

REPORT ON SELECTIVE ACYLATION OF BENZYLIC ALCOHOL TO BENZYL ACETATE WITH CATALYTIC SYSTEM Ni/SiO₂: AN ENVIRONMENTALLY BENEVOLENT APPROACH

M. ALAM^a, A. RAHMAN^b, N. M. ALANDIS^c, M. R. SHAIK^{c*}

^a*Research Center – College of Science, King Saud University, 11 451 Riyadh, Kingdom of Saudi Arabia*

^b*Department of Chemistry, Vidya Vikas College of Engineering Chevella, RR District, Hyderabad, Andhra Pradesh, India*

^c*Department of Chemistry, College of Science, King Saud University, P. O. Box 2455, 11 451 Riyadh, Kingdom of Saudi Arabia*
E-mail: rafiskm@gmail.com

ABSTRACT

An efficient and selective method was developed for the first time with 10% Ni/SiO₂ catalytic system for acylation of benzyl alcohol to benzyl acetate with 98% conversion using acetonitrile solvent under reflux with acetic anhydride. In this method we used aromatic alcohols like 4-chlorobenzyl alcohol and 4-nitrobenzyl alcohol, respectively. Ni species formed on silica surface demonstrates that Ni silica catalyst is active, while the calcined 2, 5 and 10% Ni/SiO₂ were less active compared with uncalcined 2, 5 and 10% Ni/SiO₂ catalysts, which were active for the title reaction. 10% Ni/SiO₂ catalysts were characterised by XRD, IR, BET, SEM, and UVDRS analyses. The catalysts showed remarkable reusability of 3 cycles, there is no leaching of catalysts, and finally blank reaction was also tested. The method of acylation is superactive, economic, and environmentally benevolent.

Keywords: acylation, benzyl alcohol, acetic anhydride, benzyl acetate.

AIMS AND BACKGROUND

The acylation of aliphatic and aromatic alcohols is one of the most important processes in organic synthesis¹. Acylation using acid anhydrides provides a cheap and an efficient method for protecting OH-groups during oxidation, and coupling reactions^{1,2} or synthesis of esters with high potential applications as fragrances, flavours, surfactants and solvents^{3,4}. On the other hand, the aromatic ketones resulting from the Friedel–Crafts

* For correspondence.

acylation of aromatic compounds are valuable intermediates for the preparation of fine chemicals pharmaceuticals, agrochemicals and cosmetics². Generally, acylation reactions are environmentally unfriendly due to using homogeneous catalysts such as organic bases (pyridine in triethylamine or pyridine with 4-(dimethylamine)pyridine), homogeneous Lewis acid catalysts (AlCl_3 , BF_3 , TaCl_5), or inorganic acids^{1,2}, which generate large amounts of toxic waste products, from which the catalysts are very difficult to recover, and reusability is also difficult. They also often necessitate the presence of environmentally unfriendly solvents like dichloromethane⁵. In order to overcome these problems, the attention was focused on the use of reusable, economic and ecofriendly heterogeneous catalysis. Some solid acid catalysts including zeolites^{6,7}, exchanged clays⁸, oxides⁹, K-10 montmorillonite¹⁰, Al-MCM-4 (Ref. 11), or supported reagents¹¹⁻¹⁴ were used in these reactions, but they require high reaction temperatures or the use of environmentally unfriendly solvents. Other types of catalysts which exhibit a high activity in these reactions are metal triflate derivatives¹⁵⁻²¹ but which are mostly used as homogeneous catalysts. These triflates possess strong Lewis acid and, in contrast to metal halides, they exhibit a very high tolerance towards water and more environmentally friendly catalysts^{22,23}. Since 1980, the amorphous metal-metalloid alloys received special attention for their excellent catalytic activity properties and selectivity. Since the past 50 years nickel-based catalysts are attracting much attention for use in various industrially important reactions such as hydrodesulphurisation, reduction of nitriles, nitro, dealkylation, etc. Ni- and Co-containing amorphous alloys have properties that are of interest in catalysis, such as the presence of a large number of surface coordinating unsaturated sites and the lack of crystal defects. Jonnalagadda et al.²⁴⁻²⁶ earlier reported on nitro-reduction, alcohol oxidation, the Knoevenagel reaction and aldehydes reduction with Ni/ SiO_2 -supported system with excellent conversion and selectivity. In view of the above encouraging results the research project was further extended to examine the efficiency of 10% Ni/ SiO_2 catalyst for acylation reaction of benzyl alcohol to benzyl acetate using acetic anhydride as acylating agent. The main objective of the present work is to evaluate the superactive 2, 5 and 10% Ni/ SiO_2 catalysts for selective acylation of benzyl alcohol to the corresponding benzyl acetate at 65°C, and to study the effect of Ni species on silica surface in order to assess its catalytic aptitude for a potential use of the reaction for industrial purposes.

