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ZnAl₂O₄@SiO₂ nanocomposite catalyst for the acetylation of alcohols, phenols and amines with acetic anhydride under solvent-free conditions

Saeed Farhadi*, Kosar Jahanara

Department of Chemistry, Lorestan University, Khoramabad 68135-465, Iran

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1. Introduction

The selective protection of alcohols, phenols, and amines has received attention for its fundamental importance and also for its role in multistep synthesis [1,2]. This important transformation is typically performed using acetic anhydride and/or acetyl chloride in the presence of either basic or acidic catalysts. Numerous catalytic systems are available for this transformation [3–13], but most of these are homogeneous catalysts and non-recoverable, and they have the disadvantages of prolonged reaction time, low yields, harsh conditions, use of harmful organic solvents, tedious work-up procedures, excessive reagents or catalysts, and the use of explosive, moisture-sensitive, or expensive catalysts.

ABSTRACT

A ZnAl₂O₄@SiO₂ nanocomposite was prepared from metal nitrates and tetraethyl orthosilicate by the sol-gel process, and characterized by X-ray diffraction, Fourier transform infrared, transmission electron microscopy, and N₂ adsorption-desorption measurements. The nanocomposite was tested as a heterogeneous catalyst for the acetylation of alcohols, phenols, and amines under solvent-free conditions. Under optimized conditions, efficient acetylation of these substrates with acetic anhydride over the ZnAl₂O₄@SiO₂ nanocomposite was obtained. Acetylation of anilines and primary aliphatic amines proceeded rapidly at room temperature, while the reaction time was longer for the acetylation of alcohols and phenols, showing that an amine NH₂ group can be selectively acetylated in the presence of alcoholic or phenolic OH groups. The catalyst can be reused without obvious loss of catalytic activity. The catalytic activity of the ZnAl₂O₄@SiO₂ nanocomposite was higher than that of pure ZnAl₂O₄. The method gives high yields, and is clean, cost effective, compatible with substrates having other functional groups and it is suitable for practical organic synthesis.

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One of the most promising solutions to overcome these problems is the use of heterogeneous solid catalysts [14,15], which can be recovered easily from the reaction mixture by simple filtration and reused to make the process more economical and environmentally viable. Solid catalysts such as HClO₄-SiO₂ [16], montmorillonites [17–19], metal oxides [20–22], H₂SO₄-SiO₂ [23], zeolites [24,25], HBF₄-SiO₂ [26], MoO₃-Al₂O₃ [27], NaHSO₄-SiO₂ [28], sulphated zirconia [29], (NH₄)_{2.5}H_{0.5}PW₁₂O₄₀ [30], silica-bonded Co(II) salen [31], silica-bonded N- and S-propyl sulfamic acids [32,33], poly(4-vinylpyridinium) perchlorate [34], polystyrene-supported GaCl₃ [35], borated zirconia modified with ammonium metatungstate [36], rice husk [37], V(IV) tetraphenylporphyrin [38], Ti^{IV}(salophen)(OTf)₂ [39], polystyrene-bound electron-defi

^{*} Corresponding author. Tel: +98-661-6200111; Fax: +98-661-6200112; E-mail: sfarhadi48@yahoo.com

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cient Sn(IV) porphyrin [40], poly(vinylpolypyrrolidoniume) tribromide [41], modified attapulgite [42], succinimide-N-sulfonic acid [43], acylimidazolium acetate [44], Ph₃P(OAc)₂ [45], poly(4-vinylpyridinium) tribromide [46], sulfonated ordered nanostructured carbon [47], iron oxide nanoparticles [48] and Ni/Silica [49], Cu based metal-organic framework [50] have been used in the acetylation of alcohols, phenols, and amines. However, each of these catalysts or reagents has disadvantages and limitations.

In recent years, transition metal mixed oxides with the perovskite (ABO₃) or spinel (AB₂O₄) structure have attracted considerable attention as promising catalytic materials for organic transformations due to their high thermal and hydrothermal stability and relatively low cost compared with their noble metal counterparts [51–56]. However, their potential catalytic applications are limited by their small surface areas. One possible way to circumvent this problem is to disperse these oxides on a medium with high specific surface area. In recent years, silica-based materials have been reported to be promising supports for a number of catalytically active species because of their high surface area and stable and well-ordered pore structure [57–59].

In the present work, we report that spinel-type ZnAl₂O₄ embedded in a silica matrix (ZnAl₂O₄@SiO₂) is a highly efficient catalyst for the acetylation reaction. The ZnAl₂O₄@SiO₂ nanocomposite was prepared by the sol-gel method and used as a heterogeneous catalyst for the acetylation of alcohols, phenols, and amines with acetic anhydride under solvent-free conditions.

