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Short Communication

Solventless acetylation of alcohols and phenols catalyzed by supported iron oxide nanoparticles



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ABSTRACT

Supported iron oxide nanoparticles on silicate catalysts were found to be efficient and easily recoverable materials in the acetylation of alcohols and phenols to their corresponding acetyl compounds using acetic anhydride under mild and solvent-less conditions. The supported iron oxide nanoparticles could be easily recovered from the reaction mixture and reused ten times without any loss in activity.

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1. Introduction

Acetylation of alcohols and phenols is a frequently utilized transformation in synthetic chemistry and widely used as protecting group in multi-step pharmaceutical synthesis and food or cosmetic industries [1,2]. The acetylation of alcohols and phenols has been typically performed using acetic anhydride or acetyl chloride in the presence of either base [3-6] or acid catalysts [7-21]. Although various acetylation methods are available, most protocols to date possessed inherent drawbacks including long reaction times, harsh conditions, harmful organic solvents, and tedious work-up procedures. One of the most promising solutions to these problems seems to be immobilization of catalysts or using eco-friendly solvent-free conditions. Supported or solid catalyst can be easily separated by filtration and the catalyst can be simply recovered and recycled in the reaction, often also providing higher selectivity to products under typically simpler work-up procedures [22-24]. These premises generally work for the use of nanomaterials and supported nanoparticles as catalysts in various types of chemistries. Such nanoentities provide a remarkable versatility in their use as heterogeneous catalysts in a wide range of processes (e.g. acid, base and redox catalysis) [25–27].

Following recent research endeavors from the groups aimed to *benign by design* protocols for nanomaterials synthesis and heterogeneously catalyzed applications, this work reports the solventless

1566-7367/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.catcom.2013.11.003 acetylation of a wide range of alcohols using previously reported and characterized supported iron oxide nanoparticles on silicate materials (Fe/SBA-15). Basic characterization of the material is included in this work, readers are kindly referred to previous reports from the group for a detailed and comprehensive characterization [28–31].

2. Experimental

2.1. Synthesis of iron oxide supported nanoparticles

Supported iron oxide NPs were synthesized according to our previously reported procedure [30]. A solution of salicylaldehyde (2 mmol, 0.244 g) in an excess of absolute MeOH was added to the aminopropyl-functionalized SBA-15 materials (2.35 g, NH₂ loading 0.85 mmol g⁻¹). The solution became yellow due to imine formation. After 6 h, Fe(NO)₃·9 H₂O, (1 mmol), was added to the solution, and the mixture was gently heated at 50 °C for 24 h, until a dark red color was observed, which is due to the formation of the metal oxide nanoparticles on the SBA-15. The final product was washed with MeOH and water until the washings were colorless. Further drying of the solid product was carried out in an oven at 80 °C for 8 h. Characterization data of an analogous Fe/Al-SBA-15 material has been exclusively included for comparative purposes.

2.2. Materials characterization

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2000 volumetric adsorption analyzer from Micromeritics. The samples were outgassed for 24 h at 100 °C under vacuum ($p < 10^{-2}$ Pa) and subsequently analyzed. The linear part of the BET equation (relative

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pressure between 0.05 and 0.30) was used for the determination of the specific surface area. Mean pore size diameter (D_{BJH}) and pore volumes (V_{BIH}) were obtained from porosimetry data.

Fe content in the materials was determined using Inductively Coupled Plasma (ICP) in a Philips PU 70000 secuential spectrometer equipped with an Echelle monochromator (0.0075 nm resolution) and couple to Mass Spectrometry. Samples were digested in HNO₃ and subsequently analyzed by ICP at the SCAI of Universidad de Cordoba.

