

was used as the reference to a C 1s binding energy of 285.0 eV. The measurements have been helped by Dr. Sawazki in Groningen University.

3. RESULTS AND DISCUSSION

The main products of the oxidation of propene were carbon dioxide by the complete oxidation and 1,5-hexadiene by the oxidative dimerization via allyl intermediate on the studied oxides. These products might be formed by parallel reactions and the consecutive formation of carbon dioxide from hexadiene was negligible at low conversion level. The selectivity of 1,5-hexadiene stays constant level all over the reaction temperatures on Zn and Fe-compounds, but on the other hand it decreases with decreasing reaction temperatures sharply on α - Bi_2O_3 . At 600 °C the selectivity was observed the same level on all oxides (see fig. 1). The yield of products were examined as a function of the oxygen in fig. 2 and 3. The yield of carbon dioxide increased with increasing of oxygen pressure. On the other hand, the yield of 1,5-hexadiene has no dependency of oxygen pressure.

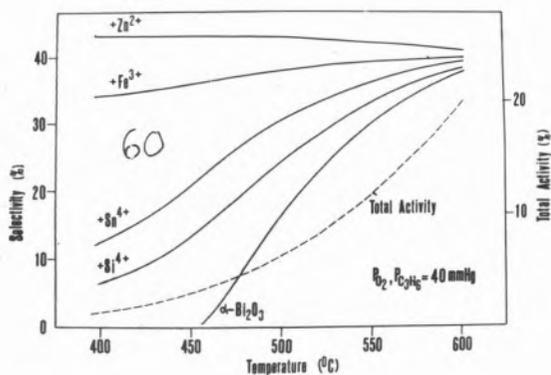


Fig. 1

Values of selectivity to 1,5-hexadiene on impregnating catalysts and α - Bi_2O_3 at different temperatures

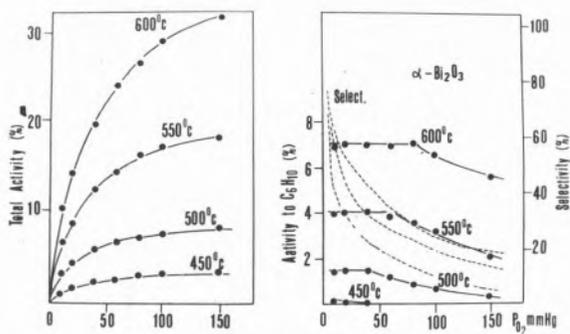


Fig. 2

The dependence of yield to 1,5-hexadiene and carbon dioxide on oxygen on α - Bi_2O_3 . Propene constant pressure is 40 mm Hg; constant time is 100 cc catalyst / 2g / min

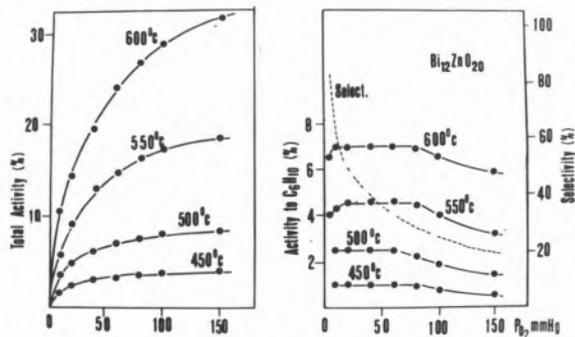


Fig. 3

The dependence of yield to 1,5-hexadiene and carbon dioxide on oxygen on $\text{Bi}_{12}\text{ZnO}_{20}$. Propene constant pressure is 40 mm Hg; contact time is 100 cc catalyst / 2g / min

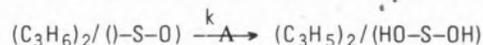
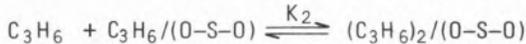
The initial rates of formation of μ products could be described by the equations

$$R_H = k_H P_{C_3H_6}$$

$$R_C = k_C P_{C_3H_6} / (1 + K P_{O_2})$$

where H and C refer to hexadiene and carbon dioxide. The rate of CO_2 formation was examined in fig. 4. The apparent activation energies of 72 kJ/mole were obtained for both reactions on Zn-compound.