2. Experimental

2.1. Preparation of the catalyst

The reagents used in the synthesis of $ZnAl_2O_4@SiO_2$ were $Al(NO_3)_3$ ·9H₂O, $Zn(NO_3)_2$ ·6H₂O, and tetraethylorthosilicate (Si(OC₂H₅)₄, TEOS, >99.5%). All these reagents were of purity >98% from Merck. Alcohols, phenols, amines, and solvents were purchased with the highest purity available (>98%) from Merck Chemical Company and used without further purification.

The ZnAl₂O₄@SiO₂ nanocomposite was synthesized by the sol-gel method as follows. A mixture of TEOS (0.35 mol, SiO₂ content 21 g), ethanol (60 mL), and water (10 mL) was prepared in a 1-L beaker, and its acidity was adjusted to pH 2 using nitric acid (0.1 mol/L). In order to hydrolyze the TEOS, the mixture was stirred at room temperature for 1 h. Then, a solution of Al(NO₃)₃·9H₂O (0.05 mol, 18.75 g) and Zn(NO₃)₂·6H₂O (0.025 mol, 7.27 g) dissolved in 90 mL of water was added. The resulting mixture was stirred for 1 h and allowed to gel at room temperature over 5 d. After gelation, it was dried and calcined at 600, 800, or 900 °C for 5 h to fix the silica network. It was washed with hot water (80 °C) three times to give ca. 30 g of the ZnAl₂O₄@SiO₂ nanocomposite. From the solid mass obtained and the initial amount of the two metal nitrates employed, we estimated that the ZnAl₂O₄@SiO₂ material prepared contained 30 wt% ZnAl₂O₄,

2.2. Characterization of the catalyst

X-ray diffraction (XRD) patterns were recorded on a Rigaku D-max C III X-ray diffractometer using Ni-filtered Cu K_{α} radiation (λ = 1.5406 Å) to determine the phases in the samples. Infrared (IR) spectra were recorded on a Shimadzu system FT-IR 160 spectrophotometer using KBr pellets. The particle size and morphology of the ZnAl₂O₄@SiO₂ nanocomposite were determined by a transmission electron microscope (TEM, Philips CM10) with an accelerating voltage of 80 kV. To prepare the TEM specimen, a small amount of the powder was dispersed in ethanol in an ultrasonic bath for 30 min, and a few drops of the resulting suspension were placed on a carbon coated copper grid. The specific surface area of the catalyst was obtained by the BET method using N2 adsorption-desorption at -196 °C with a surface area analyzer (Micromeritics ASAP 2010). Before each measurement, the sample was degassed at 200 °C for 1 h.

2.3. Catalytic tests

Alcohol, phenol, and/or amine (1 mmol) were added to a mixture of the $ZnAl_2O_4@SiO_2$ nanocomposite (100 mg) and acetic anhydride (1 mmol). The mixture was stirred at 75 °C (for alcohols and phenols) or at room temperature (for amines) for a time. The progress of the reaction was monitored by TLC and/or GC-MS. When the reaction was completed, ethyl acetate (10 mL) was added and the mixture was filtered to separate off the catalyst. The catalyst was washed twice with 7.5 mL ethyl acetate. The combined organic phases were washed with a 10% solution of NaHCO₃ and then dried over MgSO₄. The solvent was removed to yield the product. If further purification was needed, the product was passed through a short column of silica gel. All products were characterized on the basis of GC-MS, FT-IR, and ¹H-NMR spectral data by comparing these spectra with those of standard samples or literature data.

3. Results and discussion

3.1. Characterization of the ZnAl₂O₄@SiO₂ nanocomposite

Figure 1 shows the XRD patterns of the ZnAl₂O₄@SiO₂ samples calcined at 600, 800, and 900 °C for 5 h. It is clear that the sample calcined at 600 °C was amorphous, with one broad reflection at $2\theta = 22.5^{\circ}$, which is the characteristic diffraction of the amorphous SiO₂ matrix. Calcining the dried gel sample at 800 °C resulted in gradual crystallization of the sample. The increase of calcination temperature to 900 °C resulted in an increase in the crystallinity. All the peaks could be indexed as the (220), (311), (400), (422), (511), and (440) planes assigned to the ZnAl₂O₄ spinel (ICCD Card File No. 5-0669). No other crystalline phase was detected in the calcined samples. The result meant that the materials consisted of ZnAl₂O₄ nanocrystals and an amorphous phase of SiO2. Furthermore, the diffraction peaks of the ZnAl₂O₄ phase were markedly broadened due to the small size of the particles. The average particle size calculated based on the Debye-Scherrer equation [60] using the



Fig. 1. XRD patterns of ZnAl₂O₄-SiO₂ samples calcined at different temperatures for 5 h. (1) 600 °C; (2) 800 °C; (3) 900 °C.

most intense peak (311) at 2θ = 36.90° was 20 nm.

