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# Aromatization of isophorone to 3,5-xylenol over $Cr_2O_3/SiO_2$ catalysts

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**Abstract**

$SiO_2$ supported $Cr_2O_3$ catalysts with varying Cr content have been prepared and are characterized by nitrogen adsorption, low temperature oxygen chemisorption (LTOC), X-ray diffraction (XRD) and electron spin resonance (ESR) techniques. Aromatization of isophorone is carried out on these catalysts. A good correlation obtained between the oxygen uptake and aromatization yield helped to identify the nature of the active species. ©2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Aromatization; Isophorone; 3,5-xylenol; $Cr_2O_3/SiO_2$ catalysts

## 1. Introduction

With the ever increasing concern for environmental protection, the quality aspect of the catalyst (selectivity, which in turn improves the yield) attains more and more importance compared to its quantity aspect (activity); more so in case of complex reactions that exhibit several reaction pathways. Under these circumstances, it becomes imperative to look into the actual active site that drives the reaction towards the specified product. An attempt in this direction is the study on the aromatization of isophorone to produce 3,5-xylenol. 3,5-xylenol (the main component of the aromatization products) is an important intermediate in the production of Vitamin E, anti-oxidants, anti-microbial agents, laminating paper adhesives etc [1–7]. Alkylation of phenol, the conventional route to synthesizing 3,5-xylenol, gives very low selectivity. Catalytic aromatization of isophorone has subsequently been proved to be promising as an economically viable alternative for the above route. The reaction, which proceeds by the dienone–phenol re-arrangement on the catalyst surface, leads to the formation of less number of by-products [8,9]. Thus, identification of the active species is an important and challenging task to improve product selectivity.

Aromatizaion of isophorone proceeds by the formation of several side products, as illustrated in Fig. 1. Earlier work, from our laboratory, on this reaction has revealed some interesting results. The reaction carried out on $V_2O_5/Al_2O_3$ and $MoO_3/Al_2O_3$ has resulted in the production of large quantities of isoxylitones, the decomposition products of isophorone [10]. This has been explained as due to the presence of polymeric oxide species of catalysts possessing strong acidity. Reaction of isophorone on $\gamma$-$Al_2O_3$ alone has revealed that acid centres on the surface of the catalyst activate decomposition of isophorone [11] and also lead to coke formation. Once coke formation starts covering the acid centres, selectivity towards 3,5-xylenol is enhanced. These observations have been confirmed by using carbon-covered alumina (CCA) as the support

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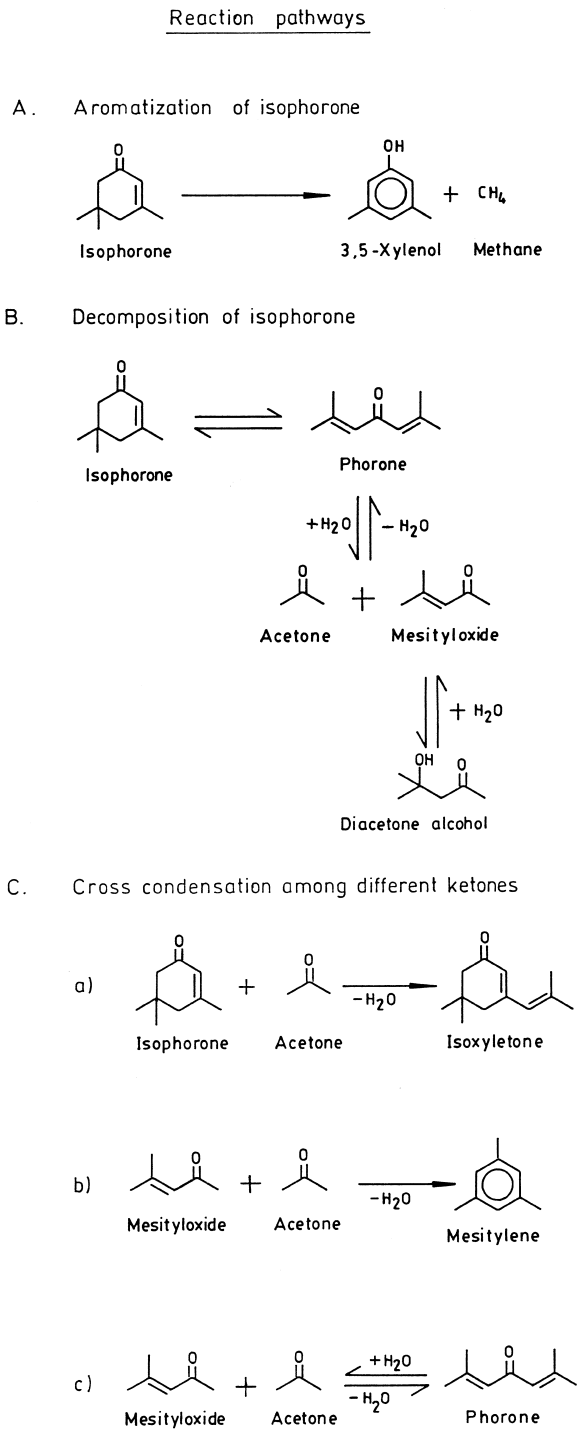