The object of the present study was to carry out acylation of benzylic alcohols to benzyl acetates with Ni/ SiO_2 catalysts system, which Ni species are associated with silica. The aim of the manuscript addresses avoiding the use of high temperature to minimise the thermal risks during industrial production. The second question addressed is the achievement of high conversion and selectivity using acylating agent, to produce the desired chemical reliability in the required quality, reusability of the catalysts, economic and ecofriendly methodology. Additional features looked for are the operational simplicity, safe and energy efficient procedure.

EXPERIMENTAL

Materials. All chemicals were synthesis grade reagents purchased from Merck, Germany.

Preparation of catalysts. The catalysts were prepared by impregnation method by dissolving nickel nitrate nonahydrate (2.5 g) in distilled water (20.0 ml) and adding to it silica gel (5.0 g) and stirring for 2 h using a magnetic stirrer at room temperature ($20\pm1^\circ\text{C}$) and ageing at room temperature for overnight. The excess water was removed by heating the mixture on water bath and using a rotavapour under vacuum to evaporate the water. The catalyst material was dried in an oven at 100°C for 12 h (Ref. 18).

Typical reaction procedure. A solution of 1.0 mmol benzyl alcohol with 10.0 ml acetonitrile as solvent and 0.5 g catalyst was prepared followed by slow addition of 1.5 mmol acetic anhydride at 65°C . In case of silica-supported catalysts, acetic anhydride was added for a 5-min period. The reaction mixture was magnetically stirred continuously. Then the reaction mixture was quenched with deionised water and extracted with ethyl acetate. The organic layer was dried on anhydrous sodium sulphate and the solvent was evaporated on rotavapour to give crude product of benzyl acetate, which was further subjected to column chromatography to afford pure benzyl acetate. The product was characterised by IR (Nicolet 460 spectrometer) and ^1H -NMR (Bruker-S-300) spectroscopy. The IR spectrum shows the characteristic ester peaks at: 1742.75, 1229.23, 1027.17 (cm^{-1}). The ^1H -NMR shows: δ = 2.09 [3H, s], 2.16 [1H, s], 4.7 [2H, s], 7.2–7.5 [5H, aromatic] in the middle of the reaction. At the end of the reaction, the singlet at 2.16 [hydroxylic proton of benzyl alcohol] disappears showing the 100% conversion to benzyl acetate.

RESULTS AND DISCUSSION

Acylation of benzyl alcohol to benzyl acetate was carried out with 10% Ni/SiO₂ (uncalcined) at 65°C and the reaction was completed in 3 h. It resulted in 97% conversion with 100% selectivity. The positive results lead the authors to investigate the catalytic activity of 2, 5 and 10%-loaded Ni/SiO₂ catalytic system under similar conditions (Table 1).

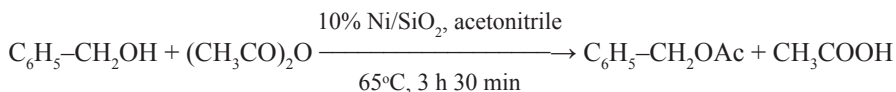
Table 1. Selective acylation of benzyl alcohol to benzyl acetate with acetic anhydride
Benzyl alcohol = 1.0 mmol, acetic anhydride = 1.5 mmol, catalyst = 0.5 g

Support	Ni loading (%)	Reaction time	Conversion (%)	Selectivity (%)
SiO ₂	2	10 h	70	100
	5	3 h 30 min	80	100
	10	3 h	97	100

Note: mean of duplicate runs.

