# Selectivity improvement in the aromatization of isophorone on carbon-covered alumina supported K₂O–Cr₂O₃ catalyst*

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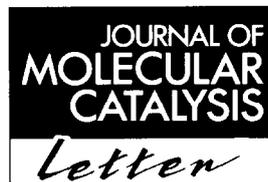
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With the growing concern for the environmental pollution and the ever increasing stringent specifications for effluents, there has been a pressing need to minimize the formation of unwanted byproducts. An example is the thrust for high selectivity in the aromatization of isophorone to 3,5-xylenol using chromia based catalysts. 3,5-Xylenol is an important intermediate in the production of vitamin E and other products used as antioxidants, laminating paper adhesives, antimicrobial agents etc. The reaction which occurs by the dienone–phenol rearrangement is almost always accompanied by the decomposition reaction, the latter proceeding by complex series–parallel steps. A detailed reaction scheme is given elsewhere [1]. Hence selectivity assumes considerable importance. Most of the data are patented. A few attempts are made to improve the selectivity by using a wide choice of catalysts [2] rather than exercising control over the reaction path by modifying the catalyst. A close look at the commercial catalyst reveals that the acid functionality of alumina leads to decomposition. In the present investigation it is shown that by using carbon-covered alumina (CCA) as support for K₂O-promoted Cr₂O₃ catalyst, the decomposition can be minimized and the aromatization functionality of Cr₂O₃ can be greatly enhanced.

Commercial γ-Al₂O₃ (Harshaw, Al-3996 R, 18/25 BSS mesh) was used in the preparation of the CCA following the method proposed by Vissers *et al.* [3], choosing ethylene as pyrolytic agent. The K₂O–Cr₂O₃ catalysts were prepared by the impregnation of Al₂O₃ and CCA with aqueous solutions of chromic anhydride (A.R. Grade, M/s Loba Chemie, India) and potassium carbonate (A.R. Grade, M/s Qualigens, India). After air drying at 393 K for 12 h, calcination at 873 K for 6 h was carried out in air for the Al₂O₃ supported catalyst and in He for CCA supported catalyst. The carbon content

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(14 wt.%) and the composition of $Cr_2O_3$ (15 wt.%) and $K_2O$ (2 wt.%) were fixed based on the acidity and aromatization yields from our detailed studies on unpromoted and $K_2O$-promoted $Cr_2O_3/Al_2O_3$ catalysts which are to be communicated shortly. Acidity measurements were made by the temperature programmed desorption of ammonia in the range 373–773 K. The reaction was performed in a 20 mm i.d., 300 mm long, glass tubular reactor in the temperature range 673–808 K with a W.H.S.V. of 1.0 $h^{-1}$.

Alumina and alumina supported catalysts showed 30–40% higher conversions at lower temperatures (673–753 K) (Fig. 1a) than the CCA and CCA supported catalysts. However, the activity of the former pair seems to have been stabilized as the conversion curve levelled off at high temperatures (753–833 K). The latter pair, instead, showed a continuous increase. The higher conversions exhibited by alumina catalyst are due to a 20% higher decomposition resulting in lower selectivity towards aromatization, as can be observed from Fig. 1b and c, respectively. Decomposition on alumina reached a maximum of 36% at 753 K and thereafter it decreased to 15% at 793 K. Impregnation of $Cr_2O_3$ and $K_2O$ on alumina had a significant effect on the decomposition, which in turn changed the selectivity pattern. CCA, on the other-hand, had a lower decomposition activity (9–19%) in the range 673–753 K but an increasing trend was shown as the temperature increased. A remarkable decrease in decomposition activity was observed on CCA supported catalyst. The influence of carbon on the alumina surface in modifying the activity and selectivity of the aromatization of isophorone has been described in a recent publication by the authors [7]. The CCA and the CCA supported catalysts showed a good linear increase of selectivity with temperature, with the CCA supported catalyst reaching almost 100% towards aromatization at 793 K.

