

Vapour phase oxidation of tetralin over Cr and Fe substituted MCM-41 molecular sieves

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Abstract

Vapour phase oxidation of tetralin to 1-tetralone using molecular oxygen is reported for the first time on Cr and Fe substituted MCM-41 molecular sieves. Mesoporous monometallic Cr-MCM-41(Si/Cr 25, 50, 75 and 100), Fe-MCM-41(Si/Fe=25) and bimetallic Cr-Fe-MCM-41(Si/(Cr + Fe) = 100) molecular sieves were synthesized by direct hydrothermal (DHT) process and characterized by XRD, ICP-AES, DR-UV-vis spectroscopy, EPR spectroscopy and SEM techniques. The conversion of tetralin and the selectivity for 1-tetralone were studied in the temperature range of 473–623 K. The efficiency of all the catalysts was evaluated and compared for the oxidation reaction under atmospheric pressure. Among various catalysts under study, Cr-MCM-41 catalyst with Si/Cr = 25 exhibited maximum efficiency. The correlation between 1-tetralone selectivity and the catalysts physico-chemical characteristics is made. A reaction scheme is proposed for the oxidation of tetralin to 1-tetralone. The reaction is considered to occur in two steps: oxidation of tetralin to tetralol and oxidation of the latter to 1-tetralone, with the former process occurring over Cr³⁺ and the latter over Cr⁶⁺.

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1. Introduction

The development of efficient catalysts for the selective oxidation reactions by molecular oxygen is of growing importance for the modern chemical industry [1]. The dominant position of molecular oxygen as the oxidant for bulk chemical oxygen functionalization is due to the fact that it is the only inexpensive and environment friendly and feasible oxidant for large scale processing. Transition metal complex—catalyzed oxidation of organic compounds is a field that has been extensively investigated in the past [2–5]. Some of these oxidation reactions are important industrially for making commodity chemicals such as 1-tetralone.

1-tetralone, an oxidation product of tetralin, is an intermediate for the production of important chemicals such as carbonyl, sertaline and 18-methyl norethisterone which are used as insecti-

cide, anti-depressant and contraceptive, respectively. In addition, this is also used as a solvent and softener of plastic. Access to a number of medicinally useful derivatives also relies on 1-tetralone [6]. However, synthetic route of this 1-tetralone remains extremely limited. In 1970, liquid phase oxidation reaction of tetralin was carried out by using soluble [7–11], and insoluble [12] catalysts such as oxides of nickel, manganese and copper. Among the catalysts, oxide of manganese (Mn₂O₃) showed higher activity towards tetralin oxidation than others. Later, Annie Liard et al. attempted to carry out this reaction by using Xanthates as starting materials in the absence of catalyst and achieved 56% of substituted tetralone. But this reaction involves multi-steps.

Tedious work up and the generation of toxic chromium residues as a result of the use of a large excess of chromium reagents are the main disadvantages often encountered in hydrocarbon oxidation under homogeneous conditions. Hence, there is a need for cleaner catalytic alternatives which do not generate excessive amount of inorganic salts as by products. Thus, considerable attention has been focused on the

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development of chromium based (heterogeneous) molecular sieves as catalysts [13–15] for several oxidation reactions [16,17].

Cr containing microporous molecular sieves such as AlPOs [14] and Zeolite Y [16] was found to be active and selective for the oxidation of olefins. However, one of the major problems with these catalysts is the leaching of active chromium from the matrix under the reaction conditions [17]. On the other hand, it is interesting to note that certain chromium incorporated mesoporous molecular sieves, e.g. Cr-MCM-41 were found to stabilize the active species and found that there is no leach out. A few studies have been reported on the synthesis, characterization of Fe-MCM-41 using different methods and catalytic activity for selective oxidation reactions of hydrocarbons [18–20]. A series of metal ions such as Fe, Co, Ni, Mn, Cu, La and Ru have been used to modify the MCM-41 silica framework [21–23]. The obtained materials have shown remarkable catalytic activity for partial liquid phase oxidation of hydrocarbons. The incorporation of two different metals might, therefore, create new materials with different redox and acidic properties. Bi-metal catalysts such as Co-V, Co-Nb, Co-La, Ni-Ru, Ni-Cr, Ni-Ti, V-Ti, V-Cu and V-Co have been explored for liquid phase oxidation. [24–26]

In the present work, vapour phase oxidation of tetralin to 1-tetralone is reported over Cr-MCM-41, Fe-MCM-41 and Cr incorporated in association with Fe-MCM-41 catalysts in the presence of air in order to study the effect of Cr content. The influence of Fe on the Cr content of the catalyst was also studied. The catalytic activity was correlated and discussed with reference to their physico-chemical properties.