For operational convenience, for most of the reactions, it is attempted to monitor the time required for 100% conversion, where the starting material is completely consumed rather than half-reaction time. With 2% Ni-loading the conversion was 70% and the time of duration 4 h and with 5% Ni-loaded the conversion was 80%, which takes 3 h and 30 min. All catalysts exhibited 100% selectivity. Thus, the order of reactivity of Ni catalyst is: 2% Ni/SiO₂ < 5% Ni/SiO₂ < 10% Ni/SiO₂. Identifying 10%Ni/SiO₂ as the ideal catalyst under the optimum conditions, all the reactions were studied in duplicate and the results were reproducible.

S c h e m e



Triflates are incorporated on the silica after the formation of the sol. For embedding *tert*-butyldimethylsilyltrifluoromethanesulphonate (BDMST) an adapted route for the synthesis of the silica gel was used, which takes 6 days for the formation of catalysts due to the limitations of the above process. Authors designed simple method of preparation of Ni/SiO₂ catalysts in order to obtain the same active species. The influence of the operation parameters such as order of reactants, speed of agitation, time of ageing is important during the impregnation process for the development of the catalytic process.

The presence of weak interaction between metal and support is due to the little impregnation²⁶. During the acylation of benzyl alcohol to benzyl acetate, the activity of the catalysts is credited to the presence of Ni uniformly distributed on the surface of the silica. All the results and the characterisation of Ni/SiO₂ identify that Ni in association with silica the active species and has major role to maximise the activation of acetic anhydride to form benzyl acetate. The observed generation of benzyl acetate with nickel on silica compared with 2, 5 and 10% Ni-loaded is noticeable for lower activity of 2 and 5% Ni/SiO₂ reinforcing the above inference. The low metallic surface of nickel on the silica support encourages the nickel oxide crystallised formation. Practically for Ni/SiO₂ inactive catalytic system reactivity with 2 and 5% Ni-loaded material is decreased possibly due to the formation of nickel basic sites. The weaker interaction between metal and support due to multilayer nickel on the support or the formation of the thick Ni particles could have contributed to the decrease of the catalytic activity. A similar observation was reported in literature, while studying the oxidation of alcohols using Ni-loaded hydrotalcites as catalysts in the presence of oxygen²⁷. Duration of time was also examined for 2, 5 and 10% Ni/SiO₂ and the data are given in Table 1. It is evident that 10% Ni/SiO₂ catalysts is suitable for acylation of benzyl alcohol to benzyl acetate with acetic anhydride as acylating reagent. Acylation reaction was tested with calcined NiO, which resulted in only 50%

conversion with 100% selectivity and shows that the bulk catalysts exhibited some catalytic activity. In view of these results the authors further evaluated the catalytic aptitude of calcined 2, 5 and 10% Ni/SiO₂ catalysts. The results showed that calcined 10%Ni/SiO₂ resulted in 60% conversions, 2, 5, and 10% Ni/SiO₂ with only 15% conversion but retained 100% selectivity in 12 h duration of time. The reactions were tested for further 24 h duration of time and it was observed that there was no change in conversion and selectivity. This specifies that the catalysts are active only for 12 h and the 10%Ni/SiO₂ uncalcined is the superactive catalysts for the reaction. Blank (without catalyst) reaction was run for benzyl alcohol with acetic anhydride in similar conditions. It is concluded that catalyst is required for this reaction. Leaching test was conducted, i.e. the Ni/SiO₂ catalysts were washed with water and acetonitrile and then the substrate and acetic anhydride were added. The reaction was run under similar conditions for a specified period of time. It was observed that the reaction did not occur which shows that the Ni metal is well adhered to the silica surface as confirmed by SEM analysis.