Fig. 1. Reaction pathways in aromatization of isophorone.

[11]. However, continuous formation of coke puts the system under unsteady state, when $\gamma$-$Al_2O_3$ is used as a support. Supported $Cr_2O_3$ is well known as an aromatization catalyst. In our work on $\gamma$-$Al_2O_3$-supported $Cr_2O_3$ catalysts [12] we have tried to reduce the acidity of the support by using CCA as the support. In addition, $K_2O$ has been added to neutralize the strong acid sites. Due to the combined effect, though maximum selectivity towards 3,5-xylenol is obtained, the nature of the $Cr_2O_3$-active site which subscribes to aromatization could not be identified. In this context it is imperative to design a suitable catalyst with a support which does not strongly influence the reaction and which optimizes the aromatization functionality of $Cr_2O_3$. In the present investigation, the $Cr_2O_3/SiO_2$ system has been selected for study, in an attempt to understand the nature of the active species on the catalyst.

## 2. Experimental

Commercial silica (Ketzen F5, S.A.: 670 $m^2/g$) was used as a support. A series of $Cr_2O_3/SiO_2$ catalysts was prepared with varying Cr-content (5–22.5 wt% $Cr_2O_3$) by impregnating the support with required quantities of aqueous $Cr(NO_3)_3 \cdot 9H_2O$ (Fluka, G.R grade). The catalyst masses were initially dried at 120°C overnight followed by calcination in air at 500°C for 6 h.

BET surface area of the catalysts was determined on an all-glass high vacuum system by adsorbing nitrogen at liquid nitrogen temperature in the relative pressure range of 0.05–0.30. LTOC of the catalysts was carried out on the same apparatus. In a typical experiment, about 0.5 g of the catalyst sample was first reduced in hydrogen flow (30 ml/min) at 500°C for 4 h. The catalyst was then evacuated at the same temperature under $10^{-6}$ Torr for 1 h and then cooled to −78°C prior to oxygen adsorption. The first adsorption isotherm representing both physisorbed and chemisorbed oxygen was generated. After evacuation under $10^{-6}$ Torr for 2 h, the second adsorption isotherm that gave only physisorbed oxygen was traced. The difference between the parallel portions of the two isotherms was taken as the oxygen uptake [13,14].

XRD patterns of the catalysts were obtained on a Phillips diffractometer (Model –PW1051) using Cu

Table 1
Characteristics of $Cr_2O_3/SiO_2$ catalysts

| Sl. No. | $Cr_2O_3$ loading, (wt%) | BET surface area ($m^2\,g^{-1}$) | $O_2$ up-take ($\mu$ mol $g^{-1}$) | Dispersion[a] (%) |
|---|---|---|---|---|
| 1 | 5.0 | 549 | 72 | 22 |
| 2 | 10.0 | 550 | 166 | 25 |
| 3 | 12.5 | 529 | 112 | 14 |
| 4 | 15.0 | 523 | 105 | 11 |
| 5 | 22.5 | 477 | 89 | 3 |
| 6 | $SiO_2$ | 672 | – | – |

[a] Calculated from $O_2$ up-take as (O/Cr) × 100.

