Optimisation of an Indium Oxide-based Catalyst for the Oxidation of Isobutene to p-Xylene

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Comparisons are drawn between the theoretical predictions and experimental results for the optimisation of an indium oxide-based catalyst used for the oxidative conversion of isobutene to the industrially important p-xylene. Experimental studies show that predictions are reasonably accurate, although significant failures were observed. Using a two-stage bed involving 6 % indium oxide on pumice, followed by 0.3 % platinum on alumina, up to 70 % selectivity to dimethylhexadiene and aromatics may be obtained for a conversion of isobutene of ca. 50 %.

Despite the fact that the theoretical design of catalysts has been described as the last refuge of alchemy, increasing understanding of the mechanisms of catalytic reactions begins to allow the possibility of developing a successful catalyst on the basis of a paper study.[1-3] In one such case, for example, theoretical arguments led to the discovery of a new catalyst (indium oxide) for the oxidative dehydrogenation, dimerisation and cyclisation of light olefins.[1] Such theoretical arguments can also be extended to consider the optimisation of the catalyst [1] and, in particular, to the predicted effect of different additives. However, this can pose several difficulties, in that a given addition may act in more than one way. No comparison of prediction and experimental testing has been carried out so far, and the present studies were intended to rectify this situation, using the oxidation of isobutene to industrially important p-xylene [4-6] as a test example.

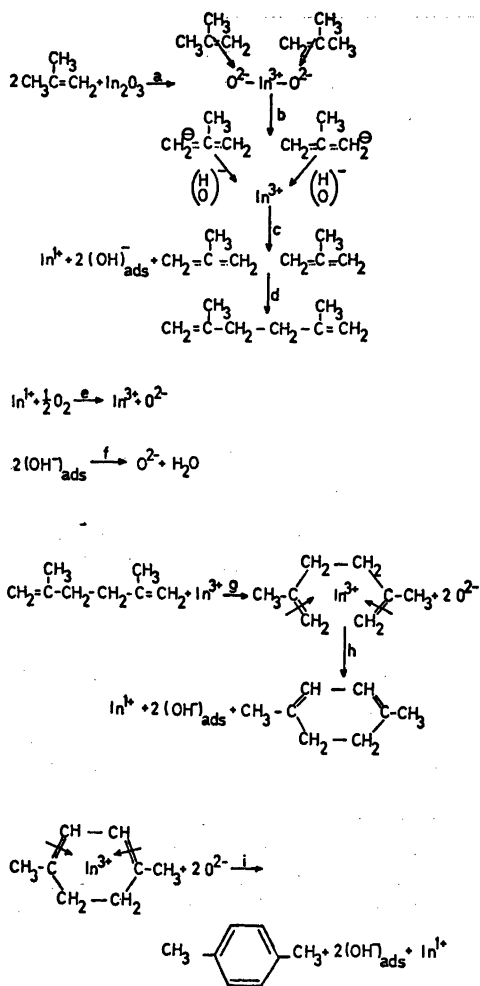The catalytic oxidation of olefins to unsaturated aldehydes and nitriles is a well-established reaction.[7] Comparatively recently, significant interest has also been focused on an analogous reaction involving the oxidation of light olefins to aromatics. Catalysts known to favour this reaction include thallium oxide,[5] indium oxide,[1,9] vanadia,[10] tin oxide [6] and bismuth oxides in the absence and presence of additives such as P_2O_5.[6,11]

Conventional routes to p-xylene, which is important in the manufacture of terephthalic acid and nylon, suffer from the disadvantage that the m- and o-isomers are also produced.[4] As a result of this, the oxidation of isobutene to p-xylene offers a new and selective route. Preliminary studies of the reaction have been carried out [5,11] and the mechanism given in Scheme 1 appears to explain most of the observations. The rate determining step has been suggested to involve the oxidative removal of allylic hydrogen (Step b).

