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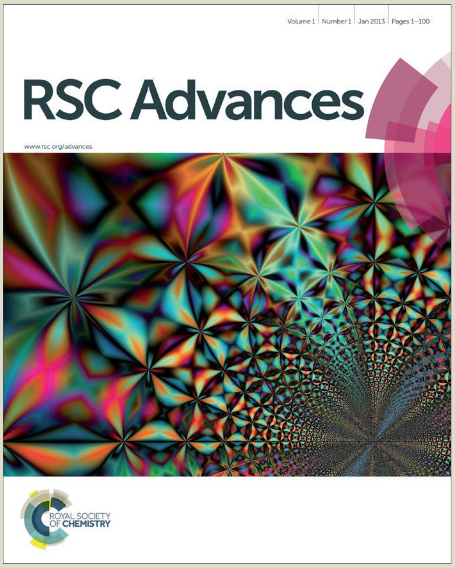

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Highly efficient solvent free synthesis of α-aminophosphonates catalyzed by recyclable nano magnetic sulfated zirconia ($Fe_3O_4@ZrO_2/SO_4^{2-}$)

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In this project, the nano magnetic sulfated zirconia $Fe_3O_4@ZrO_2/SO_4^{2-}$ was prepared and characterized by various instrumental methods. Sulfated zirconia supported on magnetic nanoparticles can act as a well-organized nanocatalyst also can be easily separated by the external magnetic field from the reaction mixture. Nano $Fe_3O_4@ZrO_2/SO_4^{2-}$ is heterogeneous acidic catalyst and has special advantages such as facile synthesis procedure, high activity, easy separation and reusability. It was applied as an efficient nanocatalyst in the synthesis of α-aminophosphonate derivatives in Kabachnik-Fields reaction. These synthetic methods has several advantages including high yields, short reaction times, easy workup and environmentally benign reaction conditions.

Introduction

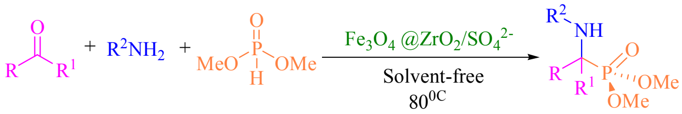
α-aminophosphonates are structurally similar to α-amino acids and also they are important class of compounds in medicinal chemistry which are involved in the metabolism of α-amino acids.[1-3] α-aminophosphonates have some biological applications such as anti-cancer drugs, strong antibiotics, nervous system activator, antibody production and anti-clotting agent.

For the first time, Arbuzov produced alkyl phosphonates from the reaction of trialkyl phosphates with alkyl halides. In 1982 Osipova understand that N- alkoxy α-aminophosphonates can be produced by nucleophiles addition of trimethyl phosphates to oximes which converted to α-aminophosphonates after one setp reduction. Some of disadvantages like low yields which could be mentioned.[4] In 1992, Genet obtained α-aminophosphonates by using trialkyl phosphite.[5] Kabachnik-Fields three component reaction includes the one pot condensation of the amine, aldehyde and di or tri-alkyl Phosphite.[3,7-15] Padvyk reaction in which the dialkyl phosphites to imine in the presence of a Lewis acid or a base is done.[16-24]

Most catalysts used in the synthesis of α-aminophosphonates have shortcomings such as high cost, the use of stoichiometric amounts of catalyst, sensitivity to moisture and difficulties of separation and the recycling. Using of reagents on mineral substrates cause to some advantages such as smooth and easy process reaction conditions, pureproducts, increased selectivity, reduce by-product and waste generated, the speed of response and recovery capabilities, recommended as catalysts.[3,11,25] Antimony trichloride stabilized on aluminum oxide bed is one of the example of catalyst which recently used in Kabachnik-Fields reaction in acetonitrile and under reflux condition.[26] Using microwave irradiation is the other method for the synthesis of α-aminophosphonate, which was done under totally different conditions.[27] Amberlite-IR 120 resin is used as a heterogeneous catalyst in many chemical reactions, including the preparation of α-aminophosphonates under microwave irradiation.[28]

