Liquid phase oxidation reactions over chromium silicalite-1 (CrS-1) molecular sieves

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Abstract

The oxidation of toluene and alkanes catalyzed by chromium silicalite-1 (CrS-1) using *t*-butyl hydroperoxide (TBHP) as oxidant is carried out under mild reaction conditions. A comparison under similar reaction conditions with vanadium silicalite-1 (VS-1) is also investigated for each reaction. The selectivities for the products strongly depend on the type of catalyst used. It is found that CrS-1 exhibits higher activity than VS-1 in the oxidation of toluene whereas CrS-1 and VS-1 are found to be comparable in the oxidation of *n*-hexane, *n*-heptane and *n*-octane. CrS-1 is not found to catalyze any reaction using H_2O_2 as the oxidant. The conversion of toluene is strongly influenced by the reaction parameters. As the reaction time and concentration of TBHP in the reaction mixture are increased, an increase in the conversion of toluene is noticed. CrS-1 is a stable catalyst and has been recycled four times with a slight decline in catalytic activity. The enhancement in the toluene conversion is not observed when CrS-1 is separated from the reaction mixture after a period of time. Mechanistically, it is assumed that catalytic properties of CrS-1 originate from the reversible transformation of Cr^{3+} and Cr^{5+} within the structure of CrS-1.

Keywords: Chromium silicalite-1; Oxidation reactions; Toluene; Alkanes

1. Introduction

Vanadium silicates (VS-1 and VS-2) and titanium silicates (TS-1 and TS-2) molecular sieves have been used widely in the synthesis of fine chemicals [1–10]. Traditionally, non-regenerable homogeneous catalysts such as acetates of transition metal ions, potassium dichromate and potassium permanganate have been used in such reactions [11–14]. Substitution of these catalysts by solid heterogeneous catalysts would result in simplified product recovery, reduction of unde-

sirable waste streams and use of catalytic amount of solid catalyst. Zeolite catalysts are effective in meeting current industrial processing objectives and more stringent environmental pollution limits which will require the development of new, more active and selective catalysts. Recently Sheldon et al. [15] and Chen et al. [16] have reported the synthesis and the use of chromium aluminophosphate molecular sieves (Cr–AlPO$_4$-5) in the oxidation reactions. More recently, the synthesis of chromium containing molecular sieves with MFI structure and their characterization have been reported in the literature but their stability is questionable because

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almost all the chromium incorporated into the molecular sieves can be leached out by ammonium (acetate) exchange [17] or by treating with acetic acid [18]. The basic media of the synthesis gel, which is maintained during synthesis, is responsible for the instability of chromium ions in the framework [19]. Chen et al. [20] reported very recently an effective catalyst for the oxidation of benzyl alcohol and ethylbenzene with TBHP. Selvam and Vinod [21] have also recently modified the synthesis procedure of CrS-1 to obtain thermally stable chromium ions in the MFI structure. However, the potential of modified CrS-1 has not yet been exploited in the oxidation of toluene and alkanes. In this paper, we disclose the report of our studies on the catalytic activity of a stable and recyclable CrS-1 catalyst in the oxidation of various organic molecules with TBHP. The influence of reaction time and toluene to TBHP ratio is also examined on the conversion of toluene using CrS-1. The results obtained for each molecule over CrS-1 are compared with that over the VS-1 catalyst.

2. Experimental

2.1. Synthesis procedure

The synthesis of CrS-1 was carried out using tetraethyl orthosilicate (TEOS, Merck), $Cr(NO_3)_3 \cdot 9H_2O$ (Loba, 98%), HF (Loba, 40%), NaOH (Loba, 99%) and tetrapropylammonium hydroxide (TPAOH, Aldrich, 20%). The molar gel composition was as follows: SiO_2 : xCr_2O_3 : 0.5 TPAOH : $0.16Na_2O$: 0.5HF : $60H_2O$. In a typical synthesis of CrS-1, 20 g TEOS was added slowly under vigorous stirring to a solution of 26 g doubly distilled water and 1.92 g $Cr(NO_3) \cdot 9H_2O$ and stirred for 30 min. The resulting mixture was added slowly to a solution of 2.4 g HF, 35 g doubly distilled water, 0.32 g NaOH and 48.6 g TPAOH. The temperature of the Teflon beaker was main-

