

Influence of K_2O addition on the aromatization functionality of Al_2O_3 -supported Cr_2O_3 catalysts in the transformation of isophorone

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Abstract

Alumina-supported unpromoted and K_2O -promoted Cr_2O_3 catalysts were prepared varying the Cr_2O_3 loading in the range of 5–25 wt.%. These were characterized for total pore area and pore size distribution by mercury porosimetry, X-ray powder diffraction (XRD), electron spin resonance spectroscopy (ESR) and for their total acidity. Transformation of isophorone was carried out on these catalysts, under vapor phase, at atmospheric pressure in the temperature range of 673–808 K. The products obtained are classified into two major groups, one due to decomposition and the other due to aromatization. Efforts have been made to delineate the Cr active species responsible for the aromatization functionality. The influence of K_2O on these active species has also been elucidated. It is observed that K_2O helps in neutralizing the strong acidity of the catalyst, minimizing the decomposition products while simultaneously enhancing the intrinsic activity of the Cr^{3+} species towards aromatization. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aromatization; Isophorone; 3,5-Xylenol; K_2O addition; Cr_2O_3/Al_2O_3 catalysts

1. Introduction

3,5-Xylenol is an important industrial intermediate [1–4] used as an anti-oxidant and in the preparation of anti-microbial powders, laminating paper adhesives and antiseptic creams. Aromatization of isophorone, the synthetic route to prepare 3,5-xylenol, is gaining more and more importance (compared to the conventional alkylation of phenol or extraction from coal-tar), as it offers higher selectivity towards the required product. However, this reaction involves a complex sequence of series and parallel steps (Fig. 1) between

the reactant and the intermediates [5,6]. The entire product can be classified into two major groups: those parts formed by the decomposition and those parts formed by aromatization. Condensation among the products and reactant (isophorone) could also occur depending upon the nature of catalyst. In view of the stringent environmental regulations imposed on waste disposal into the atmosphere, selective production of 3,5-xylenol, a major component of the aromatization product, is a challenging task. With a view to attain this goal various catalyst systems have been tried. Al_2O_3 as a catalyst [7] offers high conversion but leads to formation of substantial amounts of decomposition products because of the acidic nature of Al_2O_3 . However, formation of coke during the reaction at high temperature (>753 K) on the acid centers of the

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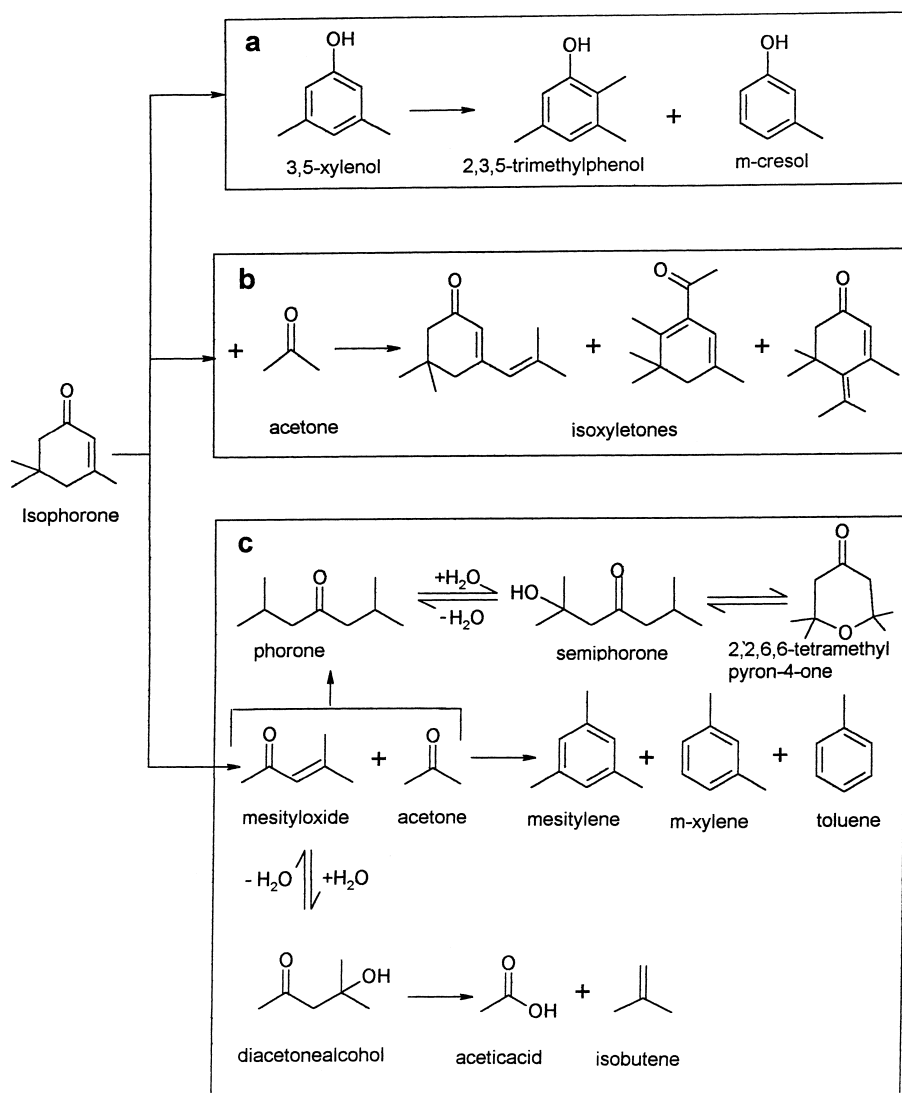