Trimm et al. (7) proposed a mechanism for the oxidative dimerization reaction on Indium oxide catalyst as follows; (1) two olefins adsorbed at an In^{3+} center, (2) the extraction of a hydrogen ion from the allylic carbon atom by oxidic oxygen, (3) In^{3+} accepts two electrons simultaneously, (4) the dimerization to diolefins, which the reaction (2) was proposed the rate controlling. The mechanism may now be rewritten :



where (O-S-O) is a reaction site. The rate of dimerization is

$$R_H = k (C_3H_6)_2/(O-S-O)$$

According to the mechanism, the concentration of the adsorbed mono-olefin and di-olefin lead to the following expressions.

$$C_3H_6/(O-S-O) = \frac{K_1 P_{C_3H_6} \{ (O-S-O)_0 - (C_3H_6)_2/(O-S-O) \}}{1 + K_1 P_{C_3H_6}}$$

$$(C_3H_6)_2/(O-S-O) = \frac{K_1 K_2 P_{C_3H_6}^2 (O-S-O)_0}{1 + K_1 P_{C_3H_6} + K_1 K_2 P_{C_3H_6}^2}$$

where $(O-S-O)_0$ is the total number of the reaction sites. The initial rate of dimerization, R_H , then becomes

$$R_H = \frac{k K_1 K_2 (O-S-O)_0 P_{C_3H_6}^2}{1 + K_1 P_{C_3H_6} + K_1 K_2 P_{C_3H_6}^2}$$

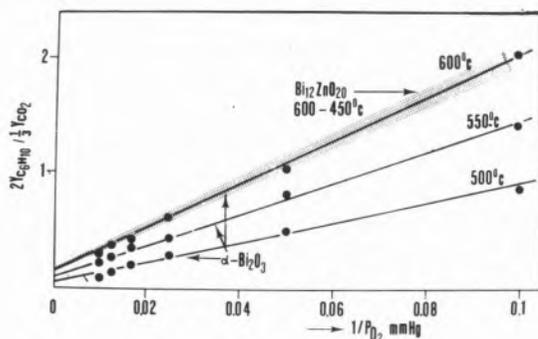


Fig. 4

Reciprocal oxygen pressure vs the ratio of 1,5-hexadiene and carbon dioxide formation according to a parallel reaction on α - Bi_2O_3 and on $Bi_{12}ZnO_{20}$

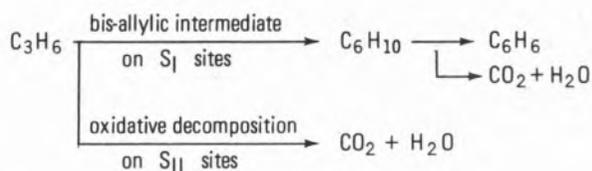
The order with respect to olefin, at constant catalyst concentration, will be variable. At very high olefin pressure R_H will approach a zero-order dependence on olefin. At very low olefin pressure R_H will approach a second order dependency. At intermediate pressure the order will be influenced by the relative values of K_1 and K_2 . If $K_1 > K_2$ then even at high olefin pressure the order could tend to level out at one. Table 1 summarizes the results obtained, the rates of hexadiene formation on different catalysts from several authors. The data are in qualitative agreement with this rate expression.

Table 1

Variation in the reaction kinetics for hexadiene formation

Catalyst	Observed by	Reaction kinetics	Activation energy (kJ/mole)
α - Bi_2O_3	Swift et al. (2)	$k P_{C_3H_6}$	90
Bi_2O_3/SnO_2	Seiyama et al. (4)	$k P_{C_3H_6}^{1.6}$	290
$Bi_{12}ZnO_{20}$	Present authors	$k P_{C_3H_6}$	78
In_2O_3	Trimm et al. (7)	$k P_{C_3H_6}^{0.4} P_{O_2}^{0.4}$	192

Also we suggest $K_1 > K_2$ which implies that adsorption of mono-olefin is more facile than is adsorption of di-olefin on an active site. From the effects of feed composition on propene conversion and the selectivity for products, it is considered that two types of adsorption centers S_I and S_{II} , the one S_I , forms an allylic intermediate and the other one, S_{II} , works for oxidative decomposition.



