

Kinetics study of the oxidative dehydrodimerisation and aromatisation of isobutene on $\text{Bi}_2\text{O}_3\text{-SnO}_2$

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Abstract

The kinetics of the oxidative dehydrodimerisation and aromatisation of isobutene has been studied on a $\text{Bi}_2\text{Sn}_2\text{O}_7$ system for a mechanistic understanding of the reaction. The rate of disappearance of isobutene has been found to be first order with respect to oxygen and second order with respect to isobutene. A good fit of the kinetic data with the Mars and van Krevelen model has been established. The k_{red} and k_{ox} have been found to be 2.3×10^6 and $32 \times 10^6 \text{ mol min}^{-1} \text{ m}^{-2} \text{ kPa}^{-1}$, respectively, proving that the reduction of the catalyst is the rate-determining step. Studies were also done to verify the mechanistic pathway of the reaction. Previous workers have suggested that the reaction is essentially a consecutive reaction proceeding from isobutene to *p*-xylene through the intermediate dimer (2,5-dimethyl-1,5-hexadiene). Studies were done at increasing contact time to verify the mechanistic pathway of the reaction and the intermediate dimer was used as the reactant. Our results showed that the intermediate dimer is mainly oxidised to CO_x while *p*-xylene is formed through some direct parallel pathway from isobutene.

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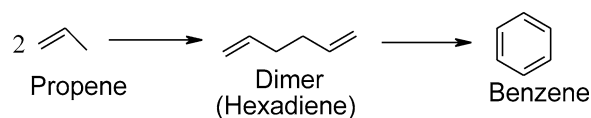
Keywords: Kinetics; Isobutene conversion; Aromatisation; Dimerisation; Order of reaction; Pathway of reaction; Consecutive reaction; Intermediate dimer

1. Introduction

The oxidative cyclodehydrogenation of propene to benzene was a well-studied reaction of the 1970s and many postulates about this reaction were published [1–7]. Some of the conclusions were from well-depicted experimental facts whereas some were simple corollaries of such findings. It has been suggested that olefin interacts with the lattice nucleophilic O^{2-} ions giving an allyl anion and a surface hydroxyl group. By electron transfer to the stabilising centre, an allyl radical is likely to be formed, which reacts with the other allyl radical and forms the dimer. This heterolytic alkene activation has been suggested to have been observed on the surface of Sn-containing catalysts (Sn–Bi, Sn–Ti, Sn–In, etc.) for which the rate of isobutene and propene dimerisation was observed to depend on the concentration of basic centres [8].

There was a general agreement that these reactions were consecutive ones with the stepwise conversion of the olefin to the dimer (hexadiene) and the dimer cyclising and aromatising to benzene in the case of the olefin being propene (Scheme 1) [9]. Studies with isobutene conversion have also suggested that the reaction may be a consecutive one proceeding from isobutene to *p*-xylene through the dimer 2,5-DMH²⁼ [10,11].

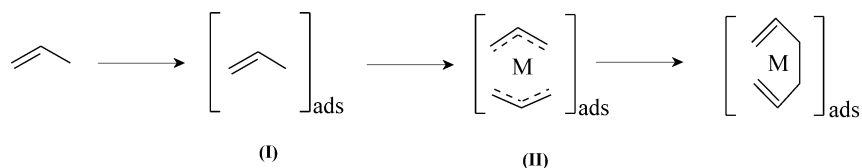
The role of oxygen in the reaction was another major area of research but the facts delivered were not unanimous. It is widely admitted from pulse experiments, e.g., on Bi_2O_3 catalysts that upon the addition of the first increments of olefin (propene, isobutene), most of the surface-sorbed oxygen is removed from the surface [12]. Usually high conversion and low selectivity to dimers and aromatics was observed first, followed by low conversion and high



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Scheme 1. Dimerisation and aromatisation of propene.



Scheme 2. Different steps of the dimerisation of propene.

selectivity. According to most of the researchers oxygen was only used to reactivate the reduced surface of the catalyst and it indirectly participated in reaction [13]. Therefore, in terms of the kinetics, the reaction was zero order with respect to oxygen and the mechanism followed the Mars and van Krevelen model [14]. According to other researchers like Trimm et al., however, oxygen did participate in the reaction through chemisorption and a multisite Langmuir Hinshelwood model fitted their data [15]. Besides, there were also suggestions that the reaction could be some negative order with respect to oxygen, where the reactivity decreases with the increase in oxygen pressure [16].

Uncertainties were also there with respect to the rate-determining step of the reaction. According to some authors it was the formation of the allyl intermediate and hence step I of Scheme 2 [17] whereas according to Seiyama et al., it was the formation of the bi-allyl intermediate that was the rate-determining step and hence step II of Scheme 2 [18]. The reaction was therefore first order with respect to olefin in the former and second order with respect to olefin in the latter.

Further, all these investigations were thoroughly done for the propene to benzene reaction with very little emphasis on the conversion of isobutene to xylene, leaving enough room for the investigation of the isobutene dimerisation and aromatisation reaction. Besides, the use of isobutene as a raw material is becoming more important since some fear of MTBE ban in reformulated gasoline has appeared in California, which should lead to a surplus in isobutene production. One application could be dimerisation to 2,5-dimethyl hexadiene and aromatisation to *p*-xylene. The former compound could be hydrogenated to branched octane for reformulated petrol and the latter being further oxidised to terephthalic acid.

