ORIGINAL PAPER



# Synthesis, kinetic study, and applications of polyethyleneimine supported nano zirconium chromate in oxidation of furfuryl alcohol to corresponding carbonyl compound

Setareh Sheikh<sup>1</sup> · Nooredin Goudarzian<sup>1</sup>

Received: 18 June 2015/Accepted: 29 December 2015 © Springer-Verlag Wien 2016

Abstract The efficiency of highly branched polyethyleneimine has been investigated as a support for nano zirconium chromate and subsequent use as a heterogeneous oxidant for selective oxidation of furfuryl alcohol to furfural. These were synthesized using polyethyleneimine to produce a polymer coordinated nano zirconium, a noble and straightforward method for screening high catalytically active polymer nano composites. The one-step systematic derivatization of the polyethyleneimine scaffold led structurally correlated to the stabilization of zirconium nanoparticles and catalysis. Analysis of this polymeric reagent identified the zirconium chromate nano composite that was able to be effective to oxidation reaction in tetrahydrofuran under mild conditions due to the surface area of the nano zirconium chromate per unit volume. Capacity of the reagent and fixation of nano zirconium chromate is confirmed by ICP and atomic absorption technique. Morphology of this nano composite is investigated by SEM and TEM. The kinetic of oxidation of furfuryl alcohol, over heterogeneous catalyst, nano zirconium chromate in THF, were investigated. Power-law rate model was applied to describe the experimental results and obtain the orders of the reaction with respect to furfuryl alcohol, catalyst, and furfural, which were found to be 0.989, 0.991, and -0.68, respectively, with the activation energy of 76.78 kJ/mol.

Setareh Sheikh sheikh@iaushiraz.ac.ir; sheikh\_set@yahoo.com Graphical abstract





# Introduction

In recent years, the effective use of more selective supported and non-toxic solid heterogeneous catalyst or polymer supported catalysts same as poly(4-vinylpyridine) supported sodium azide [1], polyethyleneimine supported silver nanoparticle [2], pyridinium chlorochromate [3], bipyridinium chlorochromate [4], tetrakis(pyridine)silver dichromate [5], and zinc borohydride supported charcoal [6] has been under more attention in various fields of organic synthesis due to their simple operation, reusability, environmental compatibility, simple isolation of the products, and high selectivity [7–12]. Most of these reagents have their deficiencies and drawbacks, e.g. need to use excess reagent [13], acidity of the reagent [14], need to use the wet reagent [15], and being expensive [16]. Polymersupported catalysts make reaction methods more economical, convenient, and environmentally safe and benign due to their ability to be used as recyclable and heterogeneous

<sup>&</sup>lt;sup>1</sup> Department of Applied Chemistry, Shiraz Branch, Islamic Azad University, Shiraz, Iran

catalysts in organic transformation. Mild conditions can be considered for the reactions and insoluble polymer support can be separated easily from the reaction medium, so simplicity of product purification is resulting. Accordingly, for oxidation reactions, application of zirconium based catalysts has also been proven [17]. Formation of zirconium bulk and zirconium agglomeration that has caused catalyst deactivation in several cases are major problems, even though there has been a significant progress in improving substrate scope, selectivity, and catalyst activity.

Although there are many different reagents described in the literature for transforming alcohol to aldehyde, we need to either enhance the existing redox procedure or to find new reagents in order to have better efficiency under milder conditions [18].

However, in mechanistic and kinetic studies, using polymer supported oxidizing agents are limited, nevertheless the application of oxidation under phase transfer catalysis in synthetic organic chemistry are common [18, 19]. The polymer supported oxidizing agent has the ability to be used and reused without losing its capacity and in addition it can be used easily and safely which are the main factors of interest in the current study. The side reaction will reduce and the process of oxidation stops just at the product aldehyde step by using polymer supported oxidizing agent. As a part of our study to develop the application of polymer supported reagents in organic syn-[18-20]. synthesis thesis application and of polyethyleneimine (PEI, Scheme 1), which is supported by nano zirconium chromate, is reported.