The selective acylation of benzyl alcohol to benzyl acetate is important and interesting area of research. Particularly, the nitro-group which is electron-withdrawing enhances the reaction when interacted on the surface of the catalysts. Using 10% Ni/SiO₂ as appropriate catalyst that facilitates the adsorption of benzyl alcohol and acetic anhydride will enhance the catalytic efficiency with high conversion and selectivity for the acylation reaction. The rate of acylation is determined by the rate of initial adsorption of the substrate on the active sites of the catalytic surface.

The efficiency of the catalytic system comprising of 10% Ni/SiO₂ for acylation of various substituted benzyl alcohols was investigated. Table 2 summarises the results obtained using 10% Ni/SiO₂ system in acetonitrile as a solvent. The best results were obtained for acylation of benzyl alcohol with 97% conversion, 4-chloro benzyl alcohol with 75% conversion, 4-nitro benzyl alcohol with 80% conversion, *p*-methoxy benzyl alcohol gave 70% conversion, 4-methyl benzyl alcohol with 76% conversion, 3-methyl benzyl alcohol with 65% conversion, 2-methyl benzyl alcohol with 60% conversion. All these substrates containing electron-withdrawing groups and electron-activating groups resulted in more than 60% conversion and 100% selectivity. The reusability of 10% Ni/SiO₂ catalysts with benzyl alcohol as model substrate is repeated. S. No 1 in Table 2 was tested after the reaction the catalysts was washed with water, acetonitrile and dried in oven at 80°C for 4 h and then the temperature was raised to remove water. The dried catalysts was ready to check reusability. It was observed that in the 1st reusability test resulted in 97% conversion. The catalyst was washed with water, acetonitrile and dried in oven at 80°C for 4 h to remove the moisture. The dried catalyst was ready to check reusability. It was observed that in the 1st reusability test 97% conversion was achieved. The same procedure was followed for other 2nd and 3rd runs with conversion 80 and 60%, respectively. It was observed that the decrease in the catalytic activity is due to the uneven distribution of nickel species on silica surface^{24–27}.

Table 2. Selective acylation of various aromatic alcohols to aromatic esters with 10% Ni/silica catalysts

Substrate – 2.0 mmol, acetic anhydride 1.5 mmol, catalyst – 0.5 g, duration time – 3h 30 min

S. No	Carbonyl + acetic anhydride	Product	Conversion (%)	Selectivity (%)
1	Ph-CH ₂ OH + (CH ₃ CO) ₂ O	PhCH ₂ OAc	97	100
2	4-Cl-C ₆ H ₄ CH ₂ OH + (CH ₃ CO) ₂ O	4-Cl-C ₆ H ₄ CH ₂ OAc	75	100
3	4-MeO-C ₆ H ₄ CH ₂ OH + (CH ₃ CO) ₂ O	4-MeO-C ₆ H ₄ CH ₂ OAc	70	100
4	4-NO ₂ -C ₆ H ₄ CH ₂ OH + (CH ₃ CO) ₂ O	4-NO ₂ -C ₆ H ₄ CH ₂ OAc	80	100
5	4-Me-C ₆ H ₄ CH ₂ OH + (CH ₃ CO) ₂ O	4-Me-C ₆ H ₄ CH ₂ OAc	76	100
6	3-Me-C ₆ H ₄ CH ₂ OH + (CH ₃ CO) ₂ O	3-Me-C ₆ H ₄ CH ₂ OAc	65	100
7	2-Me-C ₆ H ₄ CH ₂ OH + (CH ₃ CO) ₂ O	3-Me-C ₆ H ₄ CH ₂ OAc	60	100

Effect of temperature. The effect of temperature increase on the catalytic activity was tested at 120°C with 10% Ni/SiO₂ catalysts system and resulted in very little conversion of benzyl alcohol to benzyl acetate. Gosh et al.⁵ reported that the acylation of phenol and alcohols with La(OTf)₃ at 120°C proceeded with 99% conversion in 3 min. Thus, using 10% Ni/SiO₂, the conversion of benzyl alcohol was 85% after 2 h. It was demonstrated that the 10% Ni/SiO₂ catalyst was particularly superactive at 65°C compared to La(OTf)₃ (Ref. 5) and the authors avoid the use of high temperatures due for the formation of side products and the use of specialised equipment.

