Iranian Journal of Catalysis 1(2), 2011, 55-63

IRANIAN JOURNAL OF CATALYSIS

BaO/TiO_2-ZrO_2 as a green and efficient basic catalyst for Knoevenagel condensation reaction

Roozbeh Javad Kalbasi*, Zohreh S. Shahzeidi, Farzad Zamani

[a] *Department of Chemistry, Shahreza Branch, Islamic Azad University, Shahreza 311-86145, Isfahan, Iran,*
[b] *Razi Chemistry Research Center, Shahreza Branch, Islamic Azad University, Shahreza, Isfahan, Iran,*

Received 21 Jul 2011; received in revised form 2 Nov 2011; accepted 9 Nov 2011

ABSTRACT

A simple and green synthetic strategy to prepare BaO/TiO_2-ZrO_2 as a solid base catalyst was reported. These materials with various amounts of BaO were prepared by the adsorption method. The physical and chemical properties of BaO/TiO_2-ZrO_2 were investigated by X-ray diffraction, X-ray fluorescence, specific surface area and BJH pore size distribution, FT-IR spectroscopy, scanning electron microscopy and energy dispersive spectra techniques. The catalytic performance of catalyst was determined for the Knoevenagel condensation reaction between carbonyl compounds and ethyl cyanoacetate in the presence of water as a solvent. The catalyst used for this synthetically useful transformation showed considerable level of reusability besides very good activity.

Keywords: *Solid base catalyst, BaO, TiO_2-ZrO_2, Knoevenagel condensation.*

1. Introduction

Solid base catalysts have many advantages over liquid bases. They are noncorrosive and environmentally benign, presenting fewer disposal problems, while allowing easier separation and recovery of the products, catalysts and the solvents. Thus, solid base catalysis is one of the economically and ecologically important fields in catalysis and the replacement of liquid bases with heterogeneous catalysts is becoming more and more important in the chemical industries [1]. Furthermore, high activity and selectivity are often obtained only by solid base catalysts for various kinds of reaction. Recently, many solid base catalysts have been reported which is effective for a number of base-catalyzed reactions [2-7]. Nevertheless, very few references are available dealing with the application of solid base catalysts for industrial catalysis in contrast to the extensively studied solid acid catalysts [1]. However, the majority of the heterogeneous catalyst developed is quite expensive, or complicated to prepare, which limits their industrial application. Thus, the study of new simple routes to prepare solid base catalysts is very relevant in the field of heterogeneous catalyst.

The Knoevenagel condensation is a carbon-carbon bond forming reaction commonly used to evaluate both organic [8-12] and inorganic [13-15] basic catalysts, so it was used as the probe reaction. This reaction consists of the nucleophilic addition of a methylene group to a carbonyl group, where the methylene group is activated by one or two electron-withdrawing groups.

In this systematic study, the influence of alkaline earth metal oxides namely BaO on the phase stability and catalytic properties of TiO_2-ZrO_2 has been examined. A simple and green method was adopted to make the desired BaO/TiO_2-ZrO_2 mixed oxide combinations and the catalyst exhibited good activity and selectivity in the Knoevenagel condensation of aromatic carbonyl compounds with ethyl cyanoacetate in the presence of water as solvent.

2. Experimental

2.1. Materials

The chemicals used in this work include tri-block copolymer poly (ethylene oxide) poly (propylene oxide)-poly (ethylene oxide), pluronics P123 (MW: 5800, Aldrich), tetraethyl orthosilicate (TEOS, 98%, Aldrich), Aluminiumtri-*sec*-butylate (Merck), 2,4-pentandione (Merck), Zirconium(IV) isopropoxide (70 wt.% solution in 2-propanol, Aldrich), titanium(IV) n-butoxide (99%, Aldrich), *n*-butanol (Merck), cetyl pyridinium bromide (Aldrich), Barium acetate (Merck) and Strontium nitrate (Merck). All the solvents and aromatic aldehydes were purchased from Merck and deionized double distilled water was used throughout.

---

* Corresponding author: E-mail: rkalbasi@gmail.com.
Fax: +98-321-3213103; Tel.: +98-321-3213211

2.2. Instruments and characterization

The catalysts were characterized by X-ray diffraction (Bruker D8ADVANCE,Cu K_α radiation), X-ray fluorescence (XRF) (Bruker D8ADVANCE), FT-IR spectroscopy (Nicolet 400D in KBr matrix in the range of 4000–400 cm^{-1}), BET specific surface areas and BJH pore size distribution (Series BEL SORP 18, at 77 K), scanning electron microscopy (SEM) and energy dispersive spectra (EDS) (SERON, AIS-2100). In addition, the products were characterized by ^1H NMR and ^{13}C NMR spectra (Bruker DRX-500 Avance spectrometer at 500.13 and 125.47 MHz, respectively), GC (Agilent 6820 equipped with a FID detector) and GC-MS (Agilent 6890). Melting points were measured on an Electro thermal 9100 apparatus and are uncorrected. All the products are known compounds; they were characterized by FT-IR, ^1H NMR and ^{13}C NMR. All melting points were compared satisfactorily with those reported in the literature.