Development of the indium oxide catalyst for this reaction was based on theoretical design considerations.[1] These were extended to consider means of optimising the catalyst but, although illustrative examples were quoted, no direct testing of these ideas was attempted. The present paper describes such testing. The theoretical basis of the design with respect to the additives is summarised in the text, but a fuller description is given in Ref. 1.

EXPERIMENTAL

Experiments were carried out with the aid of a flow reactor in which the mixed reactants were passed over a catalyst maintained at a pre-set temperature (± 0.2 °C). The exit gases were analysed in an on-line gas chromatograph.

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$$2\,CH_3C=CH_2 + In_2O_3 \xrightarrow{a}$$

$$O^{2-}-In^{3+}_2-O^{2-}$$

$$\xrightarrow{b}$$

$$In^{+} + 2\,(OH)^-_{ads} + CH_2=C=CH_2 \quad \xrightarrow{c}$$

$$\xrightarrow{d}$$

$$CH_2=\overset{CH_3}{\underset{}{C}}-CH_2-CH_2-\overset{CH_3}{\underset{}{C}}=CH_2$$

$$In^{+} + \tfrac{1}{2}O_2 \xrightarrow{e} In^{3+} + O^{2-}$$

$$2\,(OH)^-_{ads} \xrightarrow{f} O^{2-} + H_2O$$

$$CH_2=C-CH_2-CH_2-C=CH_2 + In^{3+} \xrightarrow{g}$$

$$\xrightarrow{h}$$

$$In^{+} + 2\,(OH)^-_{ads} + CH_3-C$$

$$\xrightarrow{i}$$

$$CH_3-\!\!\!\bigcirc\!\!\!-CH_3 + 2\,(OH)^-_{ads} + In^{+}$$

Scheme 1.

Carbon dioxide was separated from other permanent gases in a 20 cm silica gel column (87 °C), while oxygen, nitrogen and carbon monoxide were separated in a molecular sieve 5 A column (1 m; 87 °C): all of these gases were detected using a Servomex microkatharometer. Organic gases were analysed using a flame ionization detector and separated in a 7 m column packed with 5 % Bentone-34 + 10 % DC 200/50 on chromosorb W (AW-DMCS) (Phase Separations Ltd.); this column allowed the separation of all three xylene isomers as well as the other products of reaction. Confirmation of product identity involved MS analysis and the comparison of retention times with known compounds on several columns.

Inorganic materials were obtained from B.D.H. in the highest purity available (normally

AnalaR; at least 95 %). Catalysts were prepared by impregnation and were calcined in air at 500 – 600 °C or at the temperature of the subsequent reaction, generally for 9 h.

There was a general tendency for the temperature in the catalyst bed to increase as a result of reaction and, on occasion, this led to the onset of homogeneous reactions. Care was taken to minimise these effects by using a small diameter reactor and by minimising the dead space in the reactor.

The results are largely reported as selectivities, defined as the percentage mol of product divided by the mol of isobutene reacted, corrected for the number of carbon atoms in the product. Conversion is defined as the fraction of mol of isobutene reacted per mol of isobutene fed × 100 %. Time parameters are expressed as the weight of catalyst (W) divided by the inlet flow rate (F), corrected to 25 °C.

RESULTS AND DISCUSSION

Preliminary experiments showed that homogeneous reactions were unimportant (< 3 % conversion) at temperatures of less than 550 °C, and that diffusion effects were negligible. The use of pure indium oxide gave a rapid and uncontrolled rise in temperature, and the experiments summarised in Fig. 1 showed that optimal amounts of the desired products were obtained with a 6 % loading of indium oxide on pumice. This loading was used in all subsequent experiments. It was necessary, however, to purchase a larger sample of pumice, which was used for all the experiments described below.

The effect of loading indium oxide on different supports was then investigated (Table 1). Surprisingly, the conversion of isobutene was found to be independent of the surface area of the support (cf. results for pumice and alumina in Table 1), and this is thought to be due to the fact that the active surface area of the indium oxide remained constant: no attempt was made to check this. The product spectrum did, however, vary. High selectivity to methacrolein was observed using an acidic silica-alumina support, and the highest yields of the desired products (dimethylhexadiene and p-xylene) were obtained using a pumice support.