2. Experimental

2.1. Synthesis of Cr-MCM-41

Cr-MCM-41(Si/Cr=25) was synthesized by hydrothermal method reported elsewhere [27] using sodium metasilicate (CDH) as silica source, cetyl trimethyl ammonium bromide (CTAB, OTTO Chemie) as the structure-directing agent with the following molar gel composition $\text{SiO}_2:0.04 \text{ Cr}_2\text{O}_3:0.2 \text{ CTAB}:0.89 \text{ H}_2\text{SO}_4:160 \text{ H}_2\text{O}$. In a typical synthesis, 21.32 g of sodium metasilicate and 1.20 g of chromium nitrate nano-hydrate were dissolved in 60 g of water. The reaction mixture was allowed to stirred for 2 h. Meanwhile, CTAB (5.47 g) was dissolved in 20 g of water. Then, the resultant mixture of sodium metasilicate and chromium nitrate nano-hydrate was added drop wise into CTAB solution. The final mixture was stirred for 1 h. The pH of the gel was adjusted to 10.5–11 using 4N sulfuric acid followed by stirring for 3 h. The obtained gel was placed into an autoclave and heated to 413 K under static condition for 12 h. The resultant precipitate was filtered, washed with deionized water and dried in air at 375 K and then finally calcined at 773 K for 1 h in N_2 flow and for 12 h in CO_2 -free air flow. The catalysts Cr-MCM-41(Si/Cr = 50, 75, 100) and Cr-Fe-MCM-41(Si/(Cr + Fe) = 100) were also synthesized in a similar manner wherein only the ratio of chromium and iron sources was adjusted.

2.2. Characterization of the catalysts

Inductively coupled plasma (ICP) optical emission spectroscopy was used for the determination of the metal content in each sample synthesized above. The measurements were performed with a Perkin-Elmer OPTIMA 3000 and the sample was dissolved in a mixture of HF and HNO_3 before the measurements. XRD analysis was performed on Rigaku Miniflex X-ray diffractometer. Liquid nitrogen cooled germanium solid state detector with $\text{Cu K}\alpha$ radiation source was used. The samples were scanned between 0.5° and 8.5° (2θ) in steps of 0.02° with the counting time of 5 s at each point. N_2 adsorption studies were carried out to examine the porous properties of each sample. The measurements were carried out on Belsorpmini II (BEL Japan Inc.). All the samples were pretreated in vacuum at 573 K for 12 h in flowing N_2 at a flow rate of 60 ml/min. Surface area and pore size were obtained from these isotherms using the conventional BET and BJH equation.

The co-ordination environment of chromium and iron containing MCM-41 catalysts was examined by diffuse reflectance UV–vis spectroscopy. The spectra were recorded between 200 and 800 nm on a Shimadzu UV–vis spectrophotometer (model 2450) using BaSO_4 as the reference. The co-ordination environment of chromium was also analyzed by EPR technique (varien E112 spectrometer operating in the X-band 9.2 GHz frequency) at room temperature. The SEM pictures of Cr-MCM-41 (25) and Cr-Fe-MCM-41(Si/(Cr + Fe) = 100) samples were recorded using a JEOL 640 scanning electron microscope (SEM) at an operating voltage of 10 kV.

2.3. Experimental procedure for the oxidation of tetralin

Oxidation of tetralin with CO_2 -free air was carried out in a fixed bed down flow quartz reactor at atmospheric pressure in the temperature range of 473–623 K with air flow of 0.02 mol h^{-1} . Prior to the reaction, the reactor packed with 0.3 g of the catalyst was preheated in a tubular furnace equipped with a thermocouple. The reactant (tetralin) was fed into the reactor through a syringe infusion pump at a predetermined flow rate. The oxidation of tetralin was carried out and the product mixture was collected at a time interval of 1 h. The products were analyzed by gas chromatograph (GC-17A, Shimadzu) equipped with a flame ionization detector and SE-30 column. After every run, the catalysts were regenerated by removing the coke deposited, by passing a stream of pure dry air at a temperature of 773 K for 6 h. The effect of various parameters, viz., temperature, weight hourly space velocity and time on stream was studied on the regenerated catalyst.

3. Results and discussion

3.1. ICP-AES

The chromium and iron contents in Cr-MCM-41, Fe-MCM-41 and Cr-Fe-MCM-41 have been determined using ICP-AES and the results are summarized in Table 1.

Table 1
Physico-chemical characteristics of the catalysts

Catalyst	Cr content (wt%) ^a	Fe content (wt%) ^a	<i>d</i> spacing (Å)	Unit cell parameter <i>a</i> ₀ (Å)	Surface area (m ² /g)	Pore diameter (Å)	Pore volume (cm ³ /g)	Wall thickness (Å)
Cr-MCM-41 (25)	1.93	–	40.01	46.20	654	24.03	0.86	22.17
Cr-MCM-41 (50)	1.17	–	39.50	45.61	796	24.04	0.89	21.57
Cr-MCM-41 (75)	0.75	–	38.41	44.36	871	24.05	0.88	20.31
Cr-MCM-1 (100)	0.59	–	37.57	43.38	924	24.05	0.90	19.33
Fe-MCM-41 (25)	–	2.39	–	–	–	–	–	–
Cr-Fe-MCM-41 Si/(Cr + Fe) = 100	1.93	0.73	–	–	–	–	–	–

^a Results obtained from ICP-AES analysis.

