J IRAN CHEM SOC
DOI 10.1007/s13738-013-0306-5

ORIGINAL PAPER

Nanocrystalline sulfated zirconia as an efficient solid acid catalyst for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones

Mohammad Abdollahi-Alibeik · Elahe Shabani

Received: 15 July 2012 / Accepted: 25 June 2013

Abstract The condensation reaction of 2-aminobenzamide and aldehydes or ketones was investigated in the presence of nanocrystalline sulfated zirconia (SO_4^{2-}/ZrO_2) as solid acid catalyst. SO_4^{2-}/ZrO_2 nanoparticles with different calcination temperatures were prepared and characterized by XRD, FT-IR and SEM techniques. The results confirm good stabilization of tetragonal phase of zirconia in the presence of sulfate. The reusability experiments show partial deactivation of the catalyst due to leaching of the sulfate and coke deposition on the catalyst.

Keywords Sulfated zirconia · Nanoparticles · Solid acid · Catalyst · 2,3-Dihydroquinazolin-4(1H)-one

Introduction

In recent years, there has been an ongoing effort to replace conventional acid catalysts with solid acid catalyst systems in many organic transformations because of environmental and economical reasons such as non-toxicity, non-corrosiveness, ease of handling, greater selectivity, simple workup and reusability of the catalyst [1]. Among the various solid acid catalysts, sulfated zirconia has received considerable attention due to its superacidity [2, 3]. However, the catalytic features of sulfated zirconia are strongly influenced by the method of preparation [3–5] crystalline phase of zirconia [6], sulfur species [7, 8], calcination temperature [9] textural properties [10] and also it can be deactivated rapidly due to coke deposition [11–13]. Much research has been devoted to modification of the method of preparation of the sulfated zirconia to improve its catalytic activity and resistance to deactivation.

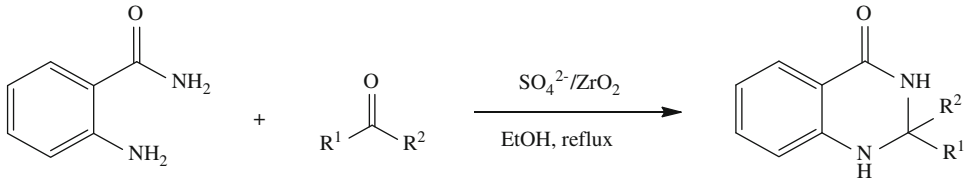
Due to its strongly acidic nature, sulfated zirconia finds application in many industrially important reactions such as hydrocarbon isomerization, alkylation, and esterification [4]. This catalyst has also been used as catalyst in many organic transformations, such as synthesis of 1,5-benzodiazepine, Friedel–Crafts acylation [14], Fries rearrangement [15], transesterification of triglycerides [11], dehydration of ethanol [16] and synthesis of hydroxycoumarins [17].

2,3-dihydroquinazolin-4(1H)-ones are an important class of heterocycles with wide range of biological activities including antibacterial [18], antifungal [19], anticancer [20] and anticonvulsant [20] activities. A number of synthetic methods have been described for the synthesis of these compounds in the past few years. Among them, the common synthetic method includes condensation of aldehydes with 2-aminobenzamide in the presence of acidic catalysts, such as zirconium (IV) chloride [21], NH_4Cl [22], $TiCl_4$-Zn [23] and $CuCl_2$ [24]. However, many of these methods suffer from limitations, such as tedious process, long reaction time and low yields of the products. Therefore, the development of simpler, environmentally benign and clean method for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones is in demand. In continuation of our studies on the application of solid-supported reagents in organic transformations [25–30], in this research, we report a green protocol for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones by the reaction of 2-aminobenzamide and aldehydes or ketones in the presence of sulfated zirconia nanoparticles as reusable solid acid catalyst Scheme 1.

M. Abdollahi-Alibeik (✉) · E. Shabani
Department of Chemistry, Yazd University,
89195-741 Yazd, Iran
e-mail: abdollahi@yazduni.ac.ir

Published online: 05 July 2013

Scheme 1 Synthesis of 2,3-dihydroquinazolin-4(1H)-ones by the reaction of 2-aminobenzamide and aldehydes or ketones in the presence of sulfated zirconia nanoparticles



R^1, R^2 = H, Alkyl, Aryl

Experimental

Materials and methods

All chemicals were commercial products. All reactions were monitored by TLC and all yields refer to isolated products. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Bruker (DRX-500 AVANCE) 500 MHz spectrometer. Infrared spectra of the catalysts and reaction products were recorded on a Bruker FT-IR Equinax-55 spectrophotometer in KBr with absorption in cm^{-1}. XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer using nickel filtered Cu Kα radiation. The morphology of nanoparticles was studied using a Philips XL30 scanning electron microscopy.

