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# Ni/Silica catalyzed acetylation of phenols and naphthols: An eco-friendly approach

Manawwer Alam <sup>a,\*</sup>, Ateeq Rahman <sup>b</sup>, Naser M. Alandis <sup>c</sup>,  
 Mohammed Rafi Shaik <sup>c</sup>

<sup>a</sup> Research Center – College of Science, King Saud University, Riyadh 11451, Saudi Arabia

<sup>b</sup> Department of Chemistry, Vidya Vikas College of Engineering Chevella, RR District, Hyderabad, Andhra Pradesh, India

<sup>c</sup> Department of Chemistry, College of Science, King Saud University, P.O. Box-2455, Riyadh 11451, Saudi Arabia

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**Abstract** A method for 10% Ni/SiO<sub>2</sub> catalyst is developed for acetylation of phenol, substituted phenols, naphthols, substituted alcohols under mild liquid phase conditions affording aromatic esters with maximum conversions of 50–80% and 100% selectivity. The catalyst showed remarkable reusability for up to 4 cycles. This methodology is eco-friendly, economic with Ni/SiO<sub>2</sub> catalysts exhibiting no loss of activity the first report for acetylation of substituted phenols to esters with 10% Ni/SiO<sub>2</sub> catalyst.

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**1. Introduction**

Acetylation is one of the fundamental reactions in organic chemistry and can be carried out by a wide variety of reagents (Ogliaruso et al., 1979). Acyl groups play an important role in the chemistry of bio-molecules (Simmonds, 1992), they are fragments of important natural products, such as peptides (Bodanszky, 1993) or modified peptide bond iso-esters (Magrath and Abeles, 1992) and also they serve as protecting groups (Greene and Wuts, 1991). *Ortho*-Hydroxy-aryl ketones, as a variety of compounds with the acyl group, are also important synthetic intermediates in the synthesis of biologically active

compounds such as chalcones, flavanones, naphthoquinones and pesticides. The acylation of alcohols, phenols, thiols, and amines is very important in various organic transformations, especially in the synthesis of natural compounds and poly-functional molecules such as nucleosides, carbohydrates, and steroids (Crouse et al., 1981).

A number of lewis acids such as TMSCl (Roux and Dubac, 1996), MoO<sub>2</sub>Cl<sub>2</sub> (Chen et al., 2005), ErCl<sub>3</sub> (Dalpozzo et al., 2007), RuCl<sub>3</sub> (De, 2004), ZrOCl<sub>2</sub> (Ghosh et al., 2005), Zn(ClO<sub>4</sub>)<sub>2</sub> (Bartoli et al., 2003), TiCl<sub>4</sub> + AgClO<sub>4</sub> (Miyashita et al., 1993), Cu(OTf)<sub>2</sub> (TfCF<sub>3</sub>SO<sub>2</sub>) (Tai et al., 2003), Er(OTf)<sub>3</sub> (Procopio et al., 2004), Al(OTf)<sub>3</sub> (Kamal et al., 2007), Ti-Cl<sub>3</sub>(OTf) (Firouzabadi et al., 2008), Ce(OTf)<sub>3</sub> (Bartoli et al., 2004), SnIV(tpp)(OTf)<sub>2</sub> (tpp = tetra phenylporphyrin) (Moghadam et al., 2004), Sc(NTf)<sub>3</sub> (Ishihara et al., 1996a,b), have been reported to show catalytic activity toward the acetylation of alcohols with acid anhydride.

Development of regio-selective reactions in organic compounds is fundamental and important viz. 2-Acylation reactions of phenol and naphthol derivatives that provide useful

\* Corresponding author. Tel.: +966 554738803.

E-mail address: malamiitd@gmail.com (M. Alam).

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synthetic methods for the preparation of 2-hydroxy phenyl or 2-hydroxy naphthyl ketone derivatives (Procopio et al., 2004). Chakraborti et al. also reported a number of good catalytic systems for the acetylation/acylation reactions (Chakraborti and Gulhane, 2003a,b,c, 2004; Chakraborti et al., 2003a,b, 2004; Chakraborti and Shivani, 2006; Shivani et al., 2007). Particularly,  $\text{Sc}(\text{OTf})_3$  (Ishihara et al., 1996a,b), a commercially available and moisture-stable lewis acid, is extremely active for this reaction. Unfortunately, due to the high price of scandium salts and its intolerance toward various functional groups,  $\text{Sc}(\text{OTf})_3$  is limited in application.  $\text{TMSOTf}$  is another catalyst for acylation of alcohols and phenols (Procopio et al., 1998). In order to overcome these limitations with lewis acids it is well known that heterogeneous catalysts have advantages over homogeneous catalysts, the recovery of catalysts, easy means of separation, ecofriendly, economic, and reusability.

The aim of this paper is to present the results of acetylation of a series of alcohols viz. 1-naphthol, 2-naphthol, substituted phenols like 2,4 dimethyl phenol and 2,4,6-trimethyl phenols etc. using acetic anhydride as acetylating agent with Ni supported silica catalysts. We also investigated the catalytic activity and various ratios of catalysts 2%, 5% and 10% Ni/SiO<sub>2</sub>. The reactions are performed under mild reflux conditions with acetonitrile as solvent.