3.2. XRD

The X-ray diffractograms were recorded at low diffraction angles for the calcined Cr-MCM-41 samples with Si/Cr atomic ratios of 100, 75, 50 and 25. Sharp *d*₁₀₀ reflection lines in the 2θ range 2.21° – 2.35° (Fig. 1.) were observed. It is clearly evident that the presence of mesoporous nature in the synthesized catalysts. The unit cell parameter (*a*₀) was calculated using the formula $a_0 = 2d_{100}/\sqrt{3}$, and *d* spacing values were obtained using the Bragg's equation $2d \sin \theta = n\lambda$, where $\lambda = 1.54 \text{ \AA}$ for the Cu K α radiation and (Table 1). The long-range regularity of hexagonal arrays of mesopores of MCM-41 is evident from the intensity of diffraction peaks after the introduction of chromium upto 1.17 wt% (Si/Cr = 50) by DHT methods. However, when Cr content was increased to 1.93 (Si/Cr = 25), the intensity of the diffraction peaks decreased largely, indicating the structural irregularity of the mesopores at higher chromium content as reported in literature [28].

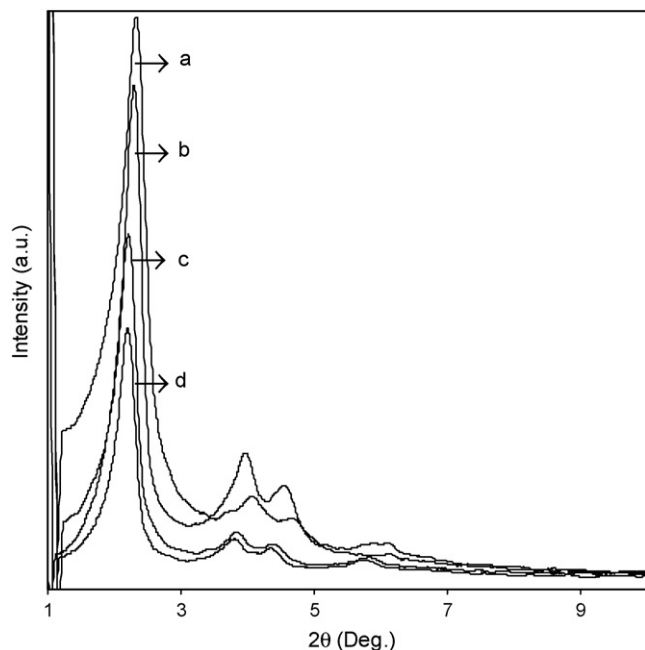


Fig. 1. X-ray diffraction patterns of (a) Cr-MCM-41 (100), (b) Cr-MCM-41 (75), (c) Cr-MCM-41 (50) and (d) Cr-MCM-41 (25) catalysts.

3.3. Nitrogen adsorption–desorption isotherms

The adsorption–desorption isotherms of the catalysts Cr-MCM-41 (Si/Cr = 25, 50, 75 and 100) are illustrated in Fig. 2. A typical type IV isotherm as defined by IUPAC for mesoporous materials [29] were obtained. A sharp inflection between relative pressures $P/P_0 = 0.2$ and 0.3 corresponding to capillary condensation within the mesopores was obtained. Hysteresis loop in the adsorption and desorption cycle upon pore condensation was also observed which can be attributed to the presence of mesopores. The surface area, pore size and pore volume, decreased with increasing metal content (Table 1).

3.4. DR-UV–vis spectroscopy

Cr-MCM-41 catalysts were initially green in colour and changed to yellow upon calcination. The former is due to the presence of trivalent chromium ions and the latter is due to the presence of hexa valent chromium ions, viz., chromate and/or polychromate ions. The DR-UV–vis spectra of the calcined Cr-MCM-41 with different Si/Cr ratio and spent catalyst (after the catalytic run) are shown in Fig. 3. Typical absorption bands