[PEI-NZrCrO $\frac{1}{4}$ ] found as a stable, clean and green polymer bond zirconium chromate for oxidation of alcohols to relative aldehydes. Many problems related to metal chromate oxidizing agent, such as the need to have an acidic solution and inconsistency of metal chromate [21] have been resolved by using polymeric oxidizing reagent.

Recently, oxidation under phase transfer catalysis spreads in a large extent in synthetic organic chemistry, but mechanistic and kinetic studies of the application of polymer supported oxidizing agents are limited [22]. Safety and easy work up of the polymer supported oxidizing agent are the main factors of interest for the new study, and moreover this oxidizing agent can be used and be reused

### Scheme 1



with no loss of activity and capacity. The oxidation reaction stops only at the aldehyde production step and the side reaction decreases by using the polymer supported oxidizing agent.

Power-law rate model is one of the proper methods for kinetic study. Reaction rate of oxidation of furfuryl alcohol (FurOH) depends on some factors. These factors are amount of catalyst (cat.), concentration of FurOH and furfural (FurH), and also temperature. Here the oxidation rate (mol dm<sup>-3</sup> min<sup>-1</sup>) is expressed in terms of the power law model as:

$$r = -(\mathrm{d}C_{\mathrm{FurOH}}/\mathrm{d}t) = k[\mathrm{FurOH}]^{a} [\mathrm{cat.}]^{b} [\mathrm{FurH}]^{c}$$
(1)

where k is the rate constant, and a, b, c, are the reaction orders with respect to the concentration of FurOH (mol/dm<sup>3</sup>), catalyst (mol/dm<sup>3</sup>), and FurH (mol/dm<sup>3</sup>), respectively. As it is known the rate constant is a temperature dependent constant and by using Arrhenius equation, it can be expressed as:

$$k = A \, \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

In this equation, A and  $E_a$  are the pre-exponential factor and the activation energy (kJ mol<sup>-1</sup>), respectively. *R* is the ideal gas law constant (kJ mol<sup>-1</sup> K<sup>-1</sup>), and *T* is the reaction temperature (K).

### **Results and discussion**

Complexation of highly branched polyethyleneimine with nano zirconium chloride prepared the highly branched polyethyleneimine-supported nano zirconium chromate by replacing the chloride anions with chromates. THF was the selected solvent, and this medium is applied for all the oxidation reactions. Polyethyleneimine-supported nano zirconium chromate is a preferable reagent to many monomeric reagents because after the oxidation reactions, the chromium ions and nano zirconium are tightly bound to the heterogonous polymer support. Evaporation of the solvent, filtration of the reaction mixture and if further separated by column or plate chromatography in order to isolate and purify the product.

There is a difference between chromium(VI)-based polymeric oxidants used for oxidation of alcohols [3, 23–27] and the discussed reagent, in which the reagent can be used in similar amounts according to the reactant. Essential recorded fact in the use of some polymeric reagents [16, 28–32] indicates that the reagent is suitable and non-acidic for oxidation of acid-sensitive materials. Additional reagent can be used, product separation is simple and filtration and evaporation of the solvent is a simple method to

obtain pure product with no by-products and waste, and this is a useful procedure to execute for selective oxidation. As a result of this study, it is proved that the polymeric reagent is a stable material and also storable for months with its initial activity. To evaluate the polymeric reagent stability [PEI-NZrCrO $_{4}^{=}$ ], which was stored 6 months in the laboratory, is used and the same results as with freshly prepared [PEI-NZrCrO $_{4}^{=}$ ] are achieved. To confirm the oxidation capability of  $[PEI-NZrCrO_4^=]$  on different types of alcohols, we used fresh and regenerate catalyst to oxidize benzvl alcohol. *p*-chlorobenzyl alcohol. 2-chlorobenzyl alcohol, and 2-nitrobenzyl alcohol under similar conditions as for oxidation of furfuryl alcohol. The results revealed that  $[PEI-NZrCrO_4^{=}]$  can be used to oxidize the foregoing alcohols successfully.