Moreover, all these investigations were done more than two decades ago and therefore there are enough opportunities to relook at the mechanistic aspects of the reaction under the light of new experimental data. It has also been found that the nature of the catalyst and also the nature of the feed play an important role in determining the mechanistic pathway of the reaction. More recent works have also shown that the presence of Mo, W, or Sb in a Bi₂O₃–SnO₂ system leads to the formation of methacrolein [19]. This paper therefore tries to make a thorough study of the isobutene conversion and also tries to resolve some of the kinetic uncertainties described above. Attempts are made to ascertain the mechanistic pathway of the reaction and ensure if it actually is a consecutive reaction.

2. Experimental and methods

2.1. Catalyst preparation

Appropriate quantities of Bi(NO₃)₃ · 5H₂O and SnCl₄ (99.99% pure, Aldrich) for Bi:Sn (1:1), in terms of atomic ratio, were dissolved separately in 2 M HCl solution. The two solutions were then mixed together. The resulting solution was highly acidic (pH ~ 0.4). To this solution 10 M aqueous NH₃ solution was added dropwise with continuous stirring till the pH was 10. The precipitate was allowed to settle for about 10 min and then filtered. The residue was then dried at 120 °C in an oven for 12 h and then calcined at 750 °C for 10 h in air followed by pelletisation of particles to diameters of 250–425 μm. The sample will be referred to as C1:1, C standing for coprecipitate.

2.2. Catalyst characterisation and testing

The sample was characterised through powder X-ray diffraction in a Siemens 5005 diffractometer, IR spectroscopy in a Nicolet FT-IR, EDX-TEM in a JEOL 2010 transmission electron microscope with an acceleration voltage of 200 kV, which is equipped with a high-resolution pole piece and an energy dispersive X-ray spectrometer (Link Isis from Oxford Instruments), and surface area measurements in a Micromeritics ASAP 2000 instrument.

All these characterisations showed that the sample C1:1 is mainly composed of Bi₂Sn₂O₇ with traces of SnO₂.

All catalytic testings were done in a fixed bed quartz microreactor connected to a GC where the reactants and products are separated by a capillary column CP Wax 52 and two packed columns Molecular Sieve 13X and Haysep C (Varian) and analysed on line by TCD and FID detectors. For catalyst activation and testing and also for analysis through the GC, the gases used were obtained from the British Oxygen Company. Isobutene (N2.0 grade), and hydrogen, air, nitrogen, and helium (all UHP grade) were used without further purification. Feed gases were delivered through Brooks 5850S Smart Mass Flow controllers (MFC) controlled from a Brooks 0154 microprocessor unit. Each gas flow was independently calibrated using a bubble flow meter.

Conversion is obtained by using the formula: Conversion (%) = ((isobutene through the bypass before reaction – isobutene after reaction)/isobutene through the bypass before reaction) * 100. Percentage selectivity of a particular product has been referred to the four carbon atoms of

isobutene in the percentage of moles of that component in the products.

3. Results and discussion

3.1. Effect of feed composition on the reactivity

It has been generally proposed [20,21] that the reaction proceeds through a Mars and van Krevelen [12] mechanism and it has been observed that the reaction proceeds more selectively in the absence of oxygen though the conversion under such a condition is very low and there is a frequent need for reactivation of the catalyst. The conversion and stability of the catalyst, however, increases with oxygen but at the cost of the selectivity to the desired product. Further, oxygen in the feed increases the exothermicity of the reaction and this might have an adverse effect on the overall performance. We investigated the effect of oxygen pressure in the feed on the overall performance of the catalyst. The pressure of oxygen was increased keeping the pressure of isobutene constant and the total pressure was maintained at atmospheric pressure (10^5 Pa), by nitrogen balance. The reaction was carried out with 0.2 g of C1:1 at 500 °C with a total flow of 90 ml min⁻¹. As air was used in the feed instead of oxygen the maximum pressure of oxygen was 15.8 kPa keeping the pressure of isobutene constant at 22.5 kPa. Fig. 1 shows how the conversion changes with increasing partial pressure of oxygen. The products of reaction were mainly 2,5-dimethyl-1,5-hexadiene (2,5-DMH²⁼), *p*-xylene, and CO₂ with some benzene, toluene, ethyl benzene, *m*, *o*-xylene, 2,4-dimethyl-1,5-hexadiene, naphthalenes, and some heavier products.