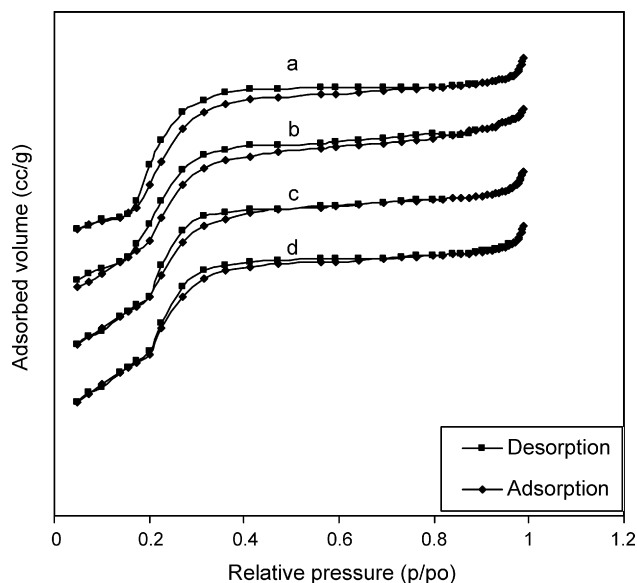


Fig. 2. N₂ adsorption–desorption isotherms of catalysts (a) Cr-MCM-41 (100), (b) Cr-MCM-41 (75), (c) Cr-MCM-41 (50) and (d) Cr-MCM-41 (25).

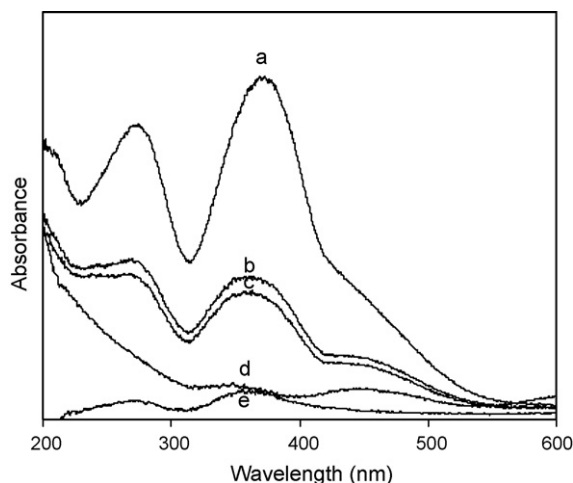


Fig. 3. DR-UV-vis spectra of catalysts (a) Cr-MCM-41 (25), (b) Cr-MCM-41 (50), (c) Cr-MCM-41 (75), (d) Cr-MCM-41 (100) and (e) spent Cr-MCM-41 (25).

with λ_{\max} at ~ 445 , 375 and 322 nm corresponding to polychromate, chromate and dichromate species, respectively [30–32] in addition to the band at 270 nm due to trivalent chromium in octahedral co-ordination were shown in Fig. 3a–d. Also it is evident from the spectra that as the ratio of Si/Cr is increased, there is a corresponding decrease in the intensity of the peaks due to chromium. Typical spectrum is recorded for the spent Cr-MCM-41 (25) catalyst (Fig. 3e). In the DR-UV-vis spectrum of spent catalyst two absorption bands were observed with λ_{\max} at 350 and 275 nm. These bands may be assigned due to Cr^{5+} and Cr^{4+} species, respectively and the peaks corresponding to Cr^{3+} and Cr^{6+} states are absent.

The DR-UV-vis spectra of Fe-MCM-41 (25) and Cr-Fe-MCM-41(Si/(Cr+Fe)=100) are presented in Fig. 4. An absorption band at around 265 nm, similar to that observed for ferrisilicate containing tetrahedrally coordinated iron species is shown in the spectrum of Fe-MCM-41 (25). This band could be assigned to the $d_{\Pi}-p_{\Pi}$ charge transfer between Fe and O atoms in the framework of Fe–O–Si as in the case of zeolites [33]. But

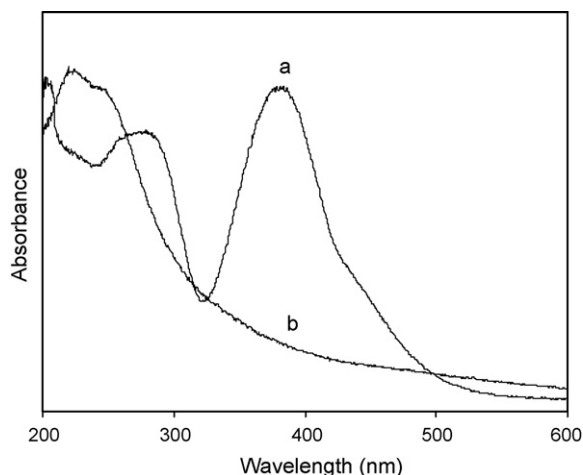


Fig. 4. DR-UV-vis spectra of catalysts (a) Fe-Cr-MCM-41(Si/(Cr+Fe)=100) and (b) Fe-MCM-41 (25).

this band is shifted to longer wavelength in Cr-Fe-MCM-41 catalyst (Fig. 4a). This shift towards longer wavelength can be attributed to the reorientation of the electrons between Cr-Fe bonds. Since chromates and polychromates pull electrons from Fe in the framework, the framework Fe possesses high degree of positive charge. Hence, the absorption maximum of Fe in the bi-metal catalyst is shifted to longer wavelength due to charge transfer of Fe–O bond. This observation illustrates clearly that there is interaction of Fe with chromium in the bimetal catalyst. Peaks due to Cr^{6+} oxidation state remain unaffected.