Using heteropolyacid as catalyst for efficient and green condition have been reported in many heterogeneous reactions. These classes of compounds are eco-friendly, reusable, non-toxic and easily removed. Producing α-aminophosphonates in the presence of $H_3PW_{12}O_{40}$ as catalysts by using trimethyl Phosphite in CH_2Cl_2 at room temperature is also reported.[29, 30] Tosyl chloride in catalyst amount used in the preparation α-aminophosphonates in CH_2Cl_2 in the presence of alcohols and in the room temperature. One of the weaknesses of this catalyst is non-recyclability.[31]Hydrous zirconium chloride at 35°C and under solvent-free conditions or in temperatures above 80°C

and a shorter duration, can be catalyzed the α-aminophosphonate synthesis. [32]
The other new method for the synthesis of these materials that has been developed, using a catalytic amount of sulfonium bromide. In the presence of this catalyst the reaction is carreid out with a short time, low temperature and high efficiency. But is limited to aliphatic aldehydes.[33] In other work on the synthesis of α-aminophosphonate is using sulfamic acid as a heterogeneous and recyclable catalyst.[34] Another method for this synthesis is the usage of magnesium ferrite magnetic nanoparticles as the catalyst. The catalyst is reusable and can be easily separated from the reaction mixture.[35] The use of magnetic nanoparticles catalyst coated with dehydroascorbic acid as a heterogeneous catalyst with magnetism properties and the recent approach is recyclability in the synthesis of α-aminophosphonates.[36] α-aminophosphonates are also prepared by $Mg(ClO_4)_2$.[37]
Recycling problem of bronsted acids and lewis acids cause to use these only for one time. The separation of them from the reaction environment is difficult and causes to remaining of impurities in the reaction. In continuation of our previous research on the development of new synthetic methods of nano magnetic sulfated zirconia as a solid acid catalyst in organic synthesis, [38-39] here in, we investigated the catalytic properties of $Fe_3O_4@ZrO_2/SO_4^{2-}$ in the Kabachnik-Fields reaction which in this case in addition of the benefits of having a super acid catalyst and heterogeneous catalyst, ease recovery and can be resolved the separation difficulties by using magnetic property. To assess the efficiency of the synthesized catalyst, it was applied in the Kabachnik-Fields reaction for the synthesis of α-aminophosphonates, three component Kabachnik-Fields reaction between 2-chlorobenzaldehyde, aniline and dimethyl phosphite as a model reaction in the presence of nano magnetic sulfated zirconia.



Scheme1. Kabachnik-Fields reaction by using nano magnetic sulfated zirconia $Fe_3O_4@ZrO_2/SO_4^{2-}$

Result and discussion

Catalyst characterization

Six characteristic peaks of Fe_3O_4 (2θ = 30.1, 35.4, 43.0, 53.5, 57.0 and 62.5) and three diffraction peaks of ZrO_2 (30.6, 51.1, 60.1) can be seen in XRD patterns in figure 1. In XRD pattern of $Fe_3O_4@ZrO_2/SO_4^{2-}$, Fe_3O_4 peaks of synthesized $Fe_3O_4@ZrO_2/SO_4^{2-}$ can be observed which no change in peak's position during the production of $Fe_3O_4@ZrO_2/SO_4^{2-}$ has not been occurred and this shown that the retention of crystalline structure of the magnetite. Due to XRD pattern of $Fe_3O_4@ZrO_2/SO_4^{2-}$ can be shown that, the major form of this catalyst is a tetragonal phase after calcinations.

From the FTIR spectrum of $Fe_3O_4@ZrO_2/SO_4^{2-}$ in figure 2, a broad peak around 3400 cm^{-1} has been seen that can be attributed to the OH stretching vibration. This peak is related to the absorption of water molecules on the catalyst surface that cause to broadening of hydrogen bond. A peak around 1630 cm^{-1} is related to the bending mode of H_2O bonds.

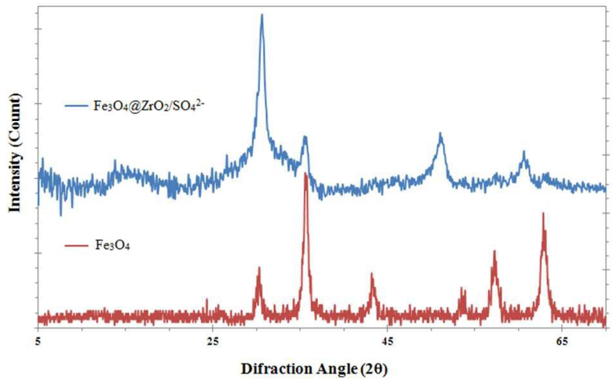


Figure 1: The X-ray diffraction patterns of Fe_3O_4 and $Fe_3O_4@ZrO_2/SO_4^{2-}$

A strong peak for stretching vibration of S=O was appeared in 1126 cm^{-1} and a peak in 1400 cm^{-1} can be attributed to asymmetric stretching vibration of S=O covalent bond. Peaks around 1600 cm^{-1} was appeared in Zr-O bond and the absorption at 500 cm^{-1} is related to Fe-O bond.