tained at 273 K and the resulting gel (pH = 5.3) was stirred for 2 h before transferring it into the autoclave. The crystallization was carried out in a Teflon lined autoclave under static conditions at 443 K for 4 days. After the crystallization, the autoclave was then removed from the oven and quenched in cold water. The solid material was recovered by filtration, washed thoroughly with doubly distilled water, dried at 393 K for 6 h, and calcined at 773 K in air for 12 h. VS-1 was synthesized according to a published procedure [22]. For comparison, chromium impregnated silicalite-1 (CrS-1) was also prepared by impregnating silicalite-1 (MFI structure) with $Cr(NO_3)_3 \cdot 9H_2O$ solution followed by calcination at 773 K for 12 h [21].

2.2. Characterization

The chemical composition of the samples was obtained using conventional techniques (Table 1). The crystalline samples were characterized by XRD (Rigaku, D-Max III VC model), ^{29}Si MAS NMR (Bruker MSL-300), SEM (Leica Sterioscan), framework IR spectrum (Perkin Elmer 221 infrared spectrometer), diffuse reflectance spectra (Shimadzu model UV-2101 PC), ESR (Bruker ER-200 D spectrometer) and cyclic voltammetric (CV) techniques. The sorption measurements and surface area of molecular sieves were measured using an Omnisorb 100 CX (Coulter Corporation) instrument.

2.3. Catalytic reactions

The oxidation reactions were carried out batchwise in a glass reactor. Typically, 0.5 g of catalyst, 5 g of toluene, 6.9 g of TBHP and 20 ml of acetonitrile were introduced. The reaction was continued for 24 h at 353 K.

In the case of cyclohexane, n-hexane, n-heptane and n-octane, the reactions were carried out in a stirred autoclave (Parr Instruments, USA) at a temperature of 373 K for 12 h under autogenous pressure. Typically, 0.5 g of the catalyst and 5 g of alkane were mixed with 25

ml of acetonitrile. An appropriate amount of TBHP (alkane/TBHP = 3 mole ratio) was added to the reaction mixture. Product samples were analyzed by a gas-chromatograph (HP model 5880 series II) equipped with a flame ionization detector (FID) and capillary column (50 m × 0.2 mm) of methyl silicone gum.

Conversion is reported as the wt% of the organic substrate consumed. The rate of substrate conversion (mmol g^{-1} h^{-1}) indicates the amount of mmol of substrate converted per gram of catalyst in an hour. The yield percentage of a product is calculated from the selectivity of a particular product multiplied by the conversion.

3. Results and discussion

The properties of the CrS-1, VS-1 and Cr/Si-1 are given in Table 1. The X-ray diffraction patterns of the CrS-1 samples match well that of the silicalite-1 (MFI) structure and are found to be highly crystalline (Fig. 1). The room temperature ^{29}Si MAS NMR spectra of the silicalite-1 and CrS-1 (calcined, exchanged and recalcined; Si/Cr = 52) are shown in Fig. 2. The ^{29}Si MAS NMR spectrum of silicalite-1 is well-resolved, fourteen lines (corresponding to the 24 crystallographically inequivalent Si sites) are visible between −109.9 and −117.0 ppm. These lines are characteristic of the monoclinic phase [23]. On the other hand, the ^{29}Si MAS NMR spectrum of CrS-1 exhibits seven lines between −111.6 and −118.6 ppm which are characteristic of the orthorhombic phase [24].
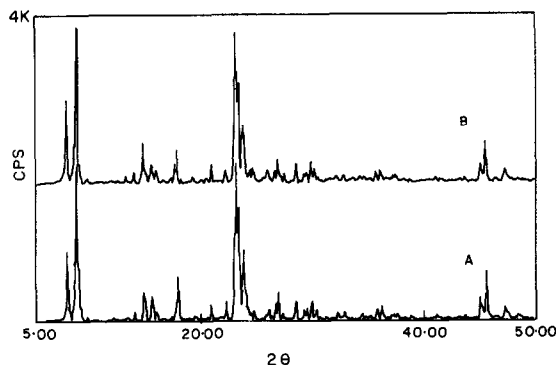

