Preparation of TiO$_2$-ZSM-5 zeolite for photodegradation of EDTA

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Abstract

Doping of TiO$_2$ into ZSM-5 zeolite has been achieved by impregnation and solid–solid interaction methods. The produced samples were characterized using X-ray diffraction (XRD), ultraviolet and visible spectroscopy (UV–vis), the Fourier transform infrared (FT-IR) and surface area measurement. The results show that the incorporation of titanium into framework of ZSM-5 using impregnation method is higher than that of solid–solid interaction method. The photocatalytic tests were carried out for degradation of EDTA. The results indicate that photodegradation of EDTA by impregnation method is much better than that of solid–solid interaction method. The EDTA removal efficiency is 99.9% at 3×10^{-3} M EDTA concentration using impregnation method whereas 75% at 3×10^{-5} M EDTA concentration using solid–solid method.
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1. 1-Introduction

Titanium atoms incorporated into the zeolite framework serve as catalytic sites, and thus the content of framework titanium in a zeolite has presented higher activity in performing some catalytic reactions [1–4]. TiO$_2$ in anatase phase is the best photocatalyst reported so far, poor adsorption and low surface area properties lead to great limitations in exploiting the photocatalyst to the best of its photoefficiency. Supporting TiO$_2$ is commonly reported to be less photoactive due to the interaction of TiO$_2$ with support during the thermal treatments [5]. Several attempts have been made to improve the photoefficiency of titania by adding adsorbents like silica, alumina, zeolites, clays, and active carbon [6–12]. This is expected to induce synergism because of the adsorption properties of the adsorbents with respect to organic molecules. Zeolite based photocatalysis is new and the work reported so far involved the use of high TiO$_2$ loadings [13–26]. The preparation of Ti/ZSM-5 by two methods namely impregna-

tion and solid–solid interaction were achieved. These samples have been characterized by XRD, surface area, FT-IR and UV–vis techniques and tested for photocatalytic degradation of EDTA.

2. Experimental

2.1. Synthesis of Ti/ZSM-5 by impregnation method

The prepared Na-ZSM-5 [27] were stirred in ethanolic solution of TiCl$_4$ to give TiO$_2$ loaded with 2, 4, 6.5 and 8.4 wt%. The samples were dehydrated in an oven for 6 h at 110 °C and calcined eventually at 550 °C for 6 h. The obtained samples were referred as M$_1$, M$_2$, M$_3$ and M$_4$, respectively.

2.2. Synthesis of Ti/ZSM-5 by solid–solid interaction method

ZSM-5 was degassed at 300 °C for 3 h to remove physisorbed water molecules prior to being mechanically mixed with TiO$_2$ anatase (Merck) at room temperature in a

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glove box filled with nitrogen (99% purity), and the mechanically mixed samples were stirred overnight. The samples were heated at 300 °C under a reduced pressure of 10^{-5} Torr for 4 h. The samples were calcined at 550 °C, in air for 6 h. Finally, the prepared samples, which gave TiO_2 loading 2, 4, 6.5 and 8.4 wt% were referred as S_1, S_2, S_3 and S_4, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns were collected with Bruker axs, D8 Advance. Surface areas were recorded using Nova 2000 series, Chromatech. The FT-IR spectra were recorded using Jasco FT-IR-460, plus Japan; the samples were characterized by UV–vis diffuse reflectance spectroscopy using a Cecil 7200, at scanning speed 4000 nm/mm and a band width 2 nm. The samples were measured in the wavelength range from 190 to 500 nm. The total organic carbon (TOC) content in the solution of EDTA before and after radiation with UV was determined using a "Phoenix 8000" Total Carbon Analyzer.

2.4. Photocatalytic experiments

The photoactivity experiments were carried out in a cylindrical Pyrex glass reactor containing different loading of catalyst and 250 ml of aqueous solution of EDTA at 5×10^{-3} M concentration at 30 °C for 60 min. A 150 W medium pressure Hg lamp (254 nm) immersed within the photoreactor was used. The EDTA was determined by comlexometeric titration with Zn^{2+} standard solution [28]. The removal efficiency of EDTA has been calculated by applying the following equation:

$$\% \text{ Removal efficiency} = \frac{C^\circ - C}{C^\circ} \times 100$$

where C° the original EDTA content, C the retained EDTA in solution.