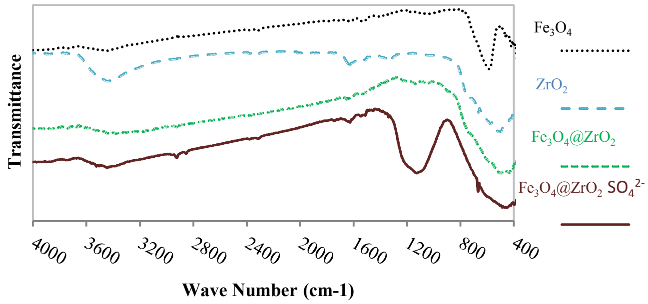


Figure 2: FT-IR spectra of the Fe_3O_4, ZrO_2, $Fe_3O_4@ZrO_2$ and $Fe_3O_4@ZrO_2/SO_4^{2-}$

Scanning electron microscope (SEM) image can be provided information about the size and morphology of the catalyst structure. SEM in figure 3 has shown that the catalyst structure is uniform. Its constituent particles are roughly the same size and the average particle size is about 30 nm. Particle size distribution curve obtained by scanning electron microscope image shows the average size of 40-30 nm for 200 particles. The graphs were plotted using Excel software (figure 4).

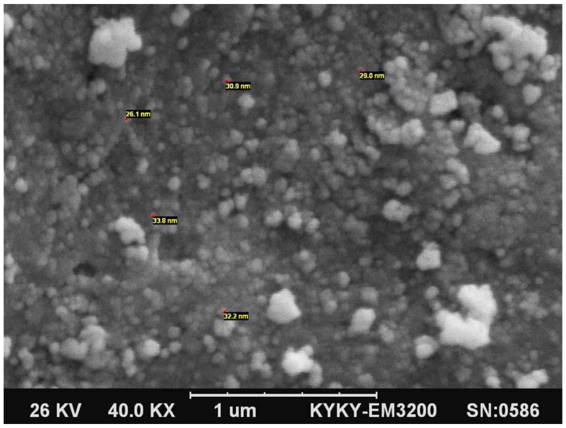
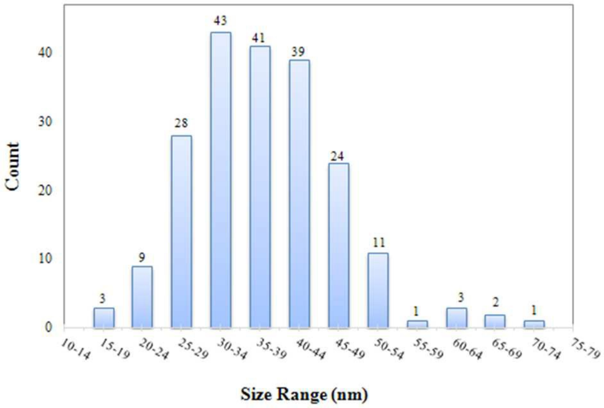


Figure 3: SEM of $Fe_3O_4@ZrO_2/SO_4^{2-}$

Figure 4: The graphs of $Fe_3O_4@ZrO_2/SO_4^{2-}$ by using Excel software



According to result of the analysis VSM, the saturation magnetizatino curve depicted in Fig. 5 there is not any hysteresis in the magnetization sweep. Therefore, the magnetic coercivity of the nano structure is zero, which suggests that the sample containing Fe_3O_4 is superparamagnetic.

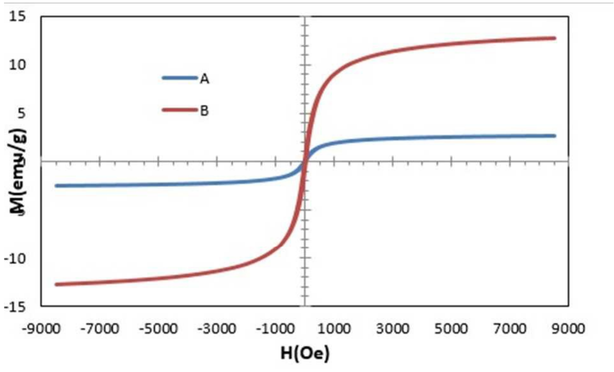


Figure 5: A) VSM of $Fe_3O_4@ZrO_2/SO_4^{2-}$, synthesized by 0.3 gr Fe_3O_4 and calcinated in at air atmosphere.B) VSM of $Fe_3O_4@ZrO_2/SO_4^{2-}$, synthesized by 3 gr Fe_3O_4 and calcinated in Nitrogen furnace .