The rapid fall in decomposition activity shown by alumina beyond 753 K could be attributed to the coke formation at high temperatures, which reduces the surface acidity. Caudus et al. [4] in their study on the oxidative dehydrogenation of ethyl benzene have also observed that both coke formation and conversion directly depend on the acidity of fresh alumina. Impregnation of alumina with $Cr_2O_3$ has led to the creation of more aromatization sites. However, the acid sites on alumina are responsible for the formation of species which poison the dehydrogenation sites on the $Cr_2O_3$ surface as proposed by Gremillion and Knox [5]. Addition of $K_2O$ neutralizes the strong acid sites on alumina [6]. This combined effect resulted in a complete reversal of the selectivity pattern shown by the alumina supported catalyst. A substantial decrease in the acidity of alumina was found after its impregnation with $Cr_2O_3$ and $K_2O$ (Table 1). There was an abnormality in the expected decomposition trend exhibited by CCA at higher temperatures. This could be due to the extent of coke formed, alumina having more coke than CCA at the instant the product analysis was made [7]. However, the alumina supported catalyst reached an optimum of about 80% selectivity towards aromatization.

The question which needs to be answered is as to how carbon coating can show nearly 100% selectivity in the case of the CCA supported catalyst.
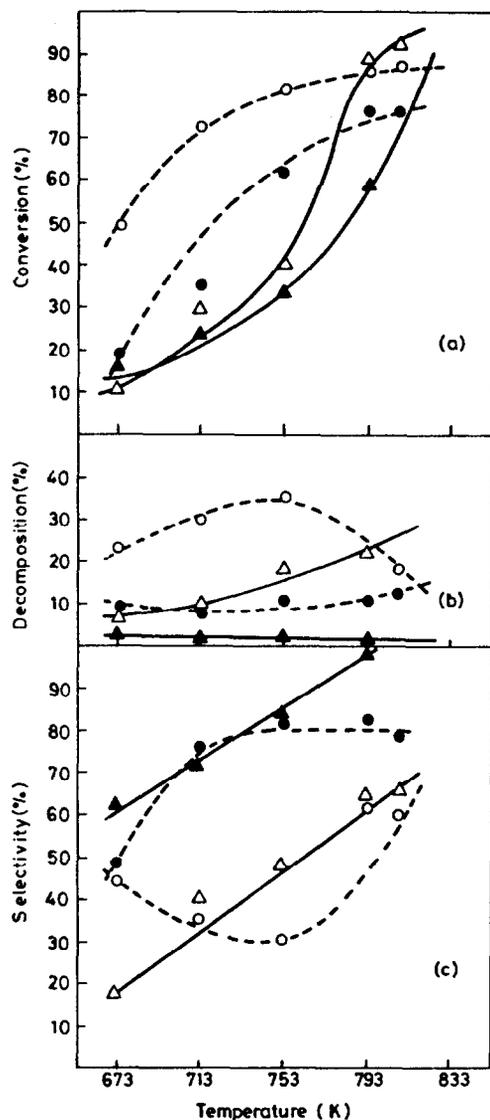
Fig. 1. Variation of conversion and decomposition of isophorone and selectivity to 3,5-xylenol with reaction temperature. (○) $Al_2O_3$; (●) $Cr_2O_3$–$K_2O$/$Al_2O_3$; (△) CCA; (▲) $Cr_2O_3$–$K_2O$/CCA.

In our earlier communication [7] we reported that with the increase in carbon coating there can be drastic reduction in acidity of the surface. The acidity values (Table 1) also agree with this proposition. However, as also expressed by Vissers *et al.* [3], it is not possible to completely cover the alumina surface with carbon, even though ethylene pyrolysis leads to uniform surface coverage. The exact role of $K_2O$ in enhancing the aromatization selectivity of CCA supported catalyst is not yet well understood. Thomson [8] described

TABLE 1

Surface area and acidity values of supports and supported chromia catalysts

| Catalyst | Surface area ($m^2$ $g^{-1}$) | Acidity (g mol/g cat) |
|---|---|---|
| $Al_2O_3$ | 178 | $13.50 \times 10^{-4}$ |
| $K_2O–Cr_2O_3/Al_2O_3$ | 146 | $5.35 \times 10^{-4}$ |
| CCA | 158 | $3.69 \times 10^{-4}$ |
| $K_2O–Cr_2O_3/CCA$ | 100 | $3.41 \times 10^{-4}$ |

the improvements in selectivity and lifetime of contact masses exhibited by alkali metal salt promoters. In general, modification of the electronic properties of metal due to the surface basicity and electron donation character of alkali is responsible for the enhanced selectivity. The carbon in the support may also facilitate the electron transport as observed by Aika et al. [9] in the case of alkali promoted Ru catalyst employed in ammonia synthesis at atmospheric pressure.

Thus it may be concluded that by reducing the surface acidity, enhancing the role of $Cr_2O_3$ and by facilitating the easy electron transport from $K_2O$, CCA support has led to enhanced selectivity in the aromatization of isophorone to 3,5-xylenol.

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