$K_\alpha$ radiation. The ESR spectra were recorded at room temperature on a Bruker ER-200-SRC X-band spectrometer.

Activity studies on the catalyst were carried out in a fixed bed glass (20 mm i.d. and 300 mm long) reactor under vapour phase at atmospheric pressure in the temperature range 400–520°C. A uniform weight hourly space velocity of $3\,h^{-1}$ 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 120 and 180°C at 3°C/min. The analysis was standardized using known mixtures of pure samples and calculating the response factors. Experiments carried out with quartz pieces in place of the catalyst did not give any observable isophorone conversions 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 is defined as the product of percentage conversion and percentage selectivity divided by 100.

## 3. Results and discussion

BET surface area, oxygen up-take and dispersion of chromium oxide of the $Cr_2O_3/SiO_2$ catalysts are presented in Table 1. With increasing $Cr_2O_3$ loading the surface area of the catalysts has shown a decreasing trend. This is generally expected due to pore blockage of $SiO_2$ with the crystallites of $Cr_2O_3$ as loading increases. Oxygen up-take increased up to 10 wt% loading of $Cr_2O_3$ and a reverse trend appears thereafter. This phenomenon could be due to carrier–active component interaction at lower loading and the formation of bigger crystallites by multi-layer deposition of $Cr_2O_3$ at higher loading. A similar argument was put forward by Nag et al. [15] for supported $MoO_3$ catalysts. These results suggest that the monolayer capacity of $SiO_2$ for $Cr_2O_3$ is 10 wt%. The formation of a patchy monolayer is postulated similar to the one suggested for $V_2O_5$ on $SiO_2$ [16]. No signals due to $\alpha$-$Cr_2O_3$ crystalline phase have been observed from the XRD patterns of the catalysts below 15 wt% $Cr_2O_3$ loading (Fig. 2). The amorphous nature of the active component at low loading is in conformity with high dispersion obtained from LTOC at 10 wt% $Cr_2O_3$. However, crystallites smaller than 40 Å size below 15 wt% $Cr_2O_3$ loading may not be ruled out. The presence of the $\alpha$-$Cr_2O_3$ crystalline phase is observed at loading beyond 10 wt%.

ESR spectra (Fig. 3) of the catalyst samples recorded at room temperature reveal the presence of electronically coupled $\beta$-phase $Cr^{3+}$ species with an average $g$-value of 1.97 and $\Delta H_{p-p}$ in the range of 220–450 gauss. Weak signals of $\gamma$-phase $Cr^{5+}$ species are found in the samples with $Cr_2O_3$ loading of upto 10 wt%. The origin and characteristics of these $\beta$- and $\gamma$-species have been described in several publications [17–20].

A close look at the data obtained from LTOC, XRD and ESR studies reveals that at loadings up to 10 wt% $Cr_2O_3$, formation of $Cr^{3+}$, the co-ordinatively unsaturated site (CUS) occurs, as the $Cr_2O_3$ monolayer is being built up. After monolayer formation, bigger crystallites of $Cr_2O_3$ decrease the number of these CUS sites.