TEM in figure 6 has shown quantitative measures of particle and grain size, size distribution, and morphology.

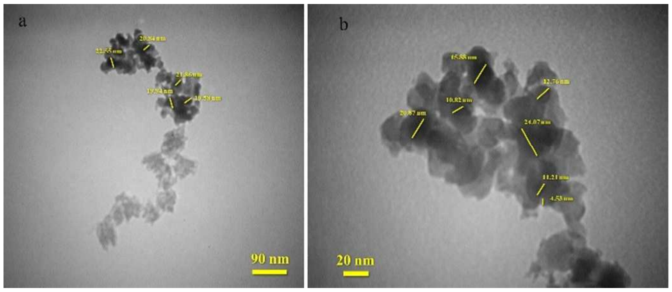


Figure 6: TEM image of $Fe_3O_4@ZrO_2/SO_4^{2}$

Finally, to confirm the structure of $Fe_3O_4@ZrO_2/SO_4^{2-}$ EDX spectrum was used. As shown in figure 7, can be cofrimed existence of iron, oxygen, and sulfur zirconium in the sample of this catalyst.

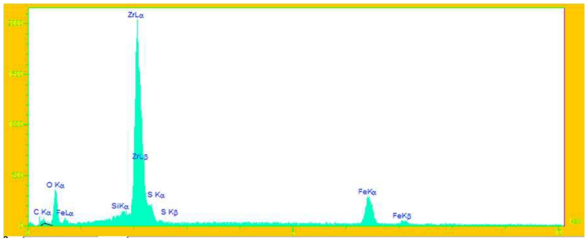


Figure 7: Energy dispersive X-ray spectroscopy of $Fe_3O_4@ZrO_2/SO_4^{2-}$

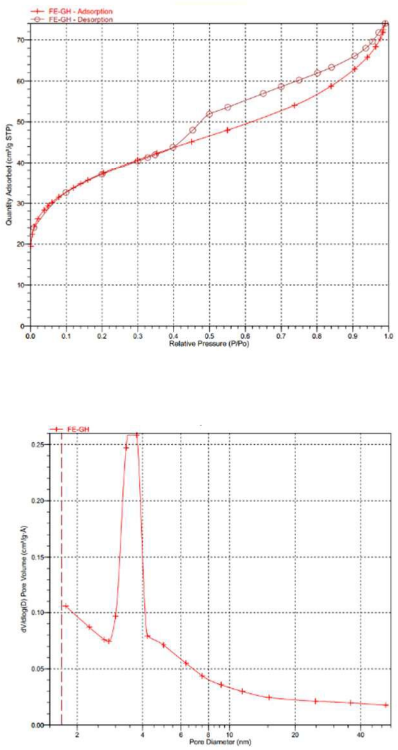


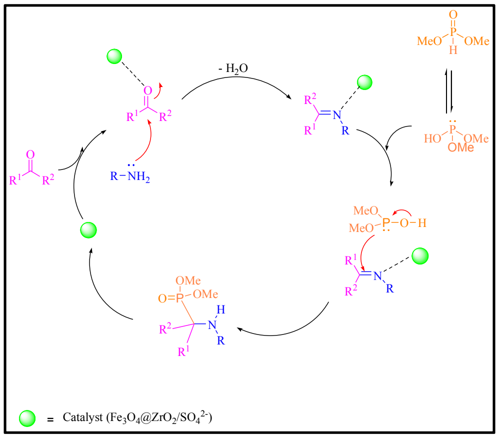
Figure 8: Nitrogen adsorption- desorption isotherm and pore- size distribution of $Fe_3O_4@ZrO_2/SO_4^{2-}$.

N_2 adsorption measurements were measured to investigate the BET specific surface area of the $Fe_3O_4@ZrO_2/SO_4^{2-}$. As can be seen from figure 8, the BET surface area of $Fe_3O_4@ZrO_2/SO_4^{2-}$ is 121 m^2/g. The high specific surface may endow the material stronger catalytic properties. The corresponding pore- size distribution determined by BJH method are also shown in figure 8 (3.77 nm).