Mechanism. Acylation of alcohols generally proceeds via an acyl-oxygen cleavage bimolecular mechanism; it can be expected that the rate of esterification could be affected due to the transient complex of the metal ion with the carbonyl group. According to the reaction mechanism, the density of the Bronsted acid sites, i.e. hydroxyl group present on silica surface facilitates the formation of Ni-acylium ion, which rapidly leads to the product formation (Table 2).

Catalysts characterisation. 10% Ni/SiO₂ catalysts were characterised by BET surface area, XRD, IR, SEM, and UV-DRS techniques.

XRD characterisation of 10% Ni/SiO₂. The XRD spectra (a Phillips-PW 1830XRD diffraction spectrometer) represented characteristic diffraction lines of the nickel phase and support, and no mixed nickel oxide support phases were identified. The pattern for the supports were of crystallised materials with the well-defined broad diffraction lines bands of amorphous SiO₂ support around 2θ = 45.

BET data for 10% Ni/SiO₂. The specific area, i.e. the BET surface area of the catalysts, is 180 mg⁻¹. During the impregnation stage of the preparation, the surface hydroxyl groups of the support are consumed by the reaction with the active phase precursor.

FT-IR spectra of 10% Ni/SiO₂. The inspection of IR spectra (a Perkin–Elmer FT-IR spectrometer) of 10% Ni/SiO₂ fresh catalysts shows that the band at 1100 cm⁻¹ (asymmetrical Si–O–Si) is very perceptive to the formation of silicates^{24–26}. SiO₂ does not

have free hydroxyl groups on the surface and confirms that nickel species are formed *in situ* during the reaction of selective acylation of benzyl alcohol. In the IR spectra of 10% Ni/SiO₂, the strong and intense absorption band between 1078–1050 cm⁻¹ shows the presence of Si–O–Ni bonds²⁶. Silica do not have free OH group on the surface. These results confirm that the aromatic alcohol obtained probably anchored to the support. This attributes to the Ni active species in association with silica for the activation of acetic anhydride for the formation of final product. The IR studies confirmed that Ni species of 10% Ni/SiO₂ catalyst is superactive for selective acylation of benzylic alcohols to benzyl acetate with good conversion and high selectivity.

SEM study of Ni/SiO₂. SEM characterisation morphology and location of Ni species on the surface of the catalyst were examined by scanning electron microscopy (SEM) using a JEOL JSM-6100 microscope equipped with an energy-dispersive X-ray analyser (EDX). The images were taken with an emission current = 100 lA by a tungsten (W) filament and an accelerator voltage = 12 kV. The SEM figures of the 2, 5 and 10% Ni-loaded silica are shown in Fig. 1*a*, *b* and *c*, respectively.

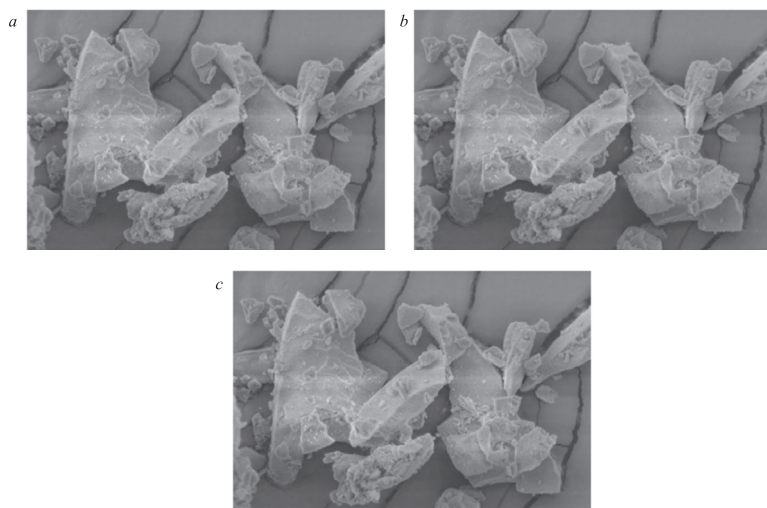


Fig. 1. SEM micrographs of: 2% Ni in silica (*a*); 5% Ni in silica (*b*), and 10% Ni in silica (*c*)