2.3.2. BaO/SBA-15

Mesoporous silica SBA-15 was prepared by the previous reported procedure [19]. Pluronic P123 (2 g) was dissolved at room temperature in H_3PO_4 (4.2 mL, 85%) and deionized water (75.4 mL), then tetraethyl orthosilicate (TEOS) (4.6 mL) was added to this solution and the synthesis was carried out by stirring at 35 °C for 24 h in sealed teflon breakers and was subsequently placed at 100 °C for 24 h. Then the solution was filtered, washed with deionized water, and finally dried at 95 °C for 12 h in air. Template removal was performed by calcinations in air using two successive steps, first heating at 250 °C for 3 h and then at 550 °C for 4 h.

BaO/SBA-15 with the optimized molar BaO loading (15 wt.%) was prepared by the previous procedure for BaO/TiO_2-ZrO_2.

2.3.3. BaO/Al_2O_3-SiO_2

SiO_2–Al_2O_3 was prepared by the sol–gel method. Aluminum tri-*sec*-butylate (97%) and tetraethyl orthosilicate (98%) were used as the precursors, and 2,4-pentandione (H-acac) as the complexing agent [20]. Appropriate amounts of aluminum tri-*sec*-butylate and tetraethylorthosilicate were dissolved, *n*-butanol. The solution was heated to 60 °C and the components were thoroughly mixed. Then the solution was cooled down to room temperature, and H-acac as the complexing agent was added. This clear solution was hydrolyzed with deionized water (11.0 mol of H_2O/mol of alkoxide). The solution was left overnight to hydrolyze the alkoxides, yielding transparent gels. The transparent gels were dried at 110 °C to remove water and solvent, and then calcined at 500 °C for 5 h to remove the organics.

According to the previous procedure for BaO/TiO_2-ZrO_2, catalyst with BaO loading (15 wt.%) was prepared with an aqueous solution of $Ba(O_2CCH_3)_2$. The material was subsequently dried at 60 °C for 1 h and then calcined in air at 500 °C for 6 h.

2.3.4. SrO/TiO_2-ZrO_2

For the preparation of other base catalyst, the relevant alkaline earth nitrate ($Sr(NO_3)_2$) solution was used to reach the same optimized molar loading (15 wt.% SrO) as we did for BaO/TiO_2-ZrO_2.

2.4. Typical procedure for the Knoevenagel condensation

A solution of benzaldehyde (0.2 mL, 2 mmol), ethylcyanoacetate (0.2 mL, 2 mmol) and catalyst (0.15 g, 15 wt.% BaO/TiO_2-ZrO_2) in water (10 mL) were stirred at 80 °C. The progress and completion of the reaction was monitored by TLC, using *n*-hexane/THF (5:1) as eluent, and by GC (Agilent 6820). For the reaction work-up, the mixture was cooled to 10 °C, to solidifiy of the product, and water was removed by Buchner filtration and the residual solids were washed with ethanol (5 mL). The solvent was evaporated and the pure product was obtained in 85 % yield. The products were identified with ^1HNMR, ^{13}CNMR, GC-Mass and FT-IR spectroscopy techniques. Quantitative analyses were conducted with an Agilent 6820 GC equipped with a FID detector. The isolated yield was obtained by using column chromatography, in addition to GC yield. Decane was added as an internal standard for GC analysis. The catalyst was recovered and reused in the reaction of ethyl cyanoacetate with benzaldehyde for four times. In addition, the selectivity, (100 % to α,β-unsaturated carbonyl compounds) and yield, (85 %) did not change by reusing the catalyst.

3. Results and discussion

3.1. Characterization of the catalyst

Fig. 1 presents the X-ray diffraction patterns of TiO_2-ZrO_2 with various amount of BaO loading. Also given in the figure, the published positions of the XRD peaks are related to $Ba_2Ti_9O_{20}$ and $BaTi_4O_9$ crystalline phases. As can be seen, the spectra of TiO_2-ZrO_2 is an amorphous form, but after this support is loaded with BaO, the diffractions corresponding to $Ba_2Ti_9O_{20}$ and $BaTi_4O_9$ were present [21]. Moreover, by

Table 1. Elemental composition of 15 wt. % BaO/TiO_2-ZrO_2 obtained from XRF.

Sample	Element/concentration (wt.%)				
	Ti	Zr	O	Ba	Others
TiO_2-ZrO_2	26.27	31.34	39.25	-	2.73
15 wt.% BaO/TiO_2-ZrO_2	21.22	26.35	40.39	8.77	2.9

Table 2. EDS results of TiO_2-ZrO_2 before and after the BaO loading.

Sample	Ti (%)	Zr (%)	O (%)	Ba(%)
TiO_2-ZrO_2	36.32	44.1	18.17	-
10 wt.% BaO/TiO_2-ZrO_2	32.72	40.2	19.33	6.3
15 wt.% BaO/TiO_2-ZrO_2	31.74	38.9	20.01	7.86
20 wt.% BaO/TiO_2-ZrO_2	27.18	34.77	23.12	13.7
30 wt.% BaO/TiO_2-ZrO_2	22.39	30.17	26.03	20.08