Fig. 1. X-ray powder patterns of (A) silicalite-1 and (B) CrS-1 (Si/Cr = 52) synthesized in the presence of fluoride ions.

ESR and cyclic voltammetric (CV) studies of CrS-1 (calcined, exchanged and recalcined) reveal that chromium is present in the form of Cr^{3+} and Cr^{5+} ions. Furthermore, the invariance of the CV pattern with cycling confirms the presence of chromium (both Cr^{3+} and Cr^{5+}) ions which are stabilized in the structure [21]. The scanning electron microscopy, surface area and sorption capacity of CrS-1 for n-hexane, cyclohexane and water show that there is no pore blocking or amorphous material inside the channels and on the external surface of the molecular sieves.

3.1. Oxidation of toluene

3.1.1. Influence of catalyst

The oxidation reaction of toluene with TBHP over CrS-1, VS-1 and Cr/S-1 yields benzaldehyde (BZD), benzyl alcohol (BZAlC), ben-

Table 1
Physico–chemical properties of the samples

Catalyst	Si/M (molar ratio) [a]	Crystal size (μm)	Surface area (m² g⁻¹)	Sorption capacity (wt%)		
				n-hexane	cyclohexane	water
CrS-1	52	5 × 25	336	9.7	5.2	3.8
VS-1	118	0.1 × 0.2	475	12.8	7.2	5.6
Cr/Si-1 [c]	52	—	273	7.4	4.3	3.1

[a] M = Cr or V.
[b] Gravimetric (Cahn balance), temperature = 298 K, p/p_o = 0.5.
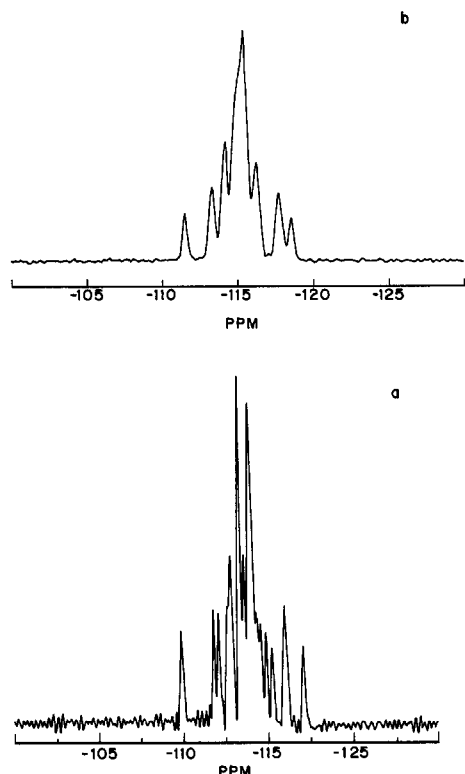[c] Chromium impregnated silicalite-1.

