FULL PAPER

A highly reactive and magnetic recyclable catalyst based on silver nanoparticles supported on ferrite for *N*-monoalkylation of amines with alcohols

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Mehdi Shakourian-Fard, Department of Chemical Engineering, Birjand University of Technology, PO Box 97175/569, Birjand, Iran. Email: shakourian@birjandut.ac.ir $Fe_3O_4@SiO_2$ -Ag catalyst was found to be highly active and selective in the *N*-alkylation of amines with a variety of aromatic and linear alcohols. The heterogeneous nature of the $Fe_3O_4@SiO_2$ -Ag catalyst allows easy recovery and regeneration by applying an external magnet for six subsequent reaction cycles. The prepared catalyst was characterized using electron microscopy techniques, X-ray diffraction, vibrating sample magnetometry and atomic absorption spectroscopy.

KEYWORDS

alcohol, green chemistry, magnetic nanoparticles, N-alkylation of amines, silver nanoparticles

1 | INTRODUCTION

The *N*-alkylation of amines is considered to be a very important reaction in synthetic organic chemistry. This process allows access to higher amines that are widely used as fundamental materials, additives, dyes and biologically active compounds.^[1-4] *N*-alkylamines are typically synthesized using alkylating agents having a good leaving group such as halide, tosylate, mesylate, triflate, etc. However, this procedure can be problematic due to over-alkylation and the toxic nature of many alkyl halides and related alkylating agents.^[5]

The use of alcohols instead of alkyl halides to obtain *N*-alkylamines is attractive because it produces only water as a by-product and does not need special equipment. A variety of transition metal complexes such as those of ruthenium, iridium, rhodium, platinum, gold, nickel, aluminium, copper, iron and silver are known to be good catalysts for the *N*-alkylation of amines with alcohols.^[6–16]

Unfortunately, the recovery and reuse of expensive catalysts is difficult and the indispensable use of co-catalysts such as stabilizing ligands is unavoidable for most of the known homogeneous catalysts.^[17–19]

One way to overcome these drawbacks is the use of an inexpensive, recoverable and reusable catalyst to accomplish the reaction. An immobilized catalytic system on the large surface area of a solid carrier can solve the problems of homogeneous systems. Although there are several reports of the *N*-alkylation process using heterogeneous catalysts, most of them require high pressure and reaction temperature and are limited in their substrate scopes.^[20–24] Therefore, the development of efficient heterogeneous catalysts for *N*-alkylation of amines with alcohols is still a challenge.

As part of our continuing effort^[25–29] to synthesize magnetic heterogeneous catalytic systems for various organic transformations, we report a magnetic recyclable heterogeneous catalyst based on silver nanoparticles supported on ferrite for one-pot selective *N*-monoalkylation of amines with alcohols. To the best of our knowledge, silver nanoparticles supported on Fe₃O₄ magnetic nanoparticles have not been reported so far for *N*-monoalkylation of amines with alcohols. Moreover, the use of the magnetic heterogeneous catalytic systems enables separation from the reaction mixture using an external magnet and reuse of the catalyst itself. This catalyst system also shows exceptionally high activity for *N*-alkylation of amines with various alcohols.

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2 | RESULTS AND DISCUSSION

2.1 | Preparation and Characterization of Fe₃O₄@SiO₂-Ag (SMNP-Ag) Catalyst

In the first step, bare Fe_3O_4 nanoparticles were synthesized via a conventional co-precipitation method using a solution of iron salts (FeCl₃·6H₂O and FeCl₂·4H₂O) (Scheme 1). In order to protect the bare Fe_3O_4 nanoparticles from oxidation and agglomeration, silica shell (SiO₂) was used as an inert and stabilizer material for coating the Fe_3O_4 nanoparticles. Then, Ag nanoparticles were deposited on the Fe_3O_4 @SiO₂ (SMNP) core–shell via reduction of AgNO₃ solution by NaBH₄ at room temperature to generate the SMNP-Ag catalyst (Scheme 1). Finally, the SMNP-Ag catalyst was characterized using various techniques.