Pyridine (PY) and 2,6-dimethylpyridine (DMPY) titration experiments were conducted at 200 °C via gas phase adsorption of the basic probe molecules utilizing a pulse chromatographic titration methodology.20,21 Briefly, probe molecules (typically 1–2 mL) were injected in very small amounts (to approach conditions of gas-chromatography linearity) into a gas chromatograph through a microreactor in which the solid acid catalyst was previously placed. Basic compounds are adsorbed until complete saturation from where the peaks of the probe molecules in the gas phase are detected in the GC. The quantity of probe molecule adsorbed by the solid acid catalysts can subsequently be easily quantified. In order to distinguish between Lewis and Bronsted acidity, the assumption that all DMPY selectively titrate Bronsted sites (methyl groups hinder coordination of nitrogen atoms with Lewis acid sites) while PY titrates both Bronsted and Lewis acidity in the materials was made. Thus, the difference between the amounts of PY (total acidity) and DMPY (Bronsted acidity) adsorbed should correspond to Lewis acidity in the materials.

2.3. General procedure for the acetylation of alcohols and phenols

To a solution of substrate (1 mmol) and acetic anhydride (1.5 mmol) was added supported iron catalyst (Fe/SBA-15) (0.005 mmol, 0.085 g) and the mixture was stirred at 40 °C. After completion of the reaction (TLC), the reaction mixture was filtered and the catalyst rinsed with ethyl acetate and heated at 70 °C prior to its reuse in the next reaction. The organic layer was washed with saturated NaHCO₃ and water, and dried over anhydrous sodium sulfate. The product was obtained after removal of the solvent.

3. Results and discussion

The preparation and characterization of supported iron oxide nanoparticles on mesoporous SBA-15 have been previously reported. The Fecontaining catalyst featured similar textural and structural properties as compared to its parent silicate in terms of high surface area (650 vs. $620 \text{ m}^2 \text{ g}^{-1}$), narrow pore size within the mesoporous range (4.8 nm), a relatively high pore volume (0.7 cm³ g⁻¹) and both Lewis (mostly) and minor Bronsted acidity as measured by a gas chromatography method using pyridine (PY) and 2,6-dimethyl pyridine (DMPY) as probe molecules (Table 1) [32]. The iron content was ca. 0.62 wt.% (as measured by ICP/MS) and the hematite Fe₂O₃ phase was found to be the active phase in the material [28–30,33]. Due to such acidity, such materials as well as analogously synthesized aluminosilicates (Table 1, last entry, included as comparison) have been previously utilized as catalyst in a range of acid-catalyzed processes [33,34].

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Catalyst	$\stackrel{S_{BET}}{(m^2g^{-1})}$	Pore size (nm)	Fe content (wt.%)	Surface acidity at 300 °C (μ mol g ⁻¹)	
				PY (total acidity)	DMPY (Bronsted acidity)
SBA-15	650	4.9	-	-	-
Fe/SBA-15	620	4.8	0.62	58	12
Fe/SBA-15 (5th reuse)	598	4.6	0.60	51	9
Fe/Al-SBA-15	688	7.8	0.63	104	88

Table 2

Acetylation of various alcohols to their corresponding products using supported iron oxide
nanoparticles as catalysts.