Before all photocatalytic runs, a fresh solution (250 ml) of EDTA were adjusted to required pH, and the catalyst was suspended at 0.4 g/l concentrations. Suspensions were kept in dark and magnetically stirred at 30 °C for 60 min. The results indicate that adsorption efficiency was about 18–20%.

3. Result and discussion

3.1. XRD

Fig. 1 presents the XRD patterns of different wt% of titanium from 2 to 8.4% loaded on ZSM-5 by impregnation method, in comparison with that of ZSM-5 synthesized in previous work [27]. The results show that increased of lines at 2-theta = "7.92, 8.76 and 23.07" are related to the presence of titanium silicate [29] which appeared for all samples, but the lines, which indicate the presence of titanium dioxide
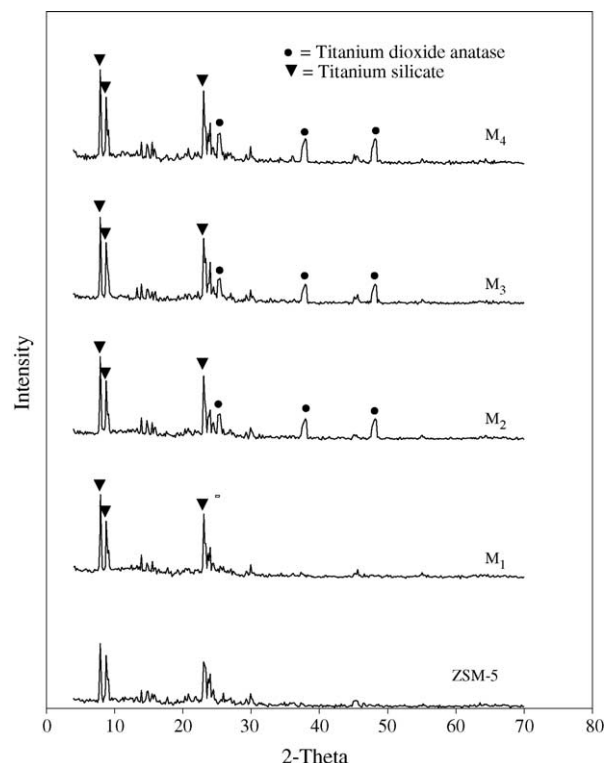

Fig. 1. XRD patterns of ZSM-5 and Ti/ZSM-5 samples prepared by imergnation method.

anatase "at 2-theta = 25.32, 37.41 and 48.04" [30] appeared with samples M_2, M_3 and M_4. Also intensity of titanium dioxide anatase was increased with increasing titanium wt% on ZSM-5. Fig. 2 presents the XRD patterns of different wt% of titanium from 2 to 8.4 % loaded on ZSM-5 by solid–solid interaction method. The results show that the lines, which indicate the presence of titanium dioxide anatase, appeared for all samples. Also intensity of titanium dioxide anatase increased with increasing titanium wt% on ZSM-5. The lattice parameters (a, b, c) and unit cell volume (V) of Ti/ZSM-5 are summarized in Table 1. Upon comparison, the unit cell parameters and thus the unit cell volume of the M_1 sample revealed an enhancement when compared with that of ZSM-5 sample, due to the successful incorporation of Ti into the

Table 1
Effect of preparation methods and different loading of titanium on unit cell parameters of the produced Ti/ZSM-5 samples

Sample	Structural parameters (Å)			V (Å)^3
	a	b	c	
ZSM-5	19.91	20.03	13.40	5343.88
M_1	19.91	20.20	13.41	5393.25
M_2	19.91	20.10	13.42	5370.56
M_3	19.89	20.08	13.38	5343.84
M_4	19.91	20.04	13.38	5338.57
S_1	19.91	20.10	13.45	5352.50
S_2	19.89	20.08	13.38	5343.84
S_3	19.90	20.05	13.39	5342.54
S_4	19.92	19.82	13.38	5282.61

Fig. 2. XRD patterns of ZSM-5 and Ti/ZSM-5 samples perpared by solid–solid interaction method.