The crystalline nature and surface state of SMNP-Ag catalyst were studied using powder X-ray diffraction (XRD), as shown in Figure 1. The peaks at 2θ values of 30.4° , 35.8° , 43.7° , 53.8° , 57.3° and 63.0° in the XRD patterns of SMNP and SMNP-Ag catalyst correspond to (220), (311), (400), (422), (551) and (440) diffraction planes of Fe₃O₄ nanoparticles, respectively. These peaks match well with the standard XRD data of the Joint Committee on Powder Diffraction Standards (JCPDS) card number and reveal a cubic inverse spinel structure for Fe₃O₄ in SMNP and SMNP-Ag catalyst.^[30] As seen in Figure 1, five

characteristic peaks for Ag nanoparticles (red peaks) are also found at 38.45°, 44.43°, 64.67°, 77.48° and 81.56° which correspond to (111), (200), (220), (311) and (222) planes of Ag nanoparticles, respectively, in accordance with the JCPDS card number. These peaks indicate the presence of Ag nanoparticles in the SMNP-Ag catalyst.^[31] A comparison between XRD patterns of SMNP and the SMNP-Ag catalyst indicates that the main peaks in the XRD patterns do not change after deposition of Ag nanoparticles, indicating retention of crystalline structure during their deposition.

In order to investigate the morphology and particle size of the SMNP-Ag catalyst, scanning electron microscopy (SEM) and transition electron microscopy (TEM) images of the catalyst were obtained, as shown in Figure 2(a) and (b), respectively. These images show that the size of the SMNP-Ag nanoparticles is between 20 and 50 nm, and the nanoparticles are also semi-spherically uniform. Energy-dispersive X-ray spectroscopy (EDS) analysis of the SMNP-Ag catalyst confirms the presence of Si, Fe, O, and Ag atoms in the catalyst structure (Figure 2c). The remaining weak peaks are due to the presence of a thin layer of gold on the sample surface. In addition, the amount of Ag deposited on the SMNP nanoparticles was measured using atomic absorption spectroscopy (AAS) analysis at about 0.192 mmol g^{-1} .

Magnetic measurements of Fe₃O₄ nanoparticles and the SMNP-Ag catalyst were conducted using a vibrating



SCHEME 1 Synthesis of magnetically recoverable heterogeneous nanocatalyst Fe₃O₄@SiO₂-Ag (SMNP-Ag)



Position [°2Theta](Copper(Cu))

FIGURE 1 XRD patterns of Fe₃O₄@SiO₂ and SMNP-Ag catalyst



FIGURE 2 (a) SEM and (b) TEM images, and (c) EDS analysis of SMNP-Ag catalyst



FIGURE 3 Magnetization curves of (a) Fe₃O₄ and (b) SMNP-Ag catalyst

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TABLE 2 Optimization of amount of SMNP-Ag catalyst^a

| | | | Yield (%) ^b | | |
|-------|--------------------------------------|----------------|------------------------|----|----|
| Entry | Catalyst (mg) | Conversion (%) | 3 a | 4a | 5a |
| 1 | _ | _ | | | |
| 2 | AgNO ₃ (85) | | — | — | — |
| 3 | Fe ₃ O ₄ (100) | 5 | 4 | 1 | _ |
| 4 | SMNP-Ag (2.6) | 67 | 64 | 2 | <1 |
| 5 | SMNP-Ag (5.2) | 82 | 78 | 3 | <1 |
| 6 | SMNP-Ag (26) | 93 | 89 | 4 | — |
| 7 | SMNP-Ag (52) | 98 | 92 | 5 | 1 |
| 8 | SMNP-Ag (104) | >99 | 93 | 6 | <1 |

^aReaction conditions: aniline (1 mmol), benzyl alcohol (1.5 mmol), KOH (20 mol %), toluene (5 ml) at 100 °C for 18 h.

^bGC yield.

sample magnetometer at room temperature. As seen in Figure 3, the magnetization curves exhibit no hysteresis loop which demonstrates superparamagnetic characteristics. Figure 3 shows that the deposition of Ag nanoparticles and the coating of the silica shell cause a decrease of the magnetization of the Fe_3O_4 nanoparticles, although the SMNP-Ag magnetic material can still be collected under an applied magnetic field.

