

Barium aluminate nano-spheres grown on the surface of BaAl₂O₄: a versatile catalyst for the Knoevenagel condensation reaction of malononitrile with benzaldehyde

M. Momayezan¹, M. Ghashang*², S. A. Hassanzadeh-Tabrizi²

¹Advanced Materials Research Center, Materials Engineering Department, Najafabad Branch, Islamic Azad University, Najafabad, Iran

²Department of Chemistry, Faculty of Sciences, Najafabad Branch, Islamic Azad University, P.O. Box: 517; Najafabad, Esfahan, Iran

Received August 20, 2014, Revised December 3, 2014

In this study, barium aluminate nano-powder was synthesized *via* homogeneous precipitation method and was investigated for its activity on the Knoevenagel condensation reaction of malononitrile with benzaldehyde. The obtained samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FT-IR) and energy-dispersive X-ray spectroscopy (EDAX). The XRD pattern showed a single phase of hexagonal structure. Two distinctive phases of BaAl₂O₄ are present in the FE-SEM micrographs. The first phase is an irregular shape of agglomerated BaAl₂O₄ nano-powders, and the second - diffused nano-spheres of BaAl₂O₄ on the outer surface of the nano-powder. The BaAl₂O₄ nano-spheres have an average size of about 70 nm. The BaAl₂O₄ nano-powder was shown to be a highly efficient catalyst for the Knoevenagel condensation reaction of malononitrile with benzaldehyde under reflux conditions in ethanol as solvent. The effects of catalyst concentration, temperature and solvent on the reaction were investigated.

Keywords: BaAl₂O₄; Knoevenagel reaction; malononitrile; benzaldehyde

INTRODUCTION

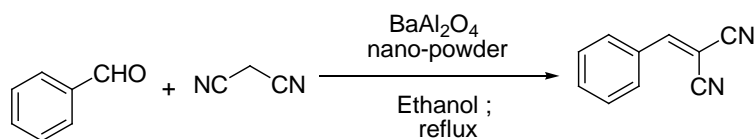
In view of homogenous and heterogeneous catalysis, basic-type catalysts and especially solid base catalysts are a challenging goal of catalysis to play a conclusive role in a lot of chemical reactions. Various solid base catalytic systems such as hydroxides, zeolites, mixed oxides, immobilized amines, metal-organic frameworks and clays are samples of the reported references [1-7].

Nowadays there is a driving force for using heterogeneous catalysts in various industries due to the environmentally friendly effect achieved, thus replacing traditional homogeneous-catalyzed reactions. Noncorrosive and environmentally benign characteristics which create fewer disposal problems are the main advantages that patronize this driving force. In addition, heterogeneous catalysts usually have higher activity, selectivity and longer catalyst life over liquid homogeneous catalysts [8-11]. However, among various acid and base heterogeneous catalysts, solid base catalysts

get much fewer applications in chemical reactions. Solid base catalysts are non-stoichiometric, non-corrosive and reusable which can be a good option for the replacement of liquid bases [12-14].

Aluminates are known to have mild basic characteristics among various bases. They are widely used in ceramics, cements, pigments, glazes, and also as industrial catalysts with superior physical properties. Among various aluminates barium aluminate (BaAl₂O₄) is of great interest in catalysis as it can be used in the treatment of air pollutions as a catalyst, for the preparation of humidity sensors and phosphor materials [15-21].

In view of the above advantages, in the present study an investigation on the phase formation of barium aluminate nano-powders and evaluation of their catalytic activity in the Knoevenagel condensation reaction of malononitrile with benzaldehyde [22-25] was taken up (Scheme 1).



Scheme 1. Knoevenagel condensation reaction of malononitrile with benzaldehyde

* To whom all correspondence should be sent:
E-mail: ghashangmajid@gmail.com

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and were used without further purification. The powder X-Ray diffraction patterns were recorded with Bruker AXS D₈ Advance diffractometer using Cu-K α irradiation. FE-SEM was taken on a Hitachi S-4160 instrument to examine the shape and metallic composition of the samples. The FT-IR spectra of the materials were recorded by the standard KBr pellet technique with a Perkin Elmer 781 spectrophotometer in the range of 400-4000 cm⁻¹.

