

The Titanium and Mixed Titanium Carbon Nanoparticles Supported on Silica For Cyclohexene Conversion and of Dyes Removal

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Abstract

The two samples of nanoparticles sulfated titania over silica ST/SiO₂ and sulfated titania active carbon over silica STAC /SiO₂ were synthesized by sol- gel method and characterized by X-ray diffraction XRD , BET , thermal analysis and TEM spectroscopy . The TEM demonstrated that the average particle size of two samples were found to be in the range of (15-50 nm).The ST/SiO₂ and STAC/SiO₂ have been used as an effective catalyst for cyclohexene disproportionation which STAC/SiO₂ catalyst show much higher selectivity for benzene formation at temperature ranging from 200-280°C. Series of kinetic studies had been conducted for the removal of acid and basic dyes. The STAC/SiO₂ has a considerable potential as an adsorbent for the removal of acidic dye (eosin) than the basic dye (safranin).

Keywords: ST/SiO₂ and STAC/SiO₂ nanocatalyst, Sol- Gel method ,cyclohexene and dyes.

1. Introduction

Titania TiO₂ is a polymorphic oxide, inclusive of two common polymorphs: anatase (space group I41/amd, a₀=0.37852 nm, c₀=0.95139 nm) and rutile (space group P42/mnm, a₀=0.45933 nm, c₀=0.29592 nm) both with octahedrally coordinated tetragonal structures . Anatase is a metastable structure but more efficient than rutile and the excellent combination of electrical, mechanical, optical , photochemical and thermal properties of titania makes it a good choice for applications such as: structural material, thermal barrier coating, semiconductor material , photonics and especially dye sensitize solar cells.Theoretical study of surface energy difference of anatase can explain the fact that experimentally crystalline TiO₂ nanoparticles are found to prefer the anatase structure for diameters up to about 10 nm and prepared by sol-gel method **Michele Lazzeri et al., 2001**. The main advantage of using a sol- gel technique is the achievement of good control of surface properties such as composition , thickness and topography **J.Zita et al., 2010 & C.C Wang et al., 1999& J.Zhu et al ., 2007& Y.U.Ahu et al., 2003& O.Kesmez et al ., 2009 & L.Chen et al., 2009& J.X.Liu et al., 2003 & H.E.Chao et al ., 2003** .This method allows preparation of materials with exceptional purity, homogeneity and composition **I. Mai et al., 2009 & M.Sabramanian et al., 2008**. Titania can also act as photocatalyst in the reactions such as hydrogenation of olefins due to strong oxidizing power of its holes, its redox selectivity, high photostability, and easy preparation **Felora Heshmatpour et al., 2011**.Photochemical reactions catalyzed by semiconductors have been extensively studied for water decomposition, degradation of toxic organic pollutants, organic synthesis, dye sensitized solar cells, and energy conversion. In these reactions, photogenerated electrons and holes migrate to the semiconductor surfaces where they can induce reduction and oxidation of adsorbed molecules **Chaochin Su et al., 2006**.When titania is modified by sulfate ions, sulfated titania is formed with high acidity.Sulfate ion modified metal oxides, such as sulfated zirconia and zeolites are two important solid catalysts in acid promoted catalytic reactions, such as dehydration, isomerization and cracking. Also, they are the candidates for potential replacement of the liquid acid catalysts, such as hydrofluoric acid or sulfuric acid in commercial gasoline refining processes **Guangshan Zhu et al., 2007**. Industry is a huge source of water pollution; it produce pollutants that are extremely harmful to people and the environment. Colored water and solutions containing toxic heavy metals from many industries like dye, textile, paper plastic, plating and mining facilities produce polluted water **Gholam Reza et al., 2010& Gaanappriya et a., 2012** .The pollution must be removed from waste water before discharging it into environment . Adsorption process, an inexpensive and simple design, can be used to remove of dye contamination from aqueous environment **A.Jafar Ahmed et al.,2011&Sekaran G., et al ., 1995&Arivoil et al., 2007**.

2. Experimental

2.1 Materials

Titanium (IV) n-butoxide (98%), tetraethylorthosilicate TEOS (purity 99%) and cyclohexene were purchased from Merck company . Absolute ethanol (purity 95%) , Hydrochloric acid (32%) , sulfuric acid (98%) and Tetra hydro furan THF (purity 99%) were purchased from Elnaser company. Active carbon prepared from nuclei balah. Eosin and saffranin dye were applied.

2.2. Synthetic Method

2.2.1. ST/SiO₂

- The SiO₂ sol was obtained by hydrolyzing 31.1900 g of tetraethylorthosilicate in a mixture of 21.2600 g of THF, 6.7400 g of H₂O and 0.7500 g of 2M HCl under a magnetic stirring at 65 to 70 °C for 3h .
- Sulfated titania sol was prepared by placing 10.000 g of ethanol and 10.000 g of titanium butoxide (98%) into a flask under magnetic stirring at room temperature , followed by adding a mixture of 6.500 g of ethanol ,1.500 g of distilled water and 5.000g of H₂SO₄ (18M).
- The SiO₂ sol was then mixed with the ST sol at a proper molar ratio , depending on the desired Ti/ Si ratio in the final product, under stirring magnetically for 12 to 24 h. Finally , the cross linking agent Si(OC₂H₅)₄ was added to the system to form a transparent binary gel . The gel was dried at room temperature for 2 days , ground into fine powder and then heated at 50 °C for about 5h, followed by heating to 550 °C and calcining at 550 °C for 3h. The calcined product was stored in a desiccator for later use.

2.2.2. STAC/SiO₂

- The SiO₂ sol and sulfated titania sol were obtained by the same steps explained before and then SiO₂ sol , ST sol mixed with 0.2 g of active carbon at a proper molar ratio, under stirring magnetically for 12 to 24 h. Finally, the cross linking agent Si (OC₂H₅)₄ was added to the system to form a transparent binary gel . The gel was dried at room temperature for 2days, ground into fine powder and then heated at 50 °C for about 5h, followed by heating to 550 °C and calcining at 550 °C for 3h. The calcined product was stored in a desiccator for later use.