The XRD analysis confirmed that a high crystallinity $ZnAl_2O_4@SiO_2$ nanocomposite was formed by calcining the dried gel at 900 °C for 5 h. For further confirmation, the FT-IR spectrum of this sample was recorded. As shown in Fig. 2, bands appeared at 1078 and 800 cm⁻¹ were assigned to the stretching and bending vibrations of the Si–O–Si bonds of the silica network [61]. These bonds were formed by the hydrolysis and condensation reactions of the TEOS precursor. In addition, three bands appeared at 680, 560, and 485 cm⁻¹ that were related to the Al–O stretching and O–Al–O bending vibrations of the ZnO₄ tetrahedron group and the Zn–O stretching vibration of the ZnO₄ tetrahedron group in the spinel-type ZnAl₂O₄ structure, respectively [61,62]. This result confirmed the formation of a ZnAl₂O₄@SiO₂ nanocomposite in the silica network in agreement with the XRD result.

Since the catalytic properties of inorganic nanomaterials are highly dependent on their size, shape, and crystalline structure, TEM was conducted to determine the particle sizes and morphology of the ZnAl₂O₄@SiO₂ nanocomposite. Figure 3 shows the TEM image of the ZnAl₂O₄@SiO₂ nanocomposite obtained by calcining the gel at 900 °C. The result revealed that the ZnAl₂O₄@SiO₂ particles had a semi-spherical morphology and homogeneous shape. The nanocomposite particles have a narrow size distribution in a range from 10 to 30 nm with an average particle size of 20 nm, which was in agreement with XRD result.



Fig. 2. FT-IR spectrum of the ZnAl₂O₄@SiO₂ nanocomposite.



Fig. 3. TEM image of the ZnAl₂O₄@SiO₂ nanocomposite.

N₂ adsorption-desorption isotherm was measured to get the surface area of the ZnAl₂O₄@SiO₂ nanocomposite. As shown in Fig. 4, the specific surface area of the ZnAl₂O₄@SiO₂ nanocomposite calculated by the BET method was 147.5 m²/g, which was much higher than that of the commercial bulk ZnAl₂O₄ sample (ca. 5 m²/g). The high specific surface area of the nanocomposite product showed that it could be an efficient catalyst. The isotherm was Type IV with an evident hysteresis loop in the 0.5–1.0 range of relative pressure, indicating that the existence of SiO₂ prevented the ZnAl₂O₄ nanoparticles from aggregating, and this can be expected to give good catalytic activity to the ZnAl₂O₄@SiO₂ nanocomposite.

3.2. Acetylation reaction over ZnAl₂O₄@SiO₂ nanocomposite

The aim of this work was to evaluate the catalytic activity of $ZnAl_2O_4@SiO_2$ in the acetylation of alcohols, phenols, and amines. At the beginning, an optimization reaction was carried out to get the best conditions with benzyl alcohol as a model substrate. A mixture of benzyl alcohol (1 mmol) and acetic anhydride (1 mmol) in the presence of various amounts of the catalyst was stirred under solvent-free conditions. The acetylation at room temperature was too slow for practical application. In order to overcome this drawback, the reaction was carried out at 75°C, which resulted in the best yield. The progress of the reaction was monitored by TLC. The yield of benzyl acetate was increased from 43% to 64% and then 92% with



Fig. 4. N_2 adsorption-desorption isotherm for the $\rm ZnAl_2O_4@SiO_2$ nanocomposite.

the increase of the amount of catalyst from 25 to 50 and then to 100 mg, respectively, but further increase did not improve the yield. The appropriate amount of catalyst in the reaction mixture was 100 mg per 1 mmol of alcohol. The essential role played by the catalyst was evident from the extremely low yield of benzyl acetate found in the absence of the catalyst. In order to choose the best medium, the reaction was also studied in various organic solvents such as acetonitrile, toluene, acetone, and dichloromethane. However, the best results in terms of

reaction time and product yield were achieved without the use of any solvent (20 min, 92%). So, we performed the reactions under solvent-free conditions. The low activity of the catalyst in the presence of a solvent can be attributed to the existence of various interactions of the solvent e.g. solvation or formation of a complex with the reactants and/or product. When the reaction was performed without a solvent, these interactions or interferences were eliminated, so a higher efficiency of the catalytic system was achieved. There was probably also an in-