Fig. 1. Reaction net-work: (a) aromatization products; (b) condensation products; (c) decomposition products.

catalyst reduces the decomposition with a simultaneous decrease in activity. This observation is supported by using carbon-covered Al_2O_3 as a catalyst for the reaction [7]. Continuous formation of coke on alumina also affects the reaction in two ways, namely, fixing a limit on the operating temperature and putting the system under an unsteady state. Other catalysts like Al_2O_3 -supported V_2O_5 and MoO_3 have resulted in the formation of high amounts of isoxylitones [8], the cross condensation products, again decreasing the

required selectivity towards aromatization products. Supported Cr_2O_3 catalyst has been identified as one of the best catalysts for obtaining better aromatization selectivity [9,10]. A small quantity of K_2O addition neutralizes strong acid sites of the catalyst and improves aromatization selectivity [9,11].

In a recent study [10], we have tried to understand the nature of Cr-active sites in the absence of support influence by using silica as a support; we observed that the Cr^{3+} coordinatively unsaturated sites

(CUS) are mainly responsible for the aromatization selectivity. However, the promoting role of K_2O on Cr_2O_3 has not been studied in detail. The purpose of the present investigation is two fold: (i) deriving the benefit of high reaction temperature (beyond 753 K) for increased activity, after suppressing the decomposition with the addition of K_2O and (ii) examining the influence of K_2O on the active chromia sites in enhancing the aromatization selectivity.

2. Experimental

Commercial γ -alumina (Harshaw 3996-R, 18/25 BSS mesh) was used as a support. A series of unpromoted Cr_2O_3/Al_2O_3 catalysts was prepared with varying Cr-content (5–25 wt.% of Cr_2O_3) by impregnating the support with required quantities of aqueous solution of chromic anhydride (A.R. Grade, Loba Chemie, India). The catalyst masses were initially dried at 393 K overnight, followed by calcination in air at 823 K for 6 h. The K_2O -promoted ($K_2O-Cr_2O_3/Al_2O_3$) catalysts were then prepared by impregnating the unpromoted catalysts with an aqueous solution of potassium carbonate (A.R. Grade, Qualigens, India). A constant K_2O content of 2 wt.% for promoted catalysts was chosen as this amount was found to be optimum for Cr_2O_3/Al_2O_3 catalysts in the decomposition of isopropanol [12]. Drying and activation were followed as described above. These catalysts have been designated as CA- x and KCA- x respectively, where CA and KCA represent unpromoted and K_2O -promoted catalysts respectively and x is the loading of Cr_2O_3 expressed as weight percent. A catalyst containing 2 wt.% K_2O impregnated on Al_2O_3 (K_2O/Al_2O_3 -without Cr_2O_3) was also prepared in a similar manner for the sake of comparison.

Total pore area, pore volume and the average pore radius of the catalysts were determined by mercury penetration porosimetry technique using Autopore-9200 (M/s. Micromeritics, USA). XRD patterns of the catalysts were obtained on a Phillips diffractometer (Model-PW1051) using $Cu\ K\alpha$ radiation. The ESR spectra of the catalysts were recorded at room temperature on a Bruker ER-200-SRC X-band spectrometer. The intensity of the broad Cr^{3+} signal was calculated as the product of the height of the signal and the square of the ΔH_{p-p} (peak to peak

line width). The intensity values were normalized for instrumental factors like modulation and gain. Microwave power, attenuated to avoid saturation effects, was held constant. The acidity of the catalysts was determined by the *n*-butylamine titration method [13]. In a typical experiment, about 0.5 g of the finely powdered catalyst (calcined) was thoroughly dried at 393 K for 24 h and then taken in a stoppered bottle. About 15 ml of standard *n*-butylamine solution prepared by taking dry benzene as solvent was then added to the sample without permitting exposure to moisture and allowed to adsorb on the catalyst. After 24 h, the catalyst was separated from the solution by filtration. The residual amine in benzene was then titrated with standard HCl solution taking bromothymol blue as the indicator. After the reaction, the catalyst in the reactor was flushed with nitrogen gas at 673 K for 1 h to remove adsorbed organics prior to acidity determination.

Activity studies on the catalysts were carried out in a fixed bed glass (20 mm i.d. and 300 mm long) reactor, under vapor phase, at atmospheric pressure in the temperature range of 673–808 K. A uniform weight hourly space velocity (WHSV) of $1\ h^{-1}$ was used for all the samples. BDH analar grade isophorone was used as the feed. After 30 min of the catalyst attaining the steady-state at each reaction temperature, the product was collected for 10 min and analyzed on a Varian gas chromatograph with FID using DAB-1 capillary column by programming the oven temperature between 393 and 453 K at 3 K/min. The analysis was standardized using known mixtures of pure samples by calculating the weight response factor. An experiment carried out with quartz pieces in place of the catalyst did not give any observable isophorone conversion ruling out the possibility of a homogeneous surface/volume effect. Percentage selectivity towards a particular product, for example 3,5-xylenol, was taken as the ratio of conversion of isophorone to 3,5-xylenol to its total conversion, multiplied by 100. Percentage yield was defined as the product of percentage conversion and percentage selectivity divided by 100.