Preparation of BaAl₂O₄ nano-powder

Two different solutions were prepared as follows: solution A: a solution of Ba(II), and Al(III) was prepared by dissolving barium chloride (20 mmol), and aluminum chloride (20 mmol) in 50 mL of water. Solution B: a solution of 2-amino ethanol (100 mmol) in 50 ml of ethanol / water (50/50 v/v). Solution B was slowly poured into solution A under vigorous magnetic stirring. The resulting mixture was aged for 5 h until a gel was formed. Finally, the gel was filtered, washed with water three times, dried and calcinated at 700 °C for 2 h.

Knoevenagel condensation reaction of malononitrile with benzaldehyde: typical procedure
A mixture of benzaldehyde (1 mmol), malononitrile (1.3 mmol) and BaAl₂O₄ nano-powder (0.01 – 0.1 g) was refluxed for 10 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by simple filtration. Removal of the solvent under reduced pressure afforded the pure product as a white solid after recrystallization from ethanol.

RESULTS AND DISCUSSION

The XRD spectrum of the BaAl₂O₄ nano-powder is presented in Figure 1. The diffraction patterns demonstrated the formation of a single phase, as peak splitting for the presence of two phases could not be detected. It can be seen from the patterns that the synthesized material showed hexagonal structure with the corresponding diffractions of 28.3, 34.3, 39.8, 40.1, 45.0, 54.5, 57.8, 89.4 (2Theta [°]).

The morphology of the nano-particles was investigated using FE-SEM analysis (Figure 2). As can be seen from the FE-SEM micrographs, two distinctive particles of BaAl₂O₄ are present. The first phase is an irregularly shaped agglomerate of BaAl₂O₄ nano-powders, and the second is diffused

nano-spheres of BaAl₂O₄ on the outer surface of the nano-powder. As can be seen in Figure 2, the BaAl₂O₄ nano-spheres have an average size of about 70 nm for 20 particles.

The FT-IR absorption spectrum of the sample calcinated at 700 °C for 2 h is presented in Figure 3. The peak appeared at 1630 cm⁻¹ is related to the Al–O stretching vibration and the other peak at around 1437 cm⁻¹ indicated the formation of the BaAl₂O₄ phase. The intense and broad peaks observed in the 400- 900 cm⁻¹ region may be due to the stretching and bending vibrations of Al-O and Ba-O bonds [26-27].

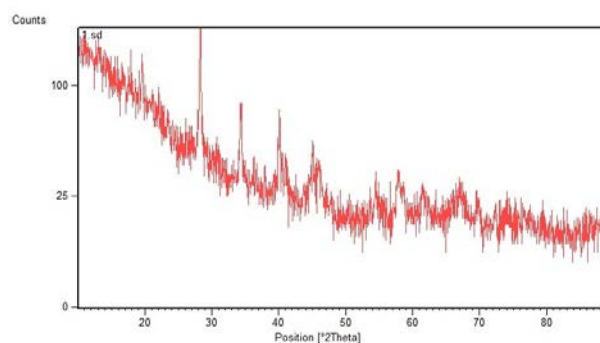


Fig. 1. XRD pattern of BaAl₂O₄ nano-powder calcined at 700 °C

Catalytic test

The BaAl₂O₄ nano-powder was assessed for its catalytic activity by studying the Knoevenagel condensation reaction of malononitrile with benzaldehyde to form 2-benzylidenemalononitrile as the targeted molecule (Scheme 1).

Solvent Selection

Initially the Knoevenagel condensation reaction of benzaldehyde and malononitrile was carried out in different solvents such as acetonitrile, ethanol, ethyl acetate, dichloromethane, *n*-hexane, H₂O and solvent-free using BaAl₂O₄ nano-powder as a catalyst (Table 1). The reaction was carried out under reflux conditions, until the starting materials disappeared (TLC indicating technique). In order to compare the catalytic performances of the different solvents, the yield of the reaction was used as indicator of catalytic activity. The use of solvent media led to higher product yields when compared with solvent-free conditions. Among the various solvents screened, ethanol was chosen as the approved reaction medium due to its higher product yield (Table 1).