Table 1

Acetylation of alcohols and phenols with acetic anhydride over the $ZnAl_2O_4@SiO_2$ nanocomposi	ite.
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Entry	Substrate	Product ^a	Time (min)	Yield ^b (%)	Entry	Substrate	Product ^a	Time (min)	Yield ^b (%)
1	OH	OAc OAc	20	92	16	OH	OAc	12	92
2	t-Bu	t-Bu-	15	94	17	OH Cl	Cl OAc	15	94
3	MeO OH	MeO-OAc	15	88	18	OH OMe OMe	OAc OMe OMe	15	92
4	OMe OH	OAc	20	92	19	ОН	OAc	30	86
5	F-C-OH	F-OAc	20	90	20	ОН	OAc	25	92
6	CI CI OH		20	92	21	ОН	OAc	30	86
7	CI OH	Cl OAc	20	89	22			36	85
8	F ₃ C-	F ₃ C-	35	85	23	ОНОН	OAc OAc	32	89
9	OH OH	OAc NO2	20	90	24 c	⟨OH	OAc	32	90
10	NO ₂ OH	NO ₂ OAc	15	90	25	ОН	OAc	38	86
11	CN-CN-OH	CN-OAc	25	90	26	Ме-ОН	Me-OAc	35	88
12	CHO OH	CHO OAc	20	90	27	O2N-OH	O ₂ N-	45	82
13	COMe OH	COMe OAc	18	92	28	OH	OAc	40	92
14	ОН	⊘Ac	15	94	29	OH	OAc	50	88
15	OH OH	OAc	15	92	30	SH SH	SAc	45	80

Reaction conditions: substrate 1 mmol, acetic anhydride one equiv. per OH, catalyst 100 mg, solvent-free, 75 °C.

^a All products were characterized by GC-MS, IR and ¹H-NMR spectral data and comparison with those of standard samples or literature data.

^bIsolated yield from weight of pure product obtained.

 $^{\rm c}{\rm The}$ reaction was carried out on a scale of 20 mmol benzyl alcohol.

crease in the number of effective collisions between reactants and catalyst. It is noteworthy that the acetylation of benzyl alcohol with acetic anhydride using a pure $ZnAl_2O_4$ sample was too slow for practical application under the optimized conditions.

The generality of this protocol was shown by utilizing various primary, secondary and tertiary alcohols, as well as diols and an allylic alcohol (Table 1). The results in Table 1 showed that all the substrates were selectively converted to the corresponding acetates in high yields without any side products. The acetylation of a wide range of ring-substituted primary benzyl alcohols having various electron-donating and electron-withdrawing groups was investigated with acetic anhydride over the ZnAl₂O₄@SiO₂ nanocomposite. These alcohols were efficiently converted to their corresponding acetates in high yields and the nature of the substituent had no significant effect on the reaction time and yields (Table 1, entries 1–13). In addition, various secondary alcohols were converted in high yields to their corresponding acetates (Table 2, entries 13-18). Cinnamyl alcohol, an α , β -unsaturated alcohol, was selectively converted to the corresponding acetate, and C=C bond remained intact under the reaction conditions (Table 1, entry 19). Also, nonbenzylic primary alcohols were selectively converted to their corresponding acetates with high efficiency at the same reaction conditions (Table 1, entries 20 and 21). A sterically hindered tertiary alcohol such as triphenylmethanol was also acetylated with high yield but it took a longer reaction time (Table 1, entry 22). In this case, no elimination product was found in the reaction mixture by GC-MS analysis. The efficiency of the catalyst can be seen clearly in the acetylation of a di-hydroxy compound under similar conditions (Table 1, entry 23). Among the various alcohols studied, secondary benzylic alcohols were the most reactive, giving the corresponding acetylated products with shorter reaction times. As we can see in Table 1, functional groups such as -OMe, -CHO, -COMe, -CN, and -NO₂ remained unchanged under the reaction conditions. Also,