Catalytic properties

The proposed mechanism of the Kabachnik-Fields reaction in the presence of a $Fe_3O_4@ZrO_2/SO_4^{2-}$ catalyst

The proposed mechanism for the synthesis of α-aminophosphonate with the $Fe_3O_4@ZrO_2/SO_4^{2-}$ catalyst has been shown in scheme 2. According to this mechanism, catalyst can be facilated the formation of imine intermediate by activating the carbonyl group. [39]



Scheme 2. The proposed mechanism of the Kabachnik-Fields reaction in the presence of a $Fe_3O_4@ZrO_2/SO_4^{2-}$ catalyst

In the presence of catalyst, carbon of imine attacked by phospite and the desired product is obtained.

The optimal conditions for the Kabachnik-Fields reaction in the presence of a $Fe_3O_4@ZrO_2/SO_4^{2-}$ catalyst

In the first, reaction done in ethanol, 80°C temperature and in the presence of 80 mg of catalyst and production was obtained in the yield of 65%. To improve the efficiency of the reaction, the effect of different solvents such as water, acetonitrile and solvent-free conditions were studied and the best yields were obtained in solvent-free conditions. The effect of temperature on the reaction efficiency was investigated. Therefore, the optimal conditions were obtained: 80 mg of the catalyst, temperature of 80°C with solvent free condition (table 1).

Table1.The various conditions for the Kabachnik-Fields reaction in the presence of a $Fe_3O_4@ZrO_2/SO_4^{2-}$ catalyst (a).

Entry	Temperature (°C)	Solvent	Time (min)	Catalyst (mg)	Yield (%)[b]
1	80	EtOH	20	80	**65**
2	80	H_2O	20	80	**low**
3	80	CH_3CN	20	80	**65**
4	80	-	20	80	**93**
5	RT	-	20	80	**10**
6	60	-	20	80	**65**
7	100	-	20	80	**93**
8	80	-	20	60	**75**
9	80	-	20	40	**73**
10	80	-	20	100	**95**

[a] Reaction conditions: 2-chlorobenzaldehyde (1.0 mmol), aniline (1.0mmol), dimethyl phosphite (1.2 eq), catalyst (aldehyde or ketone was added with catalyst), solvent (2.0 ml). [b] Isolated yields.

After obtaining the optimized conditions, the reaction for the preparation of α-aminophosphonate was carried out in solvent free and 80°C. In the first step,the reaction were studied without catalyst and then with the iron oxide magnetic nanoparticles, oxide nanoparticles zirconium and zirconium (IV) chloride as a catalyst of this reaction. The results in table 2 (4-7) are summarized.

Table 2 various conditions for the preparation of α-aminophosphonate with and without catalysts (a).

Entry	Catalyst	Catalyst (mol %)	Time (min)	Yield (%)[b]
1	-	-	24(hr)	**30**
2	Nano-Fe_3O_4	10	20	**76**
3	Nano-ZrO_2	10	20	**82**
4	$ZrCl_4$	10	20	**85**
5	ZrO_2/SO_4^{2-}	80 (mg)	20	**45**
6	$Fe_3O_4@ZrO_2$	80 (mg)	20	**36**
7	$Fe_3O_4@ZrO_2/SO_4^{2-}$	80 (mg)	20	**93**

[a] Reaction conditions: 2-chlorobenzaldehyde (1.0 mmol), aniline (1.0mmol), dimethyl phosphite (1.2 eq), catalyst, solvent-free, 80 ^{0C}. [b] Isolated yields.

In the absence of a catalyst, the reaction did not progress. Nano magnetic sulfated zirconia catalyst ($Fe_3O_4@ZrO_2/SO_4^{2-}$) in comparison with other catalysts has a higher yield. It was observed that the addition of Fe_3O_4 to sulfated zirconia dramatically affected the catalytic activity in the synthesis of α–aminophosphonates (entries 5, 7, Table 2), it was found that iron oxide (Fe_3O_4) modifies the sulfated zirconia surface by generating acidic sites of medium strength. Sufficiently doping the sulfated zirconia with iron oxide can increase the total number acidic sites with lower strength. These changes, especially the simultaneous presence of two acidic type sites with different strengths, are interesting for catalytic activity. The ionic nature of S=O imparts the Bronsted acid site to the catalyst which enhances the acidity of the material thereby reinforcing the catalytic activity (entries 6, 7, Table 2).