Preparation of sulfated zirconia (SZ)

To a solution of $ZrCl_4$ (5.6 g, 24 mmol) in deionized water (200 mL), dilute aqueous ammonia was added dropwise with vigorous stirring until the pH of the solution reached to 9.5. The mixture was stirred for 24 h, filtered, washed with deionized water and dried at 120 °C for 24 h. The uncalcined hydroxide gel was sulfated by adding a measured volume of 1 M H_2SO_4 solution, so as to reach the equivalence of 15 mL of H_2SO_4 per gram of $Zr(OH)_4$ gel. This process was performed under stirring and maintained for 24 h, subsequently dried at 120 °C for 12 h and calcined at 600 °C for 4 h.

Typical procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)ones

To a solution of 2-aminobenzamide (1 mmol) and aldehyde (1 mmol) in EtOH (3 mL), a catalytic amount of SZ (40 mg) was added and the suspension was stirred under reflux condition for appropriate period of time. After completion of the reaction as indicated by TLC (eluent; EtOAc:*n*-hexane, 1:1), EtOH (5 mL) was added and the solid catalyst was separated by centrifuge. To the obtained solution, water (9 mL) was added and precipitated product was filtered. The crude products were obtained with high purity. Further purification was achieved by recrystallization in EtOH/H_2O.

Physical and spectroscopic data for selected compound

2,3-Dihydro-2-phenylquinazolin-4(1H)-one (Table 3, entry 1)

Yield: 93 %, white solid, mp 225–227 °C; FT-IR: υ_{max} (neat) = 3,303 (NH), 3,176 (NH) and 1,651 (C = O) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 5.76 (s, 1H H2 quinazolinone), 6.68 (t, J = 7.5 Hz, 1H, H6 quinazolinone), 6.76 (d, J = 8.1 Hz, 1H, H8 quinazolinone), 7.10 (brs, 1H, NH), 7.25 (t, J = 7.3, 1H, H7 quinazolinone), 7.33–7.41 (m, 3H, ArH), 7.50 (d, 2H, J = 7.4 Hz, ArH), 7.62 (d, J = 7.8 Hz, 1H, H5 quinazolinone), 8.28 (brs, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 67.43, 115.26, 115.83, 117.97, 127.72, 128.21, 129.18, 129.31, 134.16, 142.51, 148.73, 164.45.

2,3–Dihydro-2-(4-methoxyphenyl)quinazolin-4(1H)-one (Table 3, entry 3)

Yield: 87 %, white solid, mp 193–194 °C; FT-IR: υ_{max} (neat) = 3,297 (NH), 3,176 (NH) and 1,651 (C = O) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-*d6*): δ (ppm) = 3.75 (s, 3H), 5.71 (s, 1H, H2 quinazolinone), 6.68 (t, J = 7.6 Hz, 1H, H6 quinazolinone), 6.75 (d, J = 8.1 Hz, 1H, H8 quinazolinone), 6.95 (d, J = 8.6 Hz, 2H, ArH), 7.00 (brs, 1H, NH), 7.24 (t, J = 7.6 Hz, 1H, H7 quinazolinone), 7.42 (d, J = 8.6 Hz, 2H, ArH), 7.62 (d, J = 7.7 Hz, 1H, H5 quinazolinone), 8.17 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 67.17, 114.51, 115.28, 115.88, 117.95, 128.21, 129.07, 134.09, 134.35, 148.88, 160.30, 164.55.

2,3–Dihydro-2-(3,4-dimethoxyphenyl)quinazolin-4(1H)-one (Table 3, entry 4)

Yield: 96 %, white solid, mp 218–220 °C; FT-IR: υ_{max} (neat) = 3,356 (NH), 3,181 (NH) and 1,656 (C = O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 3.75 (s, 3H, MeO), 3.76 (s, 1H, MeO), 5.71 (s, 1H, H2 quinazolinone), 6.67 (t, J = 8.0 Hz, 1H, H6 quinazolinone), 6.77 (d, J = 8.0 Hz, 1H, H8 quinazolinone), 6.94–7.03 (m, 2H,), 7.04 (s, 1H, NH), 7.15 (d, J = 2.0 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H, H7 quinazolinone), 7.63 (d, J = 7.6 Hz, 1H, H5 quinazolinone), 8.22 (s, 1H, NH); ^{13}C NMR

(100 MHz, DMSO-d_6): δ (ppm) = 55.40, 55.51, 66.52, 110.52, 111.16, 117.12, 119.19, 127.31, 133.22, 133.49, 148.05, 148.53, 148.94, 163.74.

2,3–Dihydro-2-(2-chlorophenyl)quinazolin-4(1H)-one (Table 3, entry 5)

Yield: 91 %, white solid, mp 215–216 °C; FT-IR: υ_{max} (neat) = 3,362 (NH), 3,194 (NH) and 1,645 (C = O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 6.15 (s, 1H, H2 quinazolinone), 6.72 (t, J = 7.6 Hz, 1H, H6 quinazolinone), 6.77 (d, J = 8.0 Hz, 1H, H8 quinazolinone), 7.04 (s, 1H, NH), 7.27 (t, J = 7.6 Hz, 1H, H7 quinazolinone), 7.39–7.43 (m, 2H, ArH), 7.49–7.52 (m, 1H, ArH), 7.65–7.69 (m, 2H, H5 quinazolinone, ArH), 8.22 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 63.64, 114.53, 114.63, 127.34, 127.44, 128.72, 129.55, 130.28, 131.81, 133.42, 137.81, 147.62, 163.61.