Table 2
Surface area and total pore volume of various Ti/ZSM-5 samples

Sample	S_{BET} (m^2/g)	V_p^{total} (cm^3/g)
ZSM-5	381	0.3866
M$_1$	484	0.4692
M$_2$	481	0.4429
M$_3$	468	0.4393
M$_4$	448	0.3748
S$_1$	447	0.4499
S$_2$	433	0.4459
S$_3$	432	0.4241
S$_4$	334	0.3492

sample M$_1$. In case of M$_2$, M$_3$ and M$_4$ samples, the intensity of TiO$_2$ anatase phase was less than that in case of S$_2$, S$_3$ and S$_4$ samples, So that, the S_{BET} and V_p^{total} of M$_2$, M$_3$ and M$_4$ samples are higher than that of S$_2$, S$_3$ and S$_4$ samples.

3.3. UV–vis

It is known that UV–vis spectroscopy is more sensitive to extraframework titanium than XRD spectroscopy [31] distinguished three regions in the UV–vis spectroscopy of TS-1. The band below 220 nm was assigned to isolated titanium in tetrahedral coordination. The second band around 250–280 nm was attributed to nontetrahedral species"assigned to isolated Ti incorporated in the framework". The third band above 280 characterized similar anatase species on the extraframework. Figs. 3 and 4 show diffuse reflectance spectra in UV–vis region of various Ti-ZSM-5 samples prepared by impregnation and solid–solid
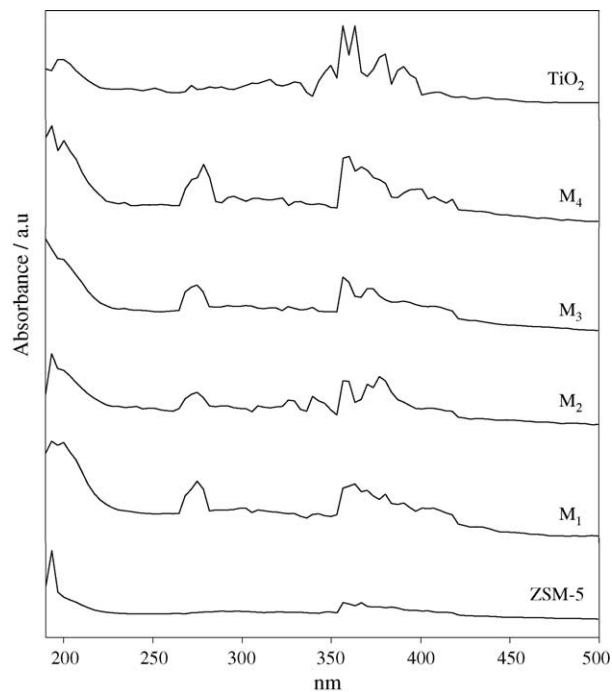
framework of ZSM-5, This is attributed to the bond distances of Si–O and Ti–O are 0.160 and 0.182 nm, respectively. So, the influence of loading of titanium on ZSM-5 on the unit cell volume can be noticed and thus indicate that partial replacement of silicon by titanium, with increasing loading of titanium above 2 wt% "samples M$_2$, M$_3$ and M$_4$" decreased lattice parameters and unit cell volume of Ti/ZSM-5 due to blocking of some pores of ZSM-5 by existing of extraframework TiO$_2$. Also, the unit cell parameters and thus the unit cell volume of the S$_1$ samples revealed small an enhancement when compared with that of M$_1$ sample, due to the presence of TiO$_2$ anatase phase, which block some pores of ZSM-5. Also, unit cell volume of the M$_2$, M$_3$ and M$_4$ samples revealed large an enhancement when compared with these of S$_2$, S$_3$ and S$_4$ samples, respectively, due to the presence of TiO$_2$ phase with small intensity when compared with these of S$_2$, S$_3$ and S$_4$ samples.

3.2. Surface area and total pore volume

The comparison between surface area (S_{BET}) and total pore volume (V_p^{total}) of titanium loading on ZSM-5 are summarized in Table 2. The results show that S_{BET} and V_p^{total} of M$_1$ sample are higher than that of S$_1$ sample, these are attributed to the appeared of titanium dioxide in the sample S$_1$ which were detected by XRD, however not detected in the