Fig. 2. Room temperature ^{29}Si MAS NMR spectra of (a) silicalite-1 and (b) CrS-1 (calcined, exchanged and recalcined; Si/Cr = 52) synthesized in the presence of fluoride ions.

as the oxidizing agent [25]. Table 2 compares the activities of catalysts under identical reaction conditions and CrS-1 showed higher activity than VS-1 and Cr/S-1. In the absence of catalyst only a very low conversion of toluene (2.1 wt%) is observed. It is believed that higher catalytic activities of CrS-1 and VS-1 compared to the Cr/S-1 are attributed to those chromium or vanadium ions which are incorporated into the MFI structure during the hydrothermal synthesis [7,20,21]. The variation of the selectivity towards products is found to be different on the three catalysts (Table 2). CrS-1 yields a higher amount of DBZ (45.1 wt%) whereas catalyst VS-1 gave only 9.2 wt% of DBZ and no DBZ formation is observed over Cr/S-1. The conversion of toluene over CrS-1, VS-1 and Cr/S-1 is found to be 18.4, 8.3 and 3.3 wt%, respectively. The corresponding rates of toluene conversions are 0.83, 0.38 and 0.15 mmol g^{-1} h^{-1}, respectively. The conversion of toluene over VS-1 is lower than over CrS-1; however, this is mainly due to the lower vanadium content in VS-1 (Si/V = 118) as compared to the chromium content in CrS-1 (Si/Cr = 52).

3.1.2. Effect of reaction time

Fig. 3 shows the conversion of toluene, ratio of BZAC/BZD and product yields at 353 K using CrS-1 as a function of reaction time. It can be seen from Fig. 3 that the conversion of toluene as well as the product yields increase

zoic acid (BZAC), dibenzyl (DBZ) and trace amounts of o-cresol (o-CRS) and p-cresol (p-CRS). A blank run was also carried out for comparison. The products are found to be similar to those reported earlier in the oxidation of toluene using VAPO-5 as the catalyst and TBHP

Table 2
Oxidation of toluene [a]

Catalyst	Conversion (wt%)	Rate of toluene conversion (mmol g^{-1} h^{-1}) [b]	Product distribution (wt%) [c]					
			BZD	BZAlC	BZAC	o-CRS	p-CRS	DBZ
CrS-1	18.4	0.83	23.3	5.2	25.7	0.4	0.3	45.1
VS-1	8.3	0.38	42.9	15.1	24.8	—	8.0	9.2
Cr/S-1 [d]	3.3	0.15	47.7	9.7	37.0	1.7	3.9	—
Blank [e]	2.1	0.10	72.0	28.0	—	—	—	—

[a] Reaction conditions: catalyst = 0.5 g, toluene = 5 g, reaction temperature = 353 K, solvent (acetonitrile) = 20 ml, TBHP/toluene (molar ratio) = 1, reaction time = 24 h.
[b] mmoles of toluene converted per gram of catalyst in an hour.
[c] BZD = benzaldehyde, BZAlC = benzylalcohol, BZAC = benzoic acid, o-CRS = ortho-cresol, p-CRS = para-cresol, DBZ = dibenzyl.
[d] Chromium impregnated silicalite-1.
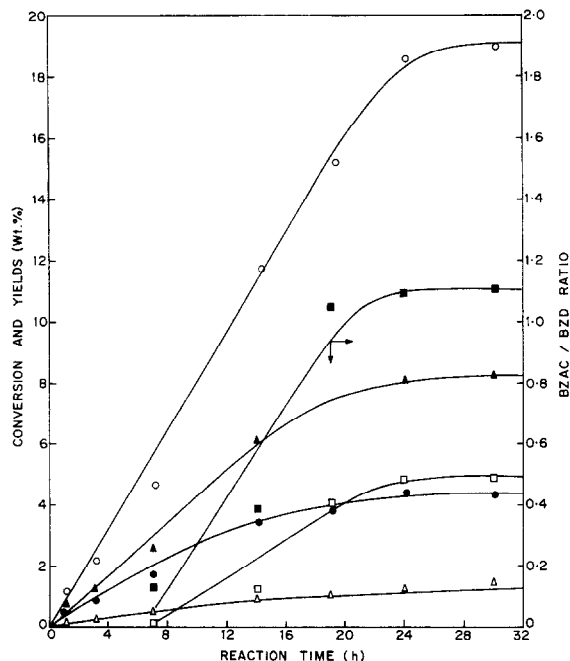[e] No catalyst was used.