3.5. EPR

The EPR spectra of the as-synthesized and calcined Cr-MCM-41 (25) catalysts are shown in Fig. 5a and b. Both the catalysts exhibited similar spectral features. It appears that Cr^{3+} might be present even after calcination, and the g value calculated is 1.98 which corresponds to Cr^{3+} and this is in good correlation with previous reports [31,32]. The EPR spectrum of the spent catalyst is shown in Fig. 5c. The g value obtained for the spent catalyst was found to be different from that of Cr^{3+} .

3.6. Scanning electron microscope

The SEM images of Cr-MCM-41 (25) and Cr-Fe-MCM-41(Si/(Cr+Fe)=100) are shown in Fig. 6a and b. Same morphology was observed for both the samples. No morphological change was noticed on the introduction of Fe. This illustrates the fact that Cr is not influenced by the presence of Fe.

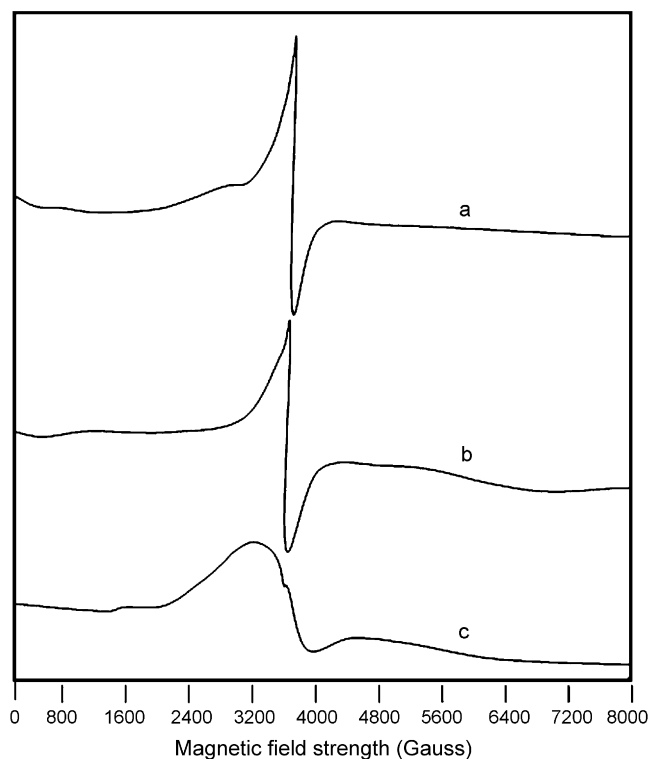


Fig. 5. EPR spectra of Cr-MCM-41 (25) (a) as synthesized, (b) calcined and (c) spent catalyst.

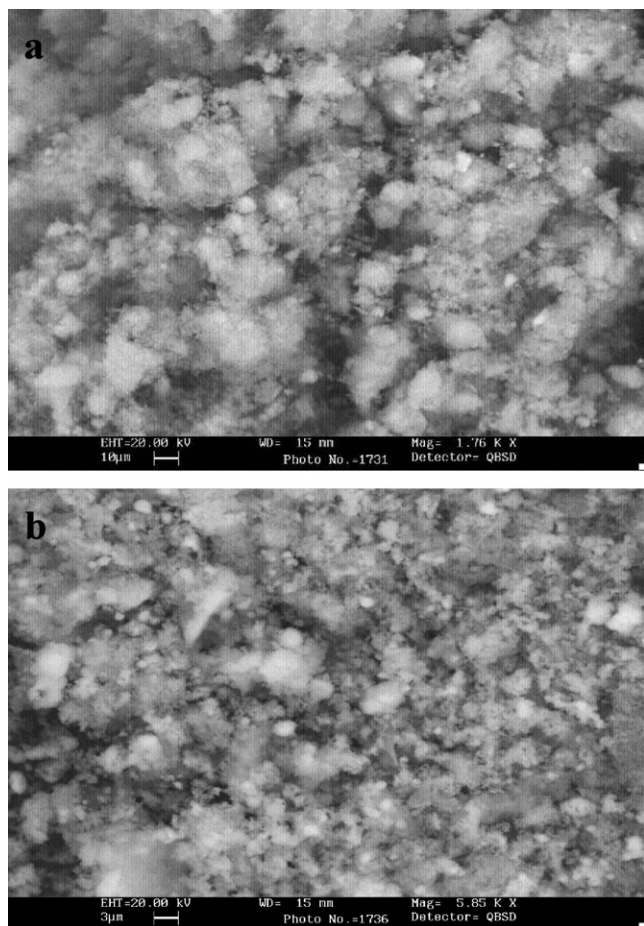


Fig. 6. (a) SEM picture of Cr-MCM-41 (25) and (b) SEM picture of Cr-Fe-MCM-41 (Si/(Cr+Fe) = 100).