The optimal conditions for the development of other derivatives of α-aminophosphonates

This reaction performed with simple and sensitive aldehydes to acid such as thiophene carbaldehyde and also several amines and the products were obtained with good yields. In addition to aldehydes, ketones were also tested. For example, cyclohexanone can be react with aniline and dimethyl phosphate and the product was obtained in good yield. All the derivatives has been shown in table 4.

Recyclability of the Fe_3O_4@ZrO_2/SO_4^{2-}catalyst in Kabachnik-Fields reaction

Reusability of catalyst for the reaction between 2-chloro benzaldehyde, aniline and dimethyl Phosphite was investigated. When the reaction was completed, catalyst separated with an external magnetic field and then was washed with ethanol and dried at room temperature and subsequent reactions without further purification was followed. The catalyst recycled and used 5 times in a row without a significant change in the catalytic capability (figure 9).

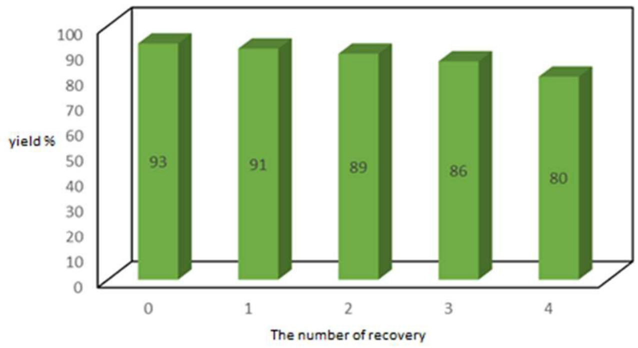


Figure 9: Recyclability of the Fe_3O_4@ZrO_2/SO_4^{2-} catalyst in Kabachnik-Fields reaction

Comparison of the results obtained in the the synthesis of α-aminophosphonat in the presence of Fe_3O_4@ZrO_2/SO_4^{2-} catalyst and other catalysts which have been reported

Finally, a comparative study of the catalytic system with some recent reported in one-pot reaction between benzaldehyde, aniline and dimethyl phosphite indicates that, the catalytic propertise of Fe_3O_4@ZrO_2/SO_4^{2-} is comparable with other catalytic reported systems (table 3).

Experimental

Chemicals and Instruments

All chemicals used, such as salts of iron (III) chloride, iron (II) chloride, zirconium (IV) chloride, ammonium sulfate, aldehydes, ketones, amines, and dimethyl phosphite and solvents used were supplied by Merck and Aldrich chemical companies. FT-IR spectra were obtained over the region 400-4000 cm^{-1} with a Nicolet IR 100 FT-IR with spectroscopic grade KBr. The powder X-ray diffraction pattern was recorded using a X-PERT- PRO diffractometer with Cu Kα, (λ= 1.54 Å) irradiation, in the range of 5 to 80 (2θ) with a scan Step of 0.026. The morphology of catalyst was studied with scanning electron microscopy using SEM (KYKY, EM 3200) on gold coated samples. The magnetic properties of Fe_3O_4@ZrO_2/SO_4^{2-} nanoparticles were measured with a vibrating magnetometer/ Alternating Gradient Force Magnetometer (VSM/, MDKFD). The BET surface area and pore volume of Fe_3O_4@ZrO_2/SO_4^{2-} was determined with a micromeritics ASAP 2020 apparatus using nitrogen as the analysis gas.

Preparation of the magnetic Fe_3O_4 nanoparticles (MN*Ps*)

Ferric acid and ferrous salts were employed as precursors for the synthesis of Fe_3O_4 nano particles. Briefly, $FeCl_3.6H_2O$ (12.2 g, 0.04 mol) and $FeCl_2.4H_2O$ (4.7 g, 0.02 mol) were dissolved in 100 ml distilled water under vigorous stirring. After 10 minutes, the solution was heated at 50 ^{0}C under nitrogen atmosphere. Consequently, the ammonium hydroxide solution (25%) was added dropwise to the reaction mixture to maintain the reaction pH about 9. Afterward, the reaction mixture was cooled at room temperature and black precipitate which was separated by external magnet from the reaction mixture, repeatedly washed with de-ionized water for several times to remove the remaining impurities. At the final step nanoparticles was dried at 60 ^{0}C in vacue.