increasing the amount of BaO loading up to 15 wt.%, XRD patterns of the samples become almost amorphous. In addition, as can be seen, when BaO amount is less than 20 wt.%, more $BaTi_4O_9$ may exist in the samples phase, but by the increase in loading, especially when that accounts for 30 wt.%, $Ba_2Ti_9O_{20}$ structure is formed on the mixed-oxide surface. The crystal structure of $Ba_2Ti_9O_{20}$ can be described as a hexagonal closest packing of oxygen and barium atoms [22]. Titanium atoms distribute in the octahedral interstices of the closest packing to form TiO_6 octahedral. This result suggests that by increase from 10 wt.% to 15 wt.% BaO loading, the Ti^{+4} sites are occupied by BaO monomers. When the BaO loading is increased to 30 wt.%, the number of BaO molecules is twice that of the Ti^{+4} sites. Therefore, if we assume an even distribution of BaO on the TiO_2-ZrO_2 support surface, and presume that BaO is only anchored to the support surface through Ti^{+4} sites, we may expect to observe two BaO molecules occupying each Ti^{+4} site. In addition, the X-ray fluorescence (XRF) results also show the elemental composition of calcined samples before and after the BaO loading (15 wt.% BaO/ZrO_2-TiO_2). It can be seen that the proportion of Ba in the catalyst is 8.77 wt.%, which is close to 70 % of the value set in the catalyst design (Table 1).

A series of FT-IR spectra obtained from TiO_2-ZrO_2, 10 wt.% BaO/TiO_2-ZrO_2, 15 wt.% BaO/TiO_2-ZrO_2, 20 wt.% BaO/TiO_2-ZrO_2 and 30 wt.% BaO/TiO_2-ZrO_2 is displayed in Fig. 2. They show two absorption bands at around 1620 cm^{-1} and 3400–3500 cm^{-1} range which correspond to O–H bending vibration and stretching vibration of the M–OH groups (Zr–OH, Ti–OH), respectively. It can be noticed that, the intensity of these peaks decreases by loading the support

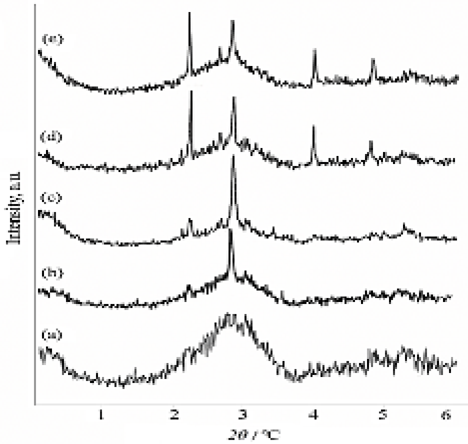


Fig.1. The powder XRD patterns of (a) TiO_2-ZrO_2, (b) 10 wt.% BaO/TiO_2-ZrO_2, (c) 15 wt.% BaO/TiO_2-ZrO_2, (d) 20 wt.% BaO/TiO_2-ZrO_2 and (e) 30wt.% BaO/TiO_2-ZrO_2.

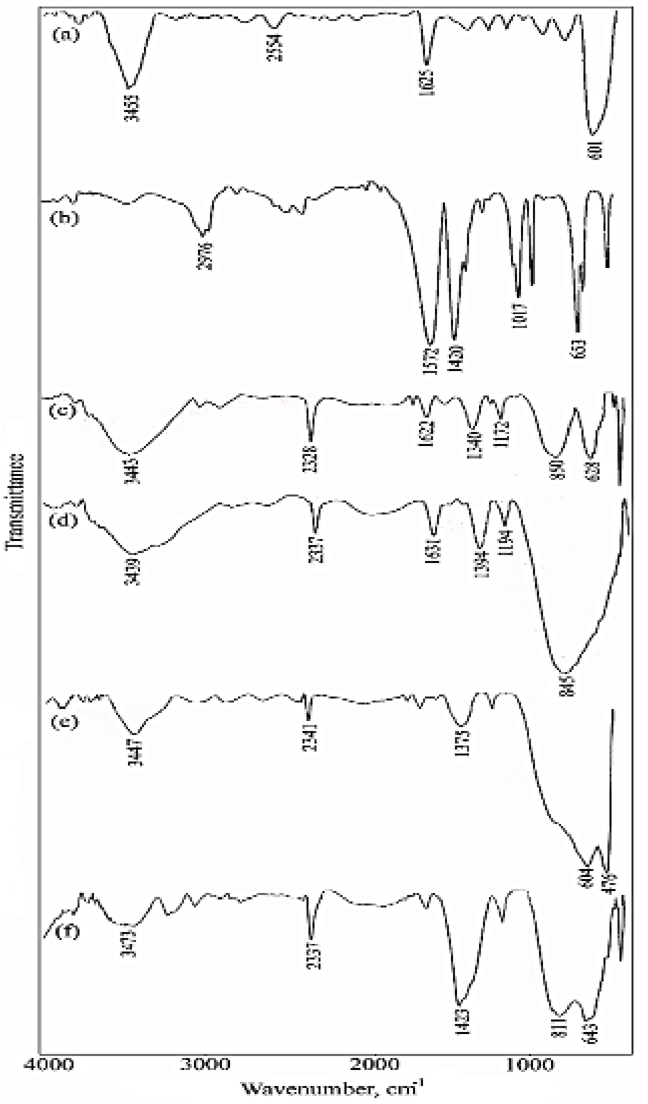


Fig. 2. The FT-IR spectra of (a) TiO_2-ZrO_2, (b) 10 wt.% BaO/TiO_2-ZrO_2, (c) 15 wt.% BaO/TiO_2-ZrO_2, (d) 20 wt.% BaO/TiO_2-ZrO_2 and (e) 30 wt.% BaO/TiO_2-ZrO_2.