[PEI-NZrCrO<sub>4</sub><sup>-</sup>] is a nontoxic, non-pollutant, and nonvolatile oxidizing reagent and does not irritate skin and mucous membrane. Scanning electron microscopy (SEM) and transmission electron microcopy (TEM) are used to assess the morphology of the polymeric reagent. Represented results about particles morphology in Fig. 1 are obtained from SEM images. A good dispersion and dissociation of the particles in the polymer bed is shown in the same image. TEM image clearly shows that spherical particles of Zr nanoparticles were formed and dispersed homogenously into the polymer matrix (Fig. 2). In comparison with the same available compounds [1–6, 13–16], the achieved products showed the same results of structure and properties based on melting point, boiling point, <sup>1</sup>H NMR spectra, and FT-IR.

Using power-law rate model, which is a proper model [33–36], orders of reaction are determined. By fitting the model to the experimental data, the kinetic parameters can be determined. The orders of reaction can be obtained by changing the concentrations of FurOH, FurH, and the amount of catalyst, respectively, while other factors should be maintained constant. The change in the initial reaction rates as a function of the initial concentration of FurOH



Fig. 1 Scanning electron microscopy images of [PEI-NZrCrO<sub>4</sub>]



Fig. 2 Transmission electron microscopy images of [PEI-NZrCrO<sub>4</sub>]

was studied in the coexistence of catalysts (0.073 g/dm<sup>3</sup>) at 66 °C. The results are illustrated in Fig. 3a, b. It can be observed that in Fig. 3b, the plot of ln (initial oxidation rate) versus ln (concentration of FurOH) shows a good linear relationship ( $R^2 = 0.995$ ) and the slope of this linear



**Fig. 3 a** Plot of FurOH concentration versus reaction time with different initial concentration of FurOH, (*filled diamond*)  $2.98 \times 10^{-4}$  mol/dm<sup>3</sup>, (*filled square*)  $6.24 \times 10^{-4}$  mol/dm<sup>3</sup>, (*filled triangle*)  $7.02 \times 10^{-4}$  mol/dm<sup>3</sup>, at 66 °C. **b** The plot of ln(initial oxidation rate) vs ln(concentration of FurOH) to obtain the reaction order with respect to FurOH. Reaction condition: initial [FurH] = 0 mol/dm<sup>3</sup>, amount of catalyst = 0.073 g/dm<sup>3</sup>, at 66 °C

equation is 0.989, which is the reaction order with respect to concentration of FurOH.

Figure 4a shows the effect of catalyst loading on the initial oxidation rates at 66 °C and in the coexistence of FurOH ( $6.28 \times 10^{-4}$  mol/dm<sup>3</sup>). It is observed in Fig. 4a that, with the increase in the catalyst amount, the oxidation rate increases sharply. Figure 4b is similar to Fig. 3b and illustrates that the slope of the straight line is 0.991 which is the reaction order with respect to catalyst and the linear regression is 0.996. This obtained order indicates that this oxidation reaction can be considered as a first order reaction with respect to the amount of the catalysts. Also a first order in the catalyst concentration suggests that the substances in the heterogeneous catalysis system will not likely poison the active sites [37].

Small amount of FurH is added to the solution at the beginning of the reaction for obtaining the order of FurH. Also this part indicates the effect of product on the reaction rate. Figure 5a shows FurOH concentration as a function of reaction time with different concentrations of FurH at 66 °C. In this case, the initial concentration of FurOH and



**Fig. 4 a** Plot of FurOH concentration vs reaction time with different initial concentration of catalyst, (*filled diamond*) 0.0352 g/dm<sup>3</sup>, (*filled square*) 0.0847 g/dm<sup>3</sup>, (*filled triangle*) 0.1089 g/dm<sup>3</sup>, at 66 °C. **b** The plot of ln(initial oxidation rate) vs ln(concentration of catalyst) to obtain the reaction order with respect to catalyst. Reaction condition: initial [FurOH] =  $6.28 \times 10^{-4}$  mol/dm<sup>3</sup>, initial [FurH] = 0 mol/dm<sup>3</sup>, at 66 °C