Fig. 3. Effect of reaction time on the conversion of toluene (o), BZAC/BZD ratio (■) and product yields, BZAlC (△), BZD (●), BZAC (□) and DBZ (▲); reaction conditions: catalyst (CrS-1) = 0.5 g, toluene = 5 g, reaction temperature = 353 K, solvent (acetonitrile) = 25 ml, TBHP/toluene (molar ratio) = 1.

gradually with the progress of the reaction and level off after 24 h of reaction time. The ratio of BZAC/BZD increases linearly from 0.13 to 1.1 when the reaction time was increased from 7 to 24 h, respectively. Benzoic acid is formed only after a few hours and its yield reaches a maximum value after a period of time. Benzoic acid is formed by the subsequent oxidation of benzaldehyde (which is formed from benzyl alcohol). In addition, dibenzyl formation takes place via a radical mechanism [25]. These results are in good agreement with the reported data on the

oxidation of toluene using various catalysts [25,26].

3.1.3. Effect of molar ratios of reactants

Another aspect studied was the influence of the ratio of reactants on the conversion of toluene. The ratios were changed by keeping the amount of toluene constant. As can be observed from Table 3, measurements carried out at 353 K in the presence of CrS-1 show that the conversion of toluene is favored by an excess of TBHP. The conversion rises from 6.8 to 18.4 wt% as the TBHP/toluene molar ratio is increased from 0.33 to 1.0. The selectivity to the product is also influenced with the increase in TBHP/toluene molar ratio.

3.1.4. Effect of catalyst removal

The results of this part of work are much more significant and show whether the toluene conversion proceeds through heterogeneous or homogeneous catalysis using CrS-1 as catalyst and TBHP as the oxidant at 353 K. Fig. 4 illustrates the effect of the catalyst removal on the conversion of toluene during the reaction. The CrS-1 was removed by filtration from the reaction solution after 7 h, further the reaction was carried out using the filtered reaction solution in the absence of CrS-1 and compared with a reaction solution containing the CrS-1 catalyst. The results of the catalyst removal experiment indicate that no conversion of toluene was achieved when the catalyst was removed from the reaction solution (after 7 h). Further the final reaction mixture was analyzed for Cr using atomic absorption spectroscopy (AAS). Presum-

Table 3
Influence of TBHP/toluene molar ratio [a]

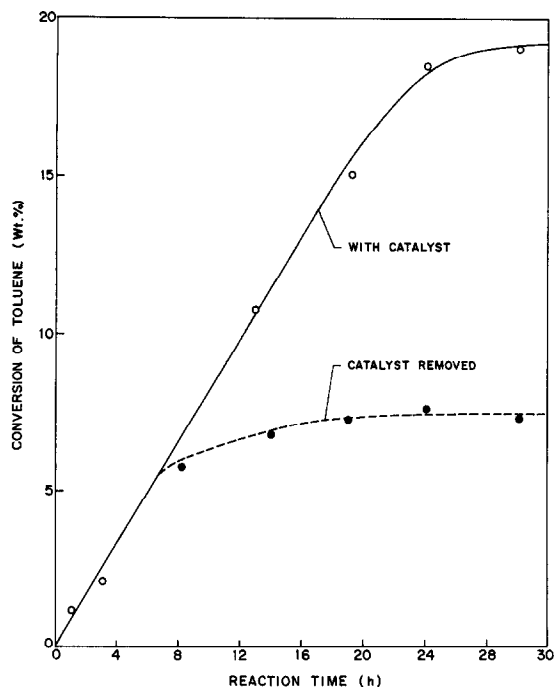| TBHP/toluene (molar ratio)	Conversion (wt%)	Rate of toluene conversion (mmol g^{-1} h^{-1}) [b]	Product distribution (wt%) [c]					
			BZD	BZAlC	BZAC	o-CRS	p-CRS	DBZ
0.3	6.8	0.31	72.6	13.3	14.1	—	—	—
0.5	11.2	0.51	58.7	9.1	17.4	0.4	0.2	14.2
1.0	18.4	0.83	23.3	5.2	25.7	0.4	0.3	45.1

[a,b,c] See footnotes to Table 2.

