FULL PAPER

Phosphomolybdic acid immobilized chitosan/Fe$_3$O$_4$: an efficient catalyst for $n$ alkylation of anilines

Mahdi Ghanimati$^a$ | Masumeh Abdoli Senejani$^{a,*}$ | Mohammad Ali Bodaghifard$^b$ | Tahereh Momeni Isfahani$^a$

$^a$Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran
$^b$Department of Chemistry, Faculty of Science, Arak University, 38156-88349, Arak, Iran

In this work, phosphomolybdic acid immobilized on chitosan/Fe$_3$O$_4$ as a green catalyst was used for the Hofmann $N$-alkylation of aniline derivatives with alcohols. H$_2$PMo$_{12}$O$_{40}$/chitosan/Fe$_3$O$_4$ (PMo/Chit/Fe$_3$O$_4$) was prepared from the phosphomolybdic acid, chitosan, and Fe$_3$O$_4$ MNPs. Several secondary amines were synthesized from primary arylamines with electron-donating, electron-withdrawing groups, and alcohols in good to excellent yields. The catalyst could be separated using an external magnet and recovered without reducing its catalytic activity. The optimization of the reaction conditions was evaluated using the response surface method (RSM), involving the Box-Behnken design matrix. The simple procedure, only one byproduct (i.e., water), good to excellent yields, easy separation of the catalyst, short reaction times, and environmentally benign conditions were some advantages of this method.

KEYWORDS
Hofmann $N$-alkylation; heterogeneous catalyst; heteropolyacids; chitosan; design of experiment; green chemistry

Introduction

$N$-alkylation of amines is of a great importance in synthetic organic chemistry because of biological activities and industrial importance of products [1,2]. Alkylation of amines with alcohols using borrowing hydrogen or "hydrogenautotransfer" strategies is an environmentally friendly and useful method for preparation of amines. This method prevents waste salt formation, and the only byproduct is water [3-10]. Heteropoly acids (HPAs) belong to the category of non-volatile polyoxometalates with special molecular architectures that have remarkable properties such as strong Brønsted acidity, high stability toward humidity, easy to handle, proper redoxpotentials, high thermal stability, environmental friendly, and low corrosiveness [11,12]. Heteropoly acids as potential solid acids are green catalysts in the synthesis of many organic compounds [13-15].

Due to the limited specific surface area, high solubility in polar solvents, and recycling performance of HPAs, supporting of HPA catalysts is important. In recent years, heterogenization of HPA catalysts, through immobilization onto the surface of modified materials has been received considerable attention [16-18]. Magnetic nanoparticles (MNPs) has received a lot of attention in case of the magnetization of solid phase [19-21]. In addition, MNPs are commonly used as potential support for the heteropoly acid catalysts because of easy separation from the...
reaction mixture using an external magnet and increasing the area of contact between the reactant particles [18-24]. Chitosan is a biodegradable and available polymer and can be modified easily to synthesize magnetic composite adsorbents [25,26]. The chitosan coordinating sites for binding onto Fe$_3$O$_4$ magnetic nanoparticles are amino and hydroxyl groups in glycosidic residue [27, 28]. In recent years, magnetic HPA-chitosan nanocomposites were used as a catalyst in some organic reactions [29,30]. Therefore, in the present study, H$_3$PMo$_{12}$O$_{40}$/chitosan/Fe$_3$O$_4$ nanoparticles were synthesized by a simple method [30]. Primarily, 0.5 g of Fe$_3$O$_4$ MNPs, 0.5 g of chitosan and 50 mL of acetic acid solution (0.05 M) were sonicated and heated at 40 °C. Then, 12 mL of glutaraldehyde aqueous solutions (4 wt%) was added and stirred. The mixture was heated for 60 min at 40 °C and then 60 min at 60 °C. Subsequently, 20 mL phosphomolybdic acid solution (0.045 g.mL$^{-1}$) was added and stirred at 60 °C for 4 h. The resulting solid was centrifuged at 4000 rpm, washed with deionized water and ethanol and dried under vacuum at 60 °C for 8 h to give the pure catalyst.