**Fig. 5 a** Plot of FurOH concentration versus reaction time with different initial concentration of FurH, (*filled circle*)  $9.41 \times 10^{-5}$  mol/dm<sup>3</sup>, (*filled square*)  $2.12 \times 10^{-4}$  mol/dm<sup>3</sup>, (*filled triangle*)  $3.14 \times 10^{-4}$  mol/dm<sup>3</sup>, at 66 °C. **b** The plot of ln(initial oxidation rate) vs ln(initial concentration of FurH) to obtain the reaction order with respect to FurH. Reaction condition: initial [FurOH] =  $12.56 \times 10^{-4}$  mol/dm<sup>3</sup>, initial amount of catalyst = 0.146 g/dm<sup>3</sup>, at 66 °C

catalyst amount are kept constant at  $12.56 \times 10^{-4}$  mol/dm<sup>3</sup> and 0.146 g/dm<sup>3</sup>, respectively. In Fig. 5b, it is indicated that related data are fitted linearly with a negative slope of -0.68 and it is the reaction order for FurH. In kinetics, negative order implies that the product and reactants undergo competitive adsorption on the surface of catalyst and adding more FurH causes occupying more adsorption sites on the surface of catalyst. Therefore the probability of surface reaction on the catalyst decreases and as a result reaction rate decreases.

Constant concentration of FurOH ( $6.28 \times 10^{-4}$  mol/dm<sup>3</sup>) and amount of catalyst (0.073 g/dm<sup>3</sup>) are applied to determine the kinetics of the reaction at different temperatures (50, 55, 60, and 66 °C). In Fig. 6a, it is observed that reaction rate increases with increasing temperature. By applying the calculated rate constants, the value of activation energy and pre-exponential factor (Eq. 2) were determined from the corresponding Arrhenius plot in Fig. 6b. The plot of ln *k* versus 1/*T* creates a straight line and  $R^2$  is 0.995. From the slope of the straight line activation energy ( $E_a$ ) was obtained that it was 76.78 kJ mol<sup>-1</sup>



Fig. 6 a Plot of FurOH concentration versus reaction time under different reaction temperature of (filled diamond) 50 °C, (filled square) 55 °C, (filled triangle) 60 °C, (filled circle) 66 °C. b Arrhenius plot of ln(k) versus 1/T. Reaction condition: initial  $[FurOH] = 6.28 \times 10^{-4} \text{ mol/dm}^3$ , initial amount of catalyst =  $0.073 \text{ g/dm}^3$ , initial [FurH] =  $0 \text{ mol/dm}^3$ 

and from the intercept of this line, the pre-exponential factor (A) was calculated to be  $8.18 \times 10^{11} \text{ mol}^{-1/3}$ dm min<sup>-1</sup>.

Based on the above results and by applying the values of reaction orders and activation parameters into Eq. (1), according to power-law model, the rate expression is:

$$r = 8.18 \times 10^{11} \times e^{-76.78/RT} [FurOH]^{0.989} [cat.]^{0.991} [FurH]^{-0.68}$$
(3)

This rate expression can be used for predicting the relative rate of oxidation of FurOH under different conditions.

# Conclusions

- . -

Unlike other reported catalysts used to oxidize alcohols,  $[PEI-NZrCrO_{4}^{=}]$  can be used in similar amounts according to the reagent and there is no need to use excessive amounts and also there is no need to wet. Since it has no acidic properties, it is suitable for oxidation of acid-sensitive alcohols besides it is not expensive. In addition to these advantages this reagent has the properties of reported polymeric reagents such as easy work-up by filtration and evaporation of the solvent to separate and obtain pure product. It is also stable and storable for months with its initial activity. Furthermore it is a nontoxic, nonvolatile, and nonpolluting oxidation reagent and it is nonirritating to skin.

In consequence, the spent reagent has been regenerated several times and no remarkable change has been observed in its activity. This polymeric reagent is economically appropriate for medium to large-scale operations because it has high stability and ability to regenerate the polymeric bed and it is a functional addition to represent methodologies.