α - Bi_2O_3 has a complex monoclinic structure with layers of bismuth atoms and oxygen atoms parallel to Y and Z-axes. There are two sorts of bismuth, one, Bi_I , has five oxygen neighbours at the corners of a distorted octahedron with bismuth lone pair occupying the sixth corner. Two more oxygen atoms are weakly bond. The other sort of bismuth Bi_{II} has six oxygen neighbours at the corners of an octahedron (8). Two combinations of Bi is shown in fig. 5. The cubic δ - Bi_2O_3 is stable above 717 °C and has a fluorite defect structure in which oxygen vacancies are randomly distributed. Sillen et al. (9) reported δ -modified Bi_2O_3 is stabilized with Al, Si, Fe, Pb, etc. Tetravalent metal oxides such as Si or Ge give stable phase approximated by the formula $Bi_{12}Me^{4+}O_{20}$. Also lower valency metals stabilize the same formula with rich oxygen. Craig and Stephenson (10) proposed the body-centered cubic structure derived above contain Bi_I ions in octahedral coordination. The 24 octahedra share corners to form a cage of $Bi_{24}O_{40}$ atoms and within this cage there is two tetrahedral sites. In the cage of the stabilized with Fe^{3+} compound, there is one Bi^{5+} and one Fe^{3+} ions per cage, and with Zn^{2+} compound, there is 4/3 Bi^{5+} and 2/3 Zn^{2+} ions distributed over the tetrahedral sites in each cage. Also they believe that γ - Bi_2O_3 is $Bi_{25}^{3+}Bi^{5+}O_{40}$.

The results of the present study seem to suggest that the oxidative decomposition site (S_{II}) might be Bi_I which consist of an inert $6s^2$ electron pair occupies an orbital pointing directly at the empty sixth corner. This electrons pair may be donated to an oxygen molecule and the adsorbed oxygen leads to waste products olefins. The selective oxidation site (S_I) may be a tetrahedral coordinated Bi^{5+} ion because the formation of 1,5-hexadiene is increased with increasing of the number of Bi^{5+} in a cage ($Zn^{2+} > Fe^{3+} \gg Si^{4+}$). Bi^{5+} with a d^{10} electron outer shall can possible to form π -adsorbed olefins, while this is not possible with Bi^{3+} which has a s^2 outer most shell. Also the reduction of Bi^{5+} appears to require two electrons effectively simultaneously.

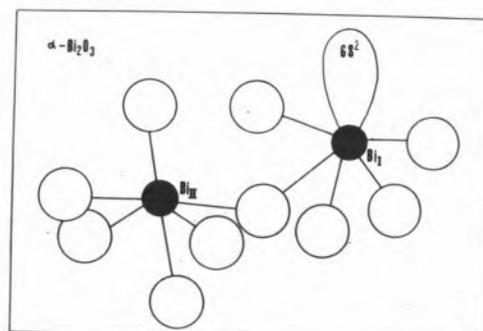
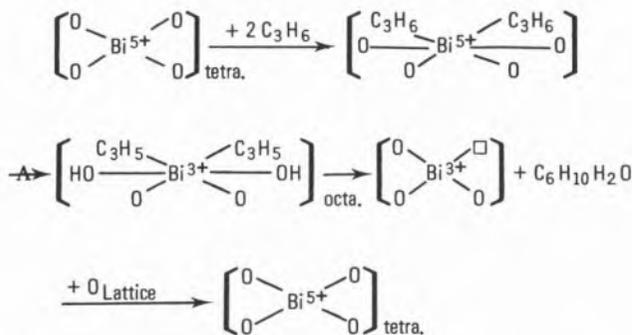


Fig. 5

The coordination polyhedra in α - Bi_2O_3

The reaction scheme on S_1 site can be shown as follows :



The first step in the proposed reaction scheme involves adsorption of the olefins at a Bi^{5+} center. Once this has occurred, the abstraction of hydrogen with electron transfer to a center from two adsorbates would appear to be favoured. Two allylic intermediates on Bi results in the reduction of Bi^{5+} to a normal oxidation state of Bi^{3+} would leave such that dimerized 1,5-hexadiene. The anion vacancy connected to Bi^{3+} can be readily filled with an oxygen from the bulk oxygen. The formation of 1,5-hexadiene upon passing propylene over $\alpha\text{-Bi}_2\text{O}_3$ was an unexpected result from our argument, since there is no tetrahedral sites in a crystal. However, in a recent paper $\gamma\text{-Bi}_2\text{O}_3$ was found in the reduced $\alpha\text{-Bi}_2\text{O}_3$ from X-ray analysis (11). Therefore we expect the formation of tetrahedral sites occupied by Bi^{5+} in the apparent reduced atmosphere at higher temperatures.