Entry	Substrate	Product	Time (min)	Yield(%) ^a
	ŎН	QAc		
1	\bigwedge	<u> </u>	15	91
	ОН	OAc		
		\square	20	94
2	\checkmark	\checkmark		
	СІ ОН	ĊI OAc		
	, a		20	02
3			20	55
	ŎН	OAc		
		\checkmark		
4			15	90
	NO ₂	NO ₂		
	ОН	OAc		
	\square	\land	15	92
5	\checkmark	\checkmark		
	ŕ OH	É		
	Br	OAc Br	25	95
6				
	ОН	OAc		
	~	, in the second		
7			20	02
	Br) Br	20	93
	ОН	OAc		
8	\land		20	01
			20	91
	OH	OAc		
9			20	94
	\sim	$\sim \downarrow$		
10			15	93
10		AcO' 😵 'O' 'O		
	ÍÌÌ	\bigwedge		
11	HO 0 0	Aco	15	90
12	ОН	OAc		
			25	98
	OH	OAc	25	95
13	H-C	Hac	25	55
	U.			
14	OH	UAC	25	93
14	но	Aco		
	~ ~ ^	~ ~ ~	20	91
15	OH OH	OAc		
	\checkmark	\checkmark	25	90
16		~~~		
10	/он	OAC		
			20	01 ^b
17	но он	AcO ² X OAc	20	91-
		<u> </u>		
18	ностон	ACO OAC	25	94°
	OH	0/10		
19	∧ ,OH	Aco		
	HO	A00	20	93 ^b
20	~ ~	4-000		
20	но 🔨 Он	ACU - UAC	20	90 ^b
	он	OAc L		
21	\frown	\bigcap		
	\smile	\sim	30	92
22	ОН	OAc		
	cr T	S		
		• •		
23	СІ ОН	CI OAc	25	94 ^b
	OH	nuu		

^a Isolated yields. ^b 3 eq of acetic anhydride. ^c 4.5 eq of acetic anhydride.



Fig. 1. Reusability of Fe/SBA-15 catalyst in acetylation of phenol. Reaction conditions: 1 mmol phenol, 1.5 mmol acetic anhydride, supported iron catalyst (0.005 mmol, 0.085 g), 40 °C, 15 min reaction.

In this work, the acetylation of a series of alcohols including phenols, naphthols, hydroxyl-substituted chromenones and polyols (e.g. glycerol) has been conducted under mild conditions, typically 15-30 min reaction and 40 °C. Acetic anhydride was utilized as acetylating agent instead of the corrosive acetyl chloride. Table 2 summarizes the main relevant results of this work. Blank reactions (in the absence of catalyst as well as with the SBA-15 support) provided negligible conversion in the selected reaction even for the simplest substrates (e.g. phenol). Comparably, supported iron oxide nanoparticle systems were able to convert a wide range of substrates into their corresponding acetylated products. A number of relevant compounds could be produced in high yields (>90%) in a short time of reaction, typically 15–30 min. The protocol was amenable to all types of substituted phenols with electron donating and electron withdrawing groups, naphthols, benzyl alcohol and cinnamyl alcohol as well as other biomass-derived relevant molecules including glycerol, propanediol and cylohexanol (Table 2).

To test the heterogeneity of the catalytic system, the catalyst was filtered after half of reaction time for acetylation of phenol during the reaction and the filtrate was allowed to react further. We found that after filtration of the supported iron catalyst, the filtration liquor did not further react. AAS confirmed that no Fe could be detected in the solution phase upon catalyst filtration after the end of the reaction.

Reuse reactions were carried out under similar conditions. The catalyst showed excellent recoverability and reusability over 10 successive runs under the same conditions to the first run (Fig. 1). No detectable metal traces in solution (<0.5 ppm) were determined by ICP of the final reaction mixture, confirming the strong coordination and stability of iron in the catalyst that prevented metal leaching during/after the reaction, something somehow expected from the mild reaction conditions (40 °C) and short times of reaction (typically minutes).

Reaction conditions: 1 mmol substrates, 1.5 mmol acetic anhydride, supported iron catalyst (0.005 mmol, 0.085 g), 40 $^{\circ}$ C (unless otherwise stated).

Furthermore, the structural and textural stability of the materials after several reuses was also observed to be excellent according to characterization and acidity data (Table 1). These indicated the stability of Fe oxide nanoparticles as well as the preserved acidity and textural properties in the materials. Even with a milder acidity as compared to Fe/Al-SBA-15 (included as comparison), Fe/SBA-15 was able to simply promote the proposed acetylation process.