General procedure for the synthesis of Fe_3O_4@ZrO_2/SO_4^{2-}

Initially 30g $ZrCl_4$ were dissolved in 1000 ml EtOH: H_2O (1:1) to form a colorless solution and aqueous ammonia (10%) was added dropwise under vigorous stirring until the pH of the solution reached 2. Then 3g Fe_3O_4NPs was added to the mixture, after that aqueous ammonia (10%) was added dropwise again under sonication up to pH 9. The precipitate was filtered, thoroughly washed with distilled water, the absence of chloride ion was confirmed by $AgNO_3$ test. Subsequently the obtained solid was dipped in $(NH_4)_2SO_4$ (3 mol.L^{-1}) aqueous solution at room temperature for 24 h. Then the solid was filtered, dried without washing overnight at 100 ^{0}C and calcined at 600 ^{0}C, for 6 h in the N_2 atmosphere.

General procedure for the synthesis of α-aminophosphonates

To a mixture of aldehydes or ketones (1 mmol), amine (1 mmol) and dimethylphosphite (1.2 mmol) in the percense of Fe_3O_4@ZrO_2/SO_4^{2-} (80.0 mg) and stirred at 80^{o}C for the appropriate reaction time (for the period of time listed in Table 4), The reaction was monitored by TLC (50:50 EtOAC/n-hexane), Dichloromethane was added after completion of the reaction, catalyst was recovered with an external magnet (or filteration). A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50:50 EtOAC/n-hexane) if necessary. The products thus obtained(in table4) were characterized by mp, IR, NMR spectroscopy; Spectral data for selected products is presented in the support information.

Back titration in aqueous media catalyst $Fe_3O_4@ZrO_2/SO_4^{2-}$
The amount of released $[H^+]$ by catalyst was determined by back titration. In a container which contained 35 ml of distilled water, 0.5 g of NaCl, 0.5 g catalyst and 10 ml NaOH (0.1 M) were added and stirred for 24 h on a magnetic stirrer until neutralized $[H^+]$ which produced from catalyst hydrolysis. Then three drops of phenolphthalein were added to the container and the solution titrated with 0.1 M solution of hydrochloric acid. The end point was reached when the colour changed from pink to colourless.

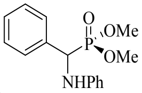
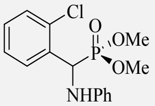
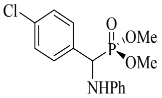
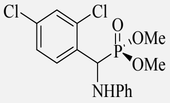
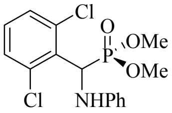
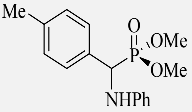
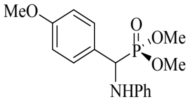
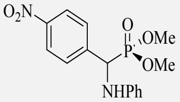
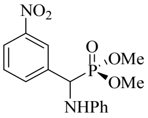
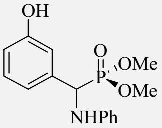
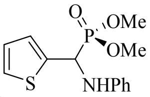
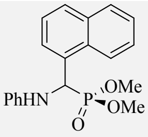
Spectral data : reported in the support information**.**

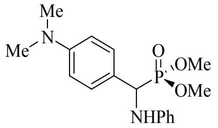
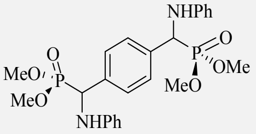
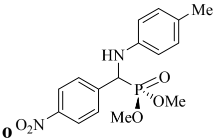
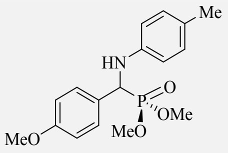
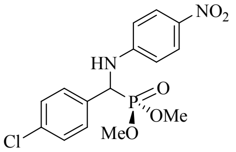
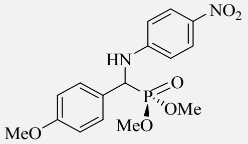
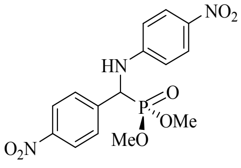
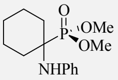
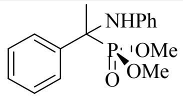
Table 3: Comparison of the results obtained in the the synthesis of α-aminophosphonate in the presence of $Fe_3O_4@ZrO_2/SO_4^{2-}$ catalyst and other catalysts

Entry	**catalyst (mol %)**	**Solvent**	**Time (hr)**	**temp (^oC)**	**Yield (%)**	**Ref.**
1	Cat 1 (5)	CH_3CN	3	rt	90	**26**
2	Cat 2 (10)	-	2	50	98	**39**
3	Cat 3 (10)	-	2	35	94	**35**
4	Cat 4 (0.09)	-	2	40	93	**36**
5	Cat 5 (80 mg)	-	30 (min)	80	95	**Present work**