2.2 | Optimized Reaction Conditions

In order to determine the best reaction conditions, the reaction of aniline with benzyl alcohol was selected as a model reaction. The effect of various solvents on the reaction was investigated. It is found that toluene is the best solvent for the N-alkylation reaction (Table 1, entry 4).

To study the effect of base on the catalytic activity of the SMNP-Ag catalyst, various bases were examined. In the absence of base, the desired amine product is formed in only 7% (Table 1, entry 13). This observation indicates that the presence of base is helpful in deprotonation of primary alcohol to alkoxide ion and also facilitates the removal of a hydride ion from it. It is found that KOH as base not only shows good conversion of amine but also provides good selectivity for the desired amine product.

After choosing the best solvent and base, the effect of the amount of the SMNP-Ag catalyst on the *N*-alkylation reaction was investigated. As evident from Table 2, in the absence of the SMNP-Ag catalyst (entry 1), the desired amine is not

 TABLE 1
 Effect of base and solvent on N-alkylation of aniline with benzyl alcohol^a

| $ \begin{array}{c} & \downarrow & \downarrow & \downarrow \\ & \downarrow & \downarrow & \downarrow \\ & \downarrow & \downarrow & \downarrow \\ & 1a & 2a & 3a & 4a & 5a \\ \end{array} $ | | | | | | |
|--|------------------|---------------------------------|--------------------------|----|------------------------|----|
| Entw | Solvent | Page | Conversion of $10^{(0)}$ | 30 | Yield (%) ^b | 50 |
| Entry | Solvent | Dase | Conversion of 1a (%) | 38 | 48 | 58 |
| 1 | H ₂ O | КОН | No reaction | 0 | 0 | 0 |
| 2 | DMF | КОН | 7 | 6 | 1 | 0 |
| 3 | EtOH | KOH | 29 | 21 | 6 | 0 |
| 4 | Toluene | КОН | 98 | 92 | 5 | 1 |
| 5 | Dioxane | КОН | 23 | 16 | 6 | <1 |
| 6 | o-Xylene | КОН | 75 | 75 | 1 | <1 |
| 7 | Toluene | LiOH | 22 | 15 | 6 | <1 |
| 8 | Toluene | NaOH | 68 | 56 | 10 | 2 |
| 9 | Toluene | K ₂ CO ₃ | 88 | 81 | 6 | 2 |
| 10 | Toluene | Na ₂ CO ₃ | 26 | 20 | 5 | <1 |
| 11 | Toluene | t-BuOK | 42 | 34 | 7 | <1 |
| 12 | Toluene | K ₃ PO ₄ | 37 | 30 | 6 | <1 |
| 13 | Toluene | | 8 | 7 | 1 | 0 |

^aReaction conditions: aniline (1 mmol), benzyl alcohol (1.5 mmol), SMNP-Ag catalyst (1 mol%, 52 mg), base (20 mol%), solvent (5 ml) at 100 °C for 18 h. ^bGC yield.

produced. The *N*-alkylation of aniline under similar conditions using AgNO₃ as catalyst does not lead to any product formation. Also, the use of Fe₃O₄ results in the formation of secondary amine with conversion of 4%. Our results show that increasing the amount of SMNP-Ag catalyst from 0.05 mol% (2.6 mg) to 1 mol% (52 mg) leads to an increase of conversion of aniline from 67 to 98%. When more catalyst (2 mol%, 104 mg) is used, the conversion of aniline and yield of the secondary amine do not change markedly. Therefore, 1 mol% of SMNP-Ag catalyst is sufficient for *N*-alkylation of amines using alcohols. Once the best reaction conditions were determined, the scope of the method was investigated for the *N*-alkylation of various amines.