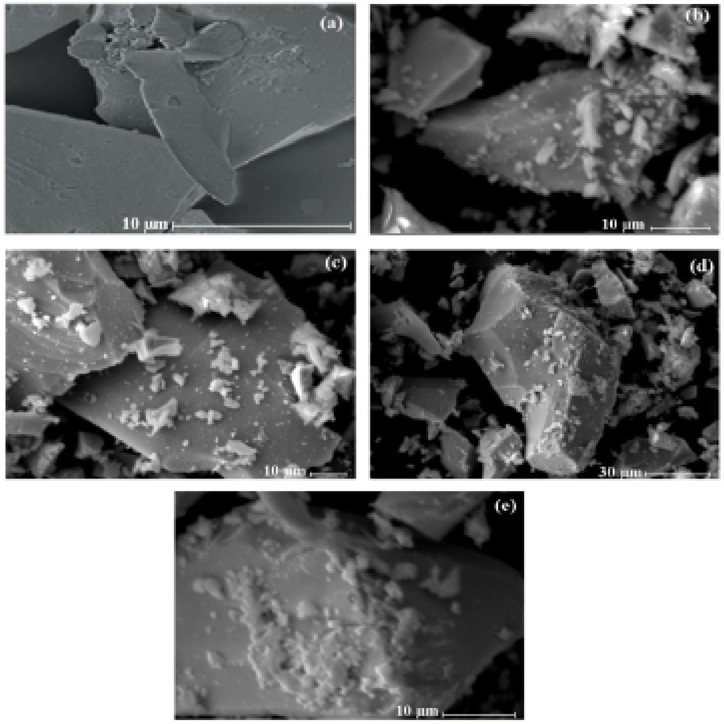


Fig. 3. Scanning electron microscopy (SEM) photographs of (a) TiO_2-ZrO_2, (b) 10 wt.% BaO/TiO_2-ZrO_2, (c) 15 wt.% BaO/TiO_2-ZrO_2, (d) 20 wt.% BaO/TiO_2-ZrO_2 and (e) 30 wt.% BaO/TiO_2-ZrO_2.

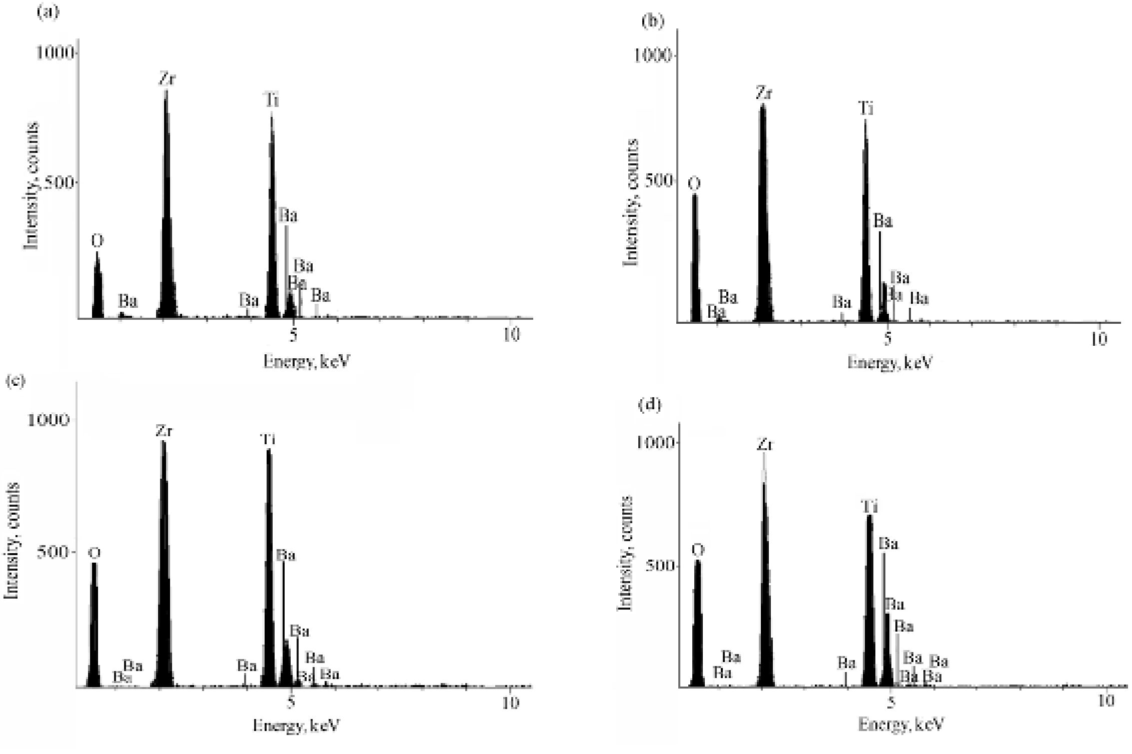


Fig. 4. Energy- dispersive spectra (EDS) analysis of (a) TiO_2-ZrO_2, (b) 10 wt.% BaO/TiO_2-ZrO_2, (c) 15 wt.% BaO/TiO_2-ZrO_2, (d) 20 wt.% BaO/TiO_2-ZrO_2 and (e) 30 wt.% BaO/TiO_2-ZrO_2.