Using the 6 % indium oxide/pumice catalyst, the first variable to be studied was temperature (Fig. 2). A significant increase in the conversion of dimethylhexadiene to p-xylene was observed at about 500 – 520 °C, the amount of benzene produced also increasing over the same range.
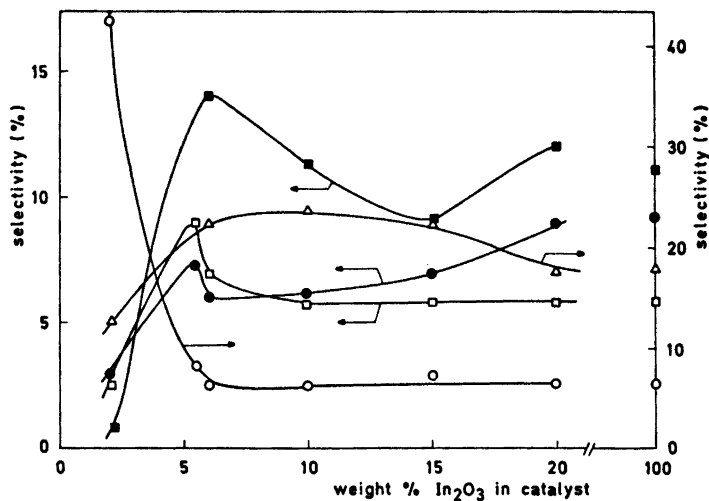
Fig. 1. The effect of catalyst loading. Isobutene = 5.0×10^{-3} mol l^{-1}, oxygen = 8.9×10^{-3} mol l^{-1}; $t = 485\,°C$; $W/F = 2.5$ g min l^{-1}. $\square$, benzene; $\blacksquare$, p-xylene; $\triangle$, dimethylhexadiene; $\triangledown$, toluene; $\bigcirc$, methacrolein; $\bullet$, CO_2.

Surprisingly, the yield of methacrolein stayed approximately constant.

The effect of contact time on yield was then studied, the catalyst being maintained at 485 °C. The conversion of isobutene to methacrolein and carbon dioxide was found to be higher at low contact times (Fig. 3), with the conversion to desired products increasing with contact time. The sharp decrease in the selectivity for hexadiene and the corresponding increase in

the production of aromatics is to be expected, in that the dimer is an intermediate in the cyclisation process. Benzene yields increase as does the yield of p-xylene, but the toluene yield remains effectively constant. The results indicate that longer contact times favour the oxidative coupling, but this may be due to depletion of oxygen in the system. This possibility was checked by studies of the effect of molar ratio of reactants on the product spectrum (Fig. 4).

Table 1. Oxidation of isobutene over 6 % In_2O_3 on different supports. Isobutene = 5.0×10^{-3} mol/l; oxygen = 8.9×10^{-3} mol/l; $W/F = 2.5$ g min l^{-1}; $t = 500$ °C.

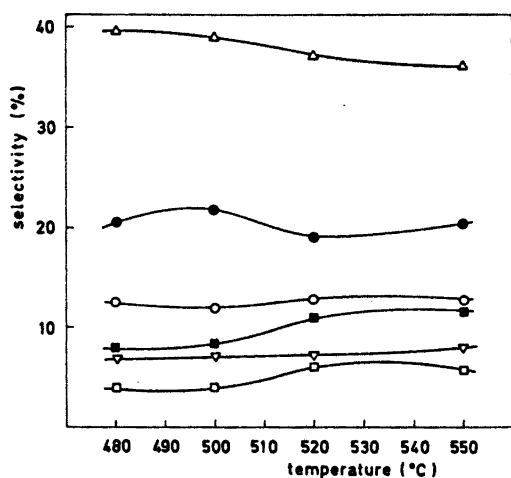| Selectivity to	Supports					
	Pumice	SiO$_2$			Al$_2$O$_3$	
a Methacrolein	12.1	21.0	12.5	37.7	8.8	30.4
b Benzene	4.4	4.20	2.2	6.0	3.1	3.6
c Dimethylhexadiene	39.4	15.8	26.6	11.6	28.9	22.2
d Toluene	6.7	5.5	3.5	3.7	3.8	3.1
e p-Xylene	8.5	11.7	11.5	5.3	10.9	12.9
f CO$_2$	22.3	31.4	36.0	34.5	36.8	24.1
(b+c+d+e)	60.4	39.0	44.9	27.4	48.2	43.6
(a+f)	34.3	52.4	48.5	72.1	45.6	54.5
Conversion (%)	31.2	24.0	23.1	33.2	34.3	35.0
Surface area m^2 g^{-1}	0.45	230	0.1	220	0.15– 0.35	12 (acidic)