The detection of Bi^{5+} in Zn-compound by XPS-analysis would not be succeeded for reasons of the lower concentration of Bi^{5+} to compare XPS-sensitivity or the reduction to Bi^{3+} for the low pressure condition at measurement ($< 10^{-8}$ mm Hg). Fig. 6 shows the 1s of O at 530.0 eV that responded to O^{2-} with strong interaction to Bi and the 4f doublet of Bi at 159 and 164 eV that assigned to Bi^{3+} at room temperature. At higher 300 °C, we observed new small oxygen peak at 532.5 eV that indicated to be present in the formal modes such as O_2^- , O_2^{2-} or O^- on surface. Also the observation of the less negative charged oxygen peak was found on bismuth-molybdate catalyst ($\text{Bi}_2\text{Mo}_2\text{O}_9$). Reduced zero valency of Bi was also found (see fig. 7). Such less negative charged oxygen than the oxide oxygen might be active and selective for olefin oxidation.

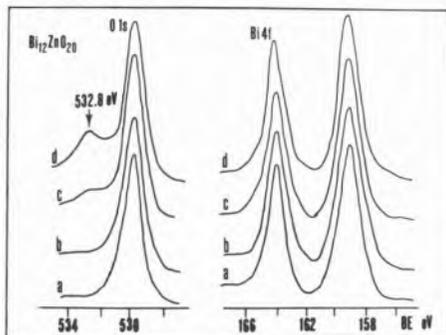


Fig. 6

Photoelectron spectra of oxygen and bismuth in $\text{Bi}_{12}\text{ZnO}_{20}$ at different temperatures. a) 20 °C; b) 200 °C; c) 300 °C; and d) 400 °C

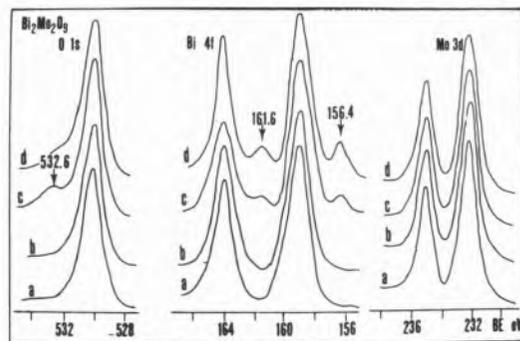


Fig. 7

Photoelectron spectra of oxygen, bismuth and molybdenum in $\text{Bi}_2\text{Mo}_2\text{O}_9$ at different temperatures. a) 20 °C; b) 200 °C; c) 300 °C; and d) 400 °C

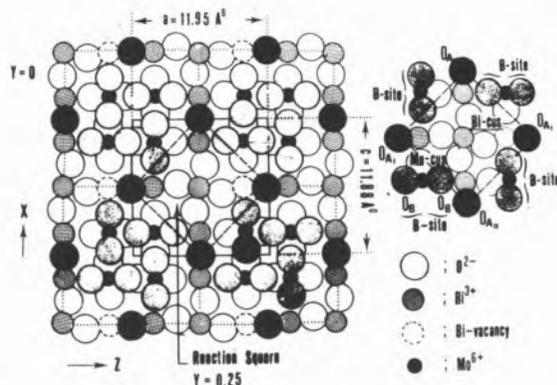


Fig. 8

Surface model of $\text{Bi}_2\text{Mo}_2\text{O}_9$ according to van der Erzen and Rieck (13) and active site model,