The scope of *N*-alkylation of amines with alcohols in the presence of the SMNP-Ag catalyst is summarized in Table 3. As seen from entries 1-4, the reaction of aniline with benzyl alcohols containing electron-donating or electron-withdrawing substituents proceeds to give good yields. The reaction of aniline derivatives with benzyl alcohol (entries 5 and 6) also proceeds efficiently. Table 3 also shows that the catalyst system is not limited to aromatic alcohols, and aliphatic alcohols can also react with amines to form higher amines in excellent yield. Alcohols with the least reactivity, such as fully saturated alcohols, were also tested in this reaction (Table 3). Secondary alcohols are challenging alkylating agents compared with primary alcohols using hydrogen borrowing strategy because the dehydrogenation of secondary alcohols to the corresponding ketones is more difficult than that of primary alcohols. In addition, aliphatic alcohols (entries 8 and 10) and secondary alcohols (entry 9) require more time to achieve higher yields of the products.

The efficiency of the SMNP-Ag catalyst in the *N*-alkylation reaction of aniline with benzyl alcohol was compared with that of other catalyst systems reported in the literature (Table 4). One of the advantages of our catalyst is that it can be easily removed from the reaction mixture by applying an external magnetic field. Thus, this property prevents the loss of the SMNP-Ag catalyst, although other methods (entries 1–3 and 5) use filtration for separation of the catalyst systems from the reaction mixture. Moreover, our magnetically recoverable nanocatalyst is not limited to aromatic amines and can also be used for aliphatic amines, although other catalysts (entries 1, 2, 4 and 5) are used

TABLE 3 Scope of catalytic activity of SMNP-Ag catalyst in *N*-alkylation of amines with various alcohols^a

| | | R ₁ -OH+ R ₂ -NH ₂ | SMNP-Ag Toluene, KOH | | |
|-------|---------------------------------|---|-------------------------|----------------|------------------------|
| Entry | R ₁ | R ₂ | Time (h) | Conversion (%) | Yield (%) ^b |
| 1 | 4-MePhCH ₂ | Ph | 17 | >99 | 95 |
| 2 | 4-BrPhCH ₂ | Ph | 24 | 98 | 97 |
| 3 | 4-ClPhCH ₂ | Ph | 24 | 96 | 97 |
| 4 | 4-MeOPhCH ₂ | Ph | 14 | >99 | 98 |
| 5 | PhCH ₂ | 4-MePh | 20 | >99 | 96 |
| 6 | PhCH ₂ | 4-ClPh | 24 | >99 | 90 |
| 7 | PhCH ₂ | PhCh ₂ | 18 | >99 | 95 |
| 8 | PhC ₃ H ₆ | Ph | 30 | 97 | 93 |
| 9 | PhCHCH ₃ | Ph | 30 | 98 | 95 |
| 10 | C ₈ H ₁₇ | Ph | 36 | 96 | 93 |
| 11 | PhCH ₂ | $-C_2H_4OC_2H_4-$ | 18 | 97 | 94 |
| 12 | PhCH ₂ | C ₆ H ₁₃ | 24 | 89 | 85 |
| 13 | PhCH ₂ | -C ₅ H ₁₀ - | 20 | 98 | 95 |

^aReaction conditions: amine (1 mmol), alcohol (1.5 mmol), SMNP-Ag catalyst (1 mol%, 52 mg), KOH (20 mol%), toluene (5 ml) at 100 °C for 18 h. ^bGC yield.

TABLE 4 Comparison of activity of various catalysts in N-alkylation of aniline with benzyl alcohol

| Entry | Catalytic system | Conditions | Yield (%) | Ref. |
|-------|--|--|-----------|-----------|
| 1 | Fe-Phthalocyanine | Toluene, N ₂ , NaOtBu, 100 °C, 12 h | 86 | [1] |
| 2 | $Ru(OH)_x/Al_2O_3$ | 132 °C, 11 h, mesitylene | 98 | [8] |
| 3 | Au/TiO ₂ -VS | 120 °C, toluene, N ₂ , 14 h | 92 | [11] |
| 4 | Cu-AcTp@Am-Si-Fe ₃ O ₄ | No solvent, KOH, 100 °C, 10 h, air | 99 | [32] |
| 5 | Ag/Al ₂ O ₃ | FeCl ₃ ·6H ₂ O, <i>o</i> -xylene, reflux, 24 h | 94 | [33] |
| 6 | Ag@polypyrrole | Cs ₂ CO ₃ , toluene, 100 °C, 12 h | 95 | [16] |
| 7 | SMNP-Ag | KOH, toluene, reflux, 18 h | 92 | This work |