In the present investigation, $Cr_2O_3$ supported on $SiO_2$ catalysts with 5–22.5% loading was studied in the temperature range of 400–520°C for its reactivity and selectivity towards aromatization of isophorone. The effect of reaction temperature on product distribution (Table 2) shows that the conversion of isophorone increases with increase in reaction temperature. The aromatization yield has increased to 43 from 19.8% with a rise in reaction temperature from 400 to 520°C. The decomposition of isophorone also rises from 12 to 30% with increase in temperature. Product distribution shows that the secondary decomposition

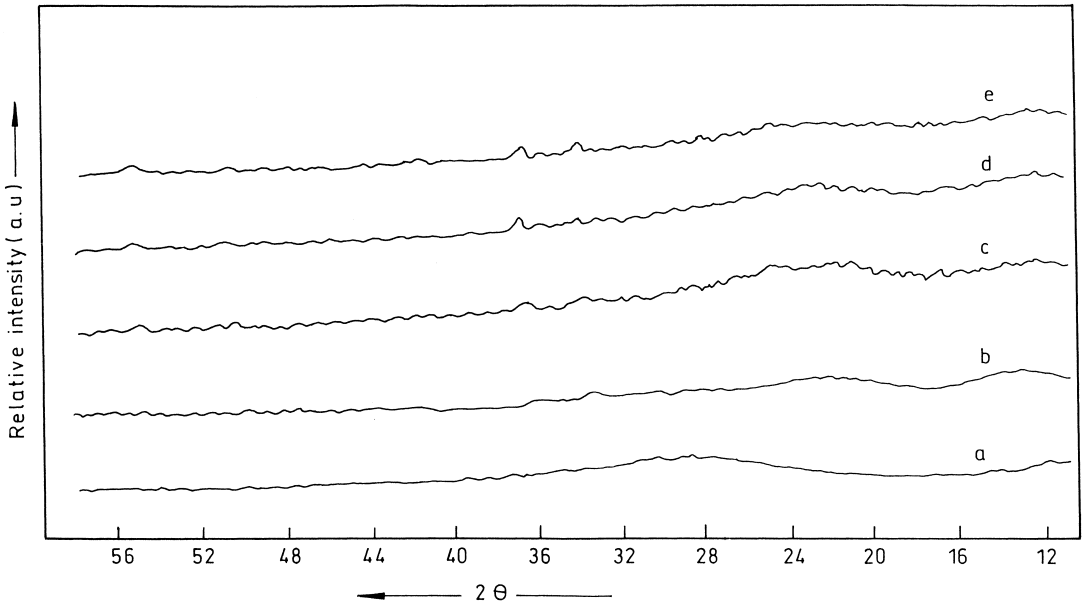


Fig. 2. XRD patterns of $Cr_2O_3/SiO_2$ catalysts (a) 5 wt% $Cr_2O_3$; (b) 10 wt% $Cr_2O_3$; (c) 12.5 wt% $Cr_2O_3$; (d) 15 wt% $Cr_2O_3$; (e) 22.5 wt% $Cr_2O_3$.

products of isophorone also increase with increase in reaction temperature (Table 2). The data reported in Table 2 are contrary to the general observation that aromatization decreases with increase in decomposition of isophorone [11]. This implies that coke formation over the catalyst at 480–520°C influences the reaction. Hence, it is reasonable to fix the temperature range 400–480°C as being favourable to study the aromatization functionality of the catalyst. The influence of $Cr_2O_3$ loading was studied at the reaction temperature of 440°C so that coke formation will not interfere with product distribution, as also reported in our earlier studies [10,11].

Table 2
Effect of temperature on product distribution with 10% $Cr_2O_3/SiO_2$ catalyst

| Product (%) | Reaction temperature (°C) | | | |
|---|---|---|---|---|
| | 400 | 440 | 480 | 520 |
| 1. Mesityl oxide | – | – | – | – |
| 2. Mesitylene | 1.9 | 2.0 | 8.4 | 11.6 |
| 3. Diacetone alcohol | 6.5 | 7.1 | 8.2 | 9.4 |
| 4. Phorone | 3.7 | 3.0 | 4.6 | 8.3 |
| 5. Isophorone | 68.1 | 59.8 | 37.6 | 27.7 |
| 6. *m*-Cresol | – | 0.5 | 2.0 | 3.3 |
| 7. 3,5-Xylenol | 19.1 | 24.9 | 32.1 | 34.6 |
| 8. 2,3,5-Trimethylphenol | 0.7 | 2.7 | 6.1 | 5.1 |