**Preparation and characterization of PMo/Chit/Fe$_3$O$_4$**

H$_3$PMo$_{12}$O$_{40}$/chitosan/Fe$_3$O$_4$nanoparticles were synthesized by a simple method [30].

**General procedure for N-alkylation of aniline derivatives using PMo/Chit/Fe$_3$O$_4$**

A mixture of amine (1.2 mmol), alcohol (1 mmol), and PMo/Chit/Fe$_3$O$_4$ (0.06 g) was stirred at 60 °C in 15 mL H$_2$O/EtOH (1:1) for an appropriate time. The progress of the reaction was followed by TLC (Petroleum ether/ethyl acetate, 7/1). After completion of the reaction, the catalyst was separated using an external permanent magnet. The crude product was purified by recrystallization from CH$_2$Cl$_2$ to give a pure product.

**Selected spectroscopic data**

N-(diphenylmethyl)aniline (1)

IR (KBr): $\nu=3379$ (N-H), 3026 (C-H aromatic), 2925 (CH aliphatic), 1597 and 1494 (C=C aromatic), 1269 cm$^{-1}$ (C-N);

$^1$HNMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta=7.65$-7.70 (m, 10H, Ar-H), 7.07-7.20 (m, 5H, Ar-H), 5.86 (s, 1H, C-H), 4.45 ppm (brs, 1H, N-H);

Anal Calcd. for C$_{19}$H$_{17}$N: C 87.99, H 6.61, N 5.40, Found: C 87.80, H 6.80, N 5.38.
N-(diphenylmethyl)-4-Chloroaniline (2)

IR (KBr): \(\nu = 3295\) (N-H), 3059 (C-H aromatic), 2953 (CH aliphatic), 1664 and 1488 (C=C aromatic), 1264 (C-N), 758 cm\(^{-1}\) (C-Cl); \(^1\)HNMR (400 MHz, CDCl\(_3\), 25°C, TMS): \(\delta = 7.20-7.32\) (m, 10H, Ar-H), 7.02 (d, 2H, J=6.4 Hz, Ar-H), 6.79 (d, 2H, J=6.4 Hz, Ar-H), 5.78 (s, 1H, C-H), 3.82 ppm (brs, 1H, N-H); Anal Calcd. for C\(_{19}\)H\(_{15}\)ClN: C 77.68, H 5.49, N 4.77, Cl 16.09.

N-(diphenylmethyl)-4-Nitroaniline (3)

IR (KBr): \(\nu = 3404\) (N-H), 3077.97 (C-H aromatic), 2911 (CH aliphatic), 1599 and 1463 (C=C aromatic), 1508 and 1303 (NO\(_2\)), 1279 cm\(^{-1}\) (C-N); \(^1\)HNMR (400 MHz, CDCl\(_3\), 25°C, TMS): \(\delta = 7.27-7.39\) (m, 10H, Ar-H), 7.13 (d, 2H, J=6.4 Hz, Ar-H), 6.67 (d, 2H, J=6.4 Hz, Ar-H), 5.36 (s, 1H, C-H), 3.86 ppm (brs, 1H, N-H); Anal Calcd. for C\(_{19}\)H\(_{14}\)NO\(_2\): C 74.98, H 5.30, N 9.20, O 10.51, Found: C 75.01, H 5.49, N 4.77, Cl 16.09.

N-(1-phenylethyl) 4-bromo aniline (6)

IR (KBr): \(\nu = 3385\) (N-H), 3026 (C-H aromatic), 2925 (CH aliphatic), 1596 and 1493 (C=C aromatic), 1269 (C-N), 697 cm\(^{-1}\) (C-Br); \(^1\)HNMR (400 MHz, CDCl\(_3\), 25°C, TMS): \(\delta = 7.50-7.55\) (m, 5H, Ar-H), 7.23 (d, 2H, J=8.4 Hz, Ar-H), 6.83 (d, 2H, J=8.4 Hz, Ar-H), 4.28 (q, 1H, J=6.9 Hz, C-H), 3.89 (brs, 1H, N-H), 1.64 ppm (d, 3H, J=6.9 Hz, CH\(_3\)); Anal Calcd. for C\(_{13}\)H\(_{13}\)BrN: C 60.89, H 5.11, N 5.07, Br 28.93, Found: C 60.80, H 5.22, N 5.07, Br 28.90.