3. Results and discussion

Total pore area, pore volume and the average pore radius values obtained by the mercury intru-

Table 1
Surface area, pore volume and average pore radius of the promoted and unpromoted Cr₂O₃/Al₂O₃ catalysts

S.No	Catalyst code	Surface area (m ² /g)	Pore volume (ml/g)	Average pore radius (Å)
1	Support	284	0.523	74
2	CA-5	236	0.480	86
3	CA-10	241	0.453	84
4	CA-15	225	0.443	97
5	CA-20	210	0.368	87
6	CA-25	189	0.328	92
7	KCA-5	223	0.468	88
8	KCA-10	209	0.439	93
9	KCA-15	199	0.392	93
10	KCA-20	219	0.356	87
11	KCA-25	216	0.338	89

sion method are given in Table 1. It can be observed that in both unpromoted and promoted catalysts the surface area has gradually decreased with increase in Cr₂O₃ loading, whereas the average pore radius remained almost constant because of corresponding decrease in pore volume. This is normally expected in impregnated catalysts where the active component is uniformly coated inside the pores. The values of the average pore radius denote medium size pores, which do not normally cause diffusional resistance. XRD patterns (Fig. 2) of the catalysts show their amorphous nature up to a Cr₂O₃ loading of 15 wt.%, beyond which there is a slight indication of the formation α -Cr₂O₃ crystallites. No compound formation of Cr₂O₃ either with the support or with the promoter is

evidenced. These results are in agreement with those of Voltz and Weller [14].

The effects of reaction temperature on the activity over Al₂O₃, K₂O/Al₂O₃-without Cr₂O₃, Cr₂O₃/Al₂O₃ and K₂O-Cr₂O₃/Al₂O₃ catalysts are shown in Fig. 3. Al₂O₃ shows higher conversion of isophorone compared to K₂O/Al₂O₃-without Cr₂O₃, Cr₂O₃/Al₂O₃ and K₂O-Cr₂O₃/Al₂O₃ catalysts. This is, however, associated with higher decomposition on Al₂O₃, possibly due to the presence of strong acid sites. It is reported that on Al₂O₃ coke formation occurs beyond 753 K [7]. The coke formed covers the strong acid sites and indirectly leads to the enhancement of aromatization selectivity. The decrease in the aromatization selectivity upto 753 K over Al₂O₃

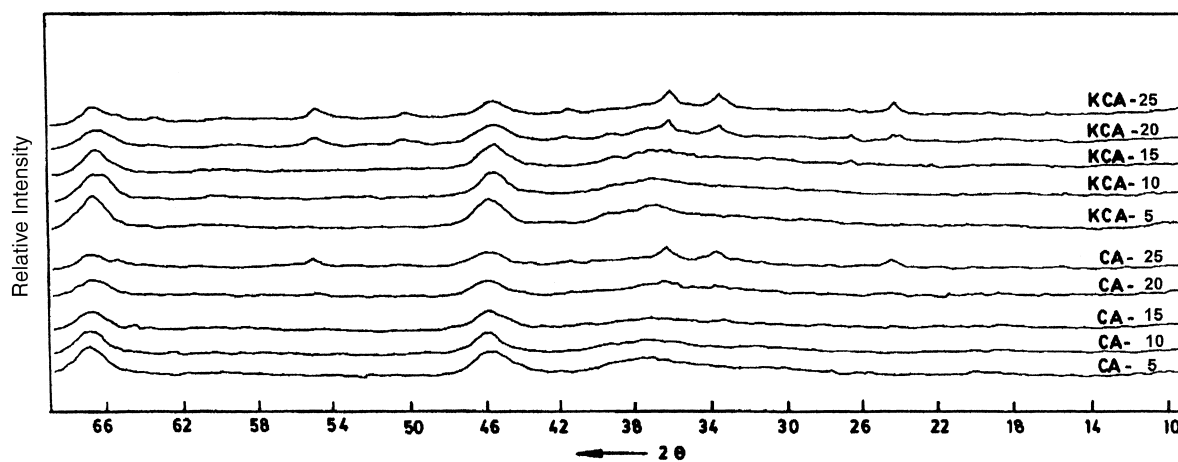


Fig. 2. XRD patterns of Cr₂O₃/Al₂O₃ and K₂O-Cr₂O₃/Al₂O₃ catalysts.