2,3–Dihydro-2-(3-bromophenyl)quinazolin-4(1H)-one (Table 3, entry 7)

Yield: 90 %, white solid, mp 225–228 °C; FT-IR: υ_{max} (neat) = 3,289 (NH), 3,198 (NH) and 1,647 (C = O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 5.78 (s, 1H, H2 quinazolinone), 6.69 (t, J = 7.6 Hz, 1H, H6 quinazolinone), 6.76 (d, J = 8.0 Hz, 1H, H8 quinazolinone), 7.23 (s, 1H, NH), 7.26 (t, J = 7.2 Hz, 1H, H7 quinazolinone), 7.36 (t, J = 8.0 Hz, 1H, ArH), 7.49 (d, J = 8.0 Hz 1H, ArH), 7.54 (d, J = 8.0 Hz, 2H, ArH), 7.61 (d, J = 7.6 Hz, 1H, H5 quinazolinone), 7.68 (s, 1H, ArH), 8.42 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 65.45, 114.43, 114.83, 117.29, 121.55, 125.76, 127.33, 129.62, 130.57, 131.14, 133.45, 144.57, 147.46, 163.38.

2,3–Dihydro-2-(4-bromophenyl)quinazolin-4(1H)-one (Table 3, entry 8)

Yield: 94 %, white solid, mp 200–202 °C; FT-IR: υ_{max} (neat) = 3,309 (NH), 3,189 (NH) and 1,655 (C = O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 5.76 (s, 1H, H2 quinazolinone), 6.69 (t, J = 7.6 Hz, 1H, H6 quinazolinone), 6.75 (d, J = 8.0 Hz, 1H, H8 quinazolinone), 7.17 (s, 1H, NH), 7.26 (t, J = 7.6 Hz, 1H, H7 quinazolinone), 7.45 (d, J = 8.4 Hz, 2H, ArH), 7.59–7.62 (m, 3H, ArH, H5 quinazolinone), 8.37 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 65.74, 114.42, 114.89, 117.25, 121.54, 127.33, 128.64, 129.06, 129.79, 131.20, 131.61, 133.38, 141.04, 147.60, 163.45.

2,3–Dihydro-2-(4-fluorophenyl)quinazolin-4(1H)-one (Table 3, entry 9)

Yield: 92 %, white solid, mp 207–209 °C; FT-IR: υ_{max} (neat) = 3,300 (NH), 3,182 (NH) and 1,653 (C = O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 5.79 (s, 1H, H2 quinazolinone), 6.69 (t, J = 7.6 Hz, 1H, H6 quinazolinone), 6.76 (d, J = 8.0 Hz, 1H, H8 quinazolinone), 7.13 (s, 1H, NH), 7.22–7.28 (m, 3H, ArH, H7 quinazolinone), 7.53–7.57 (m, 2H, ArH), 7.62 (d, J = 7.6 Hz, 1H, H8 quinazolinone), 8.33 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 65.88, 114.40, 114,90, 114,96, 115.18, 117.22, 127.33, 128.98, 129.06, 133.34, 137.71, 137.74, 147.78, 160.86, 163.28, 163.54.

2,3–Dihydro-2-(4-hydroxyphenyl)quinazolin-4(1H)-one (Table 3, entry 10)

Yield: 85 %, white solid, mp 213–216 °C; FT-IR: υ_{max} (neat) = 3,338 (NH), 3,189 (NH) and 1,632 (C = O) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 5.66 (s, 1H H2 quinazolinone), 6.67 (t, J = 7.4 Hz, 1H, H6 quinazolinone), 6.74 (d, 1H, J = 8.1 Hz, 1H, H8 quinazolinone), 6.77 (d, J = 8.4 Hz, 2H, ArH), 6.93 (brs, 1H, NH), 7.24 (t, J = 7.2 Hz, 1H, H7 quinazolinone), 7.31 (d, J = 8.3 Hz, 2H, ArH), 7.61 (d, J = 7.5 Hz, 1H, H5 quinazolinone), 8.08 (brs, 1H, NH), 9.49 (s, 1H, OH); ^{13}C NMR (125 MHz, DMSO-d_6) : δ (ppm) = 67.52, 115.24, 115.80, 115.82, 117.89, 128.21, 129.14, 132.48, 134.05, 149.01, 158.55, 164.61.

2,3–Dihydro-2-(3,4-dihydroxyphenyl)quinazolin-4(1H)-one (Table 3, entry 15)

Yield: 85 %, white solid, mp 212–214 °C; FT-IR: υ_{max} (neat) = 3,350 (NH), 3,315 (NH) and 1,636 (C = O) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 5.57 (s, 1H H2 quinazolinone), 6.66 (t, J = 8.0 Hz, 1H, H6 quinazolinone), 6.70–6.75 (m, 3H, H8 quinazolinone, ArH), 6.92 (s, 1H, ArH), 6.93 (brs, 1H, NH), 7.23 (t, J = 8.0 Hz, 1H, H7 quinazolinone), 7.60 (d, J = 8.0 Hz, 1H, H5 quinazolinone), 8.08 (brs, 1 H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 66.68, 114.21, 114.27, 114.82, 114.97, 116.86, 118.00, 127.28, 132.24, 133.13, 145.10, 145.63, 148.05, 163.61; Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N 10.93. Found: C, 65.39; H, 4.84; N 10.59.