2. 3.Characterization

The high resolution TEM images were obtained on a JEOL JEM 2100 electron microscope with an acceleration voltage 200kV.

The X -ray diffraction patterns of the solid sample was recorded on film at room temperature in a Philips model diffractometer type X Pert MPD at $\lambda = 1.54\text{\AA}$ with Cu-K _{α} radiation and graphite monochromator, data was collected over the range of 4 – 70 degree of 2 θ with continuous scan mode.

Measurement of nitrogen adsorption – desorption isotherms was performed on a Micromeritics ASAP 2020 USA. Before the measurement, each sample was degassed at 550°C for 3 h. The average pore diameters were calculated according to BJH method.

Thermogravimetric analysis was measured using Shimadzu-TGA (Germany) in the temperature range 0 up to 900°C using a thermobalance . The rate of heating of the samples was 10°C min⁻¹ in air atmosphere.

DTA were measured using Shimadzu-TDA (Germany) in the temperature range 0 up to 900°C using thermobalance . The rate of heating of the samples was 10°C min⁻¹ in air atmosphere.

2. 4. Heterogeneous Catalytic Conversion of Cyclohexene

A silica-glass down-flow type tubular reactor containing 0.300 0 g of a reduced catalyst was used in all conversion runs. The reactor was heated in an insulated wider silica-tube jacket **Hala G El-Shobky et al., 2007**, thermostated to + or -1 °C. Cyclohexene feed was introduced into the reactor via its continuous evaporation. The reaction temperatures investigated were 200–280 °C, with 25 °C decrements starting from 200 °C. The reaction effluent passing from the reactor was continuously heated to prevent condensation of any component of the product **E.M.Ezzo et al., 2004**. This effluent was injected twice at each reaction temperature in a Perkin-Elmer

(Perkin Elmer 8600-USA) with flame ionization detector on a DB-Wax column 30 m x 0.53 mm id, 1 μ m (USA). The temperature of injector and detector is 200 and 250°C, respectively, which is recommended to apply for hydrocarbon using nitrogen as a carrier gas.

2. 5. Adsorption Isotherm for the Removal of Dyes

The prepared samples were tested for its efficiency in removing (eosin and saffranin dyes) using UV-Vis spectrometer in the range of (340-630 nm). The parameters studied include initial dye concentration. Freundlich and Langmuir isotherm models were applied to the equilibrium data. **Langmuir 1918**. Calculate the analyze equilibrium dye adsorption quantities **Jafar, Ahmed et al., 2010 & ISI, Activated Carbon, 1992**.

3. Results and Discussion

3.1. Transmission Electron Microscope (TEM)

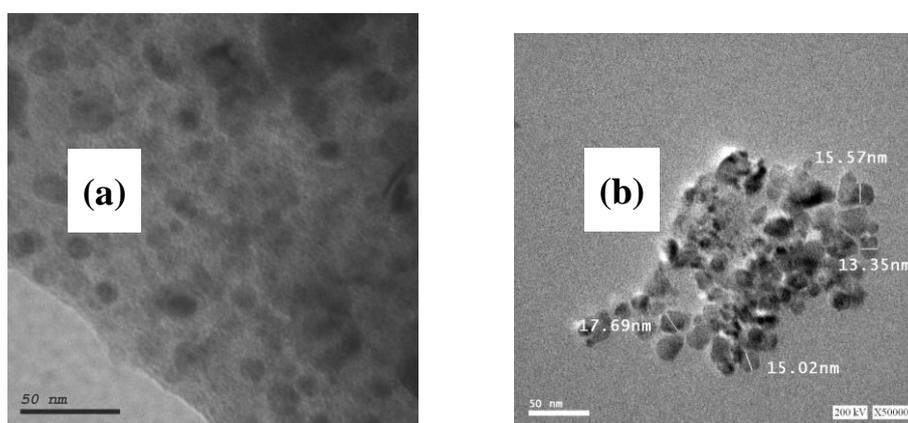


Figure 1. TEM image of a- for ST/SiO₂ and b- for STAC/SiO₂ investigated solids.

The two samples ST/SiO₂ and STA.C /SiO₂ were examined by transmission electron microscope (TEM). Fig.1a shows that the average particle size of ST/ SiO₂ in the range of 50-100 nm and showing that the titanium (darker circular) dispersed on the surface of silica referred to as primary particles, are uniform and are typically approximately 5 nm in size. Fig.1b show that the particle size of the sample STAC/SiO₂ in the range of 13-18 nm and titanium collected on the surface due to adding active carbon.

3. 2. The XRD Studies

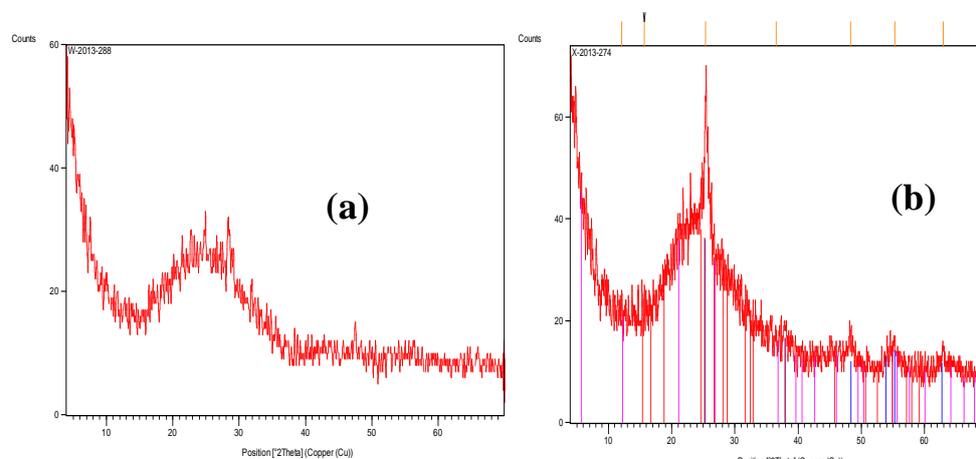


Figure 2. XRD pattern of a- for ST/SiO₂ and b- for STAC/SiO₂.