Table 3. Porosity data of 15 wt.% BaO/TiO_2-ZrO_2

Sample	BET surface area /$m^2\ g^{-1}$	V_P ($cm^3\ g^{-1}$)	D_P (nm)
TiO_2-ZrO_2	66.8	0.14	9.6
15 wt.% BaO/TiO_2-ZrO_2	51.8	0.11	11.3

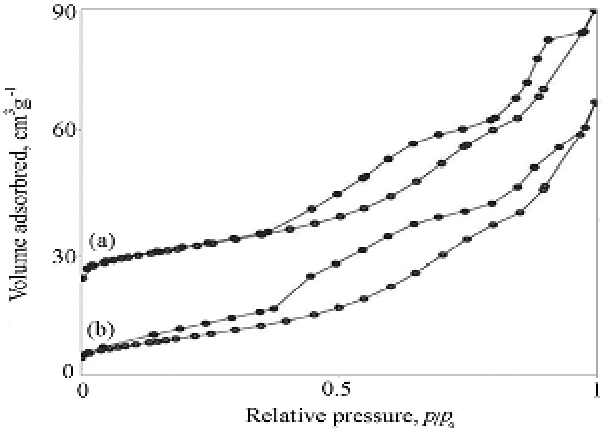


Fig. 5. Nitrogen adsorption isotherm at 77 K: (a) TiO_2-ZrO_2, (b) 15 wt.% BaO/TiO_2-ZrO_2.

of TiO_2-ZrO_2 with barium oxide, which indicated that hydroxyl groups on the surface support reacted with the BaO agent. In addition, barium crystalline oxide presents an intense band at around 473 cm^{-1} and a low one at around 510 cm-1 [23-25], which can be seen clearly from the strong overlapping of the BaO bands in the region of 475–650 cm^{-1}.

The morphology and location of BaO species on the surface of the catalyst were examined by scanning electron microscopy (SEM) using a SERON AIS-2100 microscope equipped with an energy-dispersive spectra analyzer (EDS). The SEM and EDS figures of the calcined TiO_2-ZrO_2 and loaded BaO with different amounts are shown in Fig. 3 and Fig.4, respectively. In the SEM images, there exist white and light gray regions. The contrast in these micrographs is mainly associated with the mean atomic number of each region. Bright regions correspond to low atomic numbers (Ba and O), and dark features correspond to high atomic number, (Zr and Ti in this case). The images clearly show that BaO species (bright spots) are dispersed on the surface of TiO_2-ZrO_2. The EDS data of all the calcined samples are presented in Fig. 4 and Table 2. As can be seen, Ti/Zr ratio obtained from the corresponding EDS data for them were approximately similar, as was expected. Moreover, it is revealed that barium oxide disperses well on the support surface, and the amount of it is approximately close to the value set in the theoretical design. The N_2 adsorption-desorption isotherm of calcined TiO_2-ZrO_2 and 15 wt.% BaO/TiO_2-ZrO_2 is shown in Fig. 5. The specific surface area and the pore size have been calculated by using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The structural data of all these materials (BET surface area, total pore volume, and pore size, etc.) was summarized in Table 3. During the impregnation stage of the preparation, surface hydroxyl groups of the mixed-oxide were probably consumed by reacting with the active phase precursor, resulted in the decrease of the available surface area of the support, due to the closure of the pores.

2. Catalytic activity

The Knoevenagel condensation of benzaldehyde was chosen as a model reaction to test the catalytic activity of the BaO/TiO_2-ZrO_2. Thus, effect of various reaction parameters on the condensation of benzaldehyde with ethyl cyanoacetate was studied using BaO/TiO_2-ZrO_2 as a basic catalyst and the results are as follows: Effect of reaction temperature on the Knoevenagel condensation was studied between room temperature (25°C) and reflux (95°C) in water by keeping other reaction parameters constant. Experimental results are shown in Fig. 6. The yield increased from 24 % to 80% by the increase in temperature from 25°C to 80°C. The Knoevenagel condensation is an endothermic reaction, which indicates a higher temperature can promote the reaction. By further increase in temperature, the yield remained constant but the selectivity decreased due to the formation of more condensation products. Catalytic activity of BaO/TiO_2-ZrO_2 was improved by

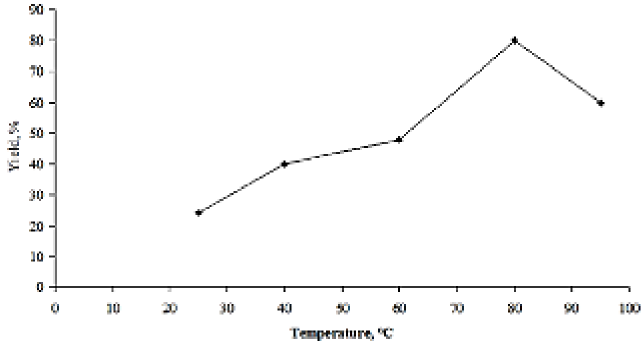


Fig. 6. Effect of reaction temperature on Knoevenagel condensation. Reaction conditions: 15 wt.% BaO/TiO_2-ZrO_2 (0.12 g), ethylcyanoacetate (2 mmol), benzaldehyde (2 mmol), H_2O (10 mL).