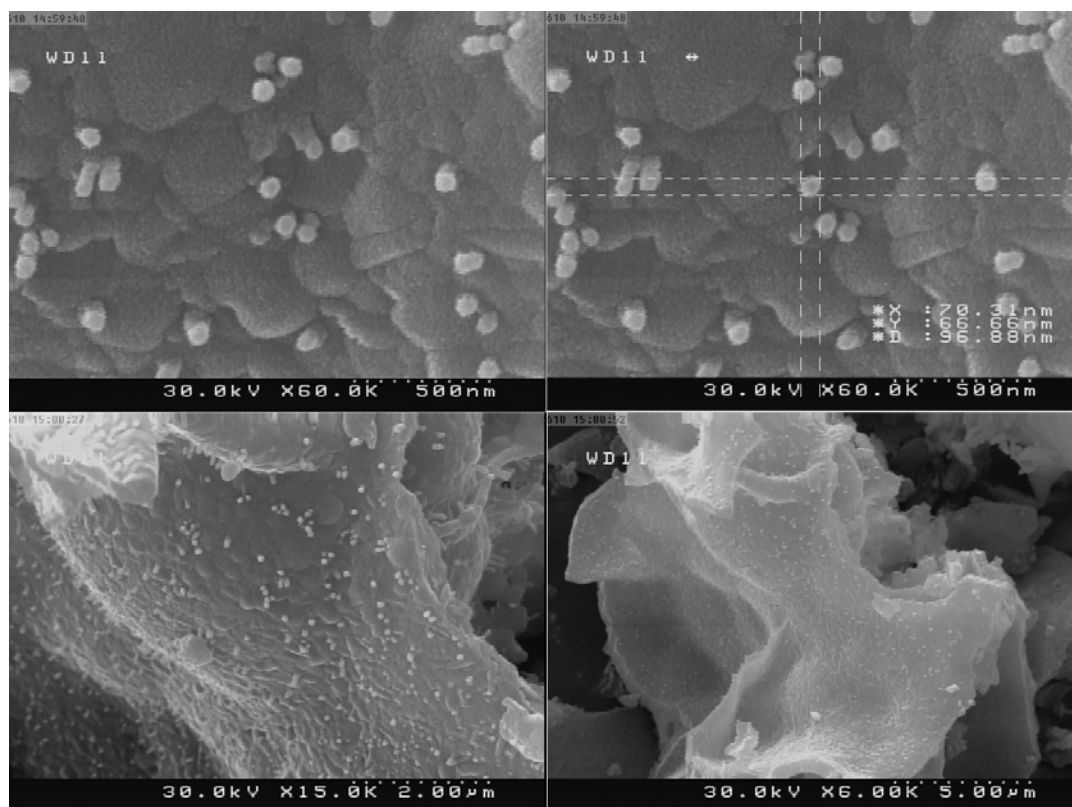


Fig. 2. FE-SEM photographs of BaAl₂O₄ nano-powder calcined at 700 °C for 2 h

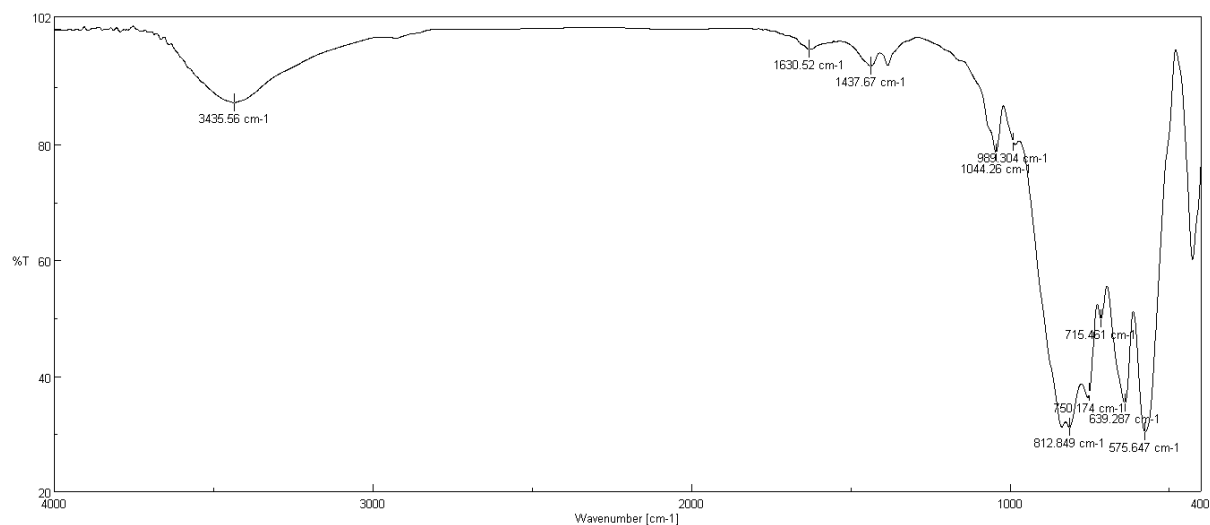


Fig. 3 FT-IR spectra of BaAl₂O₄ nano-powder calcined at 700 °C

Table 1. Solvent screening

Entry	Conditions	Yield (%) ^a
1	BaAl ₂ O ₄ nano-powder (0.20 mmol, 0.05 g), Ethanol (10 ml), reflux	80
2	BaAl ₂ O ₄ nano-powder (0.20 mmol, 0.05 g), Acetonitrile (10 ml), reflux	71
3	BaAl ₂ O ₄ nano-powder (0.20 mmol, 0.05 g), Ethyl acetate (10 ml), reflux	61
4	BaAl ₂ O ₄ nano-powder (0.20 mmol, 0.05 g), Dichloromethane (10 ml), reflux	10
5	BaAl ₂ O ₄ nano-powder (0.20 mmol, 0.05 g), <i>n</i> -Hexane (10 ml), reflux	15
6	BaAl ₂ O ₄ nano-powder (0.20 mmol, 0.05 g), H ₂ O (10 ml), reflux	45
7	BaAl ₂ O ₄ nano-powder (0.20 mmol, 0.05 g), Solvent-free, (80 °C)	55

^aIsolated yield, reaction time: 10 h

Influence of temperature and catalyst concentration

To clarify the effect of catalyst concentration, the Knoevenagel condensation reaction of benzaldehyde and malononitrile over BaAl₂O₄ nano-powder was carried out using ethanol as a solvent.