Table 2

Acety	lation of amin	es with acetic anl	nydride over the	e ZnAl ₂ O ₄ @SiO ₂	nanocomposite
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Entry	Amine	Product	Time (min)	Yield ^a (%)	Entry	Amine	Product	Time (min)	Yield ^a (%)
1	NH ₂	NHAc NHAc	3	96	12	NC-NH2	NC-NHAc	5	90
2	Me NH ₂	Me-NHAc	3	94	13	NO ₂ NH ₂	NO ₂ NHAc	5	95
3	Me NH ₂	Me NHAc	3	93	14	H ₂ N-OH	AcHN-OH	6	91
4	Et-NH2	Et-NHAc	3	96	15	HS-NH ₂	HS-NHAC	3	95
5	i-Pr-NH2	i-Pr-NHAc	3	96	16	HO-NH2	HO-NHAc	4	95
6	MeO-NH ₂	MeO-NHAc	3	96	17	OH NH ₂	OH NHAC	3	96
7	Br-NH2	Br-NHAc	4	94	18	NH ₂	NHAc	7	92
8		CI-NHAc	3	95	19	NNH2	NNHAc	5	90
9		CI NHAc	6	94	20	CH ₂ NH ₂	CH ₂ NHAc	10	88
10		H NHAc	7	89	21	NH ₂	NHAc	12	85
11	Me NH ₂	Me NHAc	8	90	22	H ₂ N-NH ₂	AcHN-NHAc	8	87

Reaction conditions: amine 1 mmol, acetic anhydride 1 eqiuv. per NH₂ group, catalyst 100 mg, without solvent, room temperature. ^a Yields are for isolated pure products.

the conversion of benzyl alcohol to benzyl acetate on a 20 mmol scale proceeded just as efficiently as the 1 mmol reaction (Table 1, entry 24).

The acetylation of phenols was also investigated using the present experimental conditions. Phenol, substituted phenols with electron-donating and electron-withdrawing groups, α - and β -naphthol and also thiophenol were acetylated with high yields (80%–92%), although with longer reaction time in comparison to alcohols (Table 1, entries 25–30). The excellent activity of the ZnAl₂O₄@SiO₂ nanocomposite was demonstrated by the high yield obtained for *para*-nitrophenol that has an electron-withdrawing group (Table 1, entry 27).

The scope of this reaction was further extended to the acetylation of amines. A wide range of anilines containing various electron-donating and withdrawing groups and also primary aliphatic amines were treated with acetic anhydride at room temperature under solvent-free conditions (Table 2). In all cases, excellent yields (85%-96%) of the corresponding acetylated derivatives were obtained within 3-12 min. The excellent activity of the ZnAl₂O₄@SiO₂ nanocomposite was demonstrated by the high yields obtained for anilines that have electron-withdrawing groups (Table 2, entries 10-13). Interestingly, the acetylation of substrates containing -NH₂, -OH, and -SH groups with one equivalent of acetic anhydride produced the corresponding acetamides as sole products; the hydroxyl or thiol moiety remained untouched (Table 2, entries 14-17). This may be due to that the -NH₂ group has greater nucleophilicity than the -OH and -SH groups. The selective acetylation of a -NH₂ group in the presence of -OH and -SH groups is of considerable synthesis importance. Furthermore, 1-naphthylamine and para-aminopyridine were converted to the corresponding acetamide in high yields (Table 2, entries 18 and 19). Benzylamine, *n*-butylamine and also 1,4-phenylenediamine gave the corresponding acetamides in high yields under the present reaction conditions (Table 2, entries 20-22). As can be seen in Table 2, functional groups such as -OMe, -CHO, -COMe, -CN, and -NO2 remained unchanged under the reaction conditions. The conversion of aniline to acetanilide on a 20 mmol scale proceeded just as efficiently as the 1 mmol reaction (10 min, 95% isolated yield). In contrast to primary aromatic amines which were readily acetylated, secondary amines such as diphenylamine did not undergo any change.

The activity of the ZnAl₂O₄@SiO₂ nanocomposite as a general catalyst was tested by the acetylation of benzyl alcohol with other anhydrides under the same reaction conditions (Table 3). In comparison to acetic anhydride, the reactions with higher anhydrides took longer time at room temperature. However, the reactions were completed in 20 to 45 min under solvent-free conditions and afforded the corresponding acylated derivatives with high yields (78.5%–92%). The rate of acylation was influenced by steric and electronic factors of the anhydrides and followed the order $Ac_2O > (CF_3CO)_2O > (EtCO)_2O$ > (iPrCO)₂O > (*tert*-BuCO)₂O > (PhCO)₂O, (EtCO)₂O, (*iso*-PrCO)₂O, and (*tert*-BuCO)₂O were mainly due to the steric effect of their alkyl groups (Table 3, entries 1–4). The longer reaction time and the requirement of two equivalents of (PhCO)₂O as op-

Table 3

Protection of benzyl alcohol with various anhydrides by the $ZnAl_2O_4@$ SiO₂ nanocomposite.