N-((4-chlorophenyl)phenylmethyl) 4-bromo aniline (15)

IR (KBr): \(\nu = 3382\) (N-H), 3030 (C-H aromatic), 2924 (CH aliphatic), 1618 and 1489 (C=C aromatic), 1284 (C-N), 818 (C-Cl), 701 cm\(^{-1}\) (C-Br); \(^1\)HNMR (400 MHz, CDCl\(_3\), 25°C, TMS): \(\delta = 7.32-7.59\) (m, 11H, Ar-H), 6.56 ppm (m, 2H, Ar-H), 5.82 (s, 1H, C-H), 3.00 ppm (brs, 1H, N-H); Anal Calcd. for C\(_{19}\)H\(_{15}\)BrClN: C 61.36, H 4.06, Br 21.27, Cl 9.53, N 3.77, Found: C 60.17, H 4.01, Br 20.16, Cl 9.95, N 4.07.

**Results and discussion**

As a part of ongoing research into the efficient synthesis of heterocyclic compounds [32-36], in the present study, we describe a green and effective procedure for the N-alkylation of aromatic amines with alcohols using H\(_3\)PMo\(_{12}\)O\(_{40}\)/chitosan/Fe\(_3\)O\(_4\) (Scheme 1).

![PMO/Chit/Fe3O4](image)

**SCHEME 1** N-alkylation of aniline derivatives using PMo/Chit/Fe\(_3\)O\(_4\) as an efficient catalyst

At first, the reaction of aniline (1 mmol) and benzhydrol (1 mmol) in the presence of 0.05 g of the catalyst in various solvents at 60 °C was selected as a model reaction (Table 1). The results indicated that, among all, C\(_2\)H\(_5\)OH/H\(_2\)O (1:1) is the most effective solvent.

In the next step, the effect of different types of catalysts on the model reaction in C\(_2\)H\(_5\)OH/H\(_2\)O (1:1) at 65 °C was studied (Table 2). As shown in Table 2, the presence of a catalyst is essential for N-alkylation of aniline derivatives with alcohols. Also, PMo/Chit/Fe\(_3\)O\(_4\) is more suitable than the other catalysts.
### TABLE 1 The effect of various solvents on the model reaction

| Entry | Solvent                | Time (h) | Yield (%) |
|-------|------------------------|----------|-----------|
| 1     | ---                    | 5        | 65        |
| 2     | H₂O                    | 5        | 78        |
| 3     | C₂H₅OH                 | 5        | 77        |
| 4     | CH₃CN                  | 5.5      | 75        |
| 5     | CH₂Cl₂                 | 5.5      | 71        |
| 6     | C₂H₅OH/H₂O (1:1)       | 4        | 91        |
| 7     | C₂H₅OH/H₂O (2:1)       | 5        | 76        |
| 8     | C₂H₅OH/H₂O (1:2)       | 5        | 80        |

### TABLE 2 The effect of various catalysts on the model reaction

| Entry | Catalyst                        | Time (h) | Yield (%) |
|-------|---------------------------------|----------|-----------|
| 1     | Fe(ClO₄)₃                       | 7        | 78        |
| 2     | Sulfamic acid                   | 6.5      | 75        |
| 3     | p-Toluenesulfonic acid          | 6.5      | 70        |
| 4     | H₃PW₁₂O₄₀                      | 6        | 76        |
| 5     | PMo/Chit/Fe₃O₄                 | 4        | 91        |
| 6     | ---                             | 6        | ---       |

### Statistical analysis and the model fitting

To assess the effect of various reaction parameters such as the amount of catalyst, temperature, and the molar ratio of amine to alcohol on the N-alkylation of aniline derivatives with alcohols, a three-level 15-run Box–Behnken design method was used by utilizing Design-Expert 7.0.0 Trial software (Stat-Ease Inc., Minneapolis). The level of parameters, the experimental design matrix and results are shown in Table 3. The input parameters in the reaction process optimization include: A) the molar ratio (i.e., 1, 1.2, and 1.4), B) the amount of catalyst (i.e., 0.02, 0.04, and 0.06 g), and C) temperature (25, 45, and 65°C). The response function (y) was a greater yield and a shorter reaction time for N-alkylation of aniline.