Fig.2a of the ST /SiO₂ pattern does not show any peaks indicating that titanium species have a good dispersion on the support surface, so show amorphous nature. While fig.2b of STAC /SiO₂ shows peaks at $2\theta = 25.3700$, 48.2713 , 12.1084 with respect to titanium oxide (anatase structure), silicon dioxide and titanium sulfate. This

indicates that presence of sulfur as titanium sulfate.

3.3. The N₂ Adsorption- Desorption Isotherm

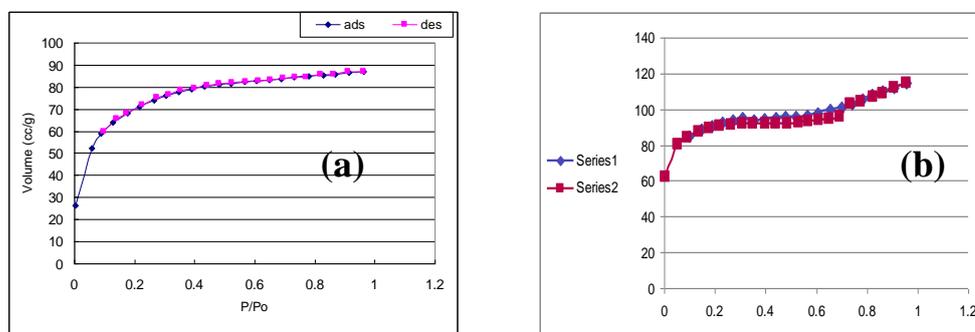


Figure 3. N₂-adsorption –desorption isotherm of a- for ST/SiO₂ and b- for STAC/SiO₂

The N₂ adsorption-desorption isotherm Fig.3a and Fig.3b suggest that a micro-mesoporous structure for the STAC/SiO₂ with a BET surface area of 317.478 which is much larger than that 236.036 m²/g of ST/SiO₂. The single pore volume of the STAC/SiO₂ is **1.773e-01** cc/g which is much larger than that 1.346e-01 cc/g for ST/SiO₂, median pore diameter is 256.7 Å, 221.6 Å for ST/SiO₂ and STAC/SiO₂ respectively. The nitrogen physisorption measurement of ST/SiO₂ show type I isotherm and STAC/SiO₂ show type II isotherm.

3.4. Thermogravimetric Analysis and Differential Thermal Analysis

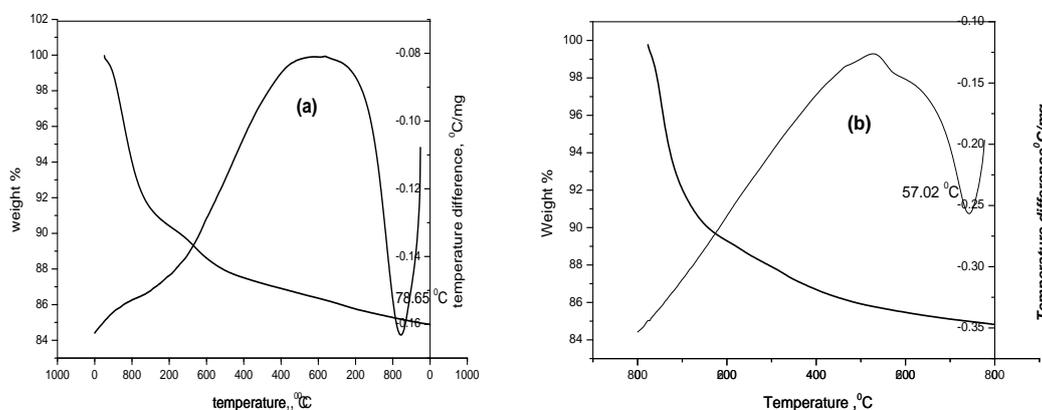


Figure 4. The thermal gravimetric analysis of solid catalyst a- for ST/SiO₂ and b- for STAC/SiO₂

The TGA thermogram confirms the amount of solvent inside or outside the coordination sphere and gives some information about the stability of the compound. The thermogram of ST/SiO₂ (Fig.4a) shows three stages of the mass loss over the temperature range 25-800°C. The first stage at 151°C corresponding to removal of water molecules outside the coordination sphere with weight loss (found= 8.5825%). The second peaks in the temperature range 151-351°C corresponding to removal of water molecules inside coordination sphere with weight loss (found = 3.46 %). The third inflection point at temperature range 351-800°C corresponding to removal of sulfate group with weight loss (found=2.997 %). The thermogram of STAC/SiO₂ (Fig.4 b) shows two stages of the mass loss over the temperature range 25-800°C. The first stage at 25-170°C corresponding to removal of water molecules outside the coordination sphere with weight loss (found= 9.939%). The second peaks in the temperature range 170-800°C corresponding to removal of water molecules inside coordination sphere and with weight loss (found = 5.176 %). The two samples show the stability over temperature range 25-900°C. The DTA curves of two samples displays one endothermic peaks at 78.5 °C and 57.02 °C respectively.

The thermodynamic activation parameters of the decomposition process of two solids were calculated using well known Coats-Redfern equation **A.W.Coats , et al., 1914**.Based on Arrhenius Eq **Arshad Adam Salema et al.,2014 (1)**:

$$k(T)=A\exp^{-E/RT} \quad (1)$$

$$d\alpha/dt=Ae^{-E/RT}(1-\alpha)^n \quad (2)$$

where A is the frequency or pre-exponential factor, E is the activation energy of the reaction, R is the universal gas constant, T is the absolute temperature, n is the order of reaction, t is the time, and α is the fraction of reactant decomposed at time t. The extent of reaction α is defined in terms of mass change in the mass sample. The simplified form of Eq. (2) is as follow after assuming the order of the reaction, n to be unity, and the ratio 2RT/E to be very small **Ahmed I. Hanafy et al., 2012**:

Table 1.Thermodynamic Parameters for two Samples.