Initially, in order to determine the conditions for maximum conversion of benzaldehyde, the reaction was performed at a temperature ranging from 25 to 80 °C for 10 h with a catalyst concentration of 0.05 g (Figure 4). As it is seen from Figure 4, with increasing temperature, the conversion increased and the complete conversion was achieved at a temperature of 80 °C.

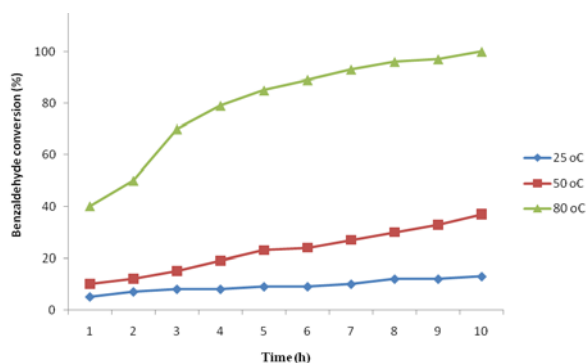


Fig. 4. Benzaldehyde conversion as a function of time for different reaction temperatures. Reaction conditions: BaAl₂O₄ nano-powder (0.05 g), ethanol (10 mL), reflux, 10 h

The percentage of benzaldehyde conversion was calculated as follows:

$$\text{Benzaldehyde conversion (\%)}: [1 - n_t] \times 100$$

where n_t is the remaining amount (in mmol) of benzaldehyde at time t .

The benzaldehyde conversion capacity of BaAl₂O₄ nano-powder was calculated using following equation:

$$\text{Benzaldehyde conversion capacity: } [1 - n_t] \times V/m$$

V is the volume of the reaction solvent and m is the mass of the catalyst in g (Figure 5).