2,3-Dihydro-2-spirocyclopentylquinazolin-4(1H)-one (Table 3, entry 17)

Yield: 81 %, white solid, mp 256–258 °C; FT-IR: υ_{max} (neat) = 3,286 (NH), 3,161 (NH) and 1,643 (C = O)

cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) = 1.65–1.67 (m, 4H), 1.74–1.81 (m, 4H), 6.62 (t, J = 7.7 Hz, 1H, H6 quinazolinone), 6.69 (d, J = 8.0 Hz, 1H, H8 quinazolinone), 6.73 (brs, 1H, NH), 7.20 (t, J = 7.6 Hz, 1H, H7 quinazolinone), 7.56 (d, J = 7.7 Hz, 1H, H5 quinazolinone), 8.07 (brs, 1 H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 22.85, 40.16, 77.94, 115.21, 115.46, 117.41, 128.11, 133.87, 148.39, 164.31.

Results and discussion

The catalyst preparation

The general method for the synthesis of ZrO_2 is hydrolysis of zirconium salts or organo zirconium compound by sol–gel method and then calcination of obtained hydrous zirconia ($Zr(OH)_4$) in various temperatures. This method is advantageous due to its ease in controlling the homogeneity and size of particles to form nano materials. The sol–gel technique for the preparation of sulfated zirconia can proceed by the two-step process. In general, this process involves the formation of a sol by the hydrolysis of the zirconium alkoxide as zirconia precursor and a three-dimensional network gel of zirconium hydroxide after condensation in the first step. This is followed by the sulfation with sulfuric acid or ammonium sulfate in the second step for the preparation of sulfated zirconia [3, 31].

In the present study, $ZrCl_4$ was used as precursor of zirconia. The hydrolysis of $ZrCl_4$ was carried out in aqueous media with pH adjusting up to 9.5 by addition of ammonium hydroxide. The sulfated zirconia was prepared by sulfation of dried $Zr(OH)_4$ using 1 M H_2SO_4 (15 mL/g) and then calcinations of dried solid at 600 °C for 4 h.

The catalyst characterization

The particle morphology of the prepared SZ was studied by scanning electron microscopy (Fig. 1). The SEM image shows the agglomerated ZrO_2 nanoparticles with the size range of <100 nm.

The presence of sulfate in the structure of the catalyst was studied by FT-IR spectroscopy. The FT-IR spectra of ZrO_2 and SZ are shown in Fig. 2. The FT-IR spectrum of the SZ shows the characteristic peaks of sulfate at 1,244, 1,136, 1,082 and 1,043 cm^{-1}, which are attributed to asymmetric and symmetric stretching frequencies of partially ionized double bond SO and single bond SO, due to the presence of inorganic chelating bidentate sulfate group on the ZrO_2 [32].

It is well known from the literature that tetragonal phase of zirconia is more active in catalysis [33]. A strong influence on the phase modification from more stable

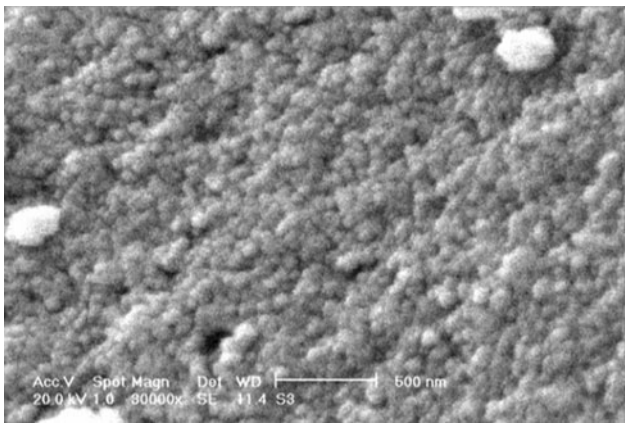


Fig. 1 SEM image of ZrO_2

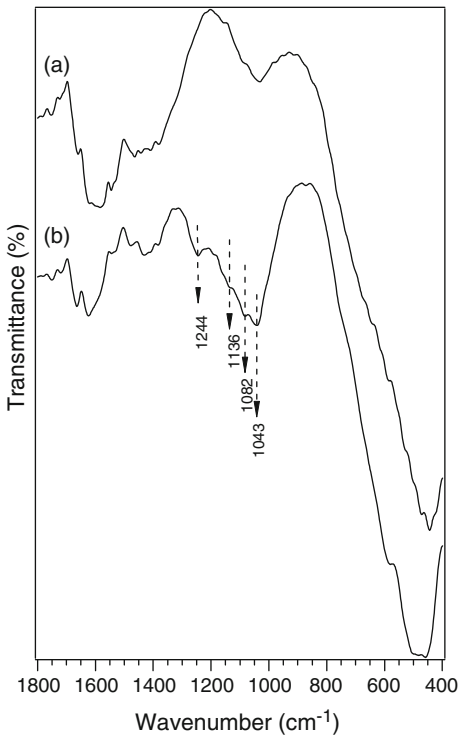


Fig. 2 FT-IR spectra of **a** ZrO_2 and **b** SZ

monoclinic to the metastable tetragonal can be observed by surface modification of zirconia [3].