Table 4. Effect of loaded BaO amounts on the Knoevenagel condensation [a].

Catalyst	Yield (%) [b]
10 wt.% BaO/TiO_2-ZrO_2	49
15 wt.% BaO/TiO_2-ZrO_2	80
20 wt.% BaO/TiO_2-ZrO_2	64
30 wt.% BaO/TiO_2-ZrO_2	12
BaO	40
TiO_2-ZrO_2	5

[a] Reaction conditions: catalyst (0.12 g), ethylcyanoacetate (2 mmol), benzaldehyde (2 mmol), H_2O (10 mL), reaction temperature = 80 °C, Time = 35 min.

[b] Isolated yield

optimizing the amount of loaded BaO. The yield increased from 49 % to 80 % as the amount of BaO loading was increased from 10 % to 15 % in water at 80 °C (Table 4). By further increase in BaO loading, the yield decreased. Above 15 %, maybe there is over-loading of BaO and some pores of TiO_2-ZrO_2 are blocked. In order to investigate effect of the support (TiO_2-ZrO_2) on the Knoevenagel reaction, we used BaO (with the same ratio of the optimized catalyst) without any support as catalyst in the Knoevenagel condensation by keeping other parameters constant. After 35 min, about 40 % yield was observed. Therefore, TiO_2-ZrO_2 as a support is very useful for the Knoevenagel reaction. The effect of catalyst amount on the reaction yield was studied and the values were shown in Fig. 7. When the catalyst amount was increased from 0.06 to 0.15 g, the yield increased from 63 % to 85 %. With excess amount of catalyst, the yield obviously increased, because of the availability of more basic sites, which favors the dispersion of more active species. With further increase in catalyst amount, the percentage of the yield remained constant. It was examined the reaction between benzaldehyde and ethylcyanoacetate with the use of 15 wt.% BaO/SBA-15 and 15 wt.% BaO/SiO_2-Al_2O_3 at the optimum conditions as shown in Table 5. The result was compared with 15 wt % BaO/TiO_2-ZrO_2 in the Knoevenagel condensation. Among these three types of catalysts, The 15 wt.% BaO/TiO_2-ZrO_2 catalyst showed higher yield of the desired product.

Table 5. Effect of different kinds of support and alkaline metal oxide on the Knoevenagel condensation

Catalyst	Yield (%)[b]
TiO_2-ZrO_2	-
15 wt.% BaO/TiO_2-ZrO_2	85
15 wt.% BaO/SBA-15	75
15 wt.% BaO/SiO_2-Al_2O_3	70
15 wt.% SrO/TiO_2-ZrO_2	78

[a] Reaction conditions: catalyst (0.15 g), ethylcyanoacetate (2 mmol), benzaldehyde (2 mmol), H_2O (10 mL), reaction temperature= 80 °C, Time = 35 min.

[b] Isolated yield.

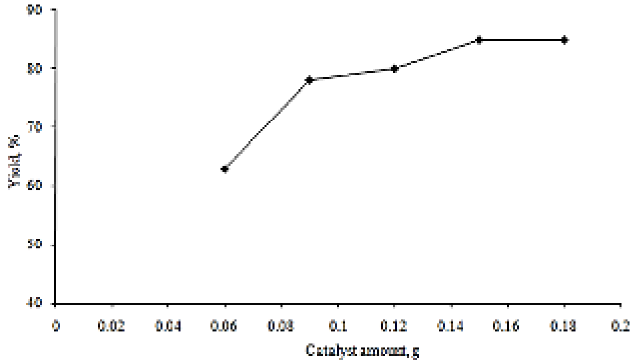


Fig. 7. Effect of catalyst amount on Knoevenagel condensation. Reaction conditions: 15 wt.% BaO/TiO_2-ZrO_2, ethylcyanoacetate (2 mmol), benzaldehyde (2 mmol), H_2O (10 mL), reaction temperature: 80°C.

Moreover, the conversion of benzaldehyde increased with the basicity character of alkaline metal oxide and the increase was more pronounced in BaO at optimum conditions (Table 5). The reusability of the catalyst was studied by using 15 wt.% BaO/TiO_2-ZrO_2 in recycling experiments. In order to regenerate the catalyst, after completion of the reaction, it was separated by filtration, washed several times with ethanol (3×5 mL), dried and calcined at 500 °C for 6 h and used in the Knoevenagel condensation with a fresh reaction mixture (Table 6). The results show that this catalyst can be reused, without any modification, for 4 times and no significant loss of activity/selectivity performance was observed. The catalytic activity of 15 wt.% BaO/TiO_2-ZrO_2 was investigated for the Knoevenagel condensation by employing various aromatic and hetero-aromatic aldehydes with ethyl cyanoacetate as an active methylene compound (Scheme 1). These reactions produce the corresponding electrophilic alkenes with 100 % selectivity to the condensation product. In addition, not any Micheal addition product was observed (Table 7). Hetero-aromatic aldehydes, such as furfural and 2-pyridine carbaldehyde (entries 2, 7) provided very good yields. Aromatic aldehydes with electron withdrawing groups (entries 5, 6) also offered good yields and the reactions were completed in short times. Also in the case of electron