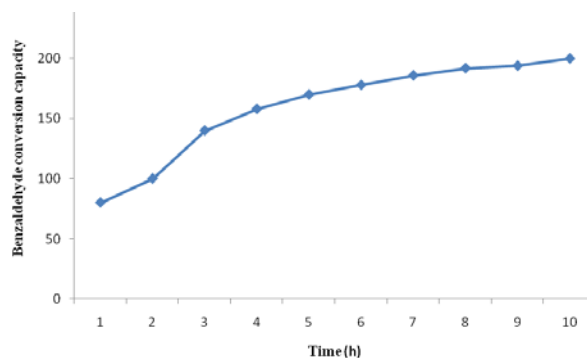


Fig. 5. Benzaldehyde conversion capacity of BaAl₂O₄ nano-powder as a function of time. Reaction conditions: BaAl₂O₄ nano-powder (0.05 g), ethanol (10 mL), reflux (80 °C), 10 h

To perform a kinetic analysis of the Knoevenagel condensation reaction, an excess of malononitrile was used to achieve pseudo first-order conditions. The data from the benzaldehyde conversion was further used to analyze the rate of the reaction by the following equation which can be further simplified as follows:

$$\text{Rate} = \frac{dC}{dt} = kC$$



$$\ln \frac{C_0}{C_t} = kt \longrightarrow \ln \frac{0.1}{C_t} = kt \longrightarrow \ln \frac{1}{n_t} = kt \longrightarrow \ln n_t = -kt$$

C_t can be calculated from the division operator of n_t (mmol amount of benzaldehyde at time t) to 10 mL (volume of ethanol as solvent).

The kinetic study shows that the conversion of benzaldehyde follows pseudo-first order kinetics and nearly linear relation of $-\ln(n_t)$ vs. t is observed (Figure 6).

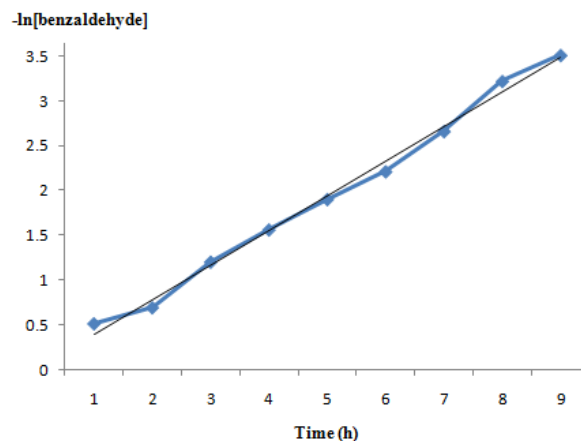


Fig. 6. Pseudo first order kinetics of $-\ln$ [benzaldehyde] vs time for the Knoevenagel condensation reaction of malononitrile with benzaldehyde. Reaction conditions: BaAl₂O₄ nano-powder (0.05 g), ethanol (10 mL), reflux (80 °C), 10 h

Since n_t is the remaining amount (in mmol) of benzaldehyde at time t and t is the time of reaction process.

It was observed that this relationship follows from the equation:

$$-\ln(n_t) = kt \quad \text{or} \quad -\ln[\text{benzaldehyde}] = kt$$

The nearly linear relationship between $-\ln(n_t)$ and t indicates that the conversion of benzaldehyde follows first-order kinetics. k is the constant of the reaction rate and can be determined from the straight-line slope of the fitted values by means of linear regression. The k value was determined as 0.007 (s⁻¹).

With these results in hand and in order to find the conditions for complete conversion of benzaldehyde, five experiments with different

concentrations of catalyst were performed at 80 °C (reflux conditions) for 10 h. The molar ratio of benzaldehyde / malononitrile was 1/1.3. The results are shown in Figure 7. It shows that the initial reaction rates increase with increasing catalyst concentration. At a catalyst amount lower than 0.025 g, the conversion of benzaldehyde is low (43%). With increasing the catalyst amount above 0.025 g, complete conversion of benzaldehyde was achieved. The increase in the number of active sites of the catalyst at higher catalyst dosage leads to an increase in the conversion of the starting materials.