The morphology exhibited crystalline Ni of 2–4 nm which is well distributed over the silica surface of 10%-Ni loaded silica, which indicates that the distribution of Ni on support is either in conglomerates or in layers, thus hindering the participation both of Ni and silica active sites in the reaction. SiO₂ individually had no catalytic effect on the reaction. The observed reactivity of Ni-supported on silica material can be possibly attributed to the metal and support interactions, and the resultant changes in surface properties of the reactive sites. Earlier studies by Urbano et al. have revealed that supported Ni catalysts prepared from Ni(NO₃)₂ by impregnation exhibit wide size distribution when compared with the prepared by more controlled and deposi-

tion method precipitation route, which generates low metallic Ni particles. The low metallic surface of nickel on the silica support encourages the crystallised nickel oxide formation. The presence of weak interaction between metal and support, due to little distribution of Ni entailing the formation of the layer of impregnated Ni, probably contributes to the increase of catalytic activity^{24,25}. The observed non-reactivity with 2 and 5% Ni-loaded material could be possibly due to the multilayer of Ni loading on the support resulting in loss of activity as suggested by Choudary et al.²⁷ This is also supported by the SEM figures of the different amounts of Ni-loaded silica in the current study. An examination of SEM figures show that Ni particles are well distributed in 2 and 5% Ni loaded material with fine particles and the 10%-loaded material shows Ni multilayers and conglomeration of Ni particles on the silica surface. Further, the broadened silica peak with the 10% Ni loading relative to lower Ni-loaded surfaces in the XRD patterns also supports the surface characteristics illustrated by SEM figures. Houi et al. have reported that the activity of Ni on silica surface depends on the particle size of the metal and lower catalytic activity is observed with increased Ni particle size. Authors observed that the surface of 10% Ni-loaded silica is almost completely covered by nickel particles^{24–26} and even suggesting that the Ni could be unevenly distributed, this has contributed to the low activity of 2 and 5% Ni-loaded silica.

UV DRS characterisation. Spectra of the supported materials, after initial drying, but before calcinations and reduction, were measured by diffuse reflectance UV diffusion spectroscopy and their absorption maxima and assignments were recorded. 10% Ni/SiO₂ of all percentages showed 740 nm⁻¹ range during UV diffusion analysis when compared with nickel nitrate aqueous solution and nickel nitrate, which showed UV range of 728 and 707 nm⁻¹. Ni silica catalysts of all samples showed particle size in the range of 20–250 Å and the moisture content observed was 7%.

CONCLUSIONS

The present study confirms that acetic anhydride silica system is superior to the other acylating agents systems for selective acylation of aromatic alcohols to aromatic acetates. Acylating species generated *in situ* by the decomposition acetic anhydride on nickel silica, which leads to the final product of acylation reaction for substituted benzylic alcohols to benzyl acetates with > 65% conversions and 100% selectivity is achieved at 65°C in 3 h 30 min duration of time (Table 2). In most cases more than 70% conversions were achieved. This system applies even to electron-withdrawing groups such as nitro, methoxy attached to 4-position of benzylic group. It is a well equipped system with no need for any specialised facilities. The catalyst is loaded without pre-addition of acetic anhydride reagent. The catalyst is reusable for 3 consecutive cycles and there is no leaching of catalysts. The NiO and 2, 5 and 10% Ni/SiO₂ calcined catalysts exhibited less activity. Finally it was concluded that 10% uncalcined Ni/SiO₂ catalysts is superactive for the reaction. Further, this process is economically viable

and can be upgraded to large-scale reactions. This forms a new alternative methodology at 65°C, which excludes the use of harsh reaction conditions.