ST/SiO ₂					STAC/SiO ₂				
Deacomp., Temp.,°C	E kJmole ⁻¹	ΔS JK ⁻¹ mole ⁻¹	ΔH kJmole ⁻¹	ΔG kJmole ⁻¹	Temp., °C	E kJmole ⁻¹	ΔS JK ⁻¹ mole ⁻¹	ΔH kJmole ⁻¹	ΔG kJmole ⁻¹
25-151	35.49	-160.39	33.02	80.82	23-170	20.81	-201.85	18.36	78.11
151-351	27.24	-216.11	23.72	115.35	170-800	6.78	-271.79	3.105	123.51
351-800	25.07	-255.67	19.89	179.43	-	-	-	-	-

$$\ln [-\ln(1-\alpha)/T^2] = \ln [AR/\beta E] - E/RT \quad (3)$$

Above equation will result in a straight line with slope $-E/R$ and an intercept of $\ln[AR/\beta E]$. The term β here refers to the heating rate. The values of E and A can be obtained by plotting graph of $\ln(-\ln(1-\alpha)/T^2)$ versus $1/T$. The activation entropy ΔS , the activation enthalpy ΔH , and free energy ΔG (Gibbs function ΔG) were calculated (Table 1) using the following equations **F.Yakuphanoglu et al., 2004**:

$$\Delta S = 2.303 (\log A_h/kT) R \quad (4)$$

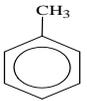
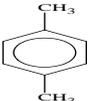
$$\Delta H = E - RT \quad (5)$$

$$\Delta G = \Delta H - T \Delta S \quad (6)$$

3.5. Activity and Selectivity of Catalysts for Cyclohexene Conversion

The superiority of ST/SiO₂ and STAC/SiO₂ catalysts for the disproportionation reaction of cyclohexene is evident from the table 2and 3.The observed products for ST/SiO₂ are benzene, cyclohexane , toluene and xylene . While the observed products for STAC/SiO₂ was benzene only **Ahmed K. Aboul- Gheit et al., 2012**.

Table 2.Catalytic Disproportionation of Cyclohexene using Reported Catalysts

Reaction temp., °C	Catalyst	Conversion %	Product %			
						
200	ST/SiO ₂	38.9	6.7	18.4	1.7	12.2
220		48.9	12.4	19.1	8.5	8.9
240		49.1	9.6	19.1	10.5	9.9
260		62.1	-	35.6	14.5	12.0
280		65.8	10.4	40.8	4.9	9.7
200	STAC/SiO ₂	48.0	-	48.0	-	-
220		52.6	-	52.6	-	-
240		59.9	-	59.9	-	-
260		60.0	-	60.0	-	-
280		65.0	-	65.0	-	-

3.5.1.Effect of Time of Contact

Figure 5 shows the activity of the ST/SiO₂ catalyst with increasing time of contact from 21.5 to 35.0 min at different temperatures from 200 to 280°C for cyclohexene disproportionation reaction and observed that the activity of the catalyst decreased and the un reacted cyclohexene increased for the same temperature at different time of contact, this phenomena observed for all temperatures, while the conversion decreased from 38.9% to 14.7% at 200°C and 65.8% to 61.0% at 280°C. For each temperature the percent of products relative to each other change according to change on temperature. For changing temperature from 200 to 280°C, the main product is benzene and the maximum yield 40.8% at 280 °C while the benzene yield decrease according to increasing in the time of contact at 200,220 and 260 °C but decrease and constant at 240 and 280°C. This observed for cyclohexane yield which increase from 6.7% to 21.1% at increasing temperature and decrease at all studying temperatures except 260°C increase with the increasing time of contact. With respect to xylene and toluene product, the yield % decrease according to increasing in the time of contact for all studying temperatures but the maximum yield appears at 260°C by 14.5% for toluene and 12.0% for xylene. From this figure obtained that ST/SiO₂ catalyst was selective for benzene formation which the selectivity increase according to increasing in the temperature.