The kinetic study of FurOH oxidation on the nano catalyst has been investigated. The reaction kinetics was initially modeled using the power-law rate expression leading to reaction orders of 0.989, 0.991, and -0.68 with respect to FurOH, catalyst, and FurH, respectively; with the activation energy of 76.78 kJ mol<sup>-1</sup>. It is our suggestion that this heterogeneous catalyst has suitable capabilities for more practical applications in industries.

### **Experimental**

All the compounds such as chemical materials were either synthesized in our laboratory or were purchased from Fluka, Sigma Aldrich Chemical Co., Merck Chemical Co. Reaction progression was monitored by TLC using silica gel Polygram SIL G/UV 254 plates or gas chromatography (GC) equipped with flame ionization detector (FID, SE-30 capillary column) and UV-Visible. Comparison was performed between all the products according to their FT-IR, <sup>1</sup>H NMR, GC-Mass spectra, TLC, and physical data with pure compounds and all the materials were characterized.

GC-Mass spectra where run on a GC aglient7890/ Mass 7000 triple quad and FT-IR spectra were run on a Perkin Elmer RXI spectrophotometer. UV-Visible was run on a HACH DR5000 Spectrophotometer and <sup>1</sup>H NMR spectra were obtained by Bruker Avance DPX instrument (250 MHz). The Zr analyses and the leaching test were analyzed by ICP-OES analyzer (Warian, Vista-Pro), TEM analyses where preformed on an EM912 Omega electron microscope with an acceleration voltage of 120 kV instrument. Scanning electron micrographs where achieved by SEM, Hitachi S-4700 microscope operated at an acceleration voltage of 10 kV. Melting points where characterized in open capillaries with an Electro thermal 9100 melting point instrument. All product yields refer to the isolated yield unless reported as GC yield. Atomic absorption was run on an Aurora instruments A11200.

# Preparation of polyethyleneimine supported nano zirconium tetrachloride

Polyethyleneimine (PEI, 1 g, 23.2 mmol) in THF was added drop wise to 1 g nanoZrCl<sub>4</sub> (4.8 mmol) solution in 20 cm<sup>3</sup> methanol. Precipitation occurred immediately. The mixture was stirred and kept warm for 30 min and then stored in refrigerator for 24 h. The precipitate was filtered and washed several times with methanol, dried in vacuum overnight. Atomic absorption and gravimetric technique was used to determine the ratio of polyethyleneimine to the metal ion, which was about 6:1. M.p.: 223–226 °C (decomposed); FT-IR (KBr):  $\bar{v} = 3400-3500$  (N–H), 1570–1620 (C–H ben), 1354 (C–N) cm<sup>-1</sup>.

# Preparation of polyethyleneimine supported nano zirconium chromate [PEI-NZrCrO<sup>=</sup><sub>4</sub>]

Polyethyleneimine supported nano zirconium tetrachloride (1 g, 4.00 mmol) was suspended in THF and added to a cold solution of 2 g chromium trioxide (10 mmol) in water/THF (10 cm<sup>3</sup>/20 cm<sup>3</sup>). The mixture was shaken magnetically at room temperature for 10 h. The pure product was filtered and washed several times by deionized water, diethyl ether

and then vacuum was used overnight to dry and produce reddish, non-hygroscopic and stable powder (Scheme 2). The FT-IR spectrum showed bonds at 852, 858, 889, 942, 1722 cm<sup>-1</sup> characteristics of chromate ion. Capacities of the reagent measured by titration method, atomic absorption and ICP technique in terms of mmol  $CrO_4^=$  per gram reagent was 2.03 mmol/g. M.p.: 218 °C (decomposed).

### Determination of the capacity of [PEI-NZrCrO<sub>4</sub>]

The principal methods which were used in determination of capacities of polymeric reagents were atomic absorption, ICP, and iodometric titration methods. For atomic absorption and ICP methods, a series of standard solutions containing 0.25–2 ppm of zirconium chloride (with respect to Zr) and potassium dichromate (with respect to Cr) in concentrated nitric acid were prepared. The catalyst [PEI-NZrCrO<sup>=</sup><sub>4</sub>], it was treated successively with 25 cm<sup>3</sup> mixture of concentrated H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and HCl, and filtered.