3.7. Activity of Cr-MCM-41 catalyst

The vapour phase oxidation of tetralin was carried out in the presence of CO₂-free air at atmospheric pressure on Cr-MCM-41 catalysts (Si/Cr = 25, 50, 75 and 100). The effect of Si/Cr ratio on the conversion of tetralin and product selectivity was studied at the optimized reaction conditions, viz., at 623 K, 0.3 g weight of the catalyst with the flow rate of tetralin being 6.46 h⁻¹ (WHSV) and CO₂-free air 0.02 mol h⁻¹. The results are presented in Fig. 7. Oxidation of tetralin involves consecutive oxidation of tetralin to tetralol and then to 1-tetralone. It is seen from the results that tetralin conversion decreased with the increase in Si/Cr ratio and the selectivity to 1-tetralone remained close to 100%. DR-UV-vis spectra of the catalysts with different Si/Cr ratio also show that there is a corresponding decrease in the intensity of the absorption bands corresponding to Cr³⁺ and Cr⁶⁺ species. The decrease in activity with an increase in Si/Cr ratio may be attributed to the decrease in the level of Cr³⁺ and Cr⁶⁺ species in Cr-MCM-41 catalysts.

The vapour phase oxidation of tetralin is proposed to take place as suggested in reaction scheme (Scheme 1). According to the scheme, the oxidation of tetralin proceeds through two steps. In the first step, tetralin is oxidized to tetralol followed by oxidation of tetralol to 1-tetralone. Cr³⁺ is required for the oxi-

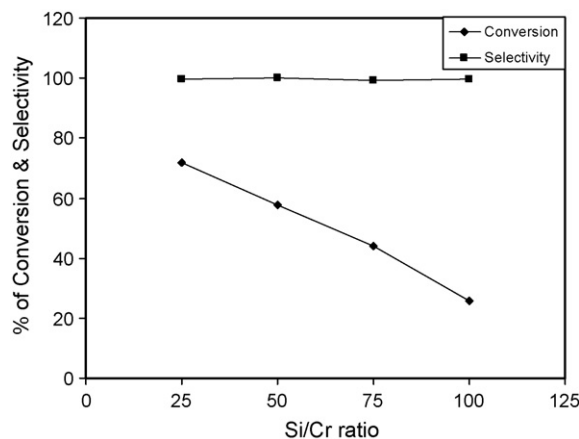


Fig. 7. Effect of Si/Cr ratio on the oxidation of tetralin over Cr-MCM-41. Reaction conditions: temperature = 623 K, catalyst weight = 0.3 g, WHSV = 6.46 h⁻¹ and flow rate of air 0.02 mol h⁻¹; reaction time = 1 h.

dation of tetralin to tetralol and Cr⁶⁺ is required for the tetralol to 1-tetralone. Based on the above fact, it is suggested that this reaction requires the co-existence of Cr³⁺ and Cr⁶⁺ which is more at the Si/Cr ratio = 25 than at other Si/Cr ratios. The reaction was also studied with N₂ in place of air. It was found that tetralin remained unreacted. This observation establishes the requirement of molecular oxygen as oxidant. However, molecular oxygen might not be adsorbed and activated by Cr⁶⁺. It is the Cr³⁺ species which can adsorb and activate O₂. Hence, presence of Cr³⁺ is necessary for the vapour phase oxidation of tetralin with molecular oxygen as the oxidant as shown in the reaction Scheme 1.