Fig. 4. Effect of catalyst (CrS-1) separation on the conversion of toluene; Reaction conditions as in Fig. 3.

Fig. 5. X-ray powder patterns of fresh CrS-1 (A) and after fourth recycling (B).

ably, the minor amount of Cr (~ 2 ppm) leached out from the CrS-1 during 7 h of reaction time may not be able to catalyze the reaction. The results confirm that CrS-1 acts as heterogeneous catalyst in the system.

3.1.5. Recycling of the catalyst

In order to check the stability of the chromium in the catalyst (CrS-1), four reaction cycles were carried out using the same catalyst in the oxidation of toluene. The results are presented in Table 4. After completion of the reaction, the catalyst was removed by filtration from the
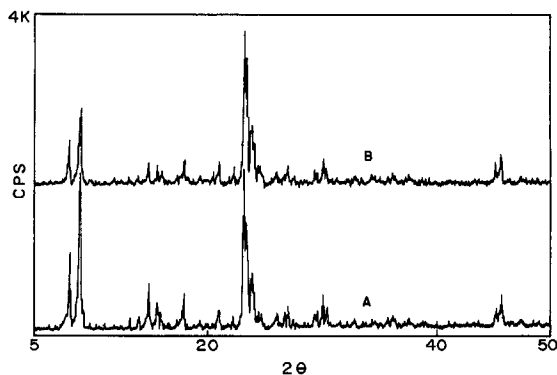
reaction mixture and washed thoroughly with acetonitrile. The reaction mixture and washings were combined and analyzed for chromium. Prior to use in the next cycle, the catalyst was calcined at 773 K for 16 h in the presence of air. AAS revealed that indeed a small amount of chromium was leached out in the reaction mixture after one reaction cycle and the Si/Cr ratio was changed from 52 to 54. The amount of chromium leached out decreased with the increase in number of cycles and the Si/Cr ratio remained constant (Si/Cr = 55) after a second recycle. These results demonstrate that CrS-1 is an active and stable catalyst and conversion of toluene decreases from 18.4 to 17.4 wt% after the first reaction cycle. However, nearly similar conversion is obtained over CrS-1 in the third (15.3 wt%) and fourth (15.0 wt%) recycles. The observed decrease in the catalytic activity of CrS-1 seems to be related to the leaching of the chromium from the catalyst. The product distri-

Table 4
Catalyst recycling [a]

Run	Conversion	Si/Cr	Rate of toluene conversion	Product distribution (wt%) [c]					
	(wt%)	(mol ratio)	(mmol g^{-1} h^{-1}) [b]	BZD	BZAlC	BZAC	o-CRS	p-CRS	DBZ
1	18.4	52	0.83	23.3	5.2	25.7	0.4	0.3	45.1
2	17.5	54	0.79	26.9	9.5	26.5	0.5	0.4	35.9
3	15.3	55	0.69	22.6	5.8	33.9	0.3	0.2	36.9
4	15.0	55	0.68	28.0	10.1	27.0	0.5	0.3	34.1

[a,b,c] See footnotes to Table 2.

Table 5
Oxidation of cyclohexane [a]

Catalyst	Conversion (wt%)	Rate of cyclohexane conversion (mmol g^{-1} h^{-1}) [b]	Product distribution (wt%)		
			cyclohexanone	cyclohexanol	others
CrS-1	8.5	0.84	49.1	50.2	0.7
VS-1	5.6	0.55	47.6	51.9	0.5

[a] Reaction conditions: catalyst = 0.5 g, cyclohexane = 5 g, reaction temperature = 373 K, solvent (acetonitrile) = 25 ml, cyclohexane/TBHP (molar ratio) = 3, reaction time = 12 h.
[b] mmoles of cyclohexane converted per gram of catalyst in an hour.

bution remained nearly similar in all recycle experiments. In order to check the structure and crystallinity of the catalyst after reaction, X-ray powder diffraction patterns were recorded. XRD patterns (Fig. 5) indicated that the catalyst retains the CrS-1 structure and the crystallinity was found to be 95% (after the fourth cycle) when compared to the fresh catalyst (100% crystallinity).