SCHEME 2 Mechanism for the SMNP-Ag-catalysed N-alkylation of amines by alcohols

only for *N*-alkylation of aromatic amines by alcohols. Entry 1 shows that the reaction yield (86%) is less than the 92% obtained in our work. In addition, in some cases (entries 2 and 5), the yield of reaction is more than 92%, while the reaction temperature is higher than that of our work.

According to reports in the literature, ^[2,14,15,33] a plausible mechanism for the SMNP-Ag-catalysed *N*-alkylation of amines by alcohols is given in Scheme 2. In the first step, alcohol is adsorbed on the catalyst surface via hydrogen bonding with Si–OH groups in the SMNP-Ag surface. Then, the base deprotonates the alcohol to give an alkoxide intermediate on the SMNP-Ag surface, which undergoes hydride abstraction by silver clusters to give a carbonyl compound on the catalyst surface. The adsorbed carbonyl compound readily reacts with a starting amine to form the corresponding imine via condensation reaction. Once the imine forms, it receives hydride ion from the silver clusters, is protonated by alcohol or base and changes to the corresponding amine.

2.3 | Recyclability

One of the most important factors for industrial catalyst systems is the recyclability and reusability of the catalyst. To clarify this issue, the recyclability of the SMNP-Ag catalyst was investigated in *N*-alkylation of aniline with benzyl alcohol under the optimized conditions (Figure 4). After completion of the first reaction, the catalyst was magnetically isolated, washed with ethanol and water, and then placed into a fresh reaction mixture. Under the described conditions, the catalyst could be reused for at least six runs without any considerable change in activity.

To explore the catalyst leaching, the SMNP-Ag catalyst was separated from the reaction mixture by applying an external magnetic field halfway through the course of the reaction (9 h) and the solution was again kept back into the reactor and the reaction was continued for an additional 9 h under the same conditions. It is found that the yield of product does not increase. Also, AAS analysis of the liquid phase confirms that the content of silver in the solution is an acceptable





FIGURE 4 Recycling experiment of SMNP-Ag catalyst in the *N*-alkylation of aniline with benzyl alcohol under optimized conditions. The reaction was quenched after 18 h in each step

amount of about 0.5%. These results reveal that the reaction is attributed to the heterogeneous catalyst and the catalyst leaching is very low.

3 | CONCLUSIONS

100

90

We have reported a simple, convenient and highly efficient heterogeneous silver catalyst system for the *N*-alkylation of amines using alcohols as green reagents. The broad substrate scope and functional group tolerance were highlighted with respect to each amine and alcohol component. The catalytic system enabled selective *N*-monoalkylation (over-alkylation <3%) in most cases. Easy recoverability and reusability of the SMNP-Ag catalyst make it a valuable economical system in comparison with other catalyst systems reported in the literature.

4 | EXPERIMENTAL

4.1 | Reagents and Analysis

All chemicals were purchased from Sigma-Aldrich and used without further purification. XRD patterns were obtained with an APD 2000, using Cu K α radiation (50 kV, 150 mA) in the range $2\theta = 10-120^{\circ}$. SEM was conducted with a KYKY-EM3200 with maximum acceleration voltage of the primary electrons between 20 and 25 kV. EDS coupled with SEM was used to identify chemical elements of the SMNP-Ag catalyst. TEM was performed with a Zeiss EM900 apparatus at 80 keV. Room temperature magnetization in an applied magnetic field was measured with a home-made vibrating sample magnetometer (Meghnatis Daghigh Kavir Company, Iran) from $-10\ 000\ to\ +10\ 000\ Oe$. The content of silver immobilized on the SMNP surface was measured using AAS.