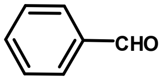
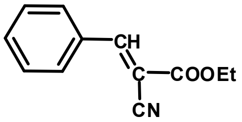
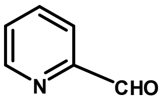
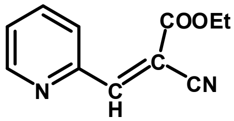
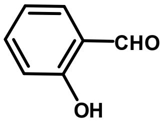
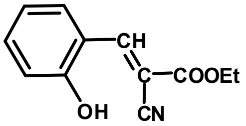
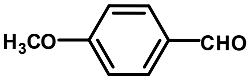
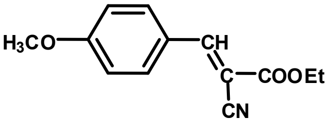
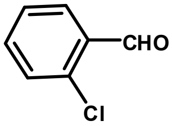
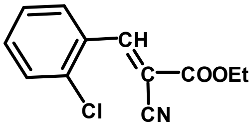
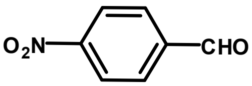
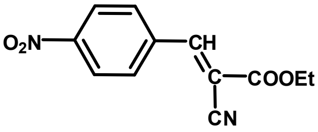
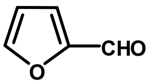
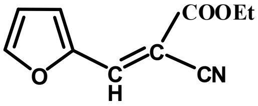
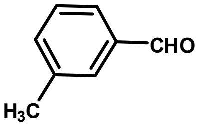
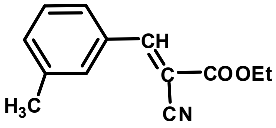
Table 6. Recyclability of the catalyst [a].

Cycle	Yield (%) [b]
Fresh	85
1st	84
2nd	84
3rd	84
4th	84

[a] Reaction conditions: 15 wt.% BaO/TiO_2-ZrO_2 (0.15 g), ethylcyanoacetate (2 mmol), benzaldehyde (2 mmol), H_2O (10 mL), 80 °C, Time = 35 min.

[b] Isolated yield.

Table 7. Knoevenagel condensation reaction of aromatic aldehydes and ethyl cyanoacetate catalyzed by 15 wt.% BaO/TiO_2-ZrO_2

Entry	Substrate	Product	Time (min)	Yield (%)[b]	mp (˚C)		Ref.
					Found	Reported	
1			35	85	49-51	50	26
2			15	95	92-94	95-96	27
3			45	40	132-134	133-135	28
4			45	40	81-82	80	26
5			20	70	52-54	53-54	29
6			10	94	165	169	26
7			15	95	85-87	89-91	30
8			20	45	85	82-85	31

[a] Reaction conditions: catalyst (0.15 g), ethyl cyanoacetate (2 mmol), substrate (2 mmol), H_2O (10 mL), 80 ˚C.
[b] Isolated yield.

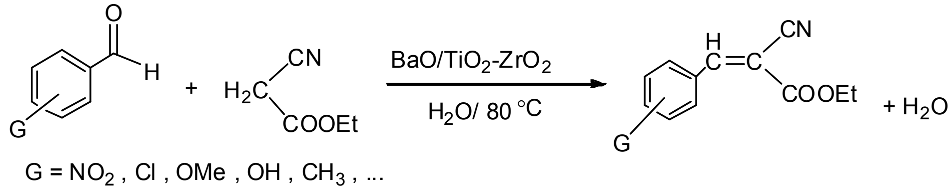
donating groups (entries, 3, 4), reasonably good yields were observed but demanded a little more reaction time. Moreover, moderately activated aromatic compound (entry 8) provided good yields. In order to examine the chemoselectivity of the present method, equimolar mixtures of ketone (4-nitro acetophenone) and aldehyde (4-nitro benzaldehyde) were allowed to react with ethyl cyanoacetate in water in the presence of the 15 wt.% BaO/TiO_2-ZrO_2 as a**.** catalyst. As shown in Scheme 2, the catalyst was able to discriminate between ketone and aldehyde and showed a high chemoselectivity.

4. Conclusion

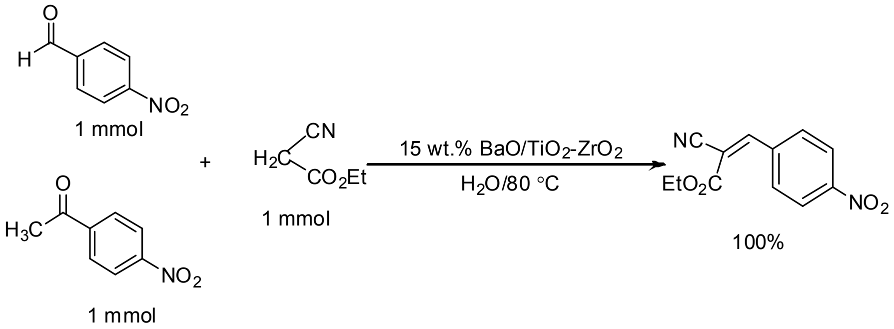
In this work, we have reported a green chemical method for preparation of a basic catalyst using Barium oxide supported on porous TiO_2-ZrO_2 support. After immobilization of Barium oxide, it was observed that the BaO molecules are preferentially anchored on the surface of the solid support. The catalyst BaO/TiO_2-ZrO_2 is efficient and selective catalyst for the Knoevenagel condensation of aromatic carbonyl compounds. Moreover, the solid catalyst can be reused and there is no evidence of Barium oxide leaching from the support during the catalytic reactions. Not requiring any particular skill to prepare the basic catalyst is another advantage of this protocol.