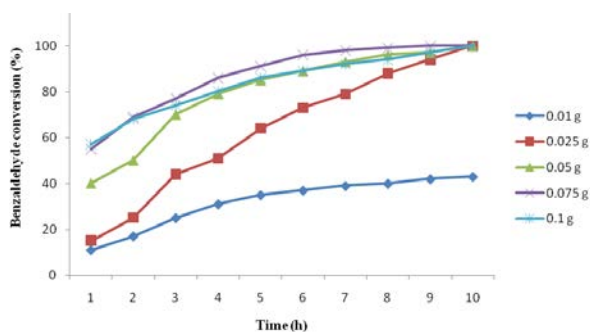


Fig. 7. Benzaldehyde conversion as a function of time for different catalyst concentrations. Reaction conditions: ethanol (10 mL), reflux (80 °C), 10 h.

The effect of catalyst concentration on the product yield was investigated by performing four runs of the Knoevenagel condensation reaction of benzaldehyde and malononitrile over different dosages of BaAl₂O₄ nano-powder ranging from 0.025-0.1 g (Table 2). Higher yield was obtained using 0.05 g of catalyst and increasing the amount of catalyst did not significantly improve the yield.

Table 2. Effect of the amount of BaAl₂O₄ nano-powder as a catalyst on the product yield (%)

Entry	Catalyst (g)	Yield (%) ^a
1	0.025	72
2	0.05	80
3	0.075	73
4	0.1	70

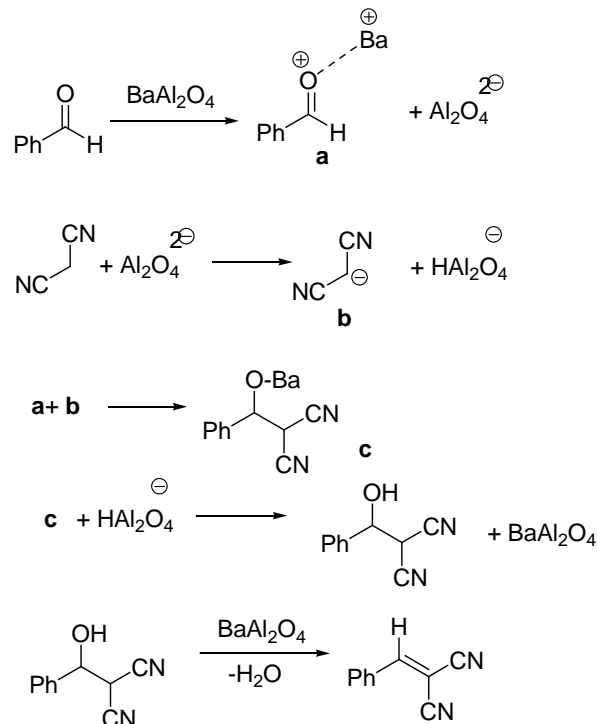
^aIsolated yield, reaction conditions: time: 10 h, solvent: ethanol (10 ml), reflux (80 °C)

Thus the optimized conditions are: 0.05 g of BaAl₂O₄ nano-powder as the catalyst and ethanol as solvent under reflux.

It was found that complete conversion of benzaldehyde can be achieved when BaAl₂O₄ nano-powder (0.05 g, 0.2 mmol) was used. With other metal oxides such as BaO (0.2 mmol, 80%), CaO (0.2 mmol, 89%) and Al₂O₃ (0.2 mmol, 30%) in the same conditions a lower conversion efficiency was achieved.

The proposed mechanism for the Knoevenagel condensation reaction of benzaldehyde and malononitrile over BaAl₂O₄ nano-powder is shown in Scheme 2. In this reaction, BaAl₂O₄ could act as a bifunctional catalyst, by activating both the carbonyl oxygen in the aldehyde and the acidic hydrogen in malononitrile. Since BaAl₂O₄ contains Ba atoms attached to O atoms, it is likely that Ba²⁺ would be released *in situ*, and this species would act as a catalyst in the reaction medium leading to a considerable increase in the electrophilicity of the aldehyde (intermediate **a**).

It is proposed that BaAl₂O₄ produces two different species: Ba²⁺ and Al₂O₄²⁻. The latter species reacts with malononitrile to form a carbanion form (intermediate **b**). This reaction is followed by the attack of intermediate **b** on the activated carbonyl to afford intermediate (**c**). The reaction proceeds till the recovery of BaAl₂O₄ and the formation of 2-(hydroxy(phenyl)methyl) malononitrile. The reaction could be continued with the removal of water to afford the targeted molecules, as is shown in scheme 2.