Fig. 3. UV-vis spectra of ZSM-5, TiO$_2$ anatase and Ti/ZSM-5 samples prepared by impergnation method with different wt% of titanium.
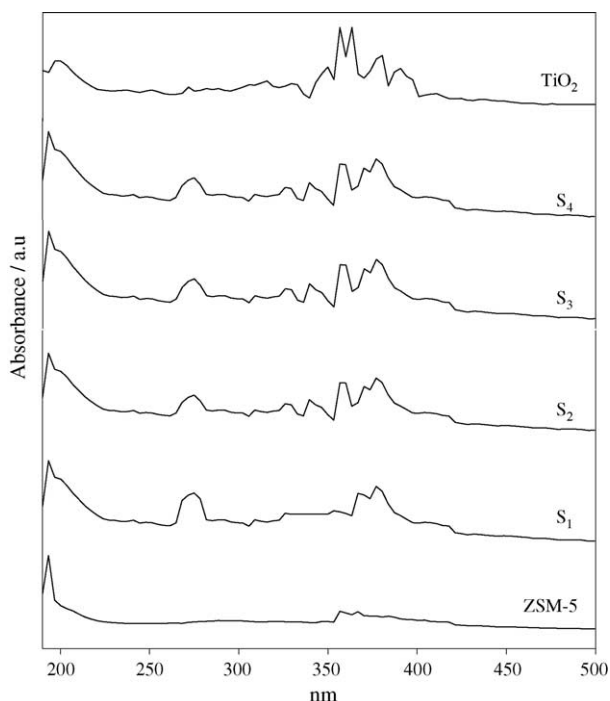
Fig. 4. UV-vis spectra of ZSM-5, TiO$_2$ anatase and different wt% of titanium loaded on ZSM-5 samples prepared by solid–solid interaction method.

interaction methods, respectively. The results show that the band at 275 nm, which represented titanium, incorporated in framework appears alone with M$_1$ sample. However, for the other samples, the bands at 350 and 275 nm, which characterized TiO$_2$ anatase and titanium in framework, are appeared. Intensity of TiO$_2$ anatase band was increased with increasing titanium loading. Therefore, in case of M$_1$, the incorporation of titanium into framework of ZSM-5 is the highest.

3.4. FT-IR spectroscopy

Figs. 5 and 6 show the FT-IR spectra of the corresponding Ti/ZSM-5 samples prepared by impregnation and
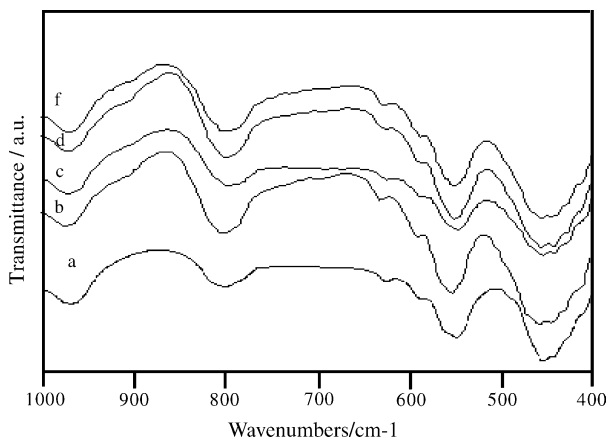

Fig. 5. FT-IR spectra of a-titanium silicate: b 2% Ti/ZSM-5; c 4% Ti/ZSM-5; d 6.5% Ti/ZSM-5; and f 8.4% Ti/ZSM-5 prepared by impregnation method.
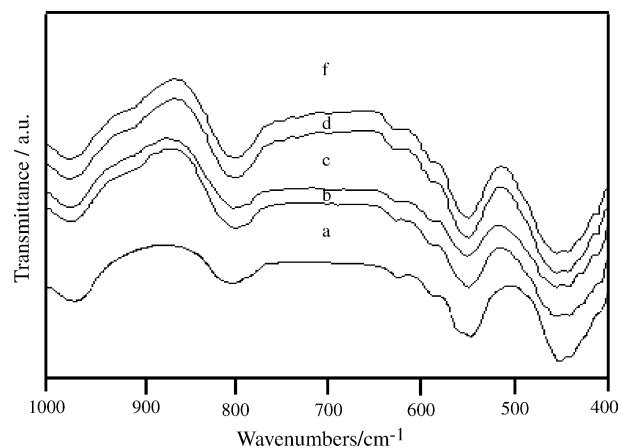

Fig. 6. FT-IR spectra of a-titanium silicate: b 2% Ti/ZSM-5; c 4% Ti/ZSM-5; d 6.5% Ti/ZSM-5; and f 8.4% Ti/ZSM-5 prepared by solid–solid interaction method.

solid–solid interaction methods, respectively. A band at 960 cm^{-1} appears in all samples and intensity of this band in M$_1$ sample is slightly larger than that of the other samples. The presence of the 960 cm^{-1} in the IR spectra of titanium–containing zeolites has been used to infer the incorporation of titanium into framework [17]. Therefore, in case of M$_1$, the percentage of incorporation of titanium into framework of ZSM-5 is the highest.