Powder X-ray diffraction technique was used to elucidate the crystalline phase and effect of sulfate on the phase change of zirconia (Fig. 3). XRD pattern of ZrO_2 exhibited the characteristic peaks of both tetragonal and monoclinic phases (Fig. 3a), while the SZ shows only characteristic peaks of tetragonal phase at 2θ = 30°, 35°, 50°, 60°. This indicates that sulfate has effect on the phase modification and makes zirconia stable in the tetragonal phase.

The catalyst acidity characters of SZ, including the acidic strength and the total number of acid sites, were

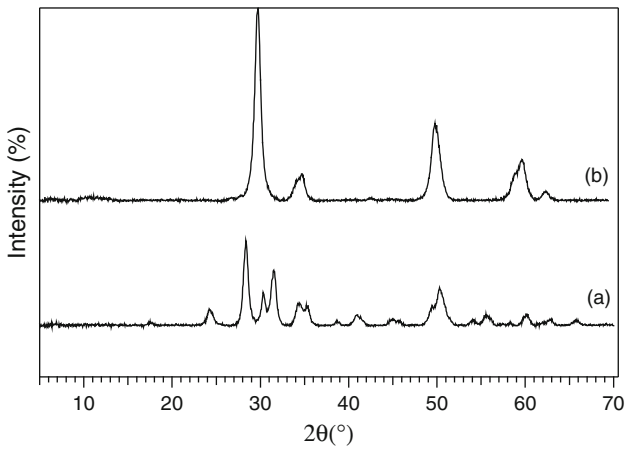


Fig. 3 XRD patterns of **a** pure ZrO_2 calcined at 600 °C and **b** SZ calcined at 600 °C

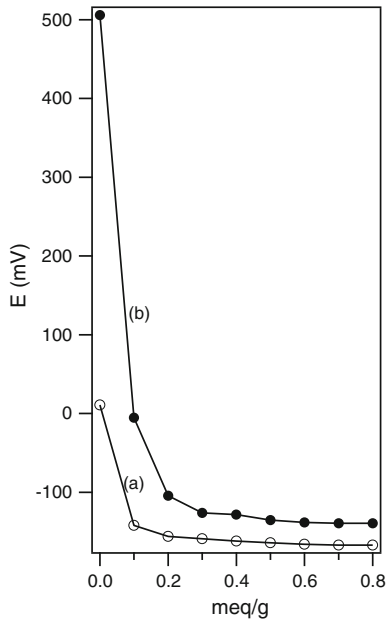


Fig. 4 Potentiometric titration curves of ZrO_2 (*filled circle*) and SZ (*open circle*)

determined by potentiometric titration. According to this method, the initial electrode potential (E_i) indicates the maximum acid strength of the surface sites and the range where a plateau is reached (meq/g solid) indicates the total number of acid sites [34]. Therefore, a suspension of the catalyst in acetonitrile was potentiometrically titrated with a solution of 0.02 N *n*-butylamine in acetonitrile. As shown in Fig. 4, very low initial potential shows that ZrO_2 is very weak acid relative to SZ. The pattern 4a also shows that the initial potential of 11 mV reaches to a value of −142 mV for 0.1 meq/g, while in the pattern of 4b initial potential of 492 mV reaches to a value of −142 mV for 0.4 meq/g. This confirms the presence of higher number of acid sites on the SZ.

Catalytic activity of sulfated zirconia nanoparticles in the synthesis of quinazolines

The catalytic performance of sulfated zirconia nanoparticles was investigated in the reaction of various types of aldehydes and ketones with 2-aminobenzamide for the synthesis of quinazolines.

Initially, the optimization experiments were performed in the reaction of benzaldehyde (1 mmol) and 2-aminobenzamide (1 mmol) in EtOH under reflux condition as the model reaction and the results are shown in Table 1.

To optimize the amount of the catalyst, the model reaction was performed with various amounts of the catalyst and in terms of time and the yield of the product; 40 mg of the catalyst for the reaction of 1 mmol 2-aminobenzamide in the model reaction was selected as the best amount (Table 1, entries 1–5).

To investigate the effect of sulfate on the catalytic activity of the sulfated zirconia, the model reaction in the presence of 40 mg ZrO_2 was carried out and results showed only 10 % yield of the product (Table 1, entry 6).

To investigate the effect of the solvent on the catalytic reaction, the model reaction in the presence of 40 mg SZ was carried out in various solvents in the same reaction times (Table 2). The results show that the reaction is faster in EtOH and 100 % conversion was achieved in EtOH in less time (Table 2, entry 1).