### TABLE 3 The experimental factors, levels, and results for the Box–Behnken design

| Factors               | Unit | Symbol | levels                | Actual levels | Coded levels | Actual levels | Coded levels | Actual levels | Experimental | Predict ed | Experimental | Predict ed | Independent variables |
|-----------------------|------|--------|-----------------------|---------------|--------------|---------------|--------------|---------------|--------------|-------------|-------------|-------------|-----------------------|
| Molar ratio           | ---  | A      | Low (-1)              | 1             | -1           | 1.2           | 1.4          |               |             |             |             |             | A                     |
| Catalyst amount       | g    | B      | Central (O)           | 0.02          | 0            | 0.04          | 0.06         |               |             |             |             |             | B                     |
| Temperature           | °C   | C      | High (+1)             | 25            | 45           | 65            |              |               |             |             |             |             | C                     |
| Run                   | A    | B      | C                     | 45            | 50.38        | 70            | 70.38        |               |             |             |             |             |                       |
| 1                     | -1   | 1.00   | 0                     | 0.04          | -1           | 25.00         | 495          | 50            |             |             |             |             |                       |
| 2                     | 0    | 1.20   | -1                    | 0.02          | -1           | 25.00         | 500.63       | 47            |             |             |             |             |                       |
| 3                     | 0    | 1.20   | 0                     | 0.04          | 0            | 45.00         | 250          | 243.33        | 77          |             |             |             |                       |
| 4                     | 0    | 1.20   | 0.06                  | 1             | 65.00        | 180           | 189.38       | 94            |             |             |             |             |                       |
| 5                     | 0    | 1.20   | 0.06                  | -1            | 25.00        | 360           | 350.63       | 65            |             |             |             |             |                       |
| 6                     | +1   | 1.40   | 0                     | 0.04          | +1           | 65.00         | 270          | 255           | 85          |             |             |             |                       |
| 7                     | +1   | 1.40   | 0.06                  | 0             | 45.00        | 300           | 305.63       | 86            |             |             |             |             |                       |
| 8                     | +1   | 1.40   | 0                     | 0.04          | -1           | 25.00         | 450          | 453.75        | 55          |             |             |             |                       |
| 9                     | +1   | 1.40   | 0.02                  | 0             | 45.00        | 300           | 305.63       | 70            |             |             |             |             |                       |
The BBD method also was applied to investigate the interaction of three factors on the yield and reaction times, and the obtained results are summarized in Tables 4 and 5. The analysis of variance (ANOVA) test at 95% confidence level was used to estimate the quality of the proposed model. The results of the ANOVA test demonstrated that the process factors with a p-value of less than 0.05 should be considered significant which could have substantial effects on the time and yield of the reaction. The results revealed that A, B, C, A², B², and C², were statistically significant. A second-order polynomial model for time and yield based on significant levels and actual values were proposed by the Equations 1 and 2.

| TABLE 4 | Analysis of variance (ANOVA) for Box–Behnken quadratic model for the reaction time of N-alkylation of aniline |
|---------|------------------------------------------------------------------------------------------------------------------|
| Source  | SS         | Df | MS     | F-value | p-Value | Remark                |
|---------|------------|----|--------|---------|---------|-----------------------|
| Model   | 2571.52    | 9  | 285.72 | 192.62  | < 0.0001 | significant           |
| A-molar ratio | 40.5       | 1  | 40.5   | 27.3    | 0.0034  |                       |
| B-Amount of catalyst | 496.12     | 1  | 496.12 | 334.47  | < 0.0001 |                       |
| C-Temperature | 1770.12    | 1  | 1770.12| 1193.34 | < 0.0001 |                       |
| AB      | 1          | 1  | 1      | 0.67    | 0.449   |                       |
| AC      | 1          | 1  | 1      | 0.67    | 0.449   |                       |
| BC      | 2.25       | 1  | 2.25   | 1.52    | 0.2729  |                       |
| A²      | 23.85      | 1  | 23.85  | 16.08   | 0.0102  |                       |
| B²      | 10.78      | 1  | 10.78  | 7.26    | 0.043   |                       |
| C²      | 224.16     | 1  | 224.16 | 151.12  | < 0.0001|                       |
| Residual| 7.42       | 5  | 1.48   |         |         |                       |
| Lack of Fit | 6.75       | 3  | 2.25   | 6.75    | 0.1318  | not significant       |
| Pure Error | 0.67       | 2  | 0.33   |         |         |                       |
| Cor Total| 2578.93    | 14 |        |         |         |                       |