Recently one of us (12) proposed the reaction site structure on bismuth-molybdate catalyst is similar arrangement of $\text{Bi}_2\text{Mo}_2\text{O}_9$ structure. The structure proposed is given in fig. 8 (13). In the Y-direction layer of cations and anions alternate. The cation layer contain clusters of four distorted MoO_4 -tetrahedra. One in every four Bi-cation is connected to those oxygens, presumably distorted, β -fold surrounding. The other three form part of a set of four sites, three of which are filled and one that is empty. These Bi^{3+} have six-fold surrounding of oxygens most of which are shared by Mo-cations. However, there is also an oxygen only connected to Bi^{3+} or a vacant site. The olefins oxidation may be proceeded on $Y = 0.25$ (or 0.5) plane that is constructed with a Bi-cus in the center surrounded by four ions connected to Bi that is to be active and selective oxygen (O_A) and four MoO_4 that is to be an olefin adsorption site (B-site). The reaction could then be visualized as follows: the propene is adsorbed at the Mo-cus, it loses first hydrogen to a O_B (on B-site) (1), an allyl turns on a Bi-cus (2), second hydrogen is abstracted to a O_B (3), active oxygen (O_A) inserts into the C_3H_4 complex to form acrolein (4), desorption of H_2O occurs because the H-atoms migrate to an O_A (5). If ammonia present at this stage, the O_A reacts with NH_3 forming a NH which inserts into the C_3H_4 complex to form acrylonitril. The direct reaction to acrylonitril ammonia and propene needs three oxygen ions that can be spent by the oxygen ions of the corner (O_A).

These reactions proceed via the intermediate reaction



where one side of the Bi-cus was left unoccupied,



The Bi-cus might be a closely similar to an olefin adsorption site (S₁) on the oxygen-rich forms of bismuth oxide.

REFERENCES

1. CALLAHAN, J. L., GRASSELLI, R. K., MILBERGER, E. C., and STERECKER, H. A., *Ind. Eng. Chem. Prod. Res. Develop.* 9, 134 (1970).
2. SWIFT, H. E., ROZIK, J. E., and ONDREY, J. A., *J. Catal.* 21, 212 (1971).
3. SAKAMOTO, T., EGASHIRA, M., and SEIYAMA, T., *J. Catal.* 16, 404 (1970).
4. SEIYAMA, T., MOCHIDA, I., UDA, T., and EGASHIRA, M., *Japan-Soviet Catalyst Meeting*, 134 (1973).
5. MATSUURA, I., and SCHUIT, G. C. A., *J. Catal.* 20, 19 (1971).
6. HABER, J., and GRZYBOWSKA, B. J., *J. Catal.* 28, 489 (1973).
7. TRIMM, D. L., and DOERR, L. A., *J. Catal.* 26, 1 (1972).
8. MALMROS, G., *Acta Chem. Scand.* 24, 384 (1970).
9. AURIVILLIUS, B., and SILLEN, L. G., *Nature*, 155, 305 (1945).
10. CRAIG, D. C., and STEPHENSON, N. C., *J. Solid State Chem.* 15, 1 (1975).
11. FATTORE, V., FUHRMANN, Z. A., MANARA, G., and NOTARI, B., *J. Catal.* 37, 215 (1975).
12. MATSUURA, I., HIRAKAWA, K., and SCHUT, R., to be published.
13. VAN DEL ELZEN, A. F., and RIECK, G. D., *Mat. Res. Bull.* 10, 1163 (1975).

RESUMO

Verificou-se que a desidrodimerização oxidante do propeno é catalisada pelas formas do óxido de bismuto ricas em oxigénio.

Estudos cinéticos demonstraram que a velocidade de formação do 1,5-hexadieno é de primeira ordem em relação ao propeno e de ordem zero em relação ao oxigénio. Os resultados foram interpretados em termos de um mecanismo envolvendo várias fases, com adsorção rápida e reversível do propeno seguida de abstracção do hidrogénio como fase controladora. Admite-se que o centro de adsorção para o intermediário alílico é o bismuto pentavalente que é estabilizado por pequenas quantidades de Zn ou Fe. Detectou-se às temperaturas de reacção oxigénio com menor carga negativa do que o oxigénio do óxido, que mostrou ser activo e selectivo para a oxidação das olefinas. Propõe-se que este centro activo é o centro A dos catalisadores de molibdato de bismuto.