Table 1 Optimization of the catalyst for the synthesis of quinazolines in the presence of catalytic amount of sulfated zirconia nanoparticles in EtOH under reflux condition

Entry	Catalyst	Catalyst amount (mg)	Time (min)	Yield[a] (%)
1	SZ	20	30	91
2	SZ	40	22	93
3	SZ	60	15	93
4	SZ	80	13	95
5	SZ	100	11	93
6	ZrO_2	40	22	5

[a] Isolated yield

Table 2 Effect of solvent on the reaction rate of 2-aminobenzamide and benzaldehyde in the presence of 40 mg sulfated zirconia nanoparticles under reflux condition

Entry	Solvent	Time (min)	Conversion (%)
1	EtOH	22	100
2	CH_3OH	22	90
3	CH_3CN	22	50
4	EtOAc	22	20
5	$CHCl_3$	22	10

Table 3 Synthesis of 2-substituted 2,3-dihydroquinazoline-4(1H)-ones by the reaction of 2-aminobenzamide and aldehydes or ketones in the presence of 40 mg SZ in EtOH under reflux condition

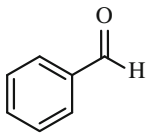
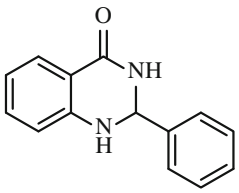
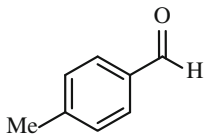
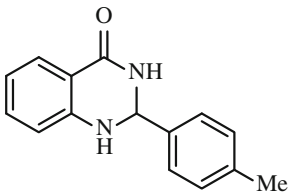
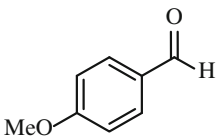
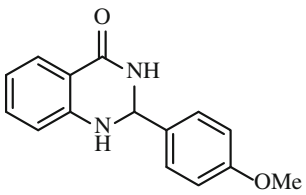
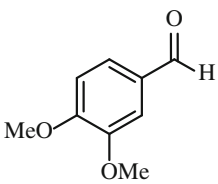
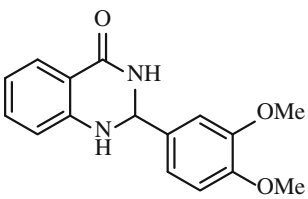
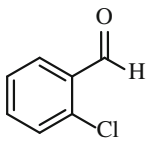
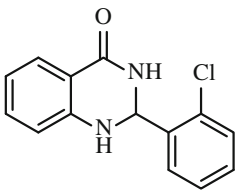
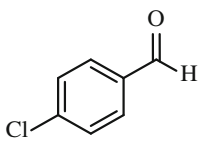
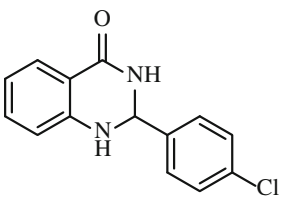
Entry	Aldehydes or ketones	Products	Time (min)	Yield[a] (%)	Mp (°C)	
					Found	Reported
1			22	93	225–227	216–218 [22]
2			13	93	231–232	233–234 [35]
3			7	87	193–194	193–195 [22]
4			17	96	213–214	212–214 [36]
5			20	91	207–209	208–210 [37]
6			30	96	202–205	205–206 [35]