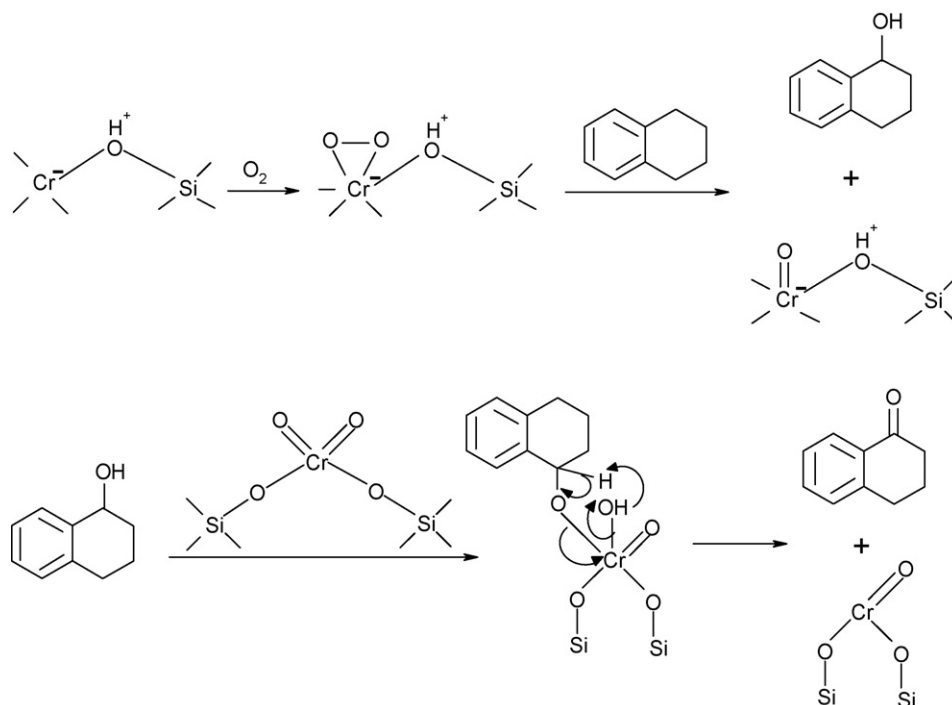
DR-UV-vis spectra of all the catalysts indicate that there is a large proportion of Cr⁶⁺ in comparison with Cr³⁺. Since it is proposed in the reaction Scheme 1, that Cr⁶⁺ is responsible for 1-tetralone formation, one would expect maximum probability for the conversion of tetralol to 1-tetralone. This may be the reason for 100% selectivity observed in all the cases for 1-tetralone formation.

During the oxidation of tetralin with air Cr³⁺ adsorbs and activates molecular oxygen leading to the formation of peroxide. One of the peroxide oxygens is inserted between C and H bond of tetralin to give tetralol. Now Cr³⁺ might become Cr⁵⁺.

Tetralol is oxidized to tetralone by framework Cr⁶⁺. Tetralol makes a nucleophilic attack on Cr⁶⁺ to give an intermediate which rapidly decomposes to 1-tetralone and water. This process facilitates the formation of Cr⁴⁺ species. In the DR-UV-vis spectrum of spent catalyst as shown Fig. 3e, two absorption bands were observed with λ_{max} at 350 and 275 nm, which are assigned to Cr⁵⁺ and Cr⁴⁺ species, respectively [34]. The suggested scheme for the formation 1-tetralone is in good agreement with the DR-UV-vis spectral features.

3.8. Effect of flow rate

The effect of flow rate of tetralin on the conversion and tetralone selectivity was studied at 623 K. The results are presented in Fig. 8. The selectivity gradually decreased with increase in flow rate of tetralin. Since the formation of 1-tetralone



Scheme 1.

involves consecutive oxidation of tetralin to tetralol and then to 1-tetralone adequate contact time is necessary. Hence the selectivity of 1-tetralone was higher at low flow rates 6.46 h^{-1} (WHSV) than other flow rates. Decrease in selectivity at high flow rates is attributed to rapid diffusion of tetralol. Similarly conversion also decreased with the increase in the flow rate.

3.9. Time on stream

The time on stream study was carried out for the vapour oxidation of tetralin at 623 K with the flow rate of tetralin 6.46 h^{-1} (WHSV) and CO_2 -free air 0.02 mol h^{-1} to test the stability of the catalyst. The plot of tetralin conversion and 1-tetralone selectivity versus time on stream (min) is shown in Fig. 9. Initially an increase in conversion was observed up to 1 h and then the conversion decreased gradually with the increase in time. The selectivity also followed similar trend as that of the conversion. The decrease in conversion may be due to the formation of Cr^{5+} which is not reactivated to Cr^{6+} sites during the course of reaction. In order to verify this, DR-UV-vis spectral analysis of both the spent and fresh catalysts was undertaken. The spectra are shown in Fig. 3a and e. In the spectrum of the spent catalyst, complete loss of polychromate and chromate species is observed. This analysis, therefore, confirms the necessity of polychromate and chromates for oxidation and also their regeneration. But they are not instantaneously regenerated. As discussed in the reaction Scheme 1, for oxidation of every tetralol to 1-tetralone

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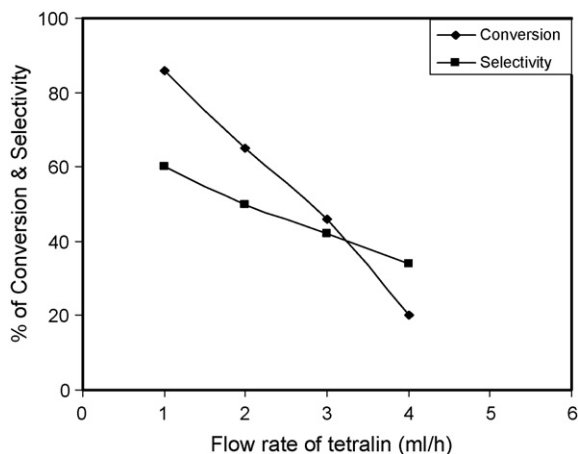


Fig. 8. Effect of flow rate on the oxidation on tetralin. Reaction conditions: catalyst: Cr-MCM-41(25), temperature = 623 K, catalyst weight = 0.3 g and flow rate of air 0.02 mol h^{-1} ; reaction time = 1 h.