3.2. Oxidation of cyclohexane

Table 5 summarizes the reaction condition and catalytic activities of CrS-1 and VS-1 in the oxidation of cyclohexane. A blank run was also carried out for comparison. The major products of the reaction are cyclohexanone and cyclohexanol. It is seen that CrS-1 sample is found to be more active than VS-1. A blank run failed to give any conversion of cyclohexane. The conversion of cyclohexane over CrS-1 and VS-1 are found to be 8.5 and 5.6 wt%, respectively. The corresponding rates of cyclohexane conversion are 0.84 and 0.55 mmol g^{-1} h^{-1}, respectively.

3.3. Oxidation of n-alkanes

The results of the oxidation of n-hexane, n-heptane and n-octane over CrS-1 and VS-1 are listed in Table 6. Both catalysts show approximately the same trends for substrate conversion as well as product distribution. The major products of the reaction are corresponding alcohols, aldehydes and ketones. Small quantities of other products with more than one functional group viz. dihydroxyalkanes and lactones are also detected. The rate of substrate

Table 6
Oxidation of n-alkanes [a]

Alkane	Catalyst	Conversion (wt%)	Rate of n-alkane conversion (mmol g^{-1} h^{-1}) [b]	Product distribution (wt%) [c]								
				4-one	3-one	2-one	4-ol	1-al	3-ol	2-ol	1-ol	others [d]
Hexane	CrS-1	11.3	1.10	—	28.2	30.9	—	4.1	4.3	6.1	0.2	26.2
Hexane	VS-1	11.6	1.12	—	28.7	31.3	—	4.0	4.7	6.6	0.1	24.6
Heptane	CrS-1	9.8	0.82	6.9	16.0	20.9	10.3	14.3	5.2	7.0	2.3	17.1
Heptane	VS-1	10.9	0.91	8.0	17.2	20.3	10.9	16.2	5.1	7.2	3.6	11.5
Octane	CrS-1	7.7	0.56	11.6	6.6	11.9	7.9	8.4	18.3	11.8	1.0	22.5
Octane	VS-1	8.7	0.64	5.7	13.7	22.5	6.1	6.8	12.6	7.3	0.2	25.1

[a] Reaction conditions: catalyst = 0.5 g (CrS-1, Si/Cr = 52; VS-1, Si/V = 118), alkane = 5 g, alkane/TBHP = 3 (mole ratio), solvent = acetonitrile (25 ml), reaction temperature = 373 K, reaction time = 12 h.
[b] mmoles of alkane converted per gram of catalyst in an hour.
[c] 1-ol = alcoh-1-ol, 2-ol = alcoh-2-ol, 3-ol = alcoh-3-ol, 4-ol = alcoh-4-ol, 1-al = 1-aldehyde, 2-one = ket-2-one, 3-one = ket-3-one and 4-one = ket-4-one of corresponding alkanes.
[d] Mostly oxygenates with more than one functional group and lactones.

conversion decreased in the order n-hexane > n-heptane > n-octane. This marked difference in the activity of alkane oxygenation between n-hexane, n-heptane and n-octane can be related to the decrease in diffusivity of these alkanes in molecular sieves with increase in chain length and molecular size [27].

3.4. Mechanism

Presumably, the oxidation of different substrates with TBHP in the presence of CrS-1 proceeds through the reversible transformation of Cr^{3+} and Cr^{5+} within the structure of CrS-1 [21]. The involvement of the redox system Cr^{5+}/Cr^{3+} present in CrS-1 is substantiated by ESR studies.