The filtrate was diluted to  $30 \text{ cm}^3$  with deionized water and used ICP method and atomic absorption technique. This solution with respect to Zr and Cr was determined and the amount of zirconium and chromium was calculated by using the calibration curve for characterized the amount of



zirconium and chromium, the Zr content and Cr content are equal to 1.97 and 2.03 mmol g<sup>-1</sup>, respectively. For iodometric titration method, 1.000 g of [PEI-NZrCrO<sub>4</sub><sup>-</sup>] was suspended in 25 cm<sup>3</sup> of sodium hydroxide (5 N). Potassium iodate (100 cm<sup>3</sup>, 0.25 N) was added immediately, and the flask stirred vigorously for 10 min. Five grams of KIO<sub>3</sub> were added, followed by 40 cm<sup>3</sup> of 4 N sulfuric acid. The flask was allowed to stand in the dark for 3–5 min before iodine was titrated with 0.1 N sodium thiosulfate (starch indicator) until the blue color disappeared. The capacity was then calculated as milimole  $CrO_4^-$  per gram [PEI-NZrCrO<sub>4</sub><sup>-</sup>] was 2 [38].

# Preparation of furfural from furfuryl alcohol: typical procedure

Under reflux condition ~0.5 g of [PEI-NZrCrO<sup>=</sup><sub>4</sub>] (equal to 1 mmol CrO<sup>=</sup><sub>4</sub>) was added to a mixture of 98.1 mg furfuryl alcohol (1 mmol) and 10 cm<sup>3</sup> THF in a 25 cm<sup>3</sup> round-bottomed flask, and the mixture was stirred for 135 min. The progression of the reaction was recorded by using TLC method (ethyl acetate: *n*-hexane, 3:1). The mixture was filtered, and the solvent was volatilized to achieve pure Furfural (96 mg, 99.9 % yield) to complete the reaction. B.p.: 161–162 °C (lit. 161 °C); FT-IR and <sup>1</sup>H NMR spectra agree with published data.

### General procedure for regeneration [PEI-NZrCrO<sub>4</sub>]

The reddish spent reagent (10 g) was treated with 50 cm<sup>3</sup> hydrochloric acid (2 N). The obtained suspension was dropped into excess aqueous sodium hydroxide (5 N). Washing with hydrochloric acid breaks the linkage of zirconium and nitrogen of PEI and then PEI precipitates in aqueous solution. After filtration and successive washings with distilled water the precipitate was dried in vacuum at 40 °C for 12 h to give PEI as a fine precipitate (0.378 g). The filtrate showed positive test for presence of chromium by atomic absorption method. The precipitate was slightly darker than original PEI. The weight loss of the obtained polymer compared to the starting PEI was only 5 %.

#### Methods for kinetic control of oxidation reactions

The oxidation of FurOH was carried out in a magnetically stirred glass reactor  $(50 \text{ cm}^3)$  by dispersing the catalysts in 25 cm<sup>3</sup> in THF medium of FurOH. Temperature was controlled using a thermocouple located in the reactor. Samples (from the reactor) were taken periodically (with a syringe) and centrifuged to separate the catalyst from the mixture. The products were analyzed using a gas chromatography and UV–Visible, identified by comparison

with known standards. External calibration method was used for quantitative analysis of the concentrations of reactants and products generated.

In this study, the initial reaction rate method was employed to conduct the kinetic investigations [39]. Samples were taken at various time intervals within the initial 30 min of this oxidation reaction. For finding the overall kinetic expression, series of experiments were performed by implementing different reaction conditions and determining the initial reaction rates. It should be mentioned that in each set of experiments only one parameter was varied and the other parameters were kept constant [33].

Acknowledgments Financial support of Shiraz Branch, Islamic Azad University (Shiraz, Iran) is gratefully acknowledged.