3.2. Order of reaction

As discussed in Section 3.1, the conversion of isobutene increased with the increase in the proportion of oxygen in the feed. The logarithmic variation of the rates of formation of different products at different oxygen pressures keeping

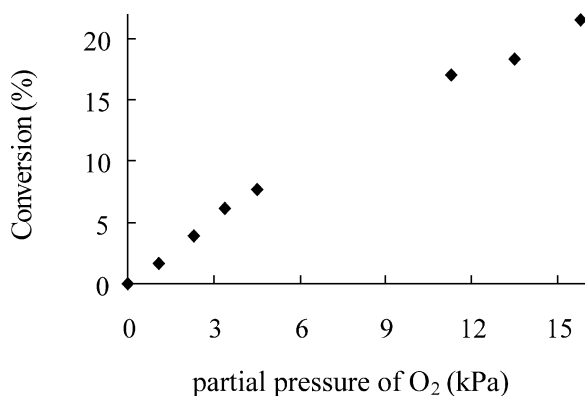


Fig. 1. Conversions of isobutene at different partial pressures of oxygen at 500 °C at a constant isobutene pressure of 22.5 kPa.

the pressure of isobutene constant is shown in Figs. 2a, 2b, and 2c. The rate of disappearance of isobutene at different oxygen pressures from 1 to 12 kPa keeping the partial pressure of isobutene fixed at 22.5 kPa is shown in Fig. 2d.

It was observed that the rate of disappearance of isobutene and formation of CO_x, 2,5-DMH²⁼, and *p*-xylene were all first order with respect to oxygen. Similarly, the dependence of rate on the partial pressure of isobutene was measured at a fixed oxygen pressure of 15.8 kPa, the pressure of isobutene being varied from 3 to 11 kPa and the total pressure was balanced by nitrogen. The temperature of reaction was 500 °C, the weight of the catalyst (C1:1) used was ~ 0.2 g at a total flow of 90 ml min⁻¹. All the values were taken after nearly 3 h of reaction, i.e., at the steady state. It has been found that the formation of 2,5-DMH²⁼ and CO_x was nearly second order with respect to isobutene whereas the rate of *p*-xylene formation was first order with respect to isobutene pressure. The overall logarithmic rate of disappearance of isobutene at different isobutene pressures is depicted in Fig. 3, which proves that the overall rate of disappearance of isobutene with respect to isobutene concentration is second order.

The second-order formation of 2,5-DMH²⁼ with respect to isobutene was comprehensible and was in accordance with the findings of Seiyama et al., indicating the formation of the bi-allyl intermediate as the possible rate-determining step [18]. The formation of CO_x was expected to be first order with respect to isobutene but its second order dependence on the concentration of isobutene indicates that its formation may go through the formation of the dimer. This means that CO_x is formed through the combustion of the dimer and hence the rate of CO_x formation is determined by the rate of formation of the dimer. The results depicted above are summarised in Table 1. The first-order dependence of *p*-xylene formation on isobutene is not easily comprehensible but it may be said that the rate-determining steps for the formation of the dimer and *p*-xylene are different. It therefore appears that the disappearance of isobutene, the formation of the dimer, and the formation of CO_x may proceed through one route whereas the formation of *p*-xylene proceeds through another and the reaction is not essentially a consecutive one. Further, the disappearance of isobutene is mainly governed by the formation of 2,5-DMH²⁼ and CO_x.

Thus, investigations of the order of formation of different products with respect to oxygen or isobutene leave us with suspicions about the mechanistic pathway of the reaction.

Table 1
Orders of various reactions with respect to isobutene and oxygen

Reaction	Order with respect to	
	Isobutene	Oxygen
Isobutene disappearance	1.9	0.95
2,5-DMH ²⁼ formation	1.9	0.7
CO _x formation	1.8	1.1
<i>p</i> -Xylene formation	1.1	1.1