Product distribution shows that aromatization of isophorone reaches a maximum with 10% $Cr_2O_3$ loading running parallel with isophorone conversion (Fig. 4). Oxygen chemisorption is also found to vary in the same way. Thus, it may be inferred that the $Cr^{3+}$ species formed in the catalysts seems to be responsible for the aromatization reaction. A direct correlation obtained (Fig. 5) between oxygen uptake and aromatization yield strengthens the fact that these sites are responsible for selectivity towards 3,5-xylenol. Isophorone decomposition remains steady at 9% in the 5–12.5% region of $Cr_2O_3$ loading and there after rises to 24% at 22.5% loading. With increased $Cr_2O_3$ loading to 22.5%, it is likely that due to increase in crystallite size, aromatization is not promoted which is also reflected in a parallel decrease in the conversion of isophorone.

The aromatization functionality of chromia may be ascribed to the co-ordinatively unsaturated $Cr^{3+}$ sites in association with the adjacent $O^{2-}$ sites by a possible reaction mechanism as described below. The carbonyl group of the isophorone gets bonded to the $Cr^{3+}$ sites, whereas the adjacent $O^{2-}$ sites

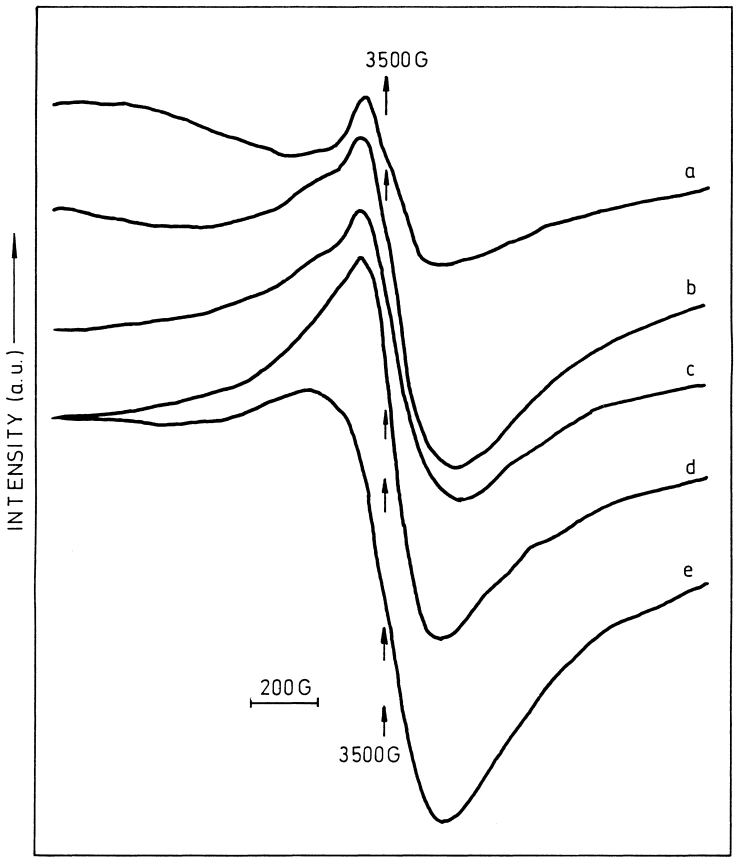


Fig. 3. ESR spectra of $Cr_2O_3/SiO_2$ catalysts (a) 5 wt% $Cr_2O_3$; (b) 10 wt% $Cr_2O_3$; (c) 12.5 wt% $Cr_2O_3$; (d) 15 wt% $Cr_2O_3$; (e) 22.5 wt% $Cr_2O_3$.