Scheme 2: Plausible Knoevenagel condensation reaction of benzaldehyde and malononitrile over BaAl₂O₄ nano-powder as a catalyst.

Catalyst reusability

Our attention then turned to the possibility of recycling the catalyst from the reaction medium since the recovery and reuse of the catalyst are preferable for a green process. At the completion of the reaction, the solid catalyst was separated by

simple filtration, dried and reused for subsequent reactions. The reusability of the catalyst was investigated in the Knoevenagel condensation reaction of malononitrile with benzaldehyde. After 10 recycles, the catalyst still had a high activity and gave the corresponding product in good yield (Figure 8).

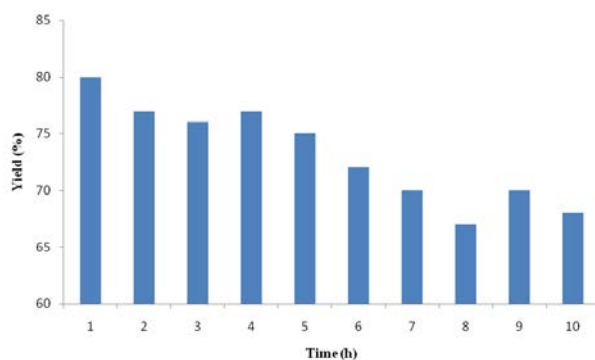


Fig. 8. Reusability of BaAl₂O₄ nano-powder.

CONCLUSION

The *in-situ* preparation of BaAl₂O₄ nano-powder via homogeneous precipitation was reported. The prepared sample was characterized using XRD, FT-IR, FE-SEM and EDAX analysis. The XRD pattern shows only hexagonal phase of BaAl₂O₄. The average particle size determined by FE-SEM is about 70 nm. The BaAl₂O₄ nano-powder was shown to be a highly efficient catalyst for the Knoevenagel condensation reaction of malononitrile with benzaldehyde under reflux conditions in ethanol as a solvent.

Acknowledgements: We are thankful to the Najafabad Branch, Islamic Azad University research council for partial support of this research