Fig. 2. The effect of temperature. Key and reaction conditions as in Fig. 1; temperature variant.
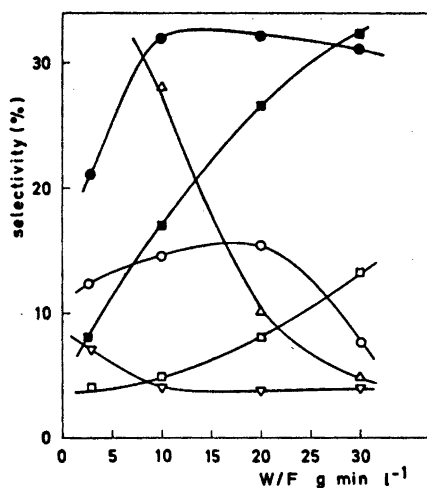

Fig. 3. The effect of contact time. Key and reaction conditions as in Fig. 1; contact time variant.

In the absence of oxygen, the reaction rate was small, and no methacrolein or carbon dioxide were detected. As oxygen increased, the conversion of isobutene increased, as did the production of toluene and carbon dioxide. The yield of methacrolein passed through a pronounced maximum, while the yields of the desired products (dimethylhexadiene and *p*-xylene) rose to a near-plateau. Similar effects, but in an inverse relation, were observed as the concentration of isobutene was increased, the production of *p*-xylene passing through a maximum at a ratio of oxygen − isobutene = 2.0.

The effect of additives on the reaction yields were then examined on the basis of the ideas proposed in Ref. 1 (Table 2). In connection with the allylic oxidation of propylene to acrolein, it has been established that the acid-base char.
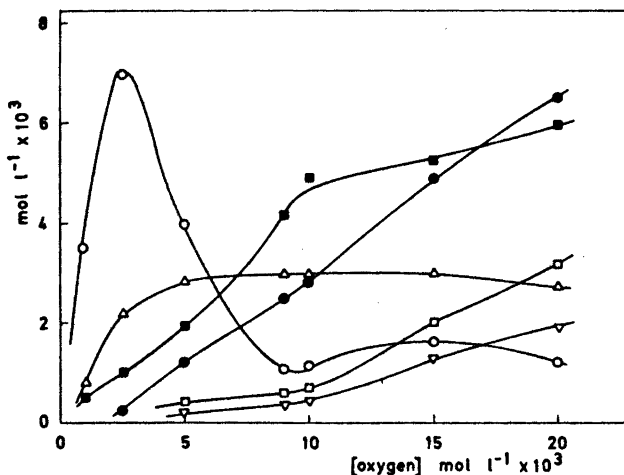

Fig. 4. The effect of varying oxygen. Isobutene = 5.0×10^{-3} mol l^{-1}; $t = 485\,°C$; $W/F = 10.0$ min l^{-1}. Key as in Fig. 1.

Table 2. The effect of additives. Isobutene$= 5.0 \times 10^{-3}$ mol l^{-1}; oxygen$= 10.0 \times 10^{-3}$ mol l^{-1}; $t = 520\,°C$; $W/F = 2.5$ g min l^{-1}.