4. Photocatalytic degradation of EDTA by Ti/ZSM-5 samples

4.1. Effect of wt% of Ti loaded on ZSM-5

A series of experiments has been carried out to study effect of wt% of Ti loaded on ZSM-5 by impregnation and solid–solid interaction methods on EDTA removal efficiency under the following conditions: 0.4 g/l M or S/EDTA solution ratio; 5×10^{-3} M Conc. of EDTA; 1 h reaction time and pH 3. The findings are summarized in Table 3. The results indicate that increasing wt% of Ti loaded on ZSM-5 from 2 to 8.4 wt%, leads to decreasing EDTA removal efficiency in the impregnation and solid–solid interaction methods from 82.3 to 58.8 and from 62.3 to 22%, respectively, This is attributed to the intensity of TiO$_2$ phase was increased by increasing

Table 3
Effect of wt% of Ti loaded on ZSM-5 by impregnation and solid–solid interaction methods on EDTA removal efficiency

Sample	EDTA removal efficiency (%)
M$_1$	82.3
M$_2$	68.2
M$_3$	62.3
M$_4$	58.8
S$_1$	62.3
S$_2$	48.2
S$_3$	32.3
S$_4$	22.0

Table 4
Effect of pH of EDTA solution on EDTA removal efficiency

pH of EDTA	EDTA removal efficiency (%)	
	M_1	S_1
3	82.3	62.3
4	90.5	69.8
7	99.9	75.0
9	99.9	75.5

TiO_2 loading as confirmed by XRD and UV–vis and hence decreasing the photocatalytic activity [17]. The optimum condition for wt% of Ti loaded on ZSM-5 by impregnation and solid–solid interaction methods is 2 wt% at 82.3 and 62.3% photodegradation of EDTA, respectively.

4.2. Effect of pH

A series of experiments has been carried out to study effect of pH on EDTA removal efficiency under aforementioned conditions but Ti loading into ZSM-5 is 2 wt%. The findings are summarized in Table 4. The results indicate that increasing pH of EDTA solution from 3 to 7, leads to increasing EDTA removal efficiency in the impregnation and solid–solid interaction methods from 82.3 to 99.9 and from 62.3 to 75%, respectively, but at pH more than 7, the EDTA removal efficiency almost remain unchanged in both two methods. The possible reason for this behaviour is that alkaline pH range favours the formation of more OH radical due to the presence of large quantity of OH^- ions in the alkaline medium, which enhance the photocatalytic degradation of EDTA significantly [33]. The optimum condition for pH in case impregnation and solid–solid interaction methods is 7 at 99.9 and 75% photodegradation of EDTA, respectively.

4.3. Effect of EDTA concentration

A series of experiments has been carried out to study effect of the EDTA concentration on EDTA removal efficiency under aforementioned conditions at pH 7. The findings are summarized in Table 5. The results indicate that in case impregnation method, increasing EDTA concentration from 5×10^{-5} to 5×10^{-3} M, has no significant effect on EDTA removal efficiency, but at concentration more than 5×10^{-3} M, the EDTA removal efficiency was decreased. In case of solid–solid interaction method, increasing EDTA con-

Table 5
Effect of EDTA concentration on EDTA removal efficiency

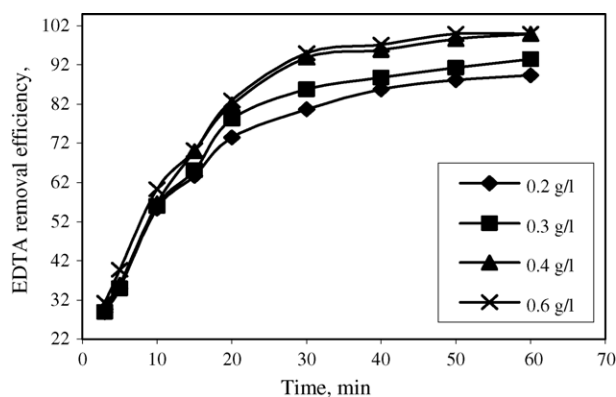| EDTA concentration (M)	EDTA removal efficiency (%)	
	M_1	S_1
5×10^{-5}	99.9	85.0
5×10^{-4}	99.9	79.0
5×10^{-3}	99.9	75.0
7.5×10^{-3}	80.0	66.6
5×10^{-2}	50.0	38.2

Fig. 7. Effect of ratio of M1/EDTA solution ratio, gm/l.on EDTA removal efficiency, %.

centration from 5×10^{-5} to 5×10^{-2} M, decreasing EDTA removal efficiency from 85 to 38.2, respectively. The optimum conditions for EDTA concentration in case impregnation and solid–solid interaction methods are 5×10^{-3} and 5×10^{-5} M, respectively at EDTA removal efficiency 99.9 and 85%, respectively.