REFERENCES

- H. Hattori, *Chem Rev.*, **95**(3), 537 (1995).
- S. Inagaki, K. Thomas, V. Ruaux, G. Clet, T. Wakihara, S. Shinoda, S. Okamura, Y. Kubota, V. Valtchev, *ACS Catal.*, **4** (7), 2333 (2014).
- M. J. Climent, A. Corma, S. Iborra, M. J. Sabater, *ACS Catal.*, **4** (3), 870 (2014).
- Y. C. Sharma, B. Singh, J. Korstad. *Fuel*, **90**, 1309 (2011).
- A. C. Alba-Rubio, J. Santamaría-González, J. M. Mérida-Robles, R. Moreno-Tost, D. Martín-Alonso, A. Jiménez-López, P. Maireles-Torres, *Catal. Today*, **149**, 281 (2010).
- M. Bolognini, F. Cavani, D. Scagliarini, C. Flego, C. Perego, M. Saba, *Catal. Today*, **75**, 103 (2002).
- D. Wang, X. Zhang, W. Wei, Y. Sun, *Catal. Commun.*, **28**, 159 (2012).
- M. R. M. Shafiee, M. Ghashang, A. Fazlinia, *Curr. Nanosci.*, **9**, 197 (2013).
- M. Ghashang, *Curr. Org. Synth.*, **9**, 727 (2012).
- M. R. M. Shafiee, A. Fazlinia, N. Yaghooti, M. Ghashang, *Lett. Org. Chem.*, **9**, 351 (2012).
- M. Ghashang, *Lett. Org. Chem.*, **9**, 497 (2012).
- D. G. Morrell, *Catalysis of Organic Reactions*, CRC Press, 2002.
- M. Lancaster, *Green Chemistry: An Introductory Text*, Royal Society of Chemistry, 2010.
- K. Wilson, A. F. Lee, *Heterogeneous Catalysts for Clean Technology: Spectroscopy, Design, and Monitoring*. John Wiley & Sons, 2013.
- S. Hodjati, P. Bernhardt, C. Petit, V. Pitchon, A. Kiennemann, *Appl Catal B: Environ.*, **19**, 209 (1998).
- M. Mohapatra, D. M. Pattanaik, S. Anand, R. P. Das. *Ceram. Inter.*, **33**, 531 (2007).
- M. Casapu, J. D. Grunwaldt, M. Maciejewski, M. Wittrock, U. Gobel, A. Baiker, *Appl. Catal. B: Environ.*, **63**, 232 (2006).
- J. J. Vijaya, L. J. Kennedy, G. Sekaran, K. S. Nagaraja, *Sens. Actuators B: Chem.*, **124**: 542 (2007).
- S. Y. Raghvendra, S. K. Pandey, A. C. Pandey, *J. Lumin.*, **131**, 1998 (2011).
- V. Singh, V. Natarajan, J. J. Zhu, *Opt. Mater*, **29**, 1447 (2007).
- Z. Qiu, Y. Zhou, M. Lu, A. Zhang, Q. Ma, *Acta Mater*, **55**, 2615 (2007).
- Sk. I. Manirul, A. R. Singha, R. D. Chandra, S. Pau, *J. Molec. Catal. A: Chem.*, **394**, 66 (2014).
- J. Zhao, J. Xie, C-T. Au, S-F. Yin, *Appl. Catal. A: Gen.*, **467**, 33 (2013).
- Y. Tan, Z. Fu, J. Zhang, *Inorg. Chem. Commun.*, **14**: 1966 (2011).
- J. Xu, K. Shen, B. Xue, Y-X. Li, *J. Molec. Catal. A: Chem*, **372**: 105 (2013).
- L-W. Zhang, L. Wang, Y-F. Zhu, *Adv. Funct. Mater.*, **17**, 3781 (2007).
- R. Stefani, L.C.V. Rodrigues, C.A.A. Carvalho, M.C.F.C. Felinto, H.F. Brito, M. Lastusaari, J. Holsa, *Opt. Mater.*, **31**, 1815 (2009).

НАНОСФЕРИ ОТ БАРИЕВ АЛУМИНАТ, ИЗРАСТНАЛИ НА ПОВЪРХНОСТТА НА
BaAl₂O₄: ОБЩО ПРИЛОЖИМ КАТАЛИЗАТОР ЗА КОНДЕНЗАЦИЯТА ПО
KNOEVENAGEL НА МАЛОНИТРИЛ С БЕНЗАЛДЕХИД

М. Момаезян¹, М. Гашанг*², С.А. Хасанзаде-Табризи²

¹ *Разширен изследователски център по материалознание, Факултет по материалознание и инженерство, Клон Наджафабад, Ислямски университет „Азад“, Наджафабад, Иран*

² *Департамент по химия, Научен факултет, Клон Наджафабад, Ислямски университет „Азад“, Наджафабад, Есфахан, Иран*

Постъпила на 20 август, 2014 г.; коригирана на 3 декември, 2014 г.

(Резюме)

Синтезиран е нано-прах от бариев алуминат по метода на хомогенното утаяване и изследван каталитичната му активност за кондензацията по Knoevenagel на малонитрил с бензалдехид. Получените образци са охарактеризирани чрез рентгено-структурен анализ (XRD), полева емисионна сканираща електронна микроскопия (FE-SEM), инфрачервена спектроскопия с Фурие-трансформация (FT-IR) и дисперсионна рентгенова спектроскопия (EDAX). Рентгенограмите показват единична фаза с хексагонална структура. Две обособени фази на BaAl₂O₄ са налице на FE-SEM-микроснимките. Първата фаза има нерегулярни форми на агломериран нано-прах от BaAl₂O₄, а втората – дифузни нано-сфери от BaAl₂O₄ на външната повърхност на нано-праховете. Сферите от BaAl₂O₄ имат среден размер около 70 nm. Показано е, че нано-прахът от BaAl₂O₄ е високо-ефективен катализатор на кондензационната реакция на Knoevenagel между малонитрил и бензалдехид с рефлукс на разтворителя (етанол). Изследвано е влиянието на концентрацията на катализатора, температурата и разтворителя върху реакцията.