Table 3 continued

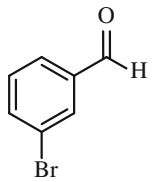
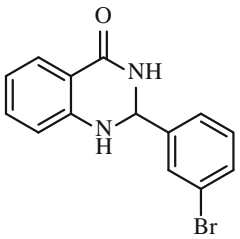
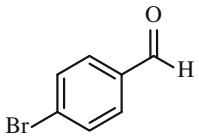
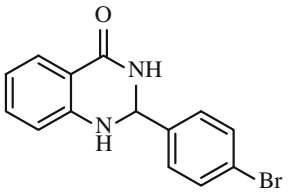
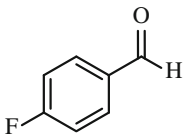
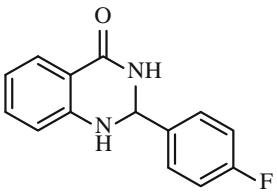
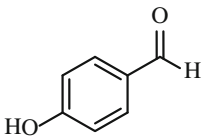
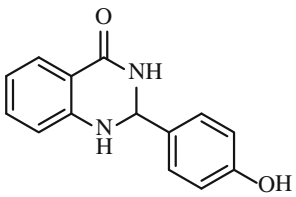
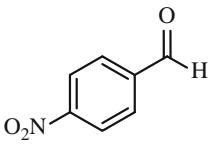
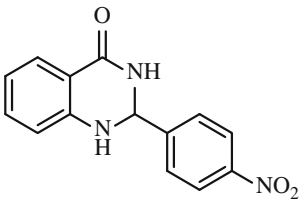
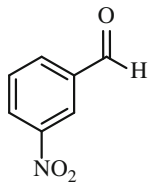
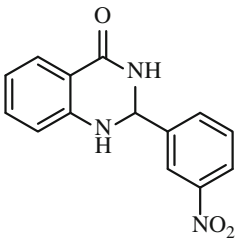
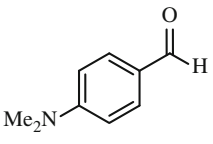
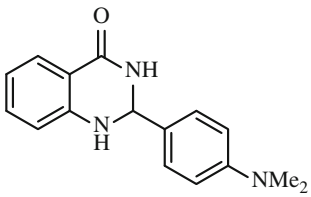
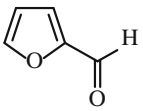
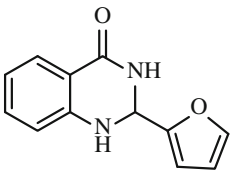
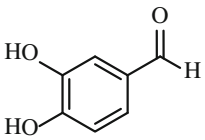
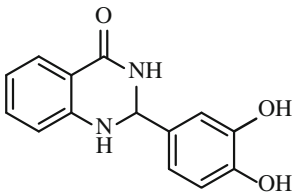
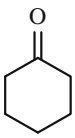
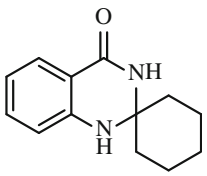
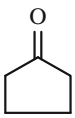
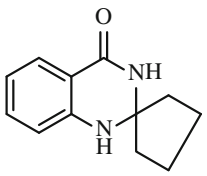
Entry	Aldehydes or ketones	Products	Time (min)	Yield[a] (%)	Mp (°C)	
					Found	Reported
7			18	90	228–230	229–230 [38]
8			35	94	198–200	197–199 [36]
9			15	92	200–201	199–200 [36]
10			20	85	213–216	278–280 [35]
11			70	90	202–205	213–214 [35]
12			160	84	200–203	216–217 [35]

Table 3 continued

Entry	Aldehydes or ketones	Products	Time (min)	Yield[a] (%)	Mp (°C)	
					Found	Reported
13			50	85	209–212	228–229 [35]
14			8	81	161–163	165–167 [39]
15			35	84	212–214	–
16			3	80	228–230	224–225 [23]
17			5	81	256–258	257–260 [22]

[a] Isolated yields

Table 4 Reusability of sulfated zirconia in the reaction of benzaldehyde and 2-aminobenzamide

Run	Time (min)[a]
1	22
2	240
3	180[b]

[a] Time for 100 % conversion

[b] The catalyst used after calcination

The scope and generality of this catalytic reaction are illustrated with respect to the reaction of different aldehydes and ketones with 2-aminobenzamide and the results are summarized in Table 3.

As shown in Table 3, the reaction of benzaldehyde with 2-aminobenzamide was carried out in the presence of 40 mg sulfated zirconia in EtOH at reflux condition and the corresponding quinazoline was obtained in 93 % yield. The reaction of various types of aldehydes with both electron donating and electron withdrawing substituents was carried out in the same reaction conditions and the corresponding quinazolines were obtained in high yields (Table 3, entries 1–15). The reaction of cyclic ketones was also carried out in the same reaction conditions and the corresponding quinazolines with spiro structure were obtained in good yields (Table 3, entries 16–17).

To study the reusability of the sulfated zirconia, the recovered catalyst from the model reaction was washed with EtOH and dried in an oven at 120 °C for 2 h. The

recovered catalyst was reused in the same reaction (Table 4, run 2). The results show that the catalyst decreased its activity after first run in comparison to the fresh catalyst. This result suggests that deactivation is due to leaching of the sulfate or the blockage of active site of the catalyst during the reaction. To clean the surface of the deactivated catalyst, the recovered catalyst after second run was calcined at 600 °C for 2 h. The catalyst was then applied in the same reaction (Table 4, run 3) and the result shows that the catalytic activity was increased. However, the activity of cleaned catalyst is not the same as fresh catalyst. This result suggests that deactivation is due to both leaching and coke deposition on the surface of the catalyst.

Conclusion

In summary, we have demonstrated that sulfated zirconia nanoparticles can be used as an efficient catalyst for the synthesis of quinazolines by the reaction of aldehydes and ketones with 2-aminobenzamide. The simple experimental procedure, high yields of the products and ease of catalyst recovery are some other advantages of this method.

Acknowledgments We are thankful to the Yazd University Research Council for partial support of this work.