abstract the α-hydrogen leads to the formation of carbanion. This carbanion undergoes dienone–phenol re-arrangement leading to 3,5-xylenol. *m*-Cresol and 2,3,5-trimethyl phenol are formed by disproportionation of 3,5-xylenol [8]. For the purpose of comparing the selectivity of the catalysts, the products 3,5-xylenol, *m*-cresol and 2,3,5-trimethyl phenol are clubbed to represent the aromatization of isophorone. Alternatively, adsorbed isophorone, in the absence of hydrogen abstraction, decomposes giving phorone, mesityl oxide, acetone and finally leading to diacetone alcohol and mesitylene. Diacetone alcohol is formed during the hydration of mesityl oxide by adsorbed water molecules over the catalyst. Mesitylene is formed from the cross-condensation reaction of either acetone with mesityl oxide anion or acetone anion with mesityl oxide and subsequent 1,6-aldol cyclization [8]. The presence of phorone in the product can be accounted by two ways. Phorone is the primary decomposition product of isophorone which can get cleaved to mesityl oxide and acetone or can undergo 1,6-Michael reaction over the catalyst to form isophorone [21]. Formation of isoxyletones was not detected in the product under the present experimental conditions. The products, phorone, mesityl oxide, diacetone alcohol and mesitylene together are represented as decomposition products. A typical product distribution is shown in Table 2.

An important question arises as to how the decomposition increases with increases in crystallite size. It may be postulated that with increase in crystallinity the availability of $Cr^{3+}$–$O^{2-}$ paired sites decreases thus restricting the hydrogen abstraction from the adsorbed

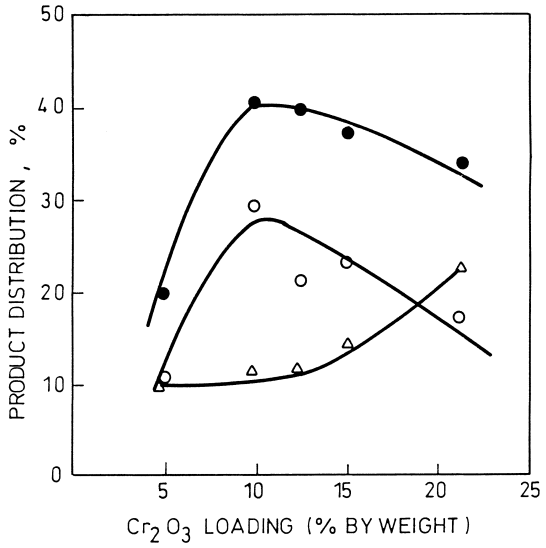


Fig. 4. Variation of product distribution as a function of $Cr_2O_3$ loading. Reaction temperature: 440°C. ● Total conversion; ○ Aromatization product yield; △ Decomposition products.

reactant molecule. On account of this the molecule may be prone for decomposition.

It may be concluded that (i) the silica-supported monolayer $Cr_2O_3$ catalysts are highly selective for the aromatization of isophorone to 3,5-xylenol, (ii) LTOC, a simple and effective technique can be used to determine the monolayer capacity of $SiO_2$-supported $Cr_2O_3$ catalysts and (iii) the $Cr^{3+}$ CUS titrated by LTOC seems to be responsible for aromatization selectivity.

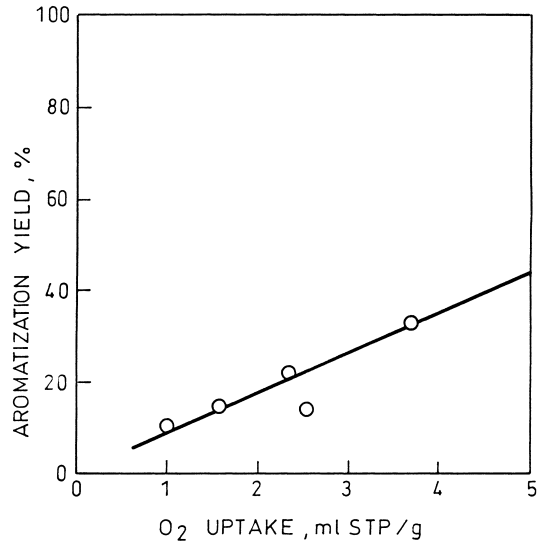


Fig. 5. Correlation between $O_2$ up-take and aromatization yield.

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