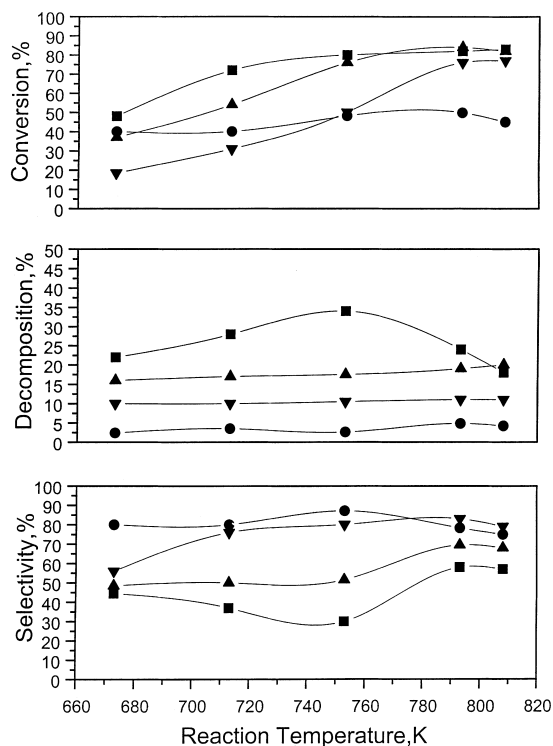


Fig. 3. Effect of reaction temperature on the catalytic activity of γ -Al₂O₃, K₂O/Al₂O₃-without Cr₂O₃, CA-15 and KCA-15 catalysts. (■) γ -Al₂O₃; (●) K₂O/Al₂O₃-without Cr₂O₃; (▲) CA-15; (▼) KCA-15.

followed by its increase and then saturation in the region 793–808 K confirms the above statement. The catalytic activity observed on K₂O/Al₂O₃-without Cr₂O₃ is found to be different from that observed on Cr₂O₃/Al₂O₃. Addition of K₂O appears to neutralize the strong acid sites on Al₂O₃ as reflected by considerable decrease in the decomposition activity and, in turn, the total isophorone conversion. Cr₂O₃/Al₂O₃, on the other hand, shows lower isophorone conversion at lower reaction temperatures, but almost equal to that of Al₂O₃ at higher temperatures. With the addition of Cr₂O₃ to Al₂O₃ the decomposition activity has decreased, though not to the extent observed on K₂O/Al₂O₃-without Cr₂O₃ catalyst. K₂O, by itself, appears to be not active for the aromatization reaction. Cr₂O₃, on the other hand, besides neutralizing the acid centres on Al₂O₃, appears to enhance the aromatization selectivity. However, in the case of pro-

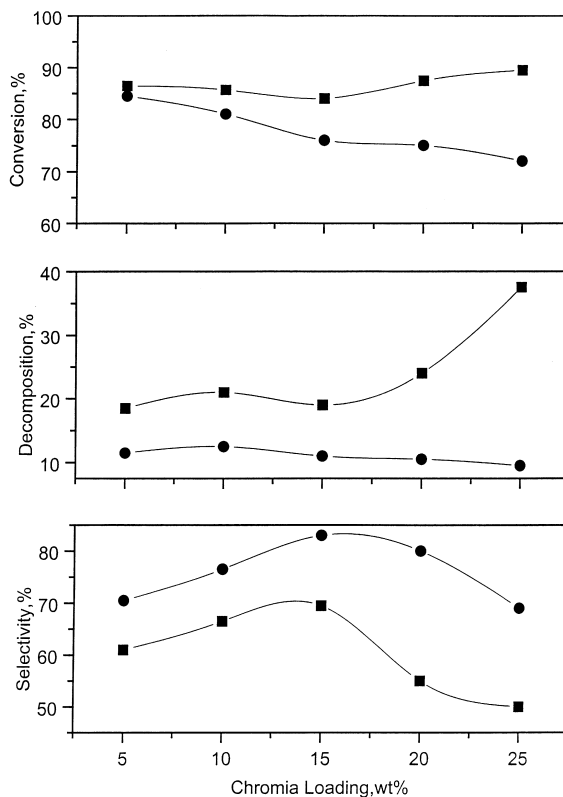


Fig. 4. Effect of chromia loading on the activity: (■) Cr₂O₃/Al₂O₃; (●) K₂O-Cr₂O₃/Al₂O₃.

moted catalysts, the selectivity towards aromatization products is higher at all temperatures studied. Moreover, at high temperatures, the conversion over the K₂O-promoted Cr₂O₃ catalyst matches with those on the Al₂O₃ and Cr₂O₃/Al₂O₃ catalysts. Thus, K₂O addition seems to be advantageous compared to the beneficial role of coke, particularly in maintaining higher aromatization yields at temperatures beyond 753 K.

In order to find out the optimum loading of Cr₂O₃, for the aromatization of isophorone a reaction temperature of 793 K has been selected. The influence of Cr₂O₃ loading on the activity and aromatization selectivity is shown in Fig. 4. In both unpromoted and K₂O-promoted catalysts the conversions are of the same order at low loading of 5 wt.% Cr₂O₃. Unpromoted catalysts show a slight increasing trend in the isophorone conversion, whereas the promoted catalysts display a slow but steady decrease in the

Table 2

Surface acidity of the promoted and unpromoted Cr₂O₃/Al₂O₃ catalysts before and after reaction