Acknowledgements

Support from Islamic Azad University, Shahreza Branch (IAUSH) Research Council and Center of Excellence in Chemistry is gratefully acknowledged.



Scheme 1. Knoevenagel condensation catalyzed by 15 wt.% BaO/TiO_2-ZrO_2.



Scheme 2. Chemoselectivity of the catalyst 15 wt.% BaO/TiO_2-ZrO_2.

References

[1] K. Tanabe, W.F. Holderich, Appl. Catal. A: 181 (1999) 399-434.

[2] T. Baba, H. Yuasa, H. Handa, Y. Ono, Catal. Lett. 50 (1998) 83-85.

[3] S. Jaenicke, G.K. Chuah, X.H. Lin, X.C. Hu, Micropor. Mesopor. Mater. 35 (2000) 143-153.

[4] K. Akutu, H. Kabashima, T. Seki, H. Hattori, Appl. Catal. A: Gen. 247 (2003) 65-74.

[5] H. Wang, M. Wang, N. Zhao, W. Wei, Y. Sun, Catal. Lett. 105 (2005) 253-257.

[6] M. Ai, Appl. Catal. A: Gen. 288 (2005) 211-215.

[7] X. Liu, H. He, Y. Wang, S. Zhu, Catal. Commun. 8 (2007) 1107-1111.

[8] J.D. Bass, A. Solovyov, A.J. Pascall, A. Katz, J. Am. Chem. Soc. 128 (2006) 3737-3747.

[9] J.D. Bass, S.L. Anderson, A. Katz, Angew. Chem. Int. Ed. 42 (2003) 5219-5222.

[10] D.J. Macquarrie, R. Maggi, A. Mazzacani, G. Sartori, R. Sartorio, Appl. Catal. A: Gen. 246 (2003) 183-188.

[11] M. Etienne, A. Walcarius, Talanta 59 (2003) 1173-1188.

[12] X. Wang, K.S.K. Lin, J.C.C. Chan, S. Cheng, J. Phys. Chem. B 109 (2005) 1763-1769.

[13] B. Siebenhaar, B. Casagrande, M. Studer, H.U. Blaser, Can. J. Chem. 79 (2001) 566-578.

[14] N. Elazarifi, A. Ezzamarty, J. Leglise, L.–C. de Menorval, C. Moreau, Appl. Catal. A: Gen. 267 (2004) 235-240.

[15] D. Hullmann, G. Wendt, G. Ziegenbalg, Chem. Eng. Technol. 24 (2001) 147-150.

[16] M. Ghiaci, A. Abbaspur, R.J. Kalbasi, Appl. Catal. A: Gen. 287 (2005) 83-88.

[17] J.M. Miller, L.J. Lakshmi, J. Phys. Chem. 102B (1998) 6465-6470.

[18] J.M. Miller, D. Wails, J.S. Belelie, J. Chem. Soc. Faraday Trans. 94 (1998) 789-796.

[19] M. Colilla, F. Balas, M. Manzano, M. Vallet-Regí, Chem. Mater. 19 (2007) 3099-3101.

[20] M. Ghiaci, B. Rezaei, R.J. Kalbasi, Talanta 73 (2007) 37-45.

[21] S.A.M. Abdel-Hameed, M.A. Azooz, Ceram. International 35 (2009) 643-648.

[22] H.M. O'Bryan, J.R.J. Thomson J. Am. Ceram. Soc. 57 (1974) 522-526.

[23] A.S. Tenny, J. Wong, J. Chem. Phys. 56 (1972) 5516-5523.

[24] I. Ardelean, F. Ciorcas, M. Peteanu, I. Bratu, V. Ioncu, Mod. Phys. Lett. B. 14 (2000) 653-661.

[25] E.I. Kamitsos, M.A. Karakassides, G.D. Cryssikos, J. Phys. Chem. 91 (1987) 1073-1079.

[26] R.M. Kumbhare, M. Sridhar, Catal. Commun. 9 (2008) 403-405.

[27] W. Flitsch, S. Kahner-Grone, Chemische Berichte 115 (1982) 871-877.

[28] G.R. Krishnan, K. Sreekumar, Euro. J. Org. Chem. 28 (2008) 4763-4768.

[29] X. Fan, X. Hu, X. Zhang, J. Wang, Australian J. Chem. 57 (2004) 1067-1071.

[30] J.S. Yadav, B.V.S. Reddy, A.K. Basak, B. Visali, A.V. Narsaiah, K. Nagaiah, Euro. J. Org. Chem. 3 (2004) 546-551.

[31] R.J. Kalbasi, M. Kolahdoozan, A.R. Massah, K. Shahabian, Bull. Korean Chem. Soc. 31 (2010) 2618-2666.