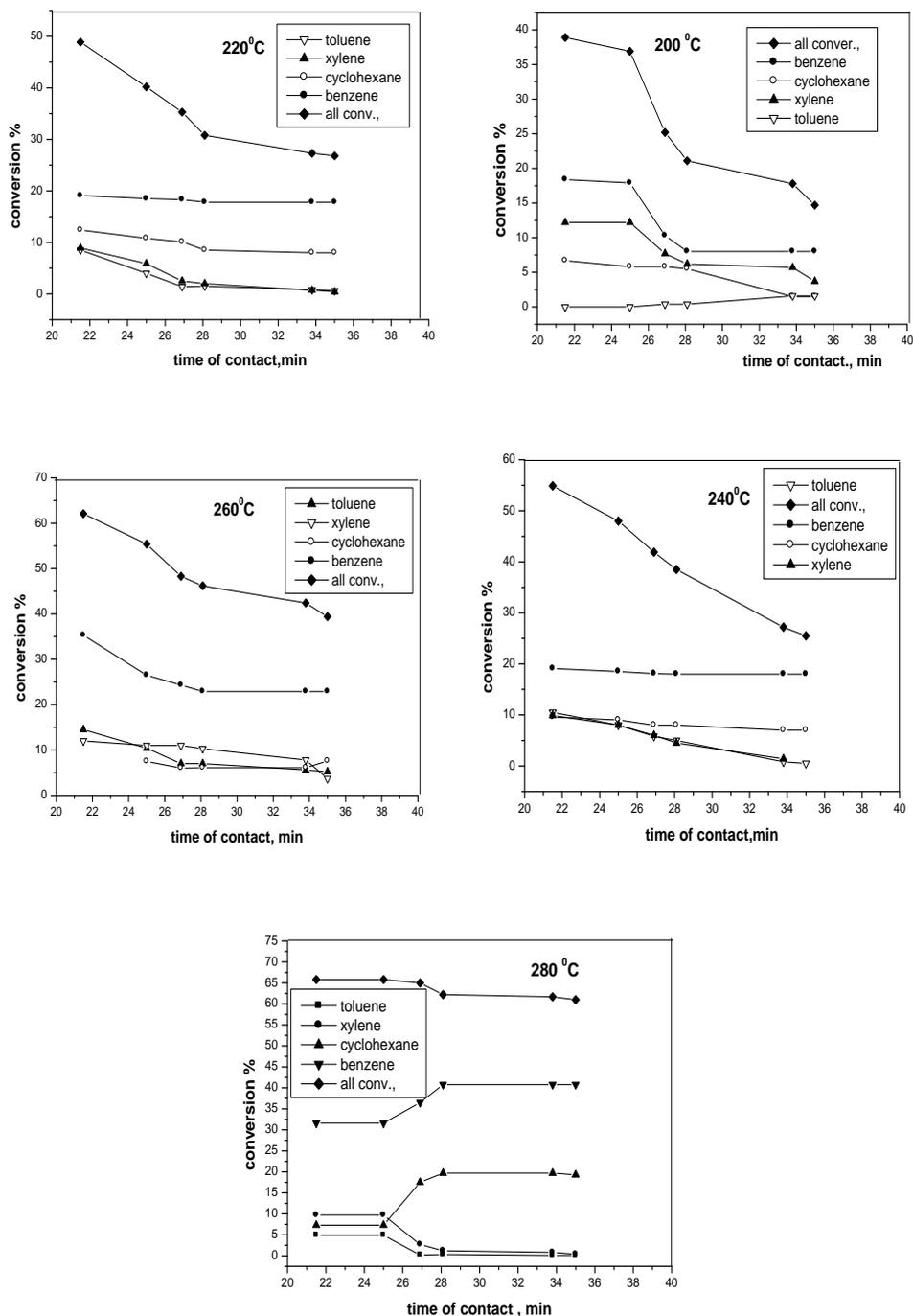


Figure 5. Effect of contact time on the conversion of cyclohexene over ST/SiO₂ at 200-280 °C

Comparatively, figure 6 shows the activity of the STAC/SiO₂ catalyst with increasing time of contact from 21.5 to 35.0 min at different temperatures from 200 to 280 °C for cyclohexene disproportionation reaction and observed that the activity of the catalyst toward benzene formation decreased at starting temperatures 200, 220 and by increasing temperature from 220 to 280 °C the activity become constant with the time of contact, this means that STAC/SiO₂ catalyst show high activity and selectivity for benzene formation than the ST/SiO₂ catalyst while we use: (1) a fixed titanium content, (2) fixed preparation procedure (e.g., sol-gel), (3) the same titanium precursor. Hence, The difference of these catalysts is using active carbon on using a fixed ratio of Ti precursor to a support. So adding active carbon to act as a competitive adsorption agent to improve the catalytic

activity. The maximum yield of benzene was 65.0% at 280°C and 52.6% at 200°C for STAC/SiO₂, for ST/SiO₂ benzene yield was 43.0% at 280 °C and 17.4% at 200°C.

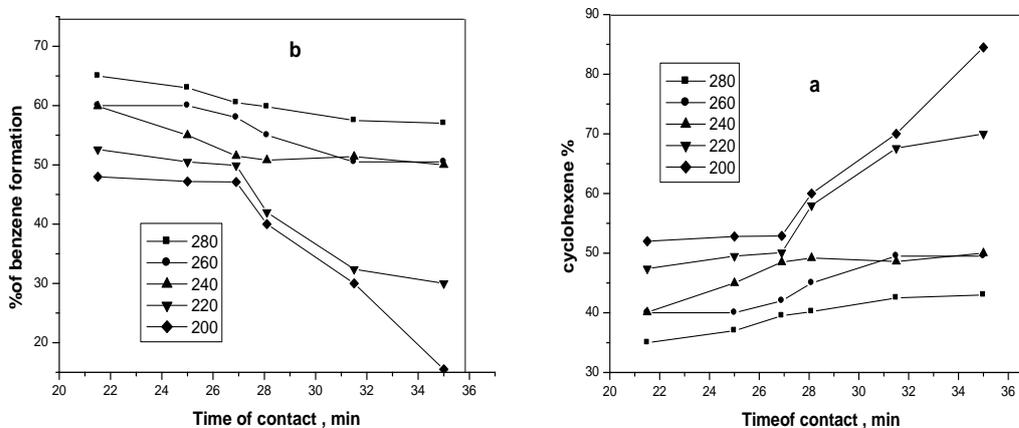


Figure 6. Effect of contact time on the conversion of cyclohexene over STAC/SiO₂

3.5.1. a. Order of reaction

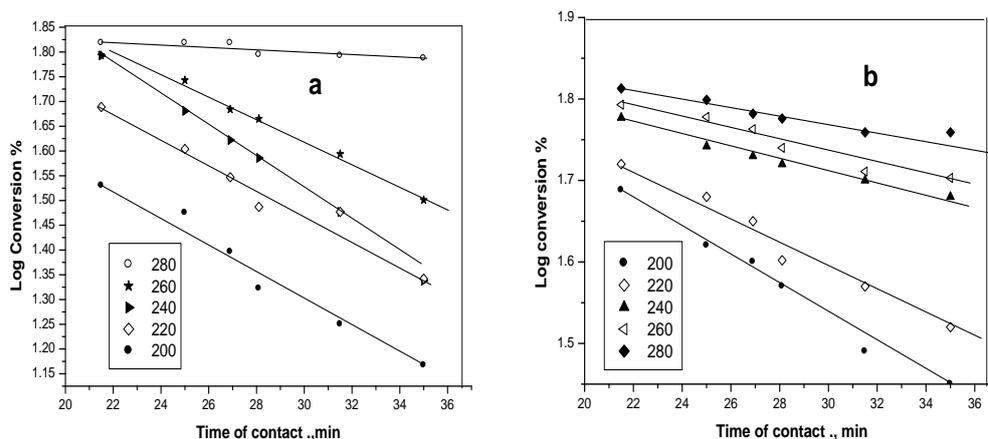


Figure 7. Effect of contact time on the conversion of cyclohexene over a-for ST/SiO₂ and b- for STAC/SiO₂ at 200°C- 280 °C