	H ₂ OC(=O)R		
Entry	Anhydride	Time (min)	Yield ^b (%)
1	Ac ₂ O	20	92
2	(CF ₃ CO) ₂ O	25	88
3	(EtCO) ₂ O	25	86.5
4	(iso-PrCO)2O	32	81
5	(tert-BuCO)20	40	80
6	(PhCO)2O	45	78.5

Reaction conditions: benzyl alcohol 1 mmol, anhydride 1 mmol, catalyst 100 mg, without solvent, 75 °C.

^a Isolated yield of corresponding acylated product.

^b 2 equiv. of (PhCO)₂O used at 85 °C.

posed to one equivalent of Ac₂O were due to the combined effect of the steric and electronic factors of the phenyl group in (PhCO)₂O. The phenyl group makes the carbonyl group in (PhCO)₂O less electrophilic by a resonance effect.

The recycling of the catalyst was investigated with the acetylation of benzyl alcohol. After completion of the reaction, ethyl acetate was added and the mixture was filtered to separate off the catalyst. The recovered catalyst was dried and reused in more runs. As can be seen in Table 4, no appreciable decrease in activity of the catalyst was observed after four runs.

We were also interested in testing the nature of the recovered catalyst. Hence, we performed XRD analysis on the spent catalyst after the fourth run. As shown in Fig. 5, the recovered catalyst did not show any significant change after four cycles

Table 4

Recyclability of the ZnAl₂O₄@SiO₂ nanocomposite.

Cycle	Yield ^a (%)
0	92
1st	90
2nd	90
3rd	88
4th	88

Reaction conditions: benzyl alcohol 1 mmol, acetic anhydride 1 mmol, catalyst 100 mg, 75 °C, 20 min.

^aYields are for isolated pure benzyl acetate.



Fig. 5. XRD pattern of the recovered $ZnAl_2O_4@SiO_2$ catalyst after the fourth run.

Table 5

Comparison	of the result obtained	ed for the acetylatio	n of benzyl alcoho	ol in the present	t work with those	e obtained by some	reported heterogen	eous
catalysts.								

Entry	Heterogeneous catalyst	Conditions	Alcohol:Ac ₂ O molar ratio	Catalyst amount (g)	Time (min)	Yield (%)	Ref.
1	Mont. KSF	Solvent-free, r.t.	1:2	0.1	60	90	[18]
2	SiO ₂ -H ₂ SO ₄	CH ₂ Cl ₂ , r.t.	1:2	0.2	240	90	[23]
3	FER zeolite	Solvent-free, 75 °C	1:1.5	0.15	120	91	[24]
4	Sulphated ZrO ₂	Solvent-free, r.t.	1:1	0.05	10	93	[29]
5	(NH4)2.5H0.5PW12O40	Solvent-free, r.t.	1:1	0.5	60	92	[30]
6	Rice husk	Solvent-free, 80 °C	1:3	0.3	60	94	[37]
7	ZnAl ₂ O ₄ @SiO ₂	Solvent-free, 75 °C	1:1	0.1	20	92	this work

compared to the fresh one (Fig. 1). This indicated that the structure of the nanocomposite was stable under the reaction conditions and was not affected by the reactants. In addition, the XRD result confirmed there was no organic impurities in the recovered catalyst.

In order to show the advantage of the present method, we compared our results in the acetylation of benzyl alcohol with those of some reported heterogeneous catalysts in the literature (Table 5). From the reaction conditions, substrate/Ac₂O molar ratio, reaction time, and product yield, it can be seen that the present method is superior. The reaction over the most of other reported catalysts required longer times for completion. The other advantages of the catalyst in this work in comparison with other previously reported catalysts are its easy preparation, no moisture sensitivity, it is not explosive or expensive, and it has very low toxicity.

Similar to other heterogeneous catalytic reactions, this reaction takes place on the surface of the catalyst and small particles make a distinct contribution to its catalytic activity [20–22]. The surface atoms behave as Lewis acid centers where the chemical reaction is activated. As shown in Scheme 1, catalytic acetylation is initiated by coordination of the carbonyl group of acetic anhydride to unsaturated Al and Zn ions on the surface of the nanocomposite as Lewis acidic sites, which activates it. The activated carbonyl group reacts with the substrate, which is a reactive nucleophile, to produce the corresponding acetate.

From the mechanism, we conclude that the chemisorption of the carbonyl group of the acetylating agents on the surface of the nanocomposite catalyst is very important for the outcome



Scheme 1. Catalytic activation pathway over the $ZnAl_2O_4@SiO_2$ nano-composite.

of the reaction. Due to the high specific surface area of the $ZnAl_2O_4@SiO_2$ nanocomposite, the number of surface atoms is a larger fraction of the total, and they provide more contact area for the reactants on the catalyst. Therefore, the higher catalytic activity of the $ZnAl_2O_4@SiO_2$ nanocomposite compared to the activity of bulk- $ZnAl_2O_4$ can be attributed to more coordination of the carbonyl group to the $ZnAl_2O_4$ due to the participation of more surface Lewis acidic sites in the reaction.