S.No	Catalyst code	Acidity of the fresh catalyst (μmol/g catalyst)	Acidity of the spent catalyst (μmol/g catalyst)	Difference in acidity of fresh and spent catalyst (μmol/g catalyst)
1	Support	1350	832	518
2	CA-5	616	430	186
3	CA-10	598	338	260
4	CA-15	666	280	386
5	CA-20	628	265	363
6	CA-25	568	204	364
7	KCA-5	518	390	128
8	KCA-10	535	385	150
9	KCA-15	525	395	150
10	KCA-20	501	370	131
11	KCA-25	443	332	111

activity of the catalysts with increase in Cr₂O₃ loading. High conversion in case of unpromoted catalysts is manifested in high decomposition of isophorone. An interesting observation is that the maximum aromatization selectivity is shown at 15 wt.% Cr₂O₃ loading in both the series of catalysts. From this figure it appears that the sites responsible for the decomposition and aromatization are different. Acidity is considered to be one of the reasons for the decomposition of isophorone [7]. Surface acidity data obtained on both the unpromoted and K₂O-promoted catalysts are given in Table 2. There is a significant decrease in the acidity of the alumina after the addition of Cr₂O₃, thus poisoning to some extent the strong acidic sites on alumina. With increase in Cr₂O₃ loading, the dehydrating (acidic) functionality of Al₂O₃ decreases while the dehydrogenating functionality of Cr₂O₃/Al₂O₃ increases [12]. From Table 2 it is clear that the K₂O-promoted catalysts may have lower acidity, due to the further neutralization of strong acid sites present on Cr₂O₃/Al₂O₃ catalysts [11]. In both the series, the acidity values start increasing with Cr₂O₃ loading up to 15 wt.% and thereafter decrease. This may be due to the fact that, in the catalysts with lower Cr loading, the Cr species are perhaps present predominantly in higher oxidation states like Cr⁵⁺ and/or Cr⁶⁺ which are more acidic than the lower oxidation states like Cr³⁺ species. The presence of Cr⁵⁺ at low loading observed from their ESR patterns (Fig. 5) strongly supports this hypothesis. The decrease in the acidity of the used catalysts compared to their fresh analogues may be due to the reduc-

tion of higher oxidation states of Cr to Cr³⁺ species during the reaction. It appears that higher oxidation states of Cr are present at low Cr₂O₃ loadings. From Table 2 it can be observed that the difference between the acidity of fresh and used catalysts increases up to 15 wt.% Cr₂O₃ loading and remains more or less constant thereafter, which may be attributed to the conversion of more and more higher oxidation states of Cr to their lower states as the loading increases up to 15 wt.%. Potassium neutralizes the strong acid centers and hence it is not surprising to note that the acidity of promoted catalysts are lower compared to their corresponding unpromoted catalysts and that the acidity difference between the fresh and used catalysts remains almost constant. However, in the present investigation we have observed that, as the Cr₂O₃ loading increases, acidity increases initially up to 15 wt.% Cr₂O₃ loading and decreases thereafter, whereas the decomposition increases more or less continually. Therefore, one may conclude that the strong acid centers on the catalyst surface rather than the total acidity may be responsible for the decomposition. Considerable decrease in the decomposition products with the addition of K₂O, strengthens this proposition.

An attempt is made to identify the nature of active sites responsible for the aromatization selectivity with the help of the ESR spectra of the catalysts. Fig. 5 shows the ESR patterns observed on both unpromoted and promoted catalysts. Cr⁵⁺, 3d¹ configuration, $S = 1/2$ and Cr³⁺, 3d³ configuration, $S = 3/2$, are the commonly visible species in the ESR spectra [15–19]. The spectra show a sharp resonance with an average