References

1. A. Corma, Chem. Rev. **95**, 559 (1995)
2. K. Arata, M. Hino, Mater. Chem. Phys. **26**, 213 (1990)
3. B.M. Reddy, M.K. Patil, Chem. Rev. **109**, 2185 (2009)
4. S. Garg, K. Soni, G.M. Kumaran, R. Bal, K. Gora-Marek, J.K. Gupta, L.D. Sharma, G.M. Dhar, Catal. Today **141**, 125 (2009)
5. R. Akkari, A. Ghorbel, N. Essayem, F. Figueras, Appl. Catal. A **328**, 43 (2007)
6. C.R. Vera, C.L. Pieck, K. Shimizu, J.M. Parera, Appl. Catal. A Gen **230**, 137 (2002)
7. E. Escalona Platero, M. Peñarroya Mentruit, C. Otero Areán, A. Zecchina, J. Catal. **162**, 268 (1996)
8. R. Barthos, F. Lónyi, J. Engelhardt, J. Valyon, Top. Catal. **10**, 79 (2000)
9. G. Resofszki, M. Muhler, S. Sprenger, U. Wild, Z. Paál, Appl. Catal. A Gen **240**, 71 (2003)
10. R. Akkari, A. Ghorbel, Stud. Surf. Sci. Catal. (2002)
11. K. Suwannakarn, E. Lotero, J.G. Goodwin Jr., C. Lu, J. Catal. **255**, 279 (2008)
12. G.D. Yadav, J.J. Nair, Microporous Mesoporous Mater. **33**, 1 (1999)
13. X. Song, A. Sayari, Catal. Rev. Sci. Eng **38**, 329 (1996)
14. G.D. Yadav, A.A. Pujari, Green Chem. **1**, 69 (1999)
15. J.H. Clark, M.G. Dekamin, F. Matloubi Moghaddam, Green Chem. **4**, 366 (2002)
16. A.I. Ahmed, S.A. El-Hakam, S.E. Samra, A.A. El-Khouly, A.S. Khder, Colloids Surf. A **317**, 62 (2008)
17. J.C. Rodríguez-Domínguez, G. Kirsch, Tetrahedron Lett. **47**, 3279 (2006)
18. P.-P. Kung, M.D. Casper, K.L. Cook, L. Wilson-Lingardo, L.M. Risen, T.A. Vickers, R. Ranken, L.B. Blyn, J.R. Wyatt, P.D. Cook, D.J. Ecker, J. Med. Chem. **42**, 4705 (1999)
19. A. Dandia, R. Singh, P. Sarawgi, J. Fluorine Chem. **126**, 307 (2005)
20. Y. Xia, Z.-Y. Yang, M.-J. Hour, S.-C. Kuo, P. Xia, K.F. Bastow, Y. Nakanishi, P. Nampoothiri, T. Hackl, E. Hamel, K.-H. Lee, Bioorg. Med. Chem. Lett. **11**, 1193 (2001)
21. M. Abdollahi-Alibeik, E. Shabani, Chin. Chem. Lett. **22**, 1163 (2011)
22. A. Shaabani, A. Maleki, H. Mofakham, Synth. Commun. **38**, 3751 (2008)
23. D. Shi, L. Rong, J. Wang, Q. Zhuang, X. Wang, H. Hu, Tetrahedron Lett. **44**, 3199 (2003)
24. R.J. Abdel-Jalil, W. Voelter, M. Saeed, Tetrahedron Lett. **45**, 3475 (2004)
25. M. Abdollahi-Alibeik, I. Mohammadpoor-Baltork, Z. Zaghaghi, B.H. Yousefi, Catal. Commun. **9**, 2496 (2008)
26. M. Abdollahi-Alibeik, S. Poorirani, Phosphorus, Sulfur Silicon Relat. Elem. **184**, 3182 (2009)
27. M. Abdollahi-Alibeik, M. Moosavifard, Synth. Commun. **40**, 2686 (2010)
28. M. Abdollahi-Alibeik, M. Pouriayevali, React. Kinet Mech. Catal **104**, 235 (2011)
29. M. Abdollahi-Alibeik, E. Heidari-Torkabad, C. R. Chim. **15**, 517 (2012)
30. M. Abdollahi-Alibeik, M. Pouriayevali, Catal. Commun. **22**, 13 (2012)
31. M.K. Mishra, B. Tyagi, R.V. Jasra, J. Mol. Catal. A: Chem. **223**, 61 (2004)
32. B. Tyagi, M.K. Mishra, R.V. Jasra, J. Mol. Catal. A: Chem. **276**, 47 (2007)
33. T. Yamaguchi, Catal. Today **20**, 199 (1994)
34. L.R. Pizzio, P.G. Vázquez, C.V. Cáceres, M.N. Blanco, Appl. Catal. A Gen **256**, 125 (2003)
35. J. Chen, D. Wu, F. He, M. Liu, H. Wu, J. Ding, W. Su, Tetrahedron Lett. **49**, 3814 (2008)
36. A. Rostami, A. Tavakoli, Chin. Chem. Lett. **22**, 1317 (2011)
37. M. Wang, T. Zhang, Y. Liang, J. Gao, Monatshefte für Chemie Chem Mon. **143**, 835 (2012)
38. S. Rostamizadeh, A.M. Amani, R. Aryan, H.R. Ghaieni, N. Shadjou, Synth. Commun. **38**, 3567 (2008)
39. M. Dabiri, P. Salehi, S. Otokesh, M. Baghbanzadeh, G. Kozehgary, A.A. Mohammadi, Tetrahedron Lett. **46**, 6123 (2005)