4. Conclusions

A ZnAl₂O₄@SiO₂ nanocomposite was prepared by the sol-gel method, and was successfully applied as an efficient and recyclable heterogeneous catalyst for the acetylation of alcohols, phenols, and amines with acetic anhydride under solvent-free conditions. The acetylation of amines proceeded rapidly, namely, selective acetylation of a $-NH_2$ group in the presence of an -OH group was observed. The ZnAl₂O₄@SiO₂ nanocomposite was reused without loss in activity. XRD showed that the structure of the catalyst did not change after the reaction. This paper provided the first description of the acetylation of amines, alcohols and phenols with acetic anhydride over a nanocomposite catalyst.

References

- Hanson J R. Protecting Groups in Organic Synthesis. 1st Ed. Malden: Blackwell Science, 1999
- [2] Greene T W, Wuts P G M. Protective Groups in Organic Synthesis. 3rd Ed. New York: Wiley, 1999
- [3] Orita A, Tanahashi C, Kakuda A, Otera J. Angew Chem Int Ed, 2000, 39: 2877
- [4] Nakae Y, Kusaki I, Sato T. Synlett, 2001: 1584
- [5] Chandra K L, Saravanan P, Singh R K, Singh V K. Tetrahedron, 2002, 58: 1369
- [6] Dalpozzo R, De Nino A, Maiuolo L, Procopio A, Nardi M, Bartoli G, Romeo R. *Tetrahedron Lett*, 2003, 44: 5621
- [7] Chakraborti A K, Gulhane R. Tetrahedron Lett, 2003, 44: 6749
- [8] Bartoli G, Bosco M, Dalpozzo R, Marcantoni E, Massaccesi M, Rinaldi S, Sambri L. Synlett, 2003: 39
- [9] Bartoli G, Bosco M, Dalpozzo R, Marcantoni E, Massaccesi M, Sambri L. Eur J Org Chem, 2003: 4611
- [10] De S K. Tetrahedron Lett, 2004, 45: 2919
- [11] Phukan P. Tetrahedron Lett, 2004, 45: 4785
- [12] Heravi M M, Behbahani F K, Bamoharram F F. J Mol Catal A, 2006,

Graphical Abstract

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 $ZnAl_2O_4@SiO_2$ nanocomposite catalyst for the acetylation of alcohols, phenols and amines with acetic anhydride under solvent-free conditions

Saeed Farhadi*, Kosar Jahanara Lorestan University, Iran

A $ZnAl_2O_4@SiO_2$ nanocomposite fabricated by a sol-gel process was a good and recyclable catalyst for the efficient acetylation of alcohols, phenols and amines with acetic anhydride under solvent-free conditions.

253:16

- [13] Moghadam M, Tangestaninejad S, Mirkhani V, Mohamadpoor-Baltork I, Taghavi S A. *J Mol Catal A*, 2007, 274: 217
- [14] Sartori G, Ballini R, Bigi F, Bosica G, Maggi R, Righi P. *Chem Rev*, 2004, 104: 199
- [15] Sakakura A, Kawajiri K, Ohkubo T, Kosugi Y, Ishihara K. J Am Chem Soc, 2007, 129: 14775
- [16] Chakraborti A K, Gulhane R. Chem Commun, 2003, 15: 1896
- [17] Choudary B M, Bhaskar V, Kantam M L, Rao K K, Raghavan K V. Green Chem, 2000, 2: 67
- [18] Bhaskar P M, Loganathan D. Tetrahedron Lett, 1998, 39: 2215
- [19] Kantam M L, Ranganath K V S, Sateesh M, Sreedhar B, Choudary B M. J Mol Catal A, 2006, 244: 213
- [20] Sarvari M H, Sharghi H. Tetrahedron, 2005, 61: 10903
- [21] Thakuria H, Borah B M, Das G. J Mol Catal A, 2007, 274: 1
- [22] Moghaddam F M, Saeidian H. Mater Sci Eng B, 2007, 139: 265
- [23] Shirini F, Zolfigol M A, Mohammadi K. Bull Korean Chem Soc, 2004, 25: 325
- [24] Ballini R, Bosica G, Carloni S, Ciaralli L, Maggi R, Sartori G. *Tetrahedron Lett*, 1998, 39: 6049
- [25] Chavan S P, Anand R, Pasupathy K, Rao B S. Green Chem, 2001, 3: 320
- [26] Chakraborti A K, Gulhane R. Tetrahedron Lett, 2003, 44: 3521
- [27] Joseph J K, Jain S L, Sain B. J Mol Catal A, 2007, 267: 108
- [28] Das B, Thirupathi P. J Mol Catal A, 2007, 269: 12
- [29] Ratnam K J, Reddy R S, Sekhar N S, Kantam M L, Figueras F. J Mol Catal A, 2007, 276: 230
- [30] Satam J R, Jayaram R V. Catal Commun, 2008, 9: 2365
- [31] Rajabi F. Tetrahedron Lett, 2009, 50: 395
- [32] Niknam K, Saberi D. *Tetrahedron Lett*, 2009, 50: 5210
- [33] Niknam K, Saberi D. Appl Catal A, 2009, 366: 220
- [34] Ghaffari-Khaligh N. J Mol Catal A, 2012, 363-364: 90
- [35] Rahmatpour A. CR Chim, 2012, 15: 1048
- [36] Osiglio L, Sathicq A G, Romanelli G P, Blanco M N. J Mol Catal A. 2012, 359: 97
- [37] Shirini F, Akbari-Dadamahaleh S, Mohammad-Khah A, Aliakbar A R. CR Chim, 2013, 16: 207
- [38] Taghavi S A, Moghadam M, Mohammadpoor-Baltork I, Tangestaninejad S, Mirkhani V, KhosropourA R. *Inorg Chim Acta*, 2011, 377:

159

- [39] Yadegari M, Moghadam M, Tangestaninejad S, Mirkhani V, Mohammadpoor-Baltork I. *Polyhedron*, 2011, 30: 2237.
- [40] Moghadam M, Tangestaninejad S, Mirkhani V, Mohammadpoor-Baltork I, Gharaati S. CR Chim, 2011, 14: 1080
- [41] Ghorbani-Choghamarani A, Pourbahar N. Chin J Catal, 2012, 33: 1470
- [42] Pushpaletha P, Lalithambika M. Appl Clay Sci, 2011, 51: 424
- [43] Shirini F, Ghaffari-Khaligh N. Chin J Catal, 2013, 34: 695
- [44] Nowrouzi N, Alizadeh S Z. Chin J Catal, 2013, 34: 1787
- [45] Iranpoor N, Firouzabadi H, Etemadi-Davan E. Tetrahedron Lett, 2013, 54: 1813
- [46] Hajjami M, Ghorbani-Choghamarani A. Norouzi M. Chin J Catal, 2012, 33: 1661
- [47] Zareyee D, Alizadeh P, Ghandali M S, Khalilzadeh M A. Chem Papers, 2013, 67: 713
- [48] Rajabi F, Luque R. Catal Commun, 2014, 45: 129
- [49] Alam M, Rahman A, Alandis N M, Shaik M R. Arab J Chem, 2014, 7: 53
- [50] Singh S J, Kale S R, Gawande M B, Velhinho A, Jayaram R V. Catal Commun, 2014, 44: 24
- [51] Spinicci R, Faticanti M, Marini P, DeRossi S, Porta P. J Mol Catal A, 2003, 197: 147
- [52] Barbero B P, Gamboa J A, Cadus L E. Appl Catal B, 2006, 65: 21
- [53] Merino N A, Barbero B P, Ruiz P, Cadus L E. J Catal, 2006, 240: 245
- [54] Grabowska H, Zawadzki M, Syper L. Appl Catal A, 2006, 314: 226
- [55] Farhadi S, Zaidi M. J Mol Catal A, 2009, 299: 18
- [56] Farhadi S, Panahandehjoo S. Appl Catal A, 2010, 382: 293
- [57] Landau M V, Titelman L, Vradman L, Wilson P. Chem Commun, 2003: 594
- [58] Liu Y M, Cao Y, Yi N, Feng W L, Dai W L, Yan R S, He H Y, Fan K N. J Catal, 2004, 224: 417
- [59] Wang X G, Landau M V, Rotter H, Vradman L, Wolfson A, Erenberg A. J Catal, 2004, 222: 565
- [60] Cullity B D, Stock S R. Elements of X-ray Diffraction. 3rd Ed. New Jersey: Prentice-Hall, Englewood Cliffs, 2001
- [61] Duan X L, Yuan D R, Sun Z H, Sun H Q, Xu D, Lü M K. J Cryst Growth, 2003, 252: 4
- [62] Mazza D, Vallino M, Busca G. J Am Ceram Soc, 1992, 75: 1929