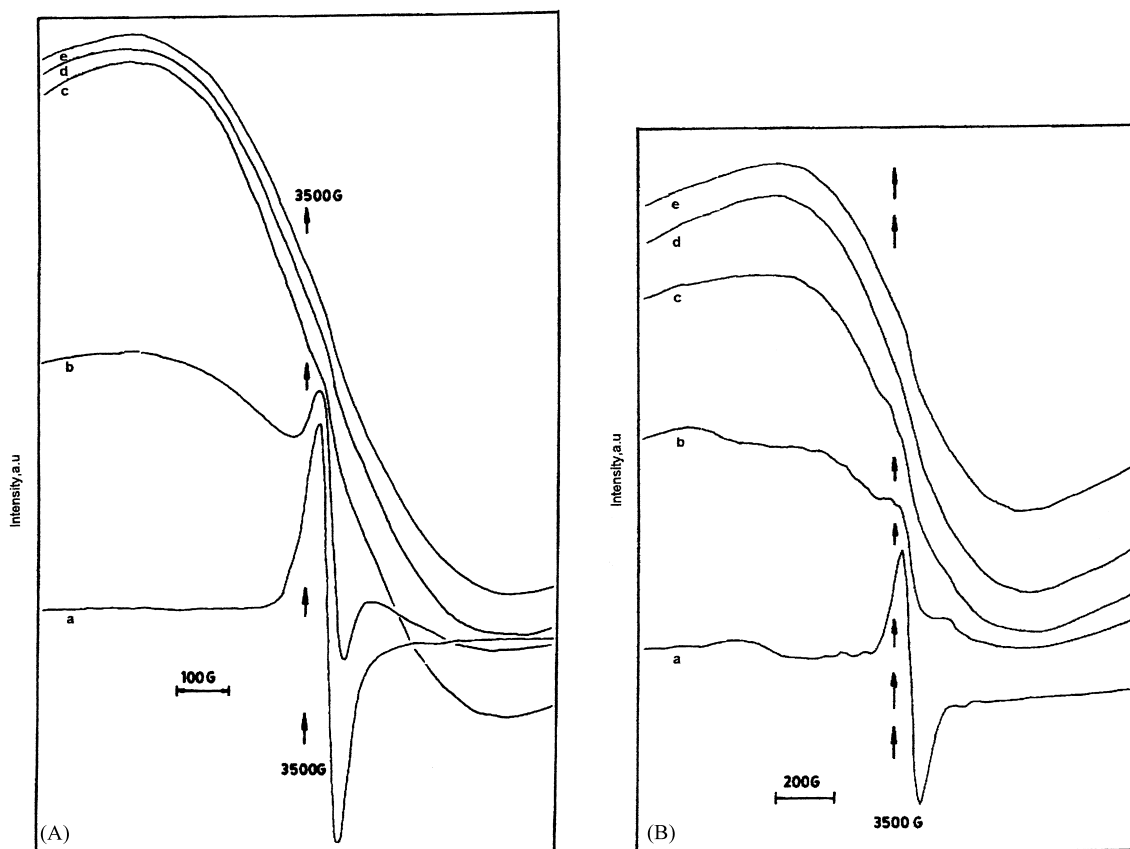


Fig. 5. (A) ESR patterns of $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts: (a) CA-5; (b) CA-10; (c) CA-15; (d) CA-20; (e) CA-25. (B) ESR patterns of $\text{K}_2\text{O}-\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts: (a) KCA-5; (b) KCA-10; (c) KCA-15; (d) KCA-20; (e) KCA-25.

g -value of 1.97 and with the average peak-peak (ΔH) value of 44 G, which correspond to the γ -phase of Cr^{5+} species. Superimposed on this is a broad resonance with a g -value of 1.98 and with an average peak-peak (ΔH) value in the range of 700–900 G, which is recognized as originating from the formation of electronically coupled β -phase Cr^{3+} species. It has been observed that there is higher Cr^{5+} concentration in the lower Cr_2O_3 loading which decreases drastically as the loading is increased. The Cr^{3+} concentration increased with increase in Cr_2O_3 loading upto 15 wt.% and thereafter decreased. Poole and MacIver [20,21] have also reported ESR spectra of $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts which displayed a rather broad symmetric absorption with a line width of 300–400 G and a value of $g = 1.96$. This spectrum is described as characteristic

of clustered Cr^{3+} ions of the β -phase. Isolated Cr^{3+} ions in distorted octahedral form (δ -phase) may also exist (not reported in the present pattern) and could be assumed as the active species based on their nature (isolated species leading to higher dispersion). In a recently reported article, it has been mentioned that these δ -phase Cr^{3+} species detected in $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst system have been most probably diffused into subsurface layers and therefore, are not involved in the catalytic action [22]. Hence, it is reasonable to think that the (β -phase) Cr^{3+} species may be the active sites for the aromatization functionality. In our recent publication on $\text{Cr}_2\text{O}_3/\text{SiO}_2$ system [11], the number of coordinatively unsaturated sites of Cr^{3+} estimated by the low temperature oxygen chemisorption (LTOC) technique have been correlated with the aromatization

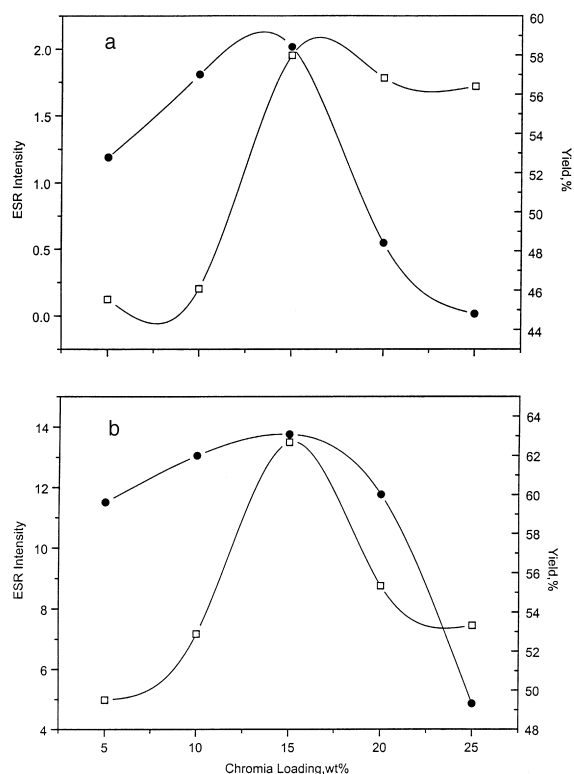


Fig. 6. Relationship between chromia loading, ESR signal intensity and aromatization yield: (a) Cr₂O₃/Al₂O₃; (b) K₂O-Cr₂O₃/Al₂O₃. (□) ESR intensity; (●) aromatization yield.

yield. It may be postulated that the aromatization is catalyzed by the CUS-Cr³⁺ sites in association with the O²⁻ sites estimated by LTOC. Fig. 6 shows the variation in intensity of β-phase Cr³⁺ against Cr₂O₃ loading in both unpromoted and promoted catalysts. The Cr³⁺ intensity bears more or less a similar relationship with the aromatization yield in the sense that when Cr³⁺ intensity increases the aromatization yield increases too and when it decreases the yield decreases. This suggests that Cr³⁺ sites may be responsible for the aromatization of isophorone. A similar correlation between the Cr⁵⁺ intensity, calculated from the ESR spectra obtained on Cr₂O₃/Al₂O₃ catalysts with the ethylene polymerization activity, has been reported earlier [23]. Grunert et al. [24,25], in their studies on the aromatization of *n*-hexane to benzene, have also reported that the coordinatively unsaturated Cr³⁺ sites (CUS) are responsible for the catalytic activity.