Catalysts: 1- $SbCl_3/Al_2O_3$, 2- Oxalic acid, 3- $MgFe_2O_4$, 4- DHAA@Fe_3O_4, 5- $Fe_3O_4@ZrO_2/SO_4^{2-}$

Table 4. synthesis derivatives of α-aminophosphonate in the presence catalyst $Fe_3O_4@ZrO_2/SO_4^{2-a}$

Entry	Time (min)	Carbonyls	amines	Products	Yield (%)^b	Mp(°C)[Ref]
1	30	PhCHO	Aniline	 **1a**	95	**90-92 [41]**
2	20	2-(Cl)C_6H_4CHO	Aniline	 **1b**	93	**128-129 [42]**
3	15	4-(Cl)C_6H_4CHO	Aniline	 **1c**	95	**139-140 [43]**
4	30	2,4-(Cl)$_2C_6H_3$CHO	Aniline	 **1d**	89	**110-112 [42]**
5	70	2,6-(Cl)$_2C_6H_3$CHO	Aniline	 **1e**	85	**98-100 [19]**
6	25	4-(Me)C_6H_4CHO	Aniline	 **1f**	93	**125-128 [45]**
7	15	4-(OMe)C_6H_4CHO	Aniline	 **1g**	90	**123-124 [41]**
8	20	4-(NO_2)C_6H_4CHO	Aniline	 **1h**	96	**127-128 [41]**
9	40	3-(NO_2)C_6H_4CHO	Aniline	 **1i**	95	**122-124 [44]**
10	20	3-(OH) C_6H_4CHO	Aniline	 **1j**	96	**130-132 Present work**
11	80	Thiophen-2-carbaldehyde	Aniline	 **1k**	80	**83-86 [19]**
12	30	1-naphthaldehyde	Aniline	 **1l**	90	**143-145 [45]**

13	20	4-(dimethyl amino) benzaldehyde	Aniline	 **1m**	85	**144** **[13]**
14^{c}	15	Terephthaldehyde	Aniline	 **1n**	90	**170-173** **[46]**
15	10	4-(NO$_2$)C$_6$H$_4$CHO	*p*-Toluidine	 **1o**	92	**209-211** **[47, 52]**
16	20	4-(OMe)C$_6$H$_4$CHO	*p*-Toluidine	 **1p**	88	**96-99** **[41]**
17	15	4-(Cl)C$_6$H$_4$CHO	4-Nitroaniline	 **1q**	76	**160-162** **[13]**
18	25	4-(OMe)C$_6$H$_4$CHO	4-Nitroaniline	 **1r**	82	**150-152** **[13]**
19	15	4-(NO$_2$)C$_6$H$_4$CHO	4-Nitroaniline	 **1s**	80	**170-173** **[13]**
20	50	Cyclohexanone	Aniline	 **1t**	75	**99-102** **[13]**
21	120	Acetophenone	Aniline	 **1u**	70	**125-129** **[13]**

^{a} Reaction conditions: aldehyde or ketone (1.0 mmol), amine (1.0 mmol), dimethyl phosphite (1.2 eq), catalyst (80 mg), under solvent-free condition, 80^{oC}, ^{b} Isolated yield, ^{c} Reaction condition: aldehyde (1.0 mmol), amine (2.0 mmol), dimethyl phosphite (2.4 eq), catalyst (100 mg) , solvent-free, 80^{oC}.

Conclusion

There are many routes to synthesized α-aminophosphonate derivatives.[49-51] In this work we introduced sulfated zirconia supported on magnetic nanoparticles as an effective nanocatalyst for Kabachnik-Fields reaction to synthesis of α-aminophosphonate derivatives. From the best advantages of Fe$_3$O$_4$@ZrO$_2$/SO$_4^{2-}$ as a nanocatalyst are easy separation by the external magnetic field and recyclability of catalyst without loss of activity, short reaction time, high yielid, and easy work up processe. Thermal durability of Fe$_3$O$_4$@ZrO$_2$/SO$_4^{2-}$ and good resistance of fanctional groups in washing process are two brilliant benefits of this compund as a catalyst in reactions.

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Notes and references

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Highly efficient solvent free synthesis of α-aminophosphonates catalyzed by recyclable nano magnetic sulfated zirconia ($Fe_3O_4@ZrO_2/SO_4^{2-}$)

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