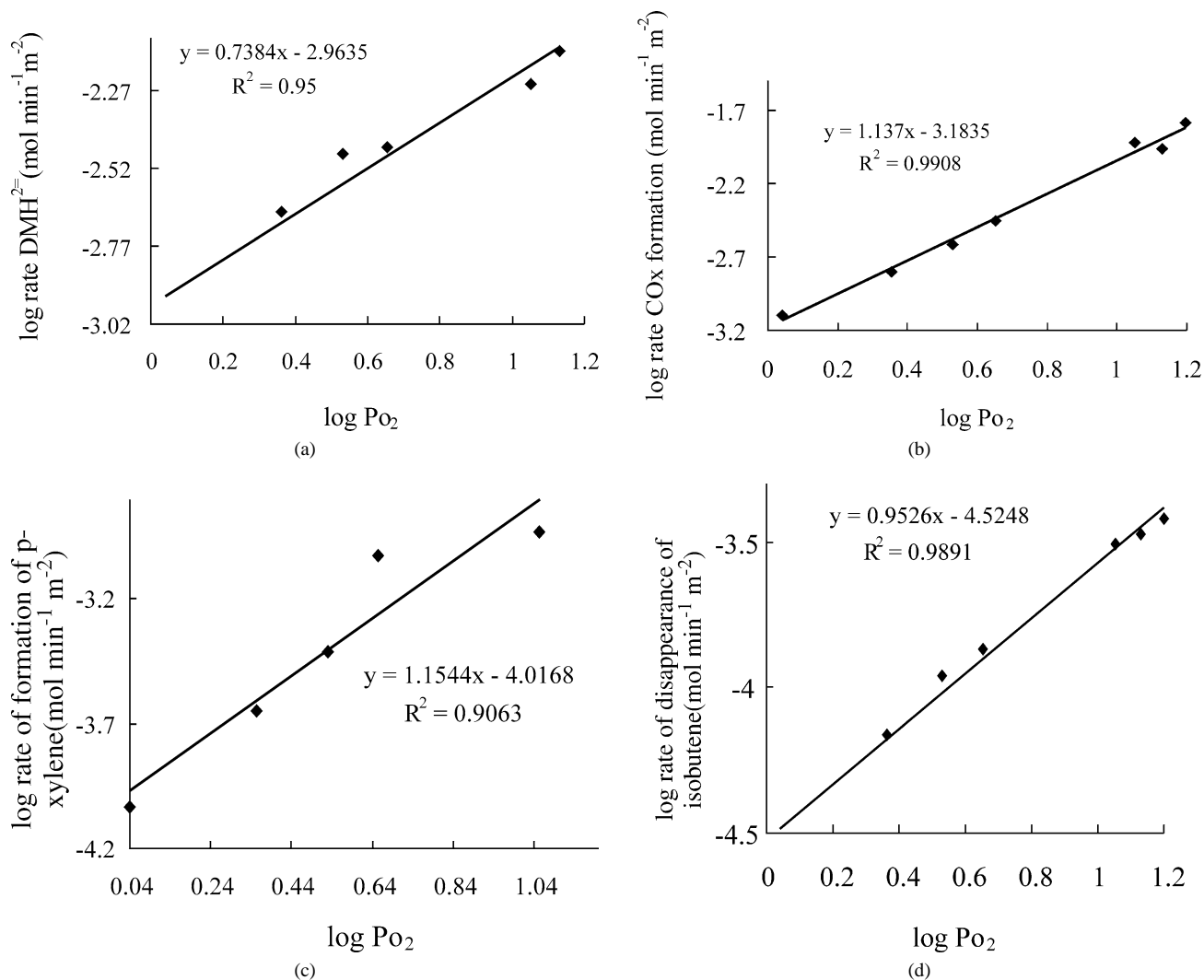


Fig. 2. (a) Log of rate of formation of 2,5-DMH²⁼ vs log of partial pressure of oxygen at a constant isobutene pressure of 22.5 kPa at 500 °C. (b) Log of rate of formation of CO_x vs log of partial pressure of oxygen at a constant isobutene pressure of 22.5 kPa at 500 °C. (c) Log of rate of formation of *p*-xylene vs log of partial pressure of oxygen at a constant isobutene pressure of 22.5 kPa at 500 °C. (d) Log of rate of disappearance of isobutene vs log of partial pressure of oxygen at a constant isobutene pressure of 22.5 kPa at 500 °C.

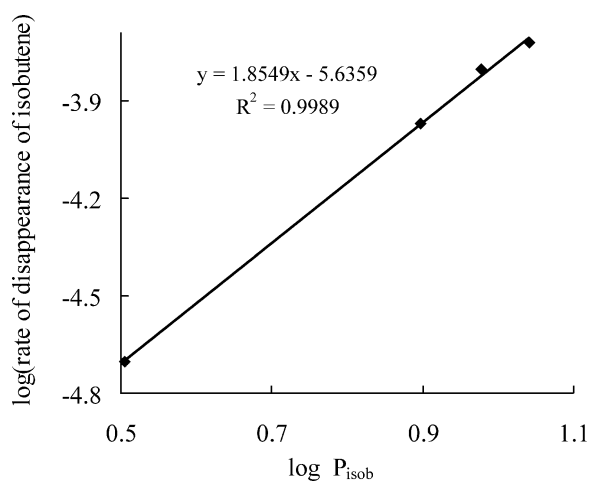


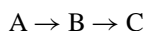
Fig. 3. Log of rate of disappearance of isobutene vs log of partial pressure of isobutene at a constant isobutene pressure of 15.8 kPa at 500 °C.

It therefore becomes necessary to know if the reaction is actually a consecutive one proceeding from isobutene to *p*-xylene through 2,5-DMH²⁼.

3.3. Mechanistic pathway

The reaction mechanism of olefin dimerisation has been widely debated in the past. A homogeneous-heterogeneous reaction has often been proposed. This involves allyl radical formation on the surface, its desorption and reaction between radicals in the gas phase as observed for Bi₂O₃ catalysts for propene dimerisation reaction [22]. The filling of the reactor by glass packing was observed to cause a disappearance of these radicals on ZnO catalysts and a decrease of conversion [23]. Thus, to avoid the homogeneous reaction, the void volume above and below the catalyst bed was filled with quartz wool in our case.

The trait of a consecutive reaction



is such that with the increase in conversion of A, the yield of B will increase and reach a maximum with the consequent increase in the yield of C. The yield of B will continue to decrease and finally go to zero when the yield of C would increase and reach the initial concentration of A. It was necessary to find out if such a trait was present in the conversion of isobutene to *p*-xylene to identify it as a consecutive reaction.