4.2 | Synthesis of Fe₃O₄ Magnetic Nanoparticles

The synthesis of Fe_3O_4 magnetic nanoparticles was performed according to our previous work.^[28] $FeCl_3 \cdot 6H_2O$ (4.8 g, 0.018 mol) and $FeCl_2 \cdot 4H_2O$ (1.8 g, 0.0089 mol) salts were first added to 100 ml of deionized water and vigorously stirred (700 rpm) under nitrogen atmosphere until the salts were completely dissolved. Then, 10 ml of aqueous ammonia (25%) was added slowly over 10 min to the mixture under nitrogen atmosphere at room temperature. A black precipitate of magnetic nanoparticles was formed immediately, followed by stirring for about 1 h with a mechanical stirrer. The Fe_3O_4 nanoparticles were separated by applying an external magnetic field, washed with double distilled water (five times) and then vacuum-dried at 50 °C overnight.

4.3 | Preparation of Fe₃O₄@SiO₂ (SMNP)

The synthesized magnetic nanoparticles (1 g) were suspended in 40 ml of ethanol and 10 ml of deionized water, and the pH of the solution was adjusted to 10 by adding aqueous ammonia. Then, 0.5 ml of tetraethyl orthosilicate (TEOS) was added slowly to the mixture, sonicated for 15 min and stirred at 50 °C for 6 h. The magnetic nanoparticles coated with a thin layer of silica were separated by applying an external magnetic field, washed three times with ethanol and then vacuum-dried.

4.4 | Deposition of Ag Nanoparticles on SMNP Surface (SMNP-Ag)

Silver was deposited on the surface of SMNP particles as follows. A AgNO₃ (0.10 g) solution was added into welldispersed SMNP (1 g) in deionized water and then 0.2 ml of aqueous ammonia (25%, *w*/w) was added and Ag(NH₃) $_2^+$ complex was formed. The pH of the suspension was adjusted to 12.0 with NaOH solution and the mixture was stirred for 30 min. Then, a solution of NaBH₄ (0.30 g) was added dropwise to the mixture to reduce Ag(NH₃) $_2^+$ complex to Ag nanoparticles on the SMNP surface. Finally, the mixture was magnetically separated, washed several times with deionized water and then dried at 50 °C overnight to afford the SMNP-Ag catalyst.

4.5 | General Procedure for Direct *N*-alkylation of Amines with Various Alcohols

A mixture of amine (1 mmol), alcohol (1.5 mmol), SMNP-Ag catalyst (1 mol% metal, 52 mg), toluene (5 ml) and base (20 mol%) was placed in a reaction vessel equipped with a condenser. The resulting mixture was vigorously stirred at 100 °C for a specified reaction time. The completion of reaction was monitored by TLC and GC. After completion of the reaction, the reaction mixture was cooled to room temperature and then the SMNP-Ag catalyst was separated by applying an external magnetic field. For isolation of products, the organic layer was washed with 10% NaHCO₃ and water solution, dried under Na₂SO₄, concentrated and purified by silica gel column chromatography with appropriate mixture of *n*-hexane and ethyl acetate. The GC yields of products were calculated on the basis of amine reactants. The conversion of amine was calculated on the basis of its weight percent as follows:

Conversion (wt%) of amine

$$= 100 \times \frac{(\text{Initial wt\% of amine}) - (\text{final wt\% of amine})}{\text{Initial wt\% of amine}}$$

In order to examine the recoverability of the SMNP-Ag catalyst, the catalyst was separated by applying an external magnetic field and then washed with ethanol and water successively. The catalyst was then used directly for the next run of the reaction without further purification.