ACKNOWLEDGEMENTS

The project was supported by King Saud University, Deanship of Scientific Research, College of Science-Research Center.

REFERENCES

1. A. N. PARVULESCU, B. C. GAGEA, G. PONCELET, V. I. PARVULESCU: Acylation of Alcohols and Activated Aromatic Compounds on Silica-embedded Triflate Catalysts. *Appl Catal A: Gen*, **301**, 133 (2006).
2. A. N. PARVULESCU, B. C. GAGEA, V. I. PARVULESCU, D. DE VOS, P. A. JACOBS: Acylation of 2-methoxynaphthalene with Acetic Anhydride over Silica-embedded Triflate Catalysts. *Appl Catal A: Gen*, **306**, 159 (2006).
3. G. BOND, J. A. GARDNER, R. W. McCABE, D. J. SHORROCK: Friedel–Crafts Acylation Reactions Using Heterogeneous Catalysts Stimulated by Conventional and Microwave Heating. *J Mol Catal A: Chem*, **278**, 1 (2007).
4. B. SREEDHAR, R. ARUNDHATHI, M. AMARNATH REDDY, G. PARTHASARATHY: Highly Efficient Heterogeneous Catalyst for Acylation of Alcohols and Amines Using Natural Ferrous Chamosite. *Appl Clay Science*, **43**, 425 (2009).
5. R. GOSH, S. MAITI, A. CHAKRABORTY: Facile Catalyzed Acylation of Alcohols, Phenols, Amines and Thiols Based on $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and Acetyl Chloride in Solution and in Solvent-free Conditions. *Tetrahedron Lett*, **46**, 147 (2005).
6. R. BALLINI, G. BOSICA, S. CARLONI, L. CIARALLI, R. MAGGI, G. SARTORI: Zeolite HSZ-360 as a New Reusable Catalyst for the Direct Acetylation of Alcohols and Phenols under Solventless Conditions. *Tetrahedron Lett*, **39**, 6049 (1998).
7. C. P. BEZOUHANOVA: Synthesis of Aromatic Ketones in the Presence of Zeolite Catalysts. *Appl Catal A: Gen*, **229**, 127 (2002).
8. J. FARKAS, S. BEKASSY, B. AGAI, M. HEGEDUS, F. FIGUERAS: Acylation of Resorcinol on Clay Catalysts. *Synth Commun*, **30**, 2479 (2000).
9. M. SARVARI, H. SHARGHI: Reactions on a Solid Surface. A Simple, Economical and Efficient Friedel–Crafts Acylation Reaction over Zinc Oxide (ZnO) as a New Catalyst. *J Org Chem*, **69**, 6953 (2004).
10. S. G. PAI, A. R. BAJPAI, A. B. DESHPANDE, S. D. SAMANT: Friedel–Crafts Benzoylation of Arenes Using FeCl_3 Impregnated Montmorillonite K10. *Synth Commun*, **27**, 2267 (1997).
11. K.G. BHATTACHARYYA, A. K. TALUKDAR, P. DAS, S. SIVASANKER: Acetylation of Phenol with Al-MCM-41. *Catal Commun*, **2**, 105 (2001).
12. C. CASTRO, A. CORMA, J. PRIO: On the Acylation Reactions of Anisole Using α , β -unsaturated Organic Acids as Acylating Agents and Solid Acids as Catalysts: A Mechanistic Overview. *J Mol Catal A: Chem*, **177**, 273 (2002).
13. V. R. CHOUDHARY, S. K. JANA, N. S. PATIL: Acylation of Aromatic Compounds Using Moisture Insensitive InCl_3 Impregnated Mesoporous Si-MCM-41 Catalyst. *Tetrahedron Lett*, **43**, 1105 (2002).
14. J. A. MELERO, R. van GRIEKEN, G. MORALES, V. NUNO: Friedel–Crafts Acylation of Aromatic Compounds over Arenesulfonic Containing Mesostructured SBA-15 Materials. *Catal Commun*, **5**, 131 (2004).

