild conditions.

RESULTS AND DISCUSSION

In the reaction of aniline and 2,5-hexandione, various metal-exchanged, montmorillonite K10 catalysts have been used to promote the condensation at room temperature (20°C). See Scheme 1.

From Table 1, the catalytic activities of metal-exchanged montmorillonite K10 catalysts in decreasing order are $Fe^{3+} > Zn^{2+} > Co^{2+} > Cu^{2+}$-



Scheme 1.

Table 1. Paal–Knorr condensation of aniline with 2,5-hexandione using various metal-exchange montmorillonite clay catalysts

Entry	Catalyst	Time (h)	Yield (%)[a]
1	Fe^{3+}-mont.	3	95
2	Zn^{2+}-mont.	5	87
3	Co^{2+}-mont.	5	81
4	Cu^{2+}-mont.	5	76
5	K10	5	72

[a] GC yield.

montmorillonite. Commercial K10 montmorillonite was also evaluated in this reaction, but its activity was slightly inferior as compared with the others. As a result, Fe^{3+}-montmorillonite proved to be a more effective catalyst for the reaction of aniline and 2,5-hexandione as compared with the others; this observation is analogous to previous investigations on Friedel–Crafts reactions[3] and esterification.[5] The high activity of the Fe^{3+}-montmorillonite catalyst may be because of the enhanced interlayer acidity with increasing ratio of charge to cation radius.[14]

The effect of reaction temperature on the Fe^{3+}-montmorillonite catalyzed Paal–Knorr condensation of aniline with 2,5-hexandione was also investigated and the results are shown in Fig. 1. When the temperature was

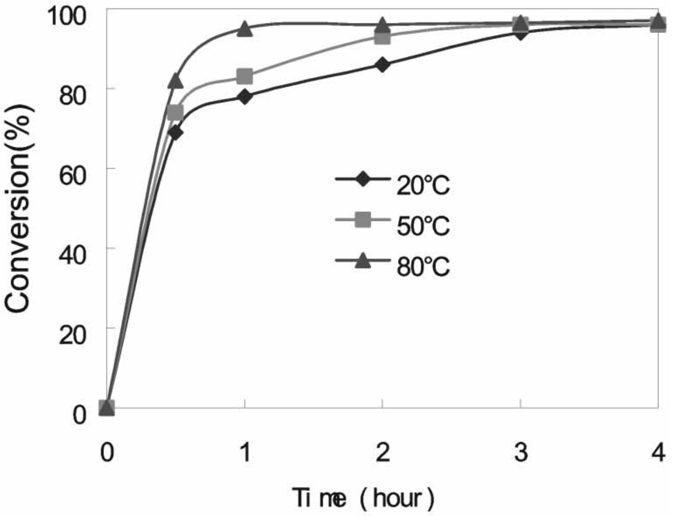


Figure 1. The effect of temperature on the Fe^{3+}-montmorillonite catalyzed Paal–Knorr condensation of aniline with 2,5-hexandione.

raised, maximum yield was reached soon. At 80°C the substrates could be completely consumed within 1 h; it is very interesting that the reaction also can be finished at room temperature (20°C) within 3 h. It should be pointed out that the dosages of catalysts are in general more than 100% (wt) in many reported solid catalytic systems.[7,9,10] In our Fe^{3+}-montmorillonite system, the dosage of catalyst was only 12% (wt), indicating the effectiveness of this catalyst.

With these results in hand, other amines have been used to react with 2,5-hexandione, and the results are listed in Table 2. To meet the requirement of minimization of energy consumption, the reactions were carried out at 20°C. It is evident that several amines could be converted to the corresponding *N*-substituted pyrroles in good to excellent yields over the Fe^{3+}-montmorillonite catalyst. It is well known that the aliphatic amines are more nucleophilic compared with aromatic amines, thus aliphatic amines give higher yields or shorter reaction times than those generally observed in other systems.[7,13] Additionally, the possibility of the large-scale production of this reaction was investigated by using aniline and 2,5-hexadione as substrates with dosages of 50 times (0.1 mol) the initial amount, and the outcome is listed in Table 2, entry 8. Compared to that of 2-mmol dosage, the reaction time of the large-scale reaction was relatively reduced but the yield of product increased to some extent. This result may be because of the increased exothermicity of the reaction.

Table 2. Pyrrole derivatives produced by Paal–Knorr condensation using Fe^{3+}-montmorillonite catalyst

Entry	R	Time (h)	Yield (%)[a]
1	*n*-Propyl	1	94
2	*n*-Butyl	1	96
3	*iso*- Butyl	2	92
4	*n*-Heptyl	2	93
5	Benzyl	2	96
6	Phenyl	3	96
7	Phenyl	3	93[b]
8	Phenyl	2	95[c]
9	*p*-Methoxyphenyl	3	94
10	Cyclohexyl	6	74
11	2-Pyridinyl	6	69

[a] Isolated yields.