4.4. Effect of M_1/EDTA and S_1/EDTA, solution ratio

A series of experiments has been carried out to study effect of M_1/EDTA and S_1/EDTA solution ratio, g/l on EDTA removal efficiency under aforementioned conditions at EDTA concentration in the impregnation and solid–solid interaction methods are 5×10^{-3} and 5×10^{-5} M, respectively. The findings are shown in Figs. 7 and 8. The results indicate that in case of impregnation method, increasing M_1/EDTA solution ratio from 0.2 to 0.4 g/l, leads to increasing EDTA removal efficiency from 89.3 to 99.9%, respectively, but at M_1/EDTA solution ratio more than 0.4 g/l the EDTA removal efficiency almost remains unchanged. In case of solid–solid
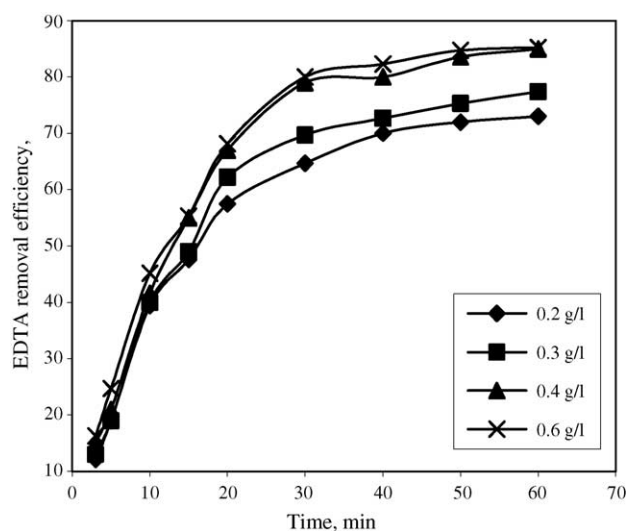

Fig. 8. Effect of S1/EDTA solution ratio, gm/l on EDTA removal efficiency, %.

Table 6
Effect of preparation methods on TOC of EDTA

Sample	TOC before radiation	TOC after radiation	EDTA removal efficiency (%)
M_1	620.0	10.00	98.4
S_1	6.2	0.94	84.8

interaction method, increasing S_1/EDTA solution ratio from 0.2 to 0.4 g/l, leads to increasing EDTA removal efficiency from 73 to 85%, respectively, but at ratio S_1/EDTA solution more than 0.4 g/l, the EDTA removal efficiency almost remains unchanged. The optimum condition of M_1/EDTA and S_1/EDTA solution ratio, g/l are 0.4 at 99.9 and 85% EDTA removal efficiency, respectively. Total organic carbons of EDTA, which were determined before and after radiation of samples by UV for 60 min, is shown in Table 6. The results show that % of EDTA removal efficiency equal 98.4 and 84.8% in case M_1 and S_1, respectively, which is in close agreement with result obtained by volumetric titration as seen above and confirm that all decomposed EDTA were degraded to carbon dioxide [32].

4.5. Kinetic of EDTA with Ti/ZSM-5 prepared by impregnation and solid–solid interaction methods

The reaction order with respect to EDTA was determined by plotting reaction time versus log[EDTA] according to the following equation for various ratios from M_1/EDTA and S_1/EDTA solution.