DISCUSSION

G. STEVENS: A question on a point of detail with the BSCN results. Perhaps I misunderstood you during your presentation. The O(15) original formed at higher temperatures had an increased binding energy. This means it is electron deficient but I thought you said the species was electron rich. Could you clarify please?

I. MATSUURA: I observed less negative charged oxygen than oxyde oxygen such as O_2^- , O_2^{2-} or O^- . However we could not suggest which type of oxygen specie is formed.

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OPTIMISATION OF CATALYSTS FOR THE OXIDATION OF ISOBUTENE TO OCTENES AND AROMATICS

OPTIMIZACION DE CATALIZADORES PARA LA OXIDACION DE ISOBUTENO A OCTENOS Y AROMATICOS

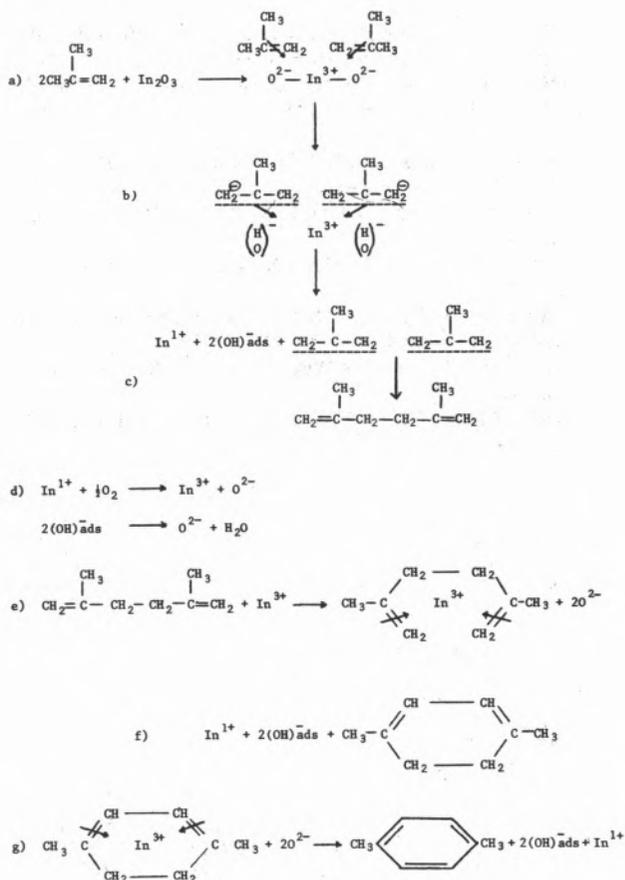
Previous studies have shown that indium oxide can be used to catalyse the oxidation of isobutene to dimethylhexadiene and to p-xylene.

The present paper reports the optimisation of the catalyst for this reaction, with respect to nature of support, catalyst loading, reaction conditions and effect of additives. The best catalyst, consisting of 6% indium oxide on pumice together with 0.3% platinum of alumina, gave up to 30% conversion of isobutene to p-xylene.

1. INTRODUCTION

As a result of the fact that it is an important intermediate in the production of terephthalic acid, attention has been focused on the production of p-xylene rather than of o- or m-xylene. Since conventional methods lead to a mixture of the isomers (1, 2, 3), some novel approaches have been attempted. In particular, the oxidative dimerisation, aromatisation and dehydrogenation of isobutene has been discovered to be a practical route to the selective production of the para isomer. Since the original discovery that the route was practicable over indium oxide catalysts (4, 5), several other catalysts have been identified (6, 7, 8). There are good grounds to suggest that the overall reaction sequence can be expressed in terms of the reactions given in scheme 1. Adsorption of two molecules of isobutene is followed by the oxidative removal of hydrogen allylic to the double bond: the adsorbed products then dimerise and react further to produce p-xylene. Methacrolein, resulting from the oxidation of one adsorbed molecule, and carbon oxides are the major unwanted products of reaction. Although indium oxide has been identified as a suitable catalyst (4, 5), no attempt has been made to optimise the system. The present paper reports studies intended to fulfil this purpose.

Scheme 1



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