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REFERENCES

- [1] M. Bala, P. K. Verma, U. Sharma, N. Kumar, B. Singh, Green Chem. 2013, 41, 1687.
- [2] A. Corma, T. Ródenas, M. J. Sabater, Chem. Eur. J. 2010, 16, 254.
- [3] R. N. Solvator, A. S. Nagle, K. W. Jung, J. Org. Chem. 2002, 67, 674.
- [4] X. H. Lu, Y. W. Sun, X. L. Wei, C. Peng, D. Zhou, Q. H. Xia, Catal. Commun. 2014, 55, 78.
- [5] R. N. Salvatore, C. H. Yoon, K. W. Jung, Tetrahedron 2001, 57, 7785.
- [6] K. N. Tayade, M. Mishra, K. Munusamy, R. S. Somani, J. Mol. Catal. A 2014, 390, 91.
- [7] J. S. Naskar, M. Bhattacharjee, Tetrahedron Lett. 2007, 48, 3367.
- [8] J. W. Kim, K. Yamaguchi, N. Mizuno, J. Catal. 2009, 263, 205.
- [9] K. I. Fujita, Z. Z. Li, N. Ozeki, R. Yamaguchi, *Tetrahedron Lett.* 2003, 44, 2687.
- [10] J. J. Brunet, N. C. Chu, M. Rodriguez-Zubiri, Eur. J. Inorg. Chem. 2007, 4711.
- [11] L. He, X. Lou, J. Ni, Y. Liu, Y. Cao, H. He, K. Fan, *Chem. Eur. J.* 2010, 16, 13965.
- [12] P. R. Likhar, R. Arundhathi, M. L. Kantam, P. S. Prathima, Eur. J. Org. Chem. 2009, 5383.
- [13] R. Martinez, D. J. Ramón, M. Yus, Org. Biomol. Chem. 2009, 2176.
- [14] K. Shimizu, N. Imaiida, K. Kon, S. M. A. Hakim Siddiki, ACS Catal. 2013, 3, 998.
- [15] T. T. Dang, B. Ramalingam, S. P. Shan, A. M. Seayad, ACS Catal. 2013, 3, 2536.
- [16] U. Mandi, S. K. Kundu, N. Salam, A. Bhaumik, S. M. Islam, J. Colloid Interface Sci. 2016, 467, 291.
- [17] M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, Adv. Synth. Catal. 2007, 349, 1555.
- [18] K. I. Fujita, Y. Enoki, R. Yamaguchi, Tetrahedron 2008, 64, 1943.
- [19] Y. Watanabe, Y. Tsuji, Y. Ohsugi, Tetrahedron Lett. 1981, 22, 2667.
- [20] R. G. Rice, E. J. Kohw, L. W. Daasch, J. Org. Chem. 1958, 23, 1352.
- [21] M. Botta, F. D. Angelis, R. Nicoletti, Synthesis 1977, 722.
- [22] K. Y. Park, S. I. Woo, Catal. Lett. 1994, 26, 169.

WILEY Organometallic 7 of 7 Chemistry

- [23] F. Valotl, F. Fachel, R. Jacquot, M. Spagnol, M. Lemairel, *Tetrahedron Lett.* 1999, 40, 3689.
- [24] R. Luque, J. M. Campelo, D. Luna, J. M. Marinas, A. A. Romero, J. Mol. Catal. A 2007, 269, 190.
- [25] A. Bayat, M. Shakourian-Fard, N. Ehyaei, M. M. Hashemi, *RSC Adv.* 2015, 5, 22503.
- [26] A. Bayat, M. Shakourian-Fard, M. M. Hashemi, *Catal. Commun.* 2014, 52, 16.
- [27] M. Shakourian-Fard, A. H. Rezayan, S. Kheirjou, A. Bayat, M. M. Hashemi, Bull. Chem. Soc. Jpn. 2014, 87, 982.
- [28] A. Bayat, M. Shakourian-Fard, N. Ehyaei, M. M. Hashemi, RSC Adv. 2014, 4, 44274.
- [29] A. Bayat, M. Shakourian-Fard, S. Ramezanpour, M. M. Hashemi, New J. Chem. 2015, 39, 3845.
- [30] S. Akbayrak, M. Kaya, M. Volkan, S. Özkar, Appl Catal B 2014, 147, 387.
- [31] R. B. N. Baig, R. S. Varma, Chem. Commun. 2012, 48, 2582.

[32] R. K. Sharma, Y. Monga, A. Puri, G. Gaba, *Green Chem.* 2013, *15*, 2800.
[33] K. Shimizu, M. Nishimura, A. Satsuma, *ChemCatChem* 2009, *1*, 497.

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