Our protocol was compared to a recent literature work [35] for the particular case of a challenging molecule such as glycerol for triacetin production. Very similar results (94% yield, 25 min reaction at 40 °C for this work vs. 100% yield after 20 min reaction at 60 °C using betazeolite or K-10 montmorillonite) were recorded for the same reaction using acetic anhydride as acetylating agent. In fact, Silva et al. showed poor triacetin yields were generally obtained when acetic acid was employed as acetylating agent, in good agreement with our findings (results not shown). With regard to phenolic-derived compounds, comparative data on Table 3 clearly demonstrates the advantages of the proposed methodology as compared to similar processes catalyzed by various materials ranging from ZnO to less environmentally friendly and not reusable bismuth, ruthenium and indium chlorides as well as magnesium perchlorate (Table 3).

4. Conclusions

Supported iron oxide nanoparticles on porous silicates have been proved to be highly active and stable catalysts for the acid-catalyzed acetylation of a series of alcohols and phenols in excellent yields to products. These included the transformation of relevant biomassderived platform chemicals (e.g. glycerol). Reactions could efficiently afford the target product at short times of reaction (typically 15–30 min) under mild reaction conditions. The catalyst was found to be highly reusable under the investigated conditions which prove the usefulness of supported transition metal oxide nanoparticle systems in heterogeneously catalyzed processes.

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References

- T.W. Green, P.C.M. Wuts, Protective Groups in Organic Synthesis, 3rd ed. Wiley, New York, 1999.
- [2] J. Otera, Esterification: Methods, Reactions and Applications, 1st ed. Wiley–VCH, 2003.
- [3] W. Steglich, G. Hofle, Angew. Chem. Int. Ed. 8 (1969) 981.
- [4] E. Vedejs, T.S. Diver, J. Am. Chem. Soc. 115 (1993) 3358.
- [5] E.F.V. Scriven, Chem. Soc. Rev. 12 (1983) 129
- [6] S. Tomohumi, O. Kousaburo, O. Takashi, Synthesis (1991) 1141.
- [7] A. Orita, C. Tanahashi, A. Kakuda, J. Otera, Angew. Chem. Int. Ed. 39 (2000) 2877.
- [8] R. Alleti, M. Perambuduru, S. Samanha, V.P. Reddy, J. Mol. Catal. A Chem. 226 (2005) 57.
- [9] B. Karimi, J. Maleki, J. Org. Chem. 68 (2003) 4951.
- [10] N. Ahmed, J.E. Van Lier, Tetrahedron Lett. 47 (2006) 5345.
- [11] R.H. Tale, R.N. Adude, Tetrahedron Lett. 47 (2006) 7263.
- T.S. Reddy, M. Narasimhulu, N. Suryakiran, K.C. Mahesh, K. Ashalatha, Y. Venkateswarlu, Tetrahedron Lett. 47 (2006) 6825.
 P. Phukan. Tetrahedron Lett. 45 (2004) 4785.
- [13] P. Phukan, Tetrahedron Lett. 45 (2004) 4785.
 [14] R. Dalpozzo, A. De Nino, L. Maiuolo, A. Procopio, M. Nardi, G. Bartoli, R. Romeo, Tetrahedron Lett. 44 (2003) 5621.

Table 3

Comparison of the activity of the present system as compared to literature reports in the acetylation of naphthalen-2-ol.

Catalyst	Compound	Time (min)	Yield	Reaction conditions	Ref.
Fe/SBA-15 ZnO	OH	20	94	1 mmol substrate, 1.5 mmol acetic anhydride, 0.005 mmol Fe (0.085 g catalyst), 40 °C No reaction with acetic anhydride	This work
RuCl ₃		600	91	1 mmol substrate, 1.2 mmol acetic anhydride, 5 mol% catalyst, RT	[37]
InCl ₃		2	95	1 mmol substrate, 1 mmol acetic anhydride, 0.1 mol% catalyst, RT	[38]
$Mg(ClO_4)_2$		20	100	1 mmol substrate, 1 mmol acetic anhydride, 1 mol% catalyst, RT	[39]