The conversion of isobutene was changed by changing the flow rates of the reactants through the same amount of the catalyst. Or in other words the contact time of the reactants was changed. The temperature of reaction was chosen as 405 °C as this is the lowest possible temperature at which aromatisation was found to happen and at this temperature the contact time could be increased three times without entering the diffusion control regime. The flow rate was varied from 45 to 150 ml min⁻¹ with the change in contact time from 0.3 to 0.1 s. The ratio of isobutene to oxygen was 1:0.6. The weight of the catalyst was 0.2 g and the reaction was carried out at atmospheric pressure. The change in conversion with the change in contact time is shown in Fig. 4a. The linear change of conversion with contact time shows that there is a negligible mass transfer limitation under these reaction conditions. The selectivities of different products change with the change in contact time/conversion and such changes are portrayed in Figs. 4b and 4c.

The curves (Figs. 4b and 4c) show that xylenes are not formed through the decomposition of the dimer but the dimers are overoxidised to CO_x and its selectivity does not go down to zero with the corresponding increase in the selectivity for *p*-xylene as would have been expected for a consecutive reaction.

All investigations so far on the mechanistic understanding of the reaction, thus do not give any clear indications that the conversion of isobutene to *p*-xylene is a consecutive reaction proceeding through the intermediate dimer. On the contrary, it indicates that 2,5-DMH²⁼ is only converted to CO_x.

To try to clarify this point, the intermediate dimer, i.e., 2,5-DMH²⁼ was injected into the reactor instead of isobutene. 2,5-DMH²⁼ is a liquid at room temperature and hence an HPLC pump was used to maintain a flow of this liquid into the reactor tube. The tubes going to the reactor were heated to a temperature of 200 °C so that the liquid turned into gas as the boiling point of the dimer is 114 °C. Calculations were made for the change of liquid to gas and the flow rate of liquid 2,5-DMH²⁼ was adjusted to get a gaseous flow rate of 2,5-DMH²⁼ of 20 ml min⁻¹, which means a partial pressure of 22.5 kPa of 2,5-DMH²⁼ as this was the partial pressure of isobutene that was used in all comparative studies. The reaction temperature was 500 °C and the weight of catalyst used was ~ 0.2 g. The results are depicted in Table 2.

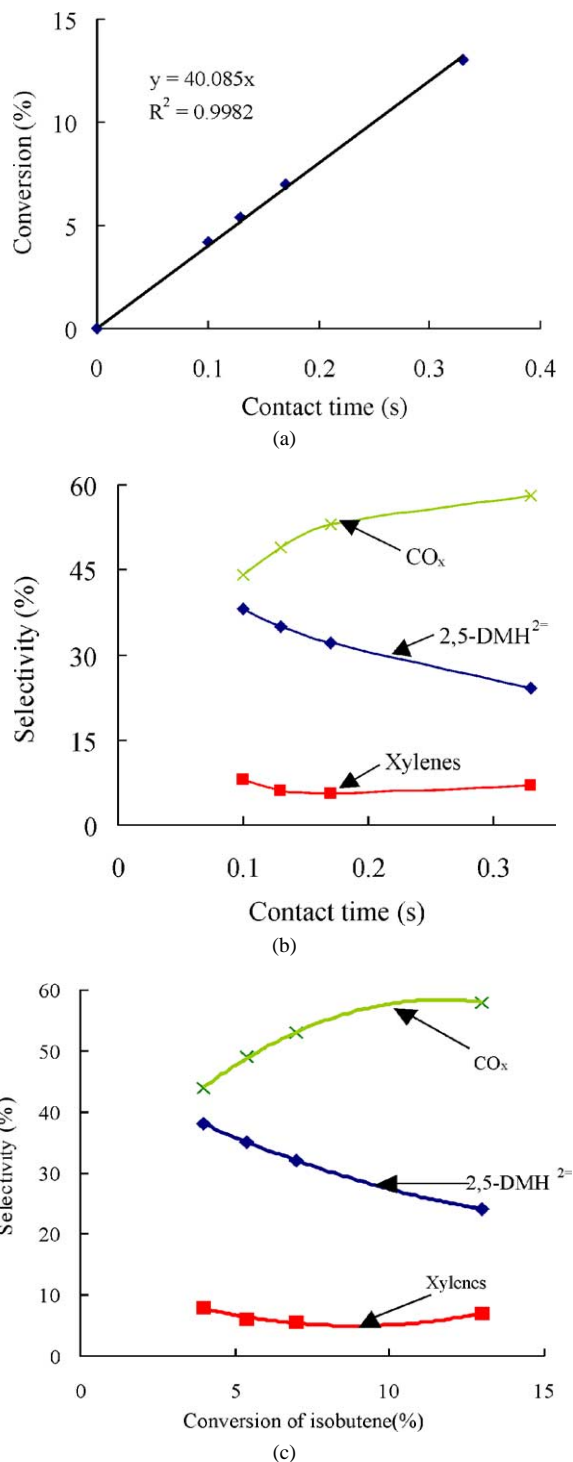


Fig. 4. (a) Conversions of isobutene at 405 °C at different contact times at an isobutene to oxygen ratio of 1:0.6. (b) Selectivities for different products at 405 °C at different contact times at an isobutene to oxygen ratio of 1:0.6. (c) Selectivities for different products at 405 °C at different conversions of isobutene.