## 2. Experimental

### 2.1. Materials

Acetic anhydride, dichloromethane, nickel nitrate hexa hydrate, ethyl acetate (BDH Chemicals, England), silica gel (ICN Pharamacitical GmbH, Germany), sodium sulfate anhydrous (Fluka Chemika), phenol (Merck, India), hexanol (Winlab, UK), 1-naphthol (Riedel-de Haen, Germany), 2-naphthol (Hopkin & Williams, England), 2,4,6-trimethyl phenol, 3,4-dimethyl phenol (Fluka AG Switzerland) were used as received.

### 2.2. Preparation of Ni/SiO<sub>2</sub> catalysts

The catalyst was prepared by the impregnation method by dissolving nickel nitrate hexa hydrate (2.5107 g) in distilled water (20.0 mL) and adding it to silica gel (5.0 g) and stirring for 2 h using a magnetic stirrer at room temperature (20 ± 1 °C) and ageing at room temperature overnight. The excess water is removed by heating the mixture on water bath and using a rota-vapor under vacuum to evaporate the water. The catalyst material is dried in an oven at 100–120 °C for 12 h (Rahman et al., 2008).

### 2.3. Typical reaction procedure

1-Naphthol (2.0 mmol) with 10.0 mL acetonitrile solvent and addition of catalyst (500 mg) followed with slow addition of acetic anhydride 1.5 mmol at room temperature was added in 5 min and the reaction mixture is refluxed continuously until starting material is consumed. The reaction progress is monitored by TLC. The reaction mixture is quenched with de-ionized water and extracted with ethyl acetate. The organic layer is dried on sodium sulfate and the solvent is evaporated on

rota-vapor to give crude product of 1-naphthol which is then subjected to column chromatography to afford pure 1-naphthyl acetate product. The final product is characterized by <sup>1</sup>H and <sup>13</sup>C NMR (400 MHz Bruker Instrument). GC–MS samples were run on Agilent 6890 GC/5973, MS Column: J&W HP5-MS. GC results were characterized on GC System 6820, Agilent Technologies equipped with flame ionization detection (FID) and a carbox OV1 capillary column and compared with standard sample.

## 3. Results and discussion

### 3.1. Characterization of 10% Ni/SiO<sub>2</sub> by BET, XRD, and IR

As reported earlier (Rahman and Jonnalagadda, 2008, 2009), the specific area, i.e., the BET surface area of the catalysts is 180 mg<sup>-1</sup>. The surface reaction may have caused the decrease of available surface area of the support, probably by uneven distribution of Ni particles on the silica surface. The hydrothermal treatment results in a surface modification, which affects the support surface area. It could be inferred from the increasing specific surface area with time and by the OH stretching band in IR however after 90 h of treatment the BET area decays. When time is increased for hydrothermal treatment, the OH bands show a maximum at 46 h. After that a degradation process can be assumed due to a decrease in the BET area and a starting crystallization process as can be seen by XRD.

IR spectra of 10% Ni/SiO<sub>2</sub> showed a band at 1100 cm<sup>-1</sup> (asymmetrical Si–O–Si) very perceptible to the formation of silicates and strong intense absorption band between 1078 and 1050 cm<sup>-1</sup>, showing the presence of Si–O–Ni bonds. Further, upon hydrothermal treatment of catalysts for 46 h, the observed degradation process can be assumed due to a decrease in the BET area. Apart from these hydrothermal treatment at 96 h shows OH stretching vibrations by IR. (Rahman and Jonnalagadda, 2008, 2009) reported the broad band at 3500–3680 cm<sup>-1</sup> is due to hydrogen bridge bonds.

### 3.2. Comparative studies of 2%, 5% and 10% Ni/SiO<sub>2</sub> catalysts

10% Ni/SiO<sub>2</sub> gave encouraging results, and further investigated with 2% and 5% Ni/SiO<sub>2</sub> catalysts. The catalyst for acetylation of alcohols by 2% and 5% Ni/SiO<sub>2</sub> resulted in 35% and 55% conversion with 100% selectivity retained which is due to Ni species uneven distribution on silica surface, which have contributed to inactivity of the catalysts. Nickel silicates with layered structure, are well known as polysilicates, hydro silicates, or surface silicates. The authors showed more interest in preparing 10% Ni/SiO<sub>2</sub> catalyst by a simple impregnation method. The fine amorphous powder of 10% Ni/SiO<sub>2</sub> was obtained, which shows that Ni particles are well distributed over the silica surface and confirmed by the XRD characterization technique. Selective acylation of alcohols is an important transformation from industry point of view (Rahman and Jonnalagadda, 2009). 10% Ni/SiO<sub>2</sub> 1-naphthol was acylated to 1-naphthyl ester in acetic anhydride. The controlled acylations of 2-naphthol to its ester product are with excellent conversion and selectivity (Rahman et al., 2008). When acetic anhydride is added to nickel silica catalysts at room temperature acylium ion is generated on the Ni silica surface due to lewis acid

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