- [15] A. Kamal, M.N.A. Khan, K.S. Reddy, Y.V.V. Srikanth, T. Krishnaji, Tetrahedron Lett. 48 (2007) 3813.
- S. Velusamy, S. Borpuzari, T. Punniyamurthy, Tetrahedron Lett. 61 (2005) 2011.
 G. Bartoli, M. Bosco, R. Dalpozzo, E. Marcantoni, M. Massaccesi, L. Sambri, Eur. J. Org. Chem. (2003) 4611.
- [18] N. Ghaffari Khaligh, J. Mol. Catal. A Chem. 363-364 (2012) 90.
- [19] F. Rajabi, Tetrahedron Lett. 50 (2009) 395.
- [20] L. Osiglio, A.G. Sathicq, G.P. Romanelli, M.N. Blanco, J. Mol. Catal. A Chem. (2012) 359.
- [21] I. López, J.L. Bravo, M. Caraballo, J.L. Barneto, G. Silvero, Tetrahedron Lett. 52 (2011) 3339.
- [22] N.J. Baldwin, A.N. Nord, B.D. O'Donnell, R.S. Mohan, Tetrahedron Lett. 53 (2012) 6946
- [23] M. Stratakis, H. Garcia, Chem. Rev. 112 (2012) 4469.
- [24] J. Kobayashi, Y. Mori, K. Okamoto, R. Akiyama, M. Ueno, T. Kitamori, S. Kobayashi, Science 304 (2004) 1305.
- [25] J.E. Mondloch, E. Bayram, R.G. Finke, J. Mol. Catal. A Chem. 355 (2012) 1(and references cited therein).
- [26] V. Zielasek, B. Juergens, C. Schulz, J. Biener, M.M. Biener, A.V. Hamza, M. Baumer, Angew. Chem. Int. Ed. 45 (2006) 8241.

- [27] N.T.S. Phan, C.S. Gill, J.V. Nguyen, Z.J. Zhang, C.W. Jones, Angew. Chem. Int. Ed. 45 (2006) 2209.
- [28] F. Rajabi, A. Pineda, S. Naserian, A.M. Balu, R. Luque, A.A. Romero, Green Chem. 15 (2013) 1232.
- [29] F. Rajabi, N. Karimi, M.R. Saidi, A. Primo, R. Luque, Adv. Synth. Catal. 354 (2012) 1707.
- [30] F. Rajabi, S. Naserian, A. Primo, R. Luque, Adv. Synth. Catal. 353 (2011) 2060.
- [31] F. Rajabi, T. Kakeshpour, M.R. Saidi, Catal. Commun. 40 (2013) 13.
- [32] J.M. Campelo, D. Luna, R. Luque, J.M. Marinas, A.A. Romero, J.J. Calvino, M.P. Rodriguez-Luque, J. Catal. 230 (2005) 327.
- [33] A. Pineda, A.M. Balu, J.M. Campelo, A.A. Romero, D. Carmona, F. Balas, J. Santamaria, R. Luque, ChemSusChem 4 (2011) 1561.
- [34] A.M. Balu, A. Pineda, D. Obermayer, A.A. Romero, C.O. Kappe, R. Luque, RSC Adv. (2013), http://dx.doi.org/10.1039/C3RA43160F.
- [35] L.N. Silva, V.I. Goncalves, C.J.A. Mota, Catal. Commun. 11 (2010) 1036.
 [36] M.H. Sarvari, H. Sharghi, Tetrahedron 61 (2005) 10903.
- [37] S.K. De, Tetrahedron Lett. 45 (2004) 2919-2922.
- [38] A.K. Chakraborti, R. Gulhane, Tetrahedron Lett. 44 (2003) 6749.
- [39] A.K. Chakraborti, L. Sharma, R. Gulhane, Shivani, Tetrahedron 59 (2003) 7661.