15. R. DALPOZZO, A. de NINO, L. MAIUOLO, A. PEROCOPIO, M. NARDI, G. BARTOLI, R. ROMEO: Highly Efficient and Versatile Acetylation of Alcohols Catalysed by Cerium(III) Triflate. *Tetrahedron Lett*, **44**, 5621 (2003).
16. A. G. M. BARRET, D. C. BRADDOCK: Scandium(III) or Lanthanide(III) Triflates as Recyclable Catalysts for the Direct Acetylation of Alcohols with Acetic Acid. *Chem Commun*, 351 (1997).
17. R. ALLETTI, M. PERAMBUDURU, S. SAMANTHA, V. R. REDDY: Gadolinium Triflate: An Efficient and Convenient Catalyst for Acetylation of Alcohols and Amines. *J Mol Catal A: Chem*, **226**, 57 (2005).
18. K. ISHIHARA, M. KUBOTA, H. YAMAMOTO: A New Scandium Complex as an Extremely Active Acylation Catalyst. *Synlett*, 265 (1996).
19. K. ISHIHARA, M. KUBOTA, H. KUNIHARA, H. YAMAMOTO: Scandium Trifluoromethanesulfonate as an Extremely Active Lewis Acid Catalyst in Acylation of Alcohols with Acid Anhydrides and Mixed Anhydrides. *J Org Chem*, **61**, 4560 (1996).
20. K. K. CHAUHAN, C. G. FROST, I. LOVE, D. WAITI: Indium Triflate: An Efficient Catalyst for Acylation Reactions. *Synlett*, **22**, 1743 (1999).
21. B. KARIMI, J. MAKEKI: Lithium Trifluoromethanesulfonate (LiOTf) as a Recyclable Catalyst for Highly Efficient Acetylation of Alcohols and Diacetylation of Aldehydes under Mild and Neutral Reaction Conditions. *J Org Chem*, **68**, 4951 (2003).
22. B. C. GAGEA, A. N. PARVULESCU, V. I. PARVULESCU, A. AUROUX, P. GRANGE, G. PONCELET: Alkylation of Phenols and Naphthols on Silica-immobilized Triflate Derivatives. *Catal Lett*, **91**, 141 (2003).
23. A. N. PARVULESCU, B. C. GAGEA, V. PARVULESCU, V. I. PARVULESCU, G. PONCELET, P. GRANGE: Comparative Behavior of Silica-embedded *tert*-butyldimethylsilyltrifluoromethanesulfonate and Lanthanum Triflate Catalysts. *Catal Today*, **73**, 177 (2003).
24. A. RAHMAN, S. B. JONNALAGADDA: Swift and Selective Reduction of Nitroaromatics to Aromatic Amines with Ni–Boride–Silica Catalysts System at Low Temperature. *Catal Lett*, **123**, 264 (2008).
25. A. RAHMAN, S. B. JONNALAGADDA: Rapid and Selective Reduction of Aldehydes, Ketones, Phenol, and Alkenes with Ni–Boride–Silica Catalysts System at Low Temperature. *J Mol Catal A*, **299**, 98 (2009).
26. V. S. R. RAJASEKHAR, A. RAHMAN, S. B. JONNALAGADDA: Selective Catalytic Knoevenagel Condensation by Ni–SiO₂ Supported Heterogeneous Catalysts: An Environmentally Benign Approach. *Catalysis Commun*, **10**, 365 (2009).
27. B. M. CHOUDARY, M. L. KANTAM, A. RAHMAN, Ch. VENKAT REDDY, K. KOTESHWAR RAO: The First Example of Activation of Molecular Oxygen by Nickel in Ni–Al Hydrotalcite: A Novel Protocol for the Selective Oxidation of Alcohols. *Angew Chem Int*, 785 (2001).

Received 17 February 2012

Revised 24 March 2012