It is observed that along with CO_x and *p*-xylene there is the formation of isobutene as well. Such a reversible conversion of the diene to olefin was also observed in the oxidative dehydrogenation reaction of propene to benzene

Table 2
Results of 2,5-DMH²⁼ injection

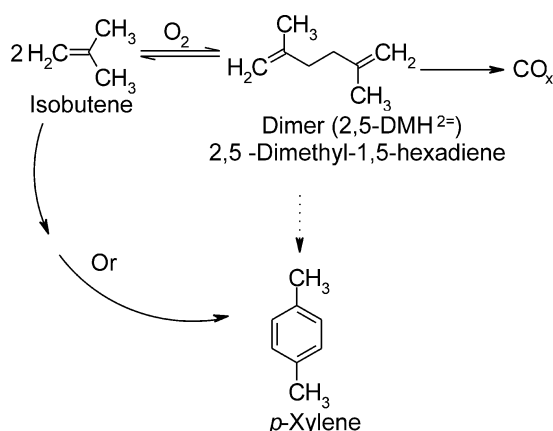
Reaction	(%)
2,5-DMH ²⁼ conversion	58
Isobutene selectivity	14
CO _x selectivity	39
Total aromatics selectivity (<i>p</i> -xylene)	25 (10)
2,4-DMH ²⁼ selectivity	17

[24,25]. Therefore it is highly possible that the *p*-xylene that is formed here comes from isobutene and not necessarily from 2,5-DMH²⁼. Further, the selectivity for *p*-xylene is of the same order of magnitude as that obtained for isobutene conversion. Hence the conversion of 2,5-DMH²⁼ to *p*-xylene is very unlikely as 45 to 60% conversion of 2,5-DMH²⁼ would then have meant a high selectivity for *p*-xylene. The pathway that can be proposed at this stage is shown in Scheme 3.

The role of 2,5-DMH²⁼ in the production of *p*-xylene could be understood without ambiguity if somehow the production of this dimer could be stopped in the conversion of isobutene to *p*-xylene. Such a reaction condition could not however be recognized.

The results regarding the mechanistic steps of the reaction show that though it is easy to comprehend a mechanism where the two molecules of isobutene dimerise and then cyclises to *p*-xylene via a sequential pathway, the results do not definitely show that the reaction is a consecutive one proceeding from isobutene to *p*-xylene. On the contrary it appears that 2,5-DMH²⁼ mainly overoxidises to CO_x whereas *p*-xylene is formed via some parallel pathway from isobutene and therefore, the reaction is much more complicated than what had been envisaged.

Further, though it had been claimed by some of the previous workers that the reaction was zero order with respect to oxygen [16], our results suggest that a certain minimum proportion of oxygen in the feed is necessary to maintain the stability of the reaction and also to increase the conversion and selectivity for the desired product.



Scheme 3. New route for the conversion of isobutene to *p*-xylene.

Thus oxygen takes part in the reaction and such a participation can either be totally at the adsorption layer through the direct interaction between the two adsorbed alkene molecules with an oxygen atom or an oxygen molecule also adsorbed on the surface, i.e., Langmuir Hinshelwood mechanism or through the interaction of the alkene molecules on the surface with gaseous oxygen, i.e., Eley Rideal mechanism [26]. The other possibility is that the process of oxidative dehydrogenation actually takes place by scavenging oxygen from the lattice and molecular oxygen is used to replenish the lattice oxygen and the rate of replenishment actually determines the rate of oxidative dehydrogenation. Or in other words, the reaction may then follow the Mars and van Krevelen mechanism [14].

The data obtained so far by changing the partial pressure of one reactant keeping the other constant fits well into the Mars and van Krevelen mechanism according to which the rate of oxidative dehydrogenation for a reaction first order in oxygen and second order in isobutene is given by [27]

$$r_m = \frac{k_{\text{ox}} k_r p_{\text{isob}}^2 p_{\text{O}}^1}{k_r p_{\text{isob}}^2 + k_{\text{ox}} p_{\text{O}}^1}, \quad (1)$$

which may be linearised to

$$\frac{1}{r_m} = \frac{1}{k_{\text{ox}} p_{\text{O}}} + \frac{1}{k_r p_{\text{isob}}^2}. \quad (2)$$

k_{ox} and k_r are the rate constants for catalyst oxidation and reduction respectively. p_{isob} and p_{O} are the partial pressures of isobutene and oxygen, respectively.

Eq. (2) is plotted in Figs. 5a and 5b keeping the pressure of isobutene and oxygen constant at 22.5 and 15.8 kPa, respectively.