[b] Yield of N-phenyl-2,5-dimethylpyrrole obtained using the Fe^{3+}-montmorillonite catalyst that had been reused three times.

[c] Yield of N-phenyl-2,5-dimethylpyrrole using substrates with dosage of 50 times of initial amount.

Because the present catalyst is a solid material, it could be easily recycled after reaction by simple filtration. After further treatments including washing and activation at 120°C, the recycled catalyst was used in the next run. In the reaction between aniline and 2,5-hexandione, the Fe^{3+}-montmorillonite catalyst could be reused three times without noticeable loss of activity.

CONCLUSION

Fe^{3+}-montmorillonite has proved to be a good catalyst for Paal–Knorr condensation between amines and 2,5-hexandione. The features of the Fe^{3+}-montmorillonite–catalyzed procedure are mild conditions, improved product yield, and simple workup. Furthermore, it is relatively inexpensive and results in less chemical waste because of the lower quantity of catalyst (12% wt) needed as compared with the reported solid catalysts. Another advantage is the reliable reusability of the catalyst; this property makes the present Fe^{3+}-montmorillonite–catalyzed Paal–Knorr condensation an attractive green procedure with previously mentioned features.

EXPERIMENTAL

Catalyst Preparation

Montmorillonite K10 (2 g) was added to 25 mL aqueous solution (1 M) of $FeCl_3$, $ZnCl_2$, $CuCl_2$, and $CoCl_2$. The mixture was stirred vigorously for 24 h. The clay suspension was centrifuged and the supernatant solution was discarded. The obtained clay catalyst was then washed with distilled water until free of chloride ions as indicated by an $AgNO_3$ test. Before catalytic reaction, the catalyst was dried in an oven at 120°C overnight.

Typical Procedure

Clay catalyst (12% wt) was added to a stirred solution of an amine (2 mmol), 2,5-hexandione (2 mmol), and a little dichloromethane (< 1 mL) in a 25-mL round-bottom flask. The mixture was stirred at room temperature (20°C) for the desired time. After reaction, the solid catalyst was filtered and washed with dichloromethane (3×2 mL). The liquid content was analyzed with GC [HP 6890 equipped with a HP 5MS column (30 m)] and GC/MS (HP 6890/5793). The concentration of reactant and product was directly given by the system of GC chemstation according to the area of each chromatograph peak. The pure products could be obtained by evaporated under vacuum.[10]

Analytical Data for Selected Compounds

2,5-Dimethyl-1-butyl-1H-pyrrole: (yellow oil); δ_H (300 MHz, $CDCL_3$) 0.96 (CH_3, t, 3H), 1.37 (CH_2, m, 2H), 1.58, (CH_2, m, 2H), 2.21 (CH_3, s, 6H), 3.69 (CH_2, s, 2H), 5.71 (pyrrolics, s, 2H).

1-Phenyl-2,5-dimethyl-1H-pyrrole: (white solid, mp 50–51°C, reported[9] 50°C); δ_H (300 MHz, $CDCl_3$,) 2.04 (CH_3, s, 6H), 5.91 (pyrrolics, s, 2H), 7.20 (PhH, m, 2H), 7.41 (PhH, m, 3H); δ_C (75 MHz, $CDCl_3$) 12.97 ($2CH_3$), 105.56 (C-3, C-4), 127.58 (C-2, C-5), 128.19, 128.76, 129.01, 138.41 (Ph).

1-Benzyl-2,5-dimethyl-1H-pyrrole: (white solid, mp 40–41°C, reported[12] 37–38°C); δ_H (300 MHz, CDCl3), 2.11 (CH_3, s, 6H), 4.99 (CH2, d, 2H), 5.86 (pyrrolics, s, 2H), 6.86 (PhH, m, 2H), 7.28 (PhH, m, 3H).

1-(4-Methoxyphenyl)-2,5-dimethyl-1H-pyrrole: (yellow solid, mp 57–59°C reported[11] 59–60°C); δ_H (300 MHz, $CDCl_3$), 2.04 (CH_3, s, 6H), 3.86 (OCH_3, s, 3H), 5.88 (pyrrolics, s, 2H), 6.93 (PhH, m, 2H), 7.14 (m, PhH, 2H).

2-(2,5-Dimethyl-1*H*-pyrrol-1-yl) pyridine: (colorless oil); δ_H (300 MHz, $CDCl_3$), 2.12 (CH_3, s, 2H), 5.90 (pyrrolics, s, 2H), 7.22 (PhH, m, 2H), 7.77 (PhH, m, 1H), 8.62 (PhH, m, 1H).

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