### References

- Karimi Zarchi MA, Escandari Z (2011) J Appl Polym Sci 121:1916
- Signori AM, Santos KO, Eising R, Albuquerque BL, Giacomelli FC, Domingos JB (2010) Langmuir 26:17772
- 3. Corey EJ, Suggs JW (1975) Tetrahedron Lett 31:2647
- 4. Guziec FS, Luzzio FA (1980) Synthesis 691
- 5. Santaniello E, Ferraboschi P (1980) Synth Commun 10:75
- 6. Setamdideh D, Rahmatollahzadeh M (2012) J Mex Chem Soc 56:169
- 7. Akelah A, Sherrington DC (1981) Chem Rev 81:557
- 8. Merrifield RB (1963) J Am Chem Soc 85:2149
- 9. Sherrington DC (1998) Chem Commun 21:2275
- 10. Akelah A, Sherrington DC (1983) Polymer 24:1369
- 11. Chanteau B, Fresnais J, Berret JF (2009) Langmuir 25:9064
- 12. McKillop A, Young DW (1979) Synthesis 6:401
- Cainelli G, Cardillo G, Osena G, Sandri S (1976) J Am Chem Soc 98:6737
- 14. Frechet JMJ, Darling P, Farrai MJ (1978) J Org Chem 43:2618
- 15. Frechet JMJ, Darling P, Farrai MJ (1981) J Org Chem 46:1728
- 16. Tamami B, Hatam M, Mohajer D (1989) Polym Bull 21:531
- 17. Tamami B, Goudarzian N (1994) J Chem Soc Chem Commun 1079
- 18. Karimi Zarchi MA, Taefi F (2011) J Appl Polym Sci 119:3462
- 19. Gaoa Y, Lama Y (2008) Adv Synth Catal 350:2937
- 20. Kaur I, Kumari V, Dhiman PK (2011) J Appl Polym Sci 121:3185
- Gonzalez-Nunez ME, Mello R, Olmos A, Acerete R, Asensio G (2006) J Org Chem 71:1039
- 22. Sonawane VY, Hilage NP (2009) J Indian Chem Soc 86:1173
- 23. Dauben WG, Lorber ME, Fullerton DS (1969) J Org Chem 34:3587
- Chaudhuria MK, Dehurya SK, Siddhartha Upasana SD, Sinhaa B (2004) Synth Commun 34:4077
- 25. Eynde JJV, Mayence A, Maquestiau A (1992) Tetrahedron 48:463
- Surya Prakash GK, Tongco EC, Mathew T, Vankar YD, Olah GA (2000) J Fluorine Chem 101:199
- 27. Firouzabadi H, Sardarian A, Gharibi H (1984) Synth Commun 14:89
- Tamami B, Iranpoor N, Karimi Zarchi MA (1993) Polymer 34:2011
- 29. Tamami B, Goudarzian N, Kiasat AR (1997) Eur Polym J 33:971

- Tajbakhsh M, Lakouraj MM, Mahalli MS (2008) Synth Commun 38:1976
- 31. Tamami B, Lakoraj MM, Yeganeh H (1997) Iran Polym J 6:159
- 32. Chanda M, Rempel GL (1993) React Polym 19:213
- 33. Demirci UB, Garin F (2008) J Mol Catal A 279:57
- Múnera JF, Irusta S, Cornaglia LM, Lombardo EA, Cesar DV, Schmal M (2007) J Catal 245:25
- 35. Heracleous E, Lemonidou AA (2006) J Catal 237:175
- 36. Martino CJ, Savage PE (1997) Ind Eng Chem Res 36:1391
- Hoek I, Nijhuis TA, Stankiewicz AI, Moulijn JA (2004) Appl Catal A 266:109
- 38. Skoog DA, West DM (1982) Fundamentals of Analytical Chemistry, 4th edn. Holt-Saunders International, Philadelphia
- Boronat M, Corma A, Illas F, Radilla J, Rodenas T, Sabater MJ (2011) J Catal 278:50