The variation of log conversion percent against time of contact show the order of reaction for cyclohexene disproportionation reaction. Fig.7a for ST/SiO₂ shows that the disproportionation reaction of cyclohexene was a first order reaction at temperature range 200-260°C while giving a zero order reaction at 280 °C. The STAC/SiO₂ catalyst shows that a first order reaction at temperature range 200-280°C (Fig.7b).

3.5.2. Effect of Reaction Temperature

In order to obtain the catalytic activity of the cyclohexene conversion. The experimental temperature was varied from 200 °C to 280°C, fig. 8a and 8b shows the effect of the reaction temperature on the disproportionation reaction of cyclohexene catalyzed by ST/SiO₂ catalyst and STAC/SiO₂ respectively.

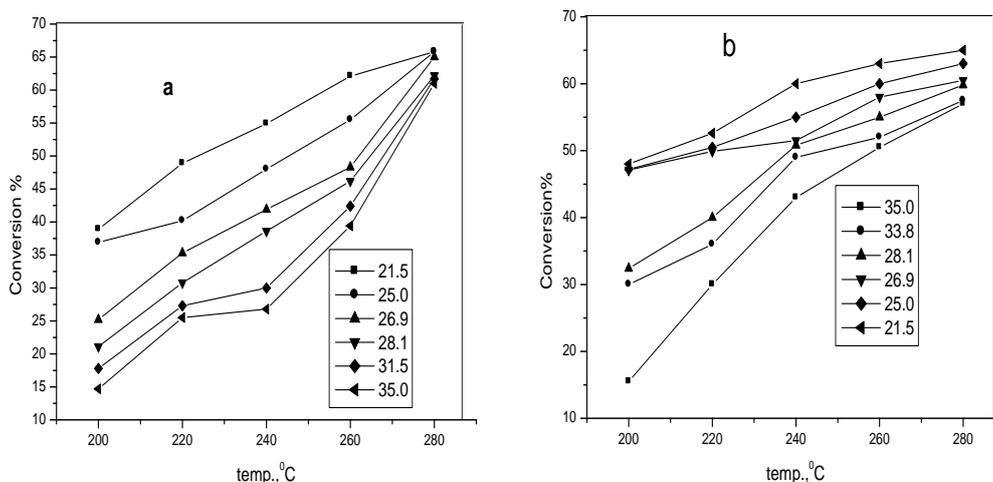


Figure 8. Effect of temperature on the conversion of cyclohexene over a-for ST/SiO₂ and b- for STAC/SiO₂ at 200°C- 280 °C

It can be seen that the increase of temperature is apparently favorable to accelerate the reaction. Mean while, it is evident from Fig. 8a that the conversion percent increases from 38.9% to 65.8% at time of contact 21.5min when the reaction temperature increases from 200 °C to 280°C, by increasing time from 21.5 to 35.0 min , the conversion decrease to 14.7% at 200 °C and to 61.0% at 280°C and the similar phenomenon is also observed in fig. 8b. The conversion percent increases from 48% to 65.8% when the reaction temperature increases from 200 °C to 280°C at time of contact 21.5min, by increasing time from 21.5 to 35.0 min the conversion decrease to 15.5% at 200 °C and to 57.0.% at 280°C .This indicates that the disproportionation of cyclohexene is a reversible exothermic reaction. For cyclohexene disproportionation reaction catalyzed by ST/SiO₂ catalyst and STAC/SiO₂, 200 °C to 280°C were considered to be the optimum reaction temperatures. It is interest to study the apparent activation energy for the samples according to Arrhenius equation Eq(1) which represent the effect of temperature on the rate of catalytic conversion of cyclohexene over two catalysts at temperature range 200-280 °C (fig.9) . It was found that the average apparent energy calculated for the reaction over ST/SiO₂ equal to 47.3 ±10 kJ/mole and for the reaction over STAC/SiO₂ was found equal to 48.3±10 kJ/mole . It can concluded that the catalytic conversion of cyclohexene over the two samples may follow by the same mechanism.

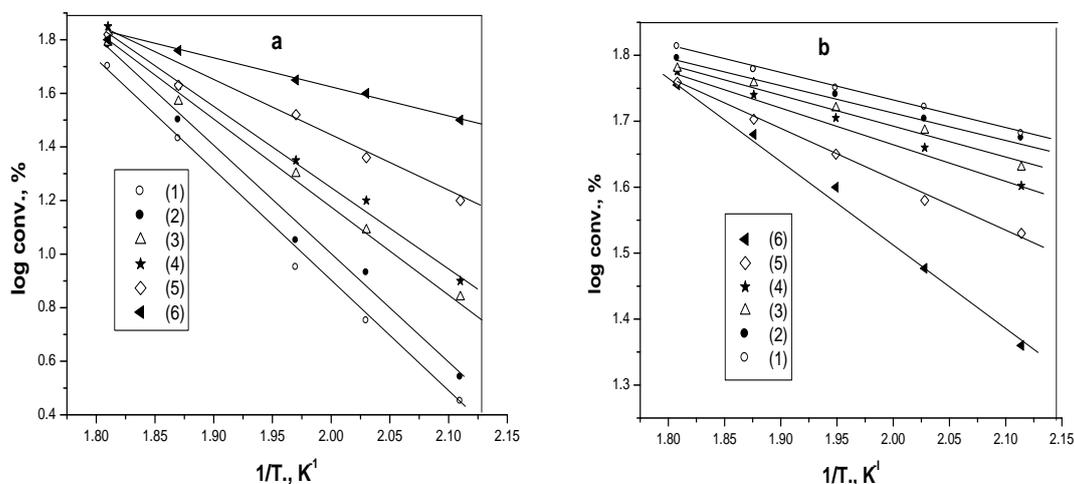


Figure 9. Effect of temperature on the conversion of cyclohexene over a-for ST/SiO₂ and b- for STAC/SiO₂ 1-fresh portion , 2- after one hour at time 25.0 min, 3- after one hour and half at 26.9 min, 4- after two hour at 28.1 min, 5- after two hour and half at 33.8 min and 6- after three hour at 35.0 min.