According to the reaction above, the rate constant for reduction and oxidation can be calculated and it corresponds to 2.3×10^{-6} and 32×10^{-6} mol min⁻¹ m⁻² kPa⁻¹, respectively. Thus, the rate of oxidation is more than 10 times faster than the rate of reduction inferring that the rate-determining step is the reduction of the catalyst. The activation energy for the reaction has been calculated to be 90 kJ mol⁻¹. These data are different from the results of Parera et al. [10] (125 kJ mol⁻¹ on In₂O₃) and Seiyama et al. [18] (205 kJ mol⁻¹ on SnO₂-Bi₂O₃) but are close to the results of White et al. [28] for the conversion of propene on Bi₂O₃ (92 kJ mol⁻¹). It may be noted at this point that the rate of disappearance of isobutene is second order in isobutene and first order in oxygen as the rate of formation of 2,5-DMH²⁼ and CO_x, whereas the rate of *p*-xylene formation was first order in isobutene and oxygen. According to this and all the discussions above, it can be said that *p*-xylene formation and 2,5-DMH²⁼ formation may happen through two different mechanisms and the rate of disappearance of isobutene is a composite of both these mechanisms. Rate equations for the formation of *p*-xylene were tested on the Mars and van Krevelen model and though the data did not fit nearly so well as for the disappearance of isobutene, it

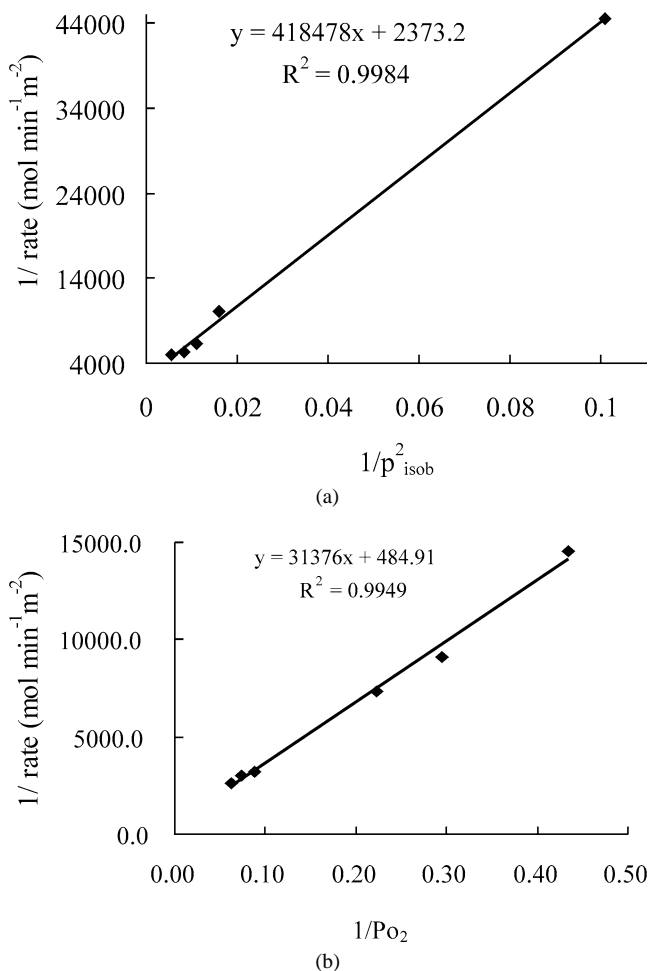


Fig. 5. (a) Mars and van Krevelen model for the overall disappearance of isobutene. Pressure of isobutene varied at a fixed oxygen pressure of 15.8 kPa at 500 °C. (b) Mars and van Krevelen model for the overall disappearance of isobutene. Pressure of oxygen varied at a fixed oxygen pressure of 22.5 kPa at 500 °C.

showed that the rate of catalyst reduction was still the rate-limiting step. For this reaction, k_r and k_{ox} are 3×10^{-5} and $8 \times 10^{-5} \text{ mol min}^{-1} \text{ m}^{-2} \text{ kPa}^{-1}$, respectively.

Thus, there is a very good fit of the data for the disappearance of isobutene with the Mars and van Krevelen model and hence it is very likely that the reaction follows this model. Further, the disruption of $\text{Bi}_2\text{Sn}_2\text{O}_7$ to Bi_2O_3 and SnO_2 during reaction also hints at this mechanism [4,29], where the oxygen of the lattice is used for the reaction. But, it may also be noted that the reaction could also obey the Langmuir Hinshelwood mechanism as described above and with the oxygen participating in the reaction it is more easy to comprehend.

The rate of the reaction first order in oxygen and second order in isobutene following Langmuir Hinshelwood model for competitive adsorption is given by Eq. (3) [28]

$$-r_{O_2} = k_2 \frac{(K_{\text{isob}} C_{\text{isob}})^2 (K_o C_o)}{(1 + K_{\text{isob}} C_{\text{isob}} + K_o C_o)^3} \quad (3)$$

k_2 is the rate constant for the reaction and K_{isob} , K_o , C_{isob} , C_o are the adsorption constants and concentrations of isobutene and oxygen, respectively. The experimental data were tested on Eq. (3), but the data did not fit nearly so well.

Thus, though mechanisms based on the Mars–van Krevelen model have usually been first order in the olefin [17], our experimental data gave a good fit in the Mars–van Krevelen model (better than for a LH mechanism). This suggests that the redox mechanism of the solid catalyst in our case proceeds with the formation of the biallyl intermediate rather than with monoallyl intermediate, i.e., with two H atom abstraction. However, a study of the kinetics of the reaction using isotopic oxygen will only authentically prove if the reaction actually follows the Mars–van Krevelen model.