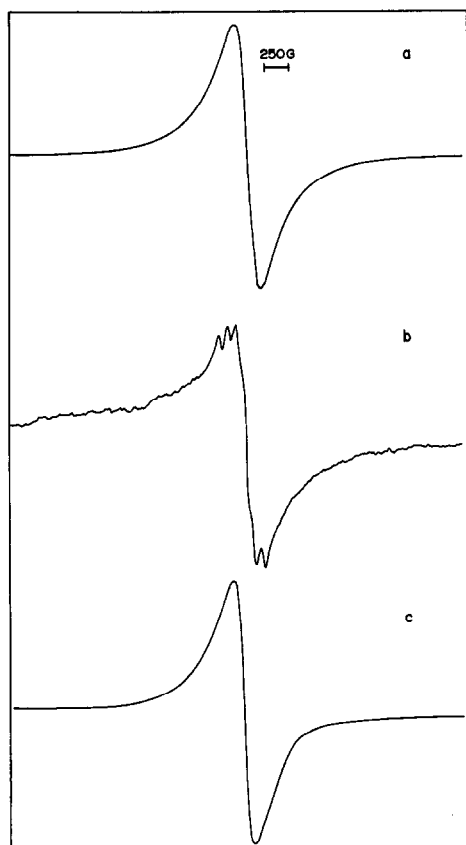The ESR spectra of as-synthesized CrS-1 (Fig. 6a) exhibit a broad singlet with a g value

Fig. 6. ESR spectra of CrS-1 (a) as-synthesized (b) calcined, exchanged and recalcined and (c) after the catalytic oxidation reaction of toluene.

of 1.945, indicating the presence of Cr^{3+} ions with octahedral coordination [28]. After calcination of the as-synthesized CrS-1 at 773 K for 12 h under air atmosphere, the sample color has changed from dark green (as-synthesized) to light yellow (calcined). Most probably, a part of Cr^{3+} ions are oxidized to Cr^{5+} and subsequently to Cr^{6+} ions. The light yellow color of the calcined CrS-1 strongly suggests that the presence of CrO_4^{2-} or $Cr_2O_7^{2-}$ species [29]. Furthermore, the presence of Cr^{6+} ions are also identified by the appearance of deep blue color after the addition of hydrogen peroxide (aqueous, 30%) [30]. These Cr^{6+} ions can easily be removed by ammonium (acetate) exchange treatment because of the freely soluble nature of these chromate species. The ESR spectrum of CrS-1 (calcined, exchanged and recalcined; Fig. 6b) exhibits a new broad five line spectrum with a g value of 1.951. This typical five line spectra is originating from the exchange interaction between Cr^{3+} and Cr^{5+} ions [31]. The presence of Cr^{5+} ions is also further corroborated by cyclic voltammetric studies [21]. ESR spectra are also obtained for CrS-1 after it was used for the catalytic reaction of toluene. The ESR spectrum of CrS-1 after the reaction (Fig. 6c) shows a broad singlet ($g = 1.946$); the characteristic spectrum of Cr^{3+} reappears indicating the reversibility of Cr^{5+}/Cr^{3+} within the structure.

4. Conclusions

In summary, CrS-1 is an active, stable, recyclable catalyst for the liquid phase oxidation of toluene, cyclohexane, n-hexane, n-heptane and n-octane with TBHP. CrS-1 exhibits higher activity than VS-1 in the oxidation of toluene whereas CrS-1 and VS-1 are found to be comparable in the oxidation of n-alkanes. The higher yield of the products can be achieved by increasing the value of reaction parameters such as reaction time and TBHP/toluene molar ratios. The activity and selectivity of CrS-1 is

quite stable after four recyclings in the oxidation of toluene. The reaction proceeds through heterogeneous catalysis and no conversion of toluene is observed when CrS-1 was removed by filtration from the reaction solution after 7 h of reaction time. Mechanistically, it is assumed that oxidation reactions involves the redox system (Cr^{3+}/Cr^{5+}) of CrS-1.

Acknowledgements

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