The basic aromatization activity was also ascribed to CUS Cr³⁺ ions by Kazansky [26], Bremer et al. [27], Marcilly and Delmon [28] and Segawa et al. [29]. One interesting observation from Fig. 6 is that the intensity of Cr³⁺ of a promoted catalyst is always higher than that of the corresponding unpromoted catalyst. It appears that the intrinsic activity of the unpromoted and promoted catalysts is different. The reason for getting more aromatization products on promoted catalysts is not yet clearly understood.

A detailed reaction network has been shown in Fig. 1. The product components can be classified into two major categories:

1. Aromatization products: the carbonyl group of isophorone gets bonded to the Cr³⁺ sites, whereas the adjacent O²⁻ sites abstract the α-hydrogen, leading to the formation of carbanion. This carbanion undergoes dienone-phenol rearrangement to form 3,5-xyleneol. 3,5-xyleneol gets converted into 2,3,5-trimethylphenol and *m*-cresol by transmethylation.
2. Decomposition products: mesityl oxide and acetone, the constituents of the decomposition products, are formed according to the retreated Michael condensation. These two, on further aldol condensation, form mesitylene, which by transmethylation gets converted into *m*-xylene and toluene. The condensation of mesityl oxide and acetone may also give phorone, which in turn transforms into semiphorone and rearranges to 2,2,6,6-tetramethylpyron-4-one. Mesityl oxide in the presence of water yields diacetone alcohol, which is subsequently converted into acetic acid and isobutene. Small quantities of condensation products like isoxyletones may also be formed from isophorone and acetone. However, we have not observed these products in this work. A typical product distribution on promoted and unpromoted catalysts (15 wt.% Cr₂O₃) at 753 K is shown in Table 3.

In order to find out the effect of K₂O addition on the intrinsic activity, the quasi turn over frequency (QTOF, defined as the number of molecules of isophorone converted per Cr site per second) values of promoted and unpromoted catalysts have been calculated at different reaction temperatures from the global rates of isophorone conversion. In a similar way, the

Table 3
Product distribution on CA-15 and KCA-15 catalysts at 793 K

S. No	Product %	CA-15 catalyst	KCA-15 catalyst
1	Aromatization products		
	(a) 3,5-xyleneol	45.20	48.90
	(b) 2,3,5-trimethyl phenol	8.70	9.30
	(c) <i>m</i> -cresol	4.50	4.88
2	Condensation products	Nil	Nil
3	Decomposition products		
	(a) mesityl oxide	3.50	2.40
	(b) mesitylene	5.70	1.20
	(c) diacetone alcohol	3.80	5.40
	(d) phorone	6.00	Nil
4	Unidentified products	6.60	3.92
5	Unreacted isophorone	16.00	24.00

QTOF of aromatization products formed (the number of molecules of aromatization products formed per Cr site per second) has been calculated. The extrapolation drawn on Cr₂O₃ loading versus QTOF of these exponential curves to Y-axis is taken as the turn over frequency (TOF) of that system at that temperature. The detailed procedure of calculation of TOF on molybdena based catalysts is described elsewhere [30]. In order to calculate the TOF by this method, an assumption has been made that both surface as well as bulk Cr-species are the same in their characteristics. Even though it is not true for all the Cr-loadings, it is known that below the monolayer coverage of Cr species on Al₂O₃ surface, most of the Cr-species lie on the surface rather than in bulk and hence it is appropriate to make this assumption to calculate the TOF of supported Cr₂O₃ system. Again at 793 K, where the activity on both unpromoted and promoted catalysts is maximum, a comparison of TOF values reveals that the number of isophorone molecules converted per Cr site per second is equal in both K₂O-Cr₂O₃/Al₂O₃ and the unpromoted Cr₂O₃/Al₂O₃ system (TOF = 7.75 × 10⁻³). However, the per site activity towards the formation of aromatization products (TOF_{aro}) is greater in the case of promoted catalyst (TOF_{aro} for K₂O-Cr₂O₃/Al₂O₃ = 5.3 × 10⁻³ and TOF_{aro} for Cr₂O₃/Al₂O₃ = 4.8 × 10⁻³). This is in agreement with the ESR observation. However, the exact role of K₂O in enhancing the aromatization needs to be understood. Thomson [31] described the improvements in selectivity and life time of con-

tact masses exhibited by alkali metal salt promoters. Sodium or potassium, because of a larger atomic radii (K⁺, 1.33 Å) than that of Cr or Al (Cr³⁺, 0.69 Å; Al³⁺, 0.50 Å), cannot go into the lattice, but occupies a position on the surface of the catalyst, thus acting as an electron donor [32]. This electron donating ability may facilitate adsorption–desorption of the reactants and/or products, favoring aromatization activity of the catalyst. K⁺ may also be influencing the reducibility of the Cr³⁺ species which, most likely, are the active centers for aromatization activity [24]. In general, modification of the electronic properties of metal oxide due to surface basicity and electron donation character of alkali may be responsible for the enhanced selectivity.