Catalyst	Selectivity (%) to						(a+f)	(b+c+d+e)	Con-version %
	Metha-crolein	Benzene	Dimeth-ylhexadi-ene	Toluene	p-xylene	CO$_2$			
	a	b	c	d	e	f			
(a) In/M = 2									
In$_2$O$_3$	12.8	5.9	36.8	7.2	10.9	18.7	31.5	62.6	39.6
In$_2$O$_3$+V$_2$O$_5$	72.8	1.3	10.7	0.11	0.3	3.5	76.3	12.3	11.6
+P$_2$O$_5$	72.8	2.5	14.9	2.4	0.4	1.8	74.6	20.1	40.2
+B$_2$O$_3$	56.0	4.8	27.8	2.4	1.6	4.4	60.4	36.6	19.7
+Sb$_2$O$_4$	67.8	1.1	13.2	0.8	0.5	15.0	82.8	15.6	14.4
+As$_2$O$_5$	63.4	2.4	20.2	0.7	0.6	10.3	73.7	23.8	10.5
+MoO$_3$	64.7	3.8	17.0	2.5	3.9	1.8	66.5	27.2	14.4
+Cr$_2$O$_3$	21.1	5.7	28.8	8.0	7.6	21.7	42.8	51.4	44.9
+WO$_3$	61.6	9.3	23.5	1.6	2.3	1.3	62.9	36.6	20.3
+Bi$_2$O$_3$	50.8	2.5	30.4	3.6	0.5	4.7	55.5	37.0	11.3
+TiO$_2$	45.7	3.0	34.0	4.8	0.1	1.7	47.7	41.9	44.9
+SnO$_2$	19.4	6.5	29.5	6.3	10.7	19.8	39.2	56.2	34.6
(b) In/M = 10									
In$_2$O$_3$+Na$_2$O	54.0	5.9	18.2	7.1	4.5	8.9	62.9	35.7	13.23
+Li$_2$O	56.5	2.8	29.8	1.5	0.2	2.7	59.6	34.3	11.58

acteristics of the catalyst may affect the course of the reaction in two ways.[1,6,12,13]

(1) By altering the electronic properties of the adsorbed allylic intermediate.

(2) By affecting the metal-oxygen bond strength.

Assuming that the initial adsorption involves reactions such as a, b, and c above, Peacock et al.[13] have shown that localisation of the electron at the adsorption site leads to strong bonding and favours complete oxidation. If the electron can be removed from the adsorption site and localised on a second metal (acceptor) ion, the allylic-surface bonding will be weaker and the production of acrolein should be favoured. As a result of these arguments, mixed catalysts involving indium oxide and oxides of vanadium, tin, molybdenum and bismuth were prepared and tested (Table 2). In all cases, this resulted in a slight decrease in selectivity for the dimer and aromatics, but a significant increase in the yield of methacrolein. These additives are, then, behaving as would be predicted.

In the case of isobutene oxidation, acidic sites would be expected to favour the production of methacrolein and of carbon dioxide, as

a result of localisation of the electron on the metal ion causing the adsorbed intermediate to become cationic, and, in consequence, susceptible to nucleophilic attack by oxygen.[1,6] Where the adsorbed intermediate is less ionic, electrostatic repulsion between two allyl groups would be less, and more dimer should be produced. As a result, basic additives should increase the selectivity to desired products, while acidic additives should increase the yields of methacrolein and carbon dioxide. The effect of acidic additives is clearly seen from Table 3, phosphorus pentoxide, antimony tetroxide and arsenic pentoxide increasing the yield of methacrolein (although possibly at the expense of carbon dioxide). However, the addition of basic additives (Na$_2$O, Li$_2$O) markedly reduces the yield of aromatics and dimethylhexadiene (Table 2), while increasing the yield of methacrolein. This is the direct opposite of what has been observed for bismuth phosphate catalysts used to oxidise propylene to benzene[6] and is difficult to explain.