4. Conclusions

This paper had started with the aim of finding the role of oxygen in the reaction and the mechanistic pathway of the reaction. It has been found that the process of oxidative dehydrogenation is first order with respect to oxygen and a certain minimum concentration is necessary to maintain the stability of the reaction, since without oxygen the system becomes highly unstable and the conversion goes down to zero within the first half an hour of the reaction and the catalyst stability (disruption retarded) is increased with the increase in O_2 concentration in the feed [29]. It has been found through the Mars and van Krevelen fit that the oxygen participates indirectly in the reaction, through replenishment of the lattice oxygen that has been scavenged in the process and the rate-determining step is the rate of catalyst reduction.

As far as the mechanistic pathway of the reaction is concerned, it has always been suggested that the reaction is a consecutive one going from isobutene to 2,5-dimethyl hexadiene and finally to *p*-xylene. Though this mechanism is easily comprehensible, our results did not prove this. According to our findings, it is shown that the conversion of isobutene to *p*-xylene is not a consecutive one. Isobutene converts to 2,5-DMH²⁼ under the reaction conditions which then gets oxidised to CO_x , while *p*-xylene is most likely to be formed by a parallel pathway directly from isobutene as described in Scheme 3.

Having identified the slow step of the reaction, it should now be possible to improve catalytic activity by incorporating additional C–H bond breaking ability into the catalyst formulation such as chromia with Bi_2O_3 [28].

References

- [1] S.M. Csicsery, J. Catal. 18 (1970) 30.
- [2] US Patent 3761536, Gulf Research & Development Company, 1973.
- [3] US Patent 3168584, 1965.
- [4] E.A. Mamedov, K.A. Mekhtiev, E.G. Gamid-Zade, R.G. Rizaev, Kinet. Katal. 14 (1977) 565.

- [5] E.A. Mamedov, Yu.D. Pankratiev, *Kinet. Catal.* 23 (1982) 772.
- [6] E.A. Mamedov, E.G. Gamid-Zade, Yu.D. Pankratiev, A.R. Kuliev, R.G. Rizaev, *React. Kinet. Catal. Lett.* 10 (1979) 19.
- [7] L.M. Kaliberdo, M.I. Tselyutina, A.S. Vaabel, V.M. Kalikhman, B.N. Shvetsov, *Russ. J. Chem.* 53 (1979) 843.
- [8] E.A. Mamedov, V.P. Vislovskii, R.G. Rizaev, *React. Kinet. Catal. Lett.* 21 (1982) 77.
- [9] T. Sakamoto, M. Egashira, T. Seiyama, *J. Catal.* 16 (1970) 407.
- [10] N.S. Parera, D.L. Trimm, *J. Catal.* 30 (1973) 485.
- [11] K. Ohdan, T. Ogawa, J. Umemura, K. Yamada, *Kogyo Kagaku Zasshi* 73 (1970) 842.
- [12] M.G. White, J.W. Hightower, *AIChE J.* 27 (1981) 545.
- [13] E.G. Gamid-Zade, E.A. Mamedov, R.G. Rizaev, *Kinet. Catal.* 20 (1978) 328.
- [14] P. Mars, D.W. van Krevelen, *Spec. Suppl. Chem. Eng. Sci.* 3 (1954) 41.
- [15] D.L. Trimm, L.A. Doerr, *J. Catal.* 26 (1972) 1.
- [16] V.S. Pashgorova, L.M. Kaliberdo, G.G. Lebedeva, *Neftekhimiya* 16 (1976) 840.
- [17] H.E. Swift, J.E. Bozik, *J. Catal.* 22 (1971) 427.
- [18] T. Seyima, T. Uda, I. Mochida, M. Egashira, *J. Catal.* 34 (1974) 29.
- [19] L. Moens, P. Ruiz, B. Delmon, M. Devillers, *Appl. Catal. A: Gen.* 171 (1998) 131.
- [20] E. Solymosi, F. Bozso, in: *Proc. 6th Intern. Congress on Catalysis*, RSC, London, 1976, p. 365.
- [21] H. Hiltner, G. Emig, *Stud. Surf. Sci. Catal.* 110 (1997) 593.
- [22] W. Martir, J.H. Lunsford, *J. Am. Chem. Soc.* 103 (1981) 3728.
- [23] A.A. Muradyan, K.G. Garigyan, K.G. Gazaryan, A.B. Nalbandyan, *Arm. Zh. Khim.* 38 (1985) 265.
- [24] A.S. Vaabel, L.B. Dubenkova, L.M. Kalibardo, *Neftekhimiya* 17 (1977) 90.
- [25] E.A. Mamedov, V.D. Sokolovskii, *Catal. Today* 14 (1992) 343.
- [26] G.C. Bond, *Heterogeneous Catalysis, Principles and Applications*, Clarendon, Oxford, 1987.
- [27] F. Benyahia, A.M. Mearns, *Appl. Catal. A: Gen.* 70 (1991) 149.
- [28] M.G. White, J.W. Hightower, *J. Catal.* 82 (1983) 185.
- [29] B. Mazumder, *Oxidative dehydrodimerisation and aromatisation of isobutene on Bi₂O₃-SnO₂*, Thesis, 2002.