Y(yield) = 77.33 + 2.254A + 7.87B + 14.88C + 0.5AB + 0.5AC + 0.75BC + 2.54A² + 1.71B² + 7.79C²

R²=0.9971

R²-Adj=0.9919

Y(time) = 243.33 + 24.38A + 60B + 95.63C + 60AB + 3.75AC + 15BC + 67.71A² + 18.96B² + 67.71C².

R²=0.9934

R²-Adj=0.9815

Where A, B, and C are molar ratios, the amount of catalyst, and temperature, respectively; AB, AC, and BC are the interaction coefficient of these factors, and Y is the predicted response as the reaction time and yield. The values of the correlation coefficient (R²) for the time and yield were found to be 0.9934 and 0.9971, respectively, demonstrating a good correlation between the observed results and the predicted regression. In order to analyze the influence of three reaction parameters, 1) the amount of catalyst, 2) temperature, 3) the molar ratio of amine to alcohol, and interaction between them, on the reaction time and yield, three-dimensional response surface method and the corresponding contour curves are shown in Figures 1 and 2. The dark blue and the dark red areas in these figures, show the optimal experimental conditions for obtaining the maximum yield and minimum time, respectively. The results of Box–Behnken design method for N-alkylation of aniline derivatives indicated that the optimal condition for the minimum reaction time of 180 min (3 hours) and maximum yield of 93% is A = 1.2, B = 006 g, and C = 60.26 °C (almost 60°C) (Figure 3). To investigate the
validity of the model, the optimum conditions were utilized in four experiments (Table 5). The results revealed that the predicted values were in good agreement with the experimental results.

FIGURE 3 Optimized process conditions

TABLE 6 The result of N-alkylation of aniline in optimal conditions

| Approach     | Factors          | Response          |
|--------------|------------------|-------------------|
|              | molar ratio      | Catalyst amount(g) | Temperature (°C) | Time (min) | Yield(%) |
| predicted    | 1.20             | 0.06              | 60.26            | 180        | 93.14    |
| Experimental | 1.20             | 0.06              | 60.00            | 180±0.47a  | 92.66±0.5a |

*Mean±SD
FIGURE 1 Response surface and contour plots corresponding to the prediction of the reaction time for N-alkylation of aniline

A: molarratio  
B: Amount of catal. (g)  
C: Temp.(0C)
After optimization of reaction conditions, the capability of PMo/Chit/Fe₃O₄ as a catalyst for N-alkylation reaction of aniline derivatives with some alcohols was investigated under the optimized reaction conditions. The results are summarized in Table 7. As shown in Table 7, a variety of aniline derivatives with both electron-donating and electron-withdrawing groups undergo N-alkylation with isopropanol, α-phenylethanol, and diphenylcarbinol derivatives using PMo/Chit/Fe₃O₄ in good to excellent yields. In addition, aniline derivatives with electron-withdrawing groups decreased the reaction rate as the electron-rich anilines are better nucleophiles and facilitate the second step of the reaction mechanism.

**TABLE 7** The N-alkylation of aniline derivatives with alcohols using PMo/Chit/Fe₃O₄

| Entry | Product | Time (h) | Yield (%) | mp (Lit. mp) [Ref.](°C) |
|-------|---------|----------|-----------|-----------------------|
| 1     | ![Aniline derivative 1](image) | 3        | 93        | 57-59 (58) [37]       |
| 2     | ![Aniline derivative 2](image) | 4        | 91        | 76-78 (75) [38]       |
3