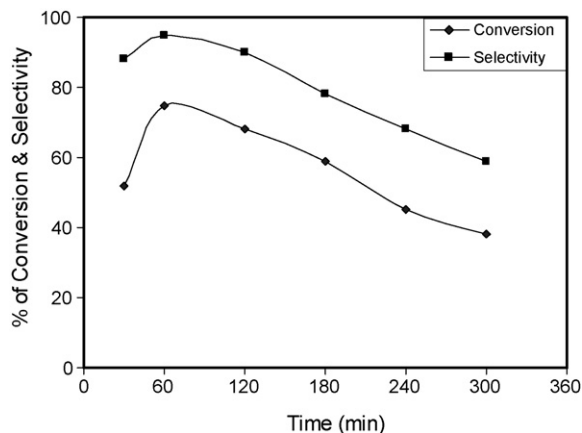


Fig. 9. Effect of reaction time on the oxidation of tetralin. Reaction conditions: temperature = 623 K, weight of Cr-MCM-41 (Si/Cr = 25) = 0.3 g, WHSV = 6.46 h^{-1} and flow rate of air 0.02 mol h^{-1} .

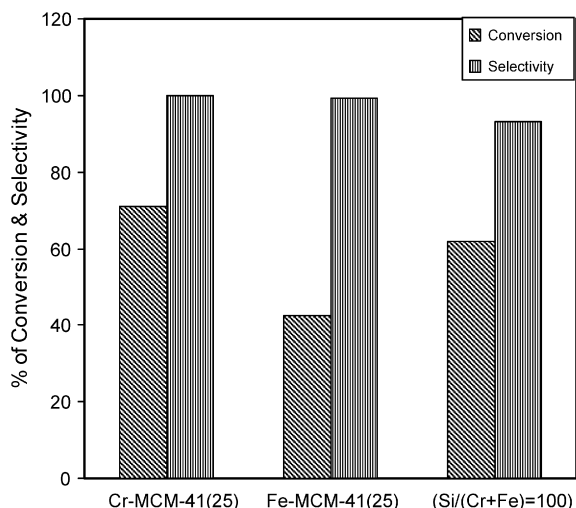


Fig. 10. Comparison of activity of the catalysts for the oxidation of tetralin. Reaction conditions: temperature = 623 K, weight of the catalyst = 0.3 g, WHSV = 6.46 h⁻¹ and flow rate of air 0.02 mol h⁻¹; reaction time = 1 h.

two hexavalent chromium sites are required but the amount of these sites decreases with the increase in time on stream. Hence the intermediate tetralol is to escape without subsequent conversion to 1-tetralone. From the above result, it is established that oxidation of tetralin requires Cr⁶⁺ species either in the form of chromates or polychromates.

3.10. Comparison of activity of the catalysts

The efficiencies of the catalysts were evaluated for the vapour phase oxidation of tetralin on Fe and Cr–Fe and compared with that of Cr-MCM-41 (Fig. 10). All the three catalysts exhibited different levels of conversion. Among the three different catalysts, Cr-MCM-41 (25) showed maximum activity for vapor phase oxidation of tetralin. However, the activity of Cr-Fe-MCM-41 was not equal to the sum of the activities of Cr-MCM-41 and Fe-MCM-41 and it is less than that of Cr-MCM-41 (25). The activity of Cr-Fe-MCM-41 catalyst is slightly reduced due to the interaction of Fe with Cr in the framework of MCM-41. It is also confirmed through the DR-UV–vis spectral analysis, wherein a shift towards longer wavelength is observed due to the charge transfer in Fe–O bond. Hence from this study it can be well understood that co-existence of Fe and Cr may not be beneficial for the vapor phase oxidation of tetralin under these experimental conditions.

4. Conclusions

Among the various Cr-MCM-41 (Si/Cr = 25, 50, 75 and 100) catalysts, the one with higher chromium content is more active than those with lower chromium content. It is established that co-existence of both Cr³⁺ and Cr⁶⁺ species in the framework is necessary for high conversion of tetralin and high selectivity to 1-tetralone. Hence adsorption and activation of molecular oxygen are a prerequisite for vapour phase oxidation. Therefore, it is concluded that Cr-MCM-41 is more active for the oxidation of

tetralin to 1-tetralone than either Fe-MCM-41 or Cr-Fe-MCM-41.

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