$$\log [C]_t = -kt + \log [C]_0$$

$$t_{1/2} = \frac{0.639}{k}$$

where $[C]_0$ and $[C]_t$ represent the concentration of the substrate in solution at zero time and t time of illumination, respectively, and k and $t_{1/2}$ represent the apparent rate constant (min^{-1}) and half life time of the reaction(min), respectively. The findings are represented in Figs. 9 and 10 and the apparent rate constants and $t_{1/2}$ are summarized in Table 7.
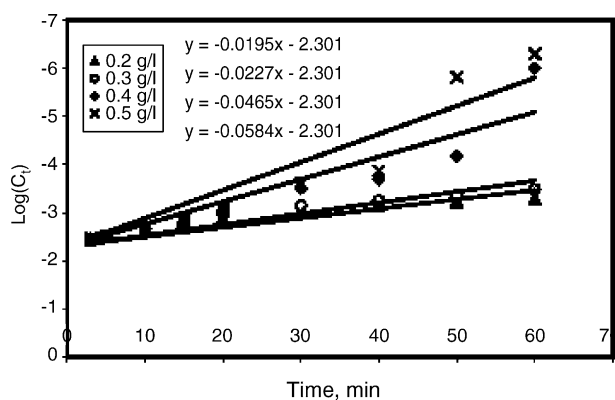

Fig. 9. Reaction kinetic of Ti/ZSM-5 prepared by impregnation method with EDTA.
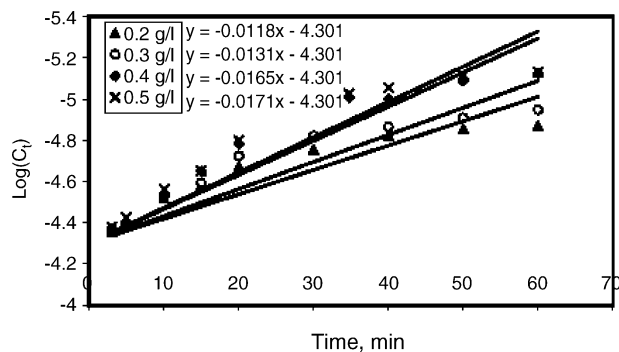

Fig. 10. Reaction kinetic of Ti/ZSM-5 prepared by impregnation method with EDTA.

Table 7
Rate constant of reaction kinetic of EDTA with Ti/ZSM-5 samples prepared by impregnation and solid–solid interaction methods

M_1/EDTA or S_1/EDTA solution ratio (g/l)	$K \times 10^{-4}$ min^{-1}		$t_{1/2}$ (min)	
	M_1	S_1	M_1	S_1
0.2	195	118	35.5	58.7
0.3	227	131	30.5	53.0
0.4	465	165	15.0	42.0
0.6	584	171	12.0	40.5

The results show that the reaction followed first order kinetics with respect to EDTA for both two methods and the rate constants were ranged in case impregnation and solid–solid interaction methods from 195×10^{-4} to 584×10^{-4} and from 118×10^{-4} to 171×10^{-4} min^{-1}, respectively. In addition, $t_{1/2}$ was decreased in case impregnation and solid–solid interaction methods from 35.5 to 12 and from 58.5 to 40.5 min, respectively by increasing M_1/EDTA or S_1/EDTA solution ratio from 2×10^{-4} to 6×10^{-4}, respectively. These indicate that impregnation method is much faster than solid–solid interaction method for photodegradation process. The first order rate equation for EDTA is given by: $R = k[EDTA]$.

5. Conclusions

Syntheses of Ti/ZSM-5 by impregnation and solid–solid interaction methods have been achieved. The lattice parameters and unit cell of S_1 revealed small an enhancement when compared with that of M_1 sample, due to the presence of TiO$_2$ anatase phase, which block pores of ZSM-5. Unit cell volume of the M_2, M_3 and M_4 samples revealed large an enhancement when compared with these of S_2, S_3 and S_4 samples, respectively. Incorporation of titanium into ZSM-5 framework is decreased in the following orders: $M_1 < M_2 < M_3 < M_4$; $S_1 < S_2 < S_3 < S_4$; $M_1 < S_1$; $M_2 < S_2$; $M_3 < S_3$ and $M_4 < S_4$. The photodegradation of EDTA by impregnation method is much better than that of solid–solid interaction method. The EDTA removal efficiency is 99.9% at 3×10^{-3} M EDTA concentration using M_1 sample whereas 75% at 3×10^{-5} M EDTA concentration using S_1 sample. The reaction of

Ti/ZSM-5 with EDTA followed first order kinetics with respect to EDTA for both two methods. The rate constants and $t_{1/2}$ for M_1 and S_1 samples at 0.4 g/l M_1/EDTA or S_1/EDTA solution ratio were (465 min^{-1}, 15 min) and (165 min^{-1}, 42 min), respectively.

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