3.5.3. Selectivity for Cyclohexene Conversion.

Table 3. Catalytic Activities Towards The Cyclohexene Disproportionation for Previously Reported Catalysts

Catalyst	Time of contact , min	Reaction temp., °C	Conversion %	benzene selectivity %
(1) ST/SiO ₂	35.0	280	65.8	48.0
(2) STAC/SiO ₂	21.5	280	65.0	100
(3) ST/SiO ₂	35.0	200	38.9	47.3
(4) STAC/SiO ₂	21.5	200	48.0	100

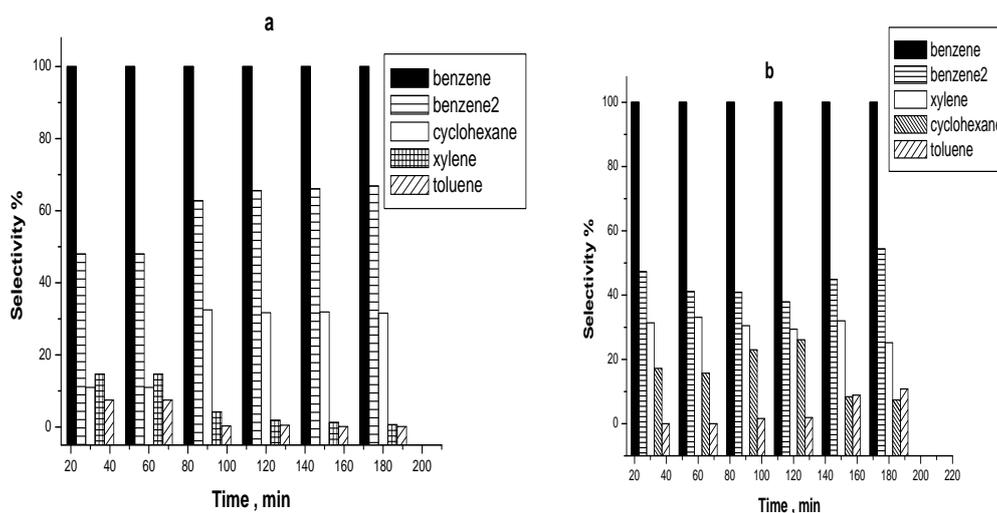
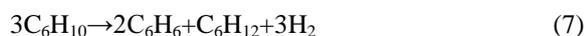
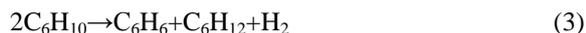


Figure 10. The selectivity of the current catalysts for cyclohexene disproportionation reaction at a- 280 and b- 200 °C

Figure 10 show that the selectivity of the current catalysts for cyclohexene disproportionation reaction and the data represented in table 3. Figure 10a shows the performance of STAC/SiO₂ during six recycles at 280 °C while benzene selectivity was stable above 100% for STAC/SiO₂ during six recycles. For ST/SiO₂, benzene selectivity was stable above 65% during the last four recycles and selectivity decreased to 48.0% in the first two cycle followed by cyclohexane selectivity to become stable above 31.0% , for xylene and toluene selectivity the catalyst show no selectivity to them relative to benzene formation at higher temperature . Figure 10b at lower temperature 200 °C also benzene selectivity was stable above 100% for STAC/SiO₂ during six recycles and decrease than that observed at 280 for ST/SiO₂ which stable above 40% during the first four recycles and then increased to 54.4% in the six recycle followed by xylene which the catalyst show selectivity to xylene above 30.0% than observed at higher temperature , also cyclohexane selectivity lower than that observed at higher temperature and show no selectivity to toluene formation. This demonstrated that good activity and selectivity as well as the excellent stability of the STAC/SiO₂ catalyst at lower and higher temperature while ST/SiO₂ show selectivity to benzene formation at higher temperature only in addition to other products . The polycondensation products observed plus benzene in the conversion of cyclohexene over ST/SiO₂ can be

explained according to structure of the catalyst which TiO_2 (anatase structure) crystals was formed by chains of distorted TiO_6 octahedra, and its tetragonal structure can be described in terms of three parameters: two cell edges a and c , and one internal parameter d . Anatase has a tetragonal unit cell containing four TiO_2 units, each Ti atom is coordinated to the six neighboring oxygens via two long (apical)and four short (equatorial) bonds of lengths 1.976 and 1.946 Å respectively, each O atom is coordinated to three Ti atoms via one long bond and two short bonds lying in the same plane. The bond length Ti-O of anatase is higher than that of C-C (1.55 Å) and C-H(1.15 Å) bond in cyclohexene ring also in titanyl sulfate, TiOSO_4 , which is very important because its crystalline structure if made of titanium-oxygen octahedra similar to those forming titania crystalline phases and sulfate tetrahedra sharing vertices with three titanium-oxygen octahedra **X.Bohklimi et al., 2004** , the O –O atomic bond lengths of the sulfate tetrahedra vary between 2.38 and 2.43 Å , the S - O atomic bond lengths between 1.45 and 1.49 Å, and the O- S- O angles, between 107.51 and 112.28 degree. This means that the cyclohexene ring enters crystal structure of titanyl sulfate during the reaction and occurs breaking for part of cyclohexene molecules then the products result then with benzene ring forming polycondensation products such as toluene and xylene .With respect to STAC/SiO_2 presence of active carbon (graphite structure with two dimensional sheet –like polymeric structure , each sheet as fused system of benzene ring) make locking for titanul sulfate group so cyclohexene molecules cover the surface of the catalyst making flat form and blocking for active centers of the catalyst forming pure benzene . Finally, the disproportionation mechanism of cyclohexene reaction change according to change on the structure of the catalyst. So the analysis of liquid products for cyclohexene conversion on reported catalysts suggests that, under our experimental conditions, the following processes may take place:



Processes (1) and (2) are monomolecular catalytic reactions which show the dehydrogenation of cyclohexene to benzene and hydrogen or methane and carbon deposition. When two molecules of cyclohexene react together (eqn.(3))benzene ,cyclohexane and hydrogen are obtained. the disproportionation of cyclohexene to benzene and cyclohexane according to (eqns (3) and (6)) is not only processes taking place under our conditions : may also occur polycondensation of benzene to toluene and *p*-xylene (eqns.(4)and(5)).Clearly , under the our conditions all the possible ways of converting of cyclohexene proceed by polymolecular mechanism through the formation of condensation products.

3.6. Adsorption Isotherm

Table 4.Equilibrium Parameters for The Adsorption of Dyes

Initial dye conc. (mg/L)	Acidic Eosin dye		basic Saffranin dye	
	Removal %		% Removal	
	ST/SiO ₂	STAC/SiO ₂	ST/SiO ₂	STAC/SiO ₂
0.1	69.23	69.50	49.10	70.50
0.01	92.00	95.00	92.40	90.40
0.001	93.87	96.20	92.40	92.30

Table 4: show The experimental data for the prepared samples ST/SiO₂ and STAC/SiO₂ adsorbed on the

surface of dyes .from the data obtained the adsorbents show high adsorption capacity for acidic dye than the basic dye with the lower concentration (0.001 mg/ L). STAC/SiO₂ show high adsorption capacity than ST/SiO₂ for acidic dye return to the structure of the adsorbents which presence carbon(graphitic structure as sheets of benzene ring) make the dye molecules available for blocking the active centers of the samples and cover the surface of it .The percent of the dye removal increased by decreasing the intial concentration of the dye, the equilibrium absorption increased due to increasing adsorbing ions on the surface of adsorbent. The experimental data were analyzed according to Freundlich and langmuir isotherm (Table 5) . The Freundlich isotherm was represented by Eq **Jia Y.F ., et al., 2002:**

$$\log Q_e = \log K_F + 1/n \log C_e$$

Where Q_e is the amount of dye adsorbed (mg/g) ,C_e is the equilibrium concentration of dye in solution (mg/L) and n , K_F are constant which 1/n is the intensity of adsorption and K_F measure adsorbent capacity which calculate from linear plot of log Q_e against log C_e . Also calculate the separation factor according to the equation

$$R = 1/ 1+K_F C$$

The langmuir isotherm was represented by Eq **Namasivayam,C., et al ., 1996:**

$$C_e / q_e = (1/q_{max}) b+ C_e /q_{max}$$

Where Q_e is the amount of dye adsorbed (mg/g) , C_e is the equilibrium concentration of dye in solution (mg/L) and Q_m and b are Langmuir constanta related to adsorption efficiency and energy of adsorption.

Table 5. Freundlich , Langmuir Constants and Statistical Parameter

Dye	ST/SiO ₂						STAC/SiO ₂					
	K _F	n	R _L	Q _M	b	R _L	K _F	n	R _L	Q _M	b	R _L
acidic	1.94	1.95	0.9548	10.23	6.392	0.9117	1.59	1.50	0.9843	13.56	9.356	0.8806
basic	4.10	2.25	0.8752	2.88	0.2038	0.9195	1.68	1.76	0.9835	7.81	4.307	0.9276

From the results ,it is clear that the value of adsorption efficiency Q_m and adsorption energy b is increased for STAC/SiO₂.We conclude that the maximum adorption corresponding to saturated monolayer of acidic dye molecules on the adsorbent surface with constant energy and no transmission of adsorbate in the plane of adsorbent surface.The observed b value show that the endothermic nature of the process involved in the system. The value of separation factor R_L were found to be between 0and 1 confirm that the ongoing adsorption process is favorable. The intensity of adsorption is an indicative of the bond energies between dye and adsorbent and the possibility of slight chemisorptions rather than physisorption. The values of n are greater than one, indicating the adsorption is much more favorable.

Conclusion

The ST/SiO₂ and STAC/SiO₂ catalysts was prepared by sol-gel method and were fully characterized by means of TEM , BET ,X ray , and thermal analysis. The diameter of ST/SiO₂ is found to be in the range of 50-100 nm which for STAC/SiO₂ is 13-18nm and showing amorphous structure . The two catalysts are mesoporos with surface area (S_{BET}) = 236.036 and 317.178 m².g⁻¹ respectively. The structure of the catalyst have important factor for determining the type of products.The ST/SiO₂ catalyst is much less active than STAC /SiO₂ due to principally the dispersion of AC which have graphitic structure in the former catalyst by 0.5%, making block for titanyl sulfate then cyclohexene covering the surface giving pure benzene so show high selectivity (100% at 200-280 °C) . The reaction was a first order reaction at temperatures (200-260°C), zero order at 280°C for ST/SiO₂ and was a first order reaction at temperature range(200-280°C) for STAC/SiO₂ . The disproportionation mechanism for cyclohexene conversion was suggested . The experimental data were very well correlated by the Langmuir and Freundlich adsorption isotherms and isotherm parameters were reported. The amount of dyes adsorbed increased with decreasing the dye concentration over ST/SiO₂ but less than that adsorberd over STAC /SiO₂ . The structure of STAC /SiO₂ catalyst making it has a considerable potential as an adsorbent for the removal of acidic dye than the basic dye. The dimensional separation factor showed that the

prepared adsorbents more effective for the removal of these dyes from aqueous solutions.

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