4. Conclusions

It may be concluded that the CUS Cr³⁺ sites are responsible for the aromatization of isophorone. K₂O also neutralizes the strong acid sites of Cr₂O₃/Al₂O₃ catalysts decreasing the overall acidity, which in turn helps in minimizing the formation of decomposition products and thus in maintaining higher aromatization products even at higher temperatures. K₂O addition to Cr₂O₃/Al₂O₃ catalytic systems enhances intrinsic activity towards aromatization.

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References

- [1] L.J. Kitchen, H.E. Albert, G.E.P. Smith Jr., *Ind. Eng. Chem.* 42 (1950) 675.
- [2] H. Juenger, F. Weissenfels, (Dynamit Nobel), German Patent, 1815897, 1970.
- [3] A.J. Golick, J.T. Stephan (westix), US Patent 3 336 246, 1959.
- [4] H.G. Noesler, H. Schnegellerger, H. Bellinger (Henkel) German Patent 1284 040, 1968.
- [5] G.S. Salvapathi, K.V. Ramanamurthy, M. Janardhana Rao, *J. Mol. Catal.* 54 (1989) 9.
- [6] G.S. Salvapathi, K.V. Ramanamurthy, M. Janardhana Rao, R. Vaidyeswaran, *Appl. Catal.* 48 (1989) 223.

- [7] P.S. Sai Prasad, B. David Raju, K.S. Rama Rao, G.S. Salvapathi, P. Kanta Rao, *Appl.Catal. A: General* 83 (1992) 141.
- [8] P.S. Sai Prasad, N. Lingaiah, G.S. Salvapathi, P. Kanta Rao, *React. Kinet. Catal. Lett.* 59 (1996) 151.
- [9] P.S. Sai Prasad, B. David Raju, K.S. Rama Rao, G.S. Salvapathi, P. Kanta Rao, *J. Mol. Catal.* 78 (1993) L19.
- [10] B. David Raju, K.S. Rama Rao, G.S. Salvapathi, P.S. Sai Prasad, P. Kanta Rao, *Appl. Catal. A: General* 193 (2000) 123.
- [11] T. Tagawa, T. Hattori, Y. Murakami, *J. Catal.* 75 (1982) 56.
- [12] A.M. Rubinshtein, N.A. Pribyutkova, V.A. Afanas'ev, A.A. Slinkin, *Kinet. Catal.* 1 (1960) 116.
- [13] H.A. Bensi, *J. Phys. Chem.* 61 (1957) 970.
- [14] S.E. Voltz, S.W. Weller, *J. Am. Chem. Soc.* 76 (1954) 4701.
- [15] S.W. Weller, *Acc. Chem. Res.* 16 (1983) 101.
- [16] J.H. Bridges, D.S. MacIver, W.H. Tobin, in: *Proceedings of the 2nd International Actes Congress on Catalysis*, Vol. 196, 1960, p. 2161.
- [17] M.P. McDaniel, R.L. Burwell Jr., *J. Catal.* 36 (1975) 394.
- [18] M.P. McDaniel, R.L. Burwell Jr., *J. Catal.* 36 (1975) 404.
- [19] D.E. O'Reilly, *Adv. Catal.* 12 (1960) 31.
- [20] C.P. Poole Jr., W.L. Kehl, D.S. MacIver, *J. Catal.* 1 (1962) 407.
- [21] C.P. Poole, D.S. MacIver, *Adv. Catal.* 17 (1968) 223.
- [22] S.D. Rossi, M.P. Casaletto, G. Ferraris, A. Cimino, G. Minelli, *Appl. Catal. A: General* 167 (1998) 257.
- [23] J.C. Kuriacose, *Catalysis*, Macmillan, New Delhi, 1991, p. 152.
- [24] W. Grunert, W. Saffert, R. Feldhaus, K. Anders, *J. Catal.* 99 (1986) 149.
- [25] W. Grunert, W. Saffert, R. Feldhaus, K. Anders, *J. Catal.* 100 (1986) 138.
- [26] V.B. Kazanski, *Kinet. Catal.* 8 (1967) 1125.
- [27] H. Bremer, J. Muche, M. Wilde, *Z. Anorg. Allg. Chem.* 407 (1974) 40, 51.
- [28] C. Marcilly, B. Delmon, *J. Catal.* 24 (1972) 336.
- [29] K.I. Segawa, N. Ishi, H. Ueda, *Sekiyu Gakkaishi* 22 (2) (1979) 84.
- [30] K.V.R. Chary, G. Kishan, T. Bhaskar, Ch. Shivraj, *J. Phys. Chem.* 102 (1998) 6792.
- [31] S.J. Thomson, *J. Chem. Soc., Faraday Trans.* 1 83 (1987) 1893.
- [32] S. Carra, L. Forni, C. Vintani, *J. Catal.* 9 (1967) 154.