It is obvious that the production of carbon dioxide requires considerably more oxygen than any other product. As a result, it could be argued that an additive that decreases the

Table 3. Mixed catalysts for the oxidation of isobutene. Isobutene $= 5.0 \times 10^{-3}$ mol l⁻¹; oxygen $=$ 10.0×10^{-3} mol l⁻¹; $W/F = 10.0$ g min l⁻¹.

t °C	Catalyst A [a] 500	Catalyst B [b] 500	520	550	Catalyst C [c] 485	500	550	600
Selectivity (%) to								
a Methacrolein	21.9	13.4	10.0	10.4	5.3	5.2	4.5	4.9
b Benzene	2.9	1.2	1.8	7.2	7.1	7.1	9.5	9.5
c Dimethylhexadiene	21.0	31.2	30.49	26.3	8.3	8.7	5.2	9.5
d Toluene	1.5	3.4	4.0	9.7	9.5	9.9	14.6	17.0
e *p*-Xylene	6.8	8.7	10.7	8.5	20.6	23.7	26.5	29.6
f *m*-Xylene	0.6	1.9	1.9	1.7	5.6	5.2	6.1	7.5
g *o*-Xylene	–	0.5	0.32	0.5	1.8	2.0	2.5	2.8
h Dimethylcyclohexadiene	1.3	0.8	1.06	0.7	13.1	10.6	4.2	2.4
i CO₂	43.0	37.8	37.9	30.6	27.4	26.4	25.4	23.4
(a+i)	68.9	51.2	47.9	41.0	32.7	31.6	29.9	28.3
(b+c+d+e+f+g+h)	34.0	47.7	50.3	54.4	65.9	67.1	68.6	69.7
Conversion (%)	26.0	37.6	42.8	47.0	45.6	45.2	49.8	53.4

[a] Catalyst A= 12 % $Cr_2O_3/Al_2O_3 + In_2O_3$/pumice (mixed randomly). [b] Catalyst B= 12 % $Cr_2O_3/Al_2O_3 + In_2O_3$/pumice (two separate layers). [c] Catalyst C= 0.3 % $Pt/Al_2O_3 + In_2O_3$/pumice (two separate layers).

amount of adsorbed oxygen should decrease the amount of carbon dioxide. Since oxygen adsorbs mainly as a charged entity,[2] electronegative additives should decrease oxygen adsorption and decrease carbon dioxide production. Addition of additives such as oxides of V, P, Sb or Mo did have this effect, although their influence may result more from their ability to attract oxygen and/or electrons to themselves [2,12] than from their acidity. The addition of basic oxides (Na, Li) also reduced the formation of carbon dioxide although, in this case, reduction of the acidity of the support (Table 1) may favour the decrease in the yield.

As a result of these studies it is clear that although the effect of additives can be predicted in some cases, the prediction is not completely accurate. This may well reflect the fact that a given additive may play more than one role, particularly in the complicated reactions represented in Scheme 1.

Examination of the results showed that the selectivity to dimethylhexadiene was often higher than to *p*-xylene. As a result, it was decided to explore the advantages of using a mixture of catalysts, such as supported indium oxide (to effect dimerisation) with supported chromia or platinum (to effect cyclisation [14,15]). Preparations involving indium oxide and chromia on the same support were unselective

(Table 2), presumably as a result of the chromia concentrating at the gas interface.

Catalysts containing 12 % chromia on alumina [15] and 0.3 % platinum on alumina [14] were prepared and mixed with supported oxide in two ways. Mixing of the pellets throughout the bed offered no particular advantage but a two-stage bed involving supported indium oxide followed by supported platinum gave a significant increase in selectivity (Table 3). Up to 70 % selectivity to desired products was obtained for conversions of the order of 50 %. Subsequent tests of the supported platinum alone showed that it was unselective, giving *ca.* 60 % of oxygenated products and only *ca.* 15 % of dimer plus aromatics.

Given that the theoretical design of catalysts is far from an exact art,[1-3] comparison of the experimental results with theoretical optimisation procedures is reasonably successful. The amount of time involved in the two procedures is such that theoretical design would appear to offer significant advantages even though it is not completely reliable. The accuracy of the prediction can be expected to improve as we understand more about the underlying catalytic mechanisms.

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