4

5

6

7

8

9

Phosphomolybdic acid immobilized chitosan ...
A plausible mechanism for N-alkylation of aniline derivatives with alcohols using PMo/Chit/Fe$_3$O$_4$ is shown in Scheme 2. The model reaction was investigated at the presence of chitosan, Fe$_3$O$_4$ or PMO as the catalyst under the optimized reaction conditions and compared with the results obtained from PMo/Chit/Fe$_3$O$_4$ (Table 8). As seen in Table 8, the PMo/Chit/Fe$_3$O$_4$ is more suitable than the others and the PMO plays the main role of catalyst in this reaction. In this work, PMO was supported on the magnetic chitosan, which boosted catalytic characteristic of PMO.
To study the recyclability of PMo/Chit/Fe₃O₄, the catalyst was magnetically separated by an external magnet from the reaction mixture, washed three times with 5 ml of diethyl ether, dried, and reused in the synthesis of 4e for five times without a considerable loss in its catalytic activity (Figure 4).

Finally, a comparison of N-alkylation of aniline derivatives with alcohols using PMo/Chit/Fe₃O₄ with a range of other methodologies proved the efficiency of this method with respect to the yields and time of reactions (Table 9).

**Conclusion**

PMo/Chit/Fe₃O₄ was synthesized from Phosphomolybdic acid, chitosan, and Fe₃O₄ MNPs. The magnetic PMo/Chit/Fe₃O₄ as heterogeneous catalyst exhibited excellent catalytic activity in the N-alkylation of variety of aniline derivatives with electron-donating as well as electron-withdrawing groups using isopropanol, α-phenylethanol and diphenylcarbinol via direct reductive amination. The optimization of the reaction conditions was evaluated using the response surface method (RSM) and adopting the Box-Behnken design matrix. The predicted values were found to be in good agreement with experimental results. The catalyst could be separated using an external magnet and...
recovered without reducing its catalytic activity. The efficiency of the PMo/Chit/Fe$_3$O$_4$ is comparable with other catalysts for N-alkylation of amines. The simple experimental procedures, the very limited byproduct (only water), good to excellent yields, easy separation, reusability of the catalyst, short reaction times, and environmentally benign conditions were distinctive advantages of this method.

**TABLE 9** A comparison of the efficiency of PMo/Chit/Fe$_3$O$_4$ with the previous procedure for the N-alkylation of aniline derivatives using alcohols

| Entry | Catalyst | Time (h) | Yield (%) | Condition[Ref.] |
|-------|----------|----------|-----------|----------------|
| 1     | PMo/Chit/Fe$_3$O$_4$ | 3-5      | 83-93     | H$_2$O:EtOH, 60 °C [this work] |
| 2     | SnCl$_4$  | 16-18    | 71-93     | CH$_3$Cl$_2$, r.t. [49] |
| 3     | Ph$_3$PCl/imidazole/I$_2$ | 0.25-48 | 50-94     | CH$_2$Cl$_2$, reflux [2] |
| 4     | Pd/Fe$_2$O$_3$ | 2-28    | 72-99     | Solvent free, 140-170 °C [51] |
| 5     | DBU$_3$, CSA$^b$ | 24      | 81-99     | Trichloroacetonitrile, CH$_3$Cl$_2$, [41] |
| 6     | Iridium Complex/K$_2$CO$_3$ | 12-24  | 19-95     | 2,2,2-trifluoroethanol, 100 °C [4] |
| 7     | CsOH. H$_2$O | 24-28   | 26-95     | Solvent free, air, 130-150 °C [52] |
| 8     | [Cp$^*$$\text{IrCl}_2$]$_2$/K$_2$CO$_3$ | 17      | 69-95     | Toluene, 110 °C [53] |
| 9     | In(OTf)$_3$ | 4-24    | 37-99     | H$_2$O, 100 °C [38] |

$^a$1,8-diazabicyclo[5.4.0]undec-7-ene, $^b$Camphorsulfonic acid, $^c$Cp$^*$=pentamethylcyclopentadienyl

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**Orcid:**

Mahdi Ghanimati: https://orcid.org/0000-0001-8536-9218

Masumeh Abdoli Senejani: https://orcid.org/0000-0002-3677-7853

Mohammad Ali Bodaghifard: https://orcid.org/0000-0001-9732-4746

Tahereh Momeni: https://orcid.org/0000-0002-6648-9625

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