

Synthesis of Maleic and Phthalic Anhydrides from the Mixture of Cyclopentene and 1-Pentene

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Abstract—The selective oxidations of cyclopentene, 1-pentene, and their mixture to maleic and phthalic anhydrides have been studied to gain information on the total utilization of olefins of C₅-fraction. The highest selectivities for maleic anhydride, a single major organic product, in individual oxidations of cyclopentene and 1-pentene were obtained at complete or almost complete conversion, and then the main byproduct was phthalic anhydride. The cooxidation of the mixture of cyclopentene and 1-pentene at ca. 100% conversion, which was selected as optimized condition, gave no interaction between cyclopentene and 1-pentene. This result indicates that two reactants can be simultaneously utilized at one oxidation unit process. In contrast, the cooxidation at low degrees of conversion gave some interaction. It was only related to the slightly stronger adsorption of cyclopentene as compared to 1-pentene.

Key words: Cooxidation, Maleic Anhydride, Phthalic Anhydride, Cyclopentene, 1-Pentene

INTRODUCTION

Today's petrochemical industry is based essentially on the use of alkenes as the main raw material, because they are easy to obtain starting from petroleum with low cost. In addition, alkenes are molecules that can be easily functionalized; thus they are versatile as raw materials. Until the present time, however, the chemical utilization of olefins of the C₅-fraction, produced in the steam cracking of naphtha, was largely limited to isoprene for the production of polymers, to methylbutenes and to cyclopentadiene [Wittcoff and Reuben, 1996; Schlepplinghoff and Schulwitz, 1985]. The reason is the similarity of their physical properties, which makes a separation into individual components uneconomical. Therefore, it is of interest to develop processes that enable the chemical utilization of olefins of the C₅-fraction without prior separation into individual components. Some time ago, a process that makes use of the acyclic branched mono- and di-olefins contained in C₅-fraction was developed [Böckler et al., 1990]. According to this process, total C₅-fraction is submitted to a mild hydrogenation which converts the diolefinic components like isoprene, piperylene and cyclopentadiene into the corresponding monoolefins. Subsequently, the hydrogenated C₅-fraction is contacted with methanol on an acidic catalyst which results in the elective reaction of the acyclic branched C₅-olefins, i.e., the isomeric 2-methylbutenes, with methanol to give tertiary amyl methyl ether, the so-called TAME [Herwig et al., 1984; Lange et al., 1985]. The latter can be used as an antiknock agent. Additionally, a proposal was advanced to make use of the olefinic components which remain in the effluent from the TAME process, the so-called C₅-raffinate [Griesbaum and Hönicke, 1986]. These C₅-olefins, cyclopentene, 1-pentene and 2-pentene, amount

to ca. 54% of the C₅-raffinate. According to the above proposal, these C₅-olefins could be separated from the saturated C₅-hydrocarbons of C₅-raffinate by an extractive distillation and subsequently oxidized to give a mixture of maleic anhydride (MA) and phthalic anhydride (PA).

On the other hand, most previous investigations on the oxidations of C₅-hydrocarbons have been focused on the conversion of n-pentane [Centi et al., 1987, 1989, 1990b], 1,3-pentadiene [Miura et al., 1992] and cyclopentadiene [Jun et al., 1986, 1991; Kim et al., 1988], which are major components in the C₅-fraction. The oxidations of cyclopentene, 1-pentene and 2-pentene, however, have rarely been recognized in the scientific literature. Only a few papers have reported on their oxidations [Hönicke et al., 1982a, 1984, 1987; Butt and Fish, 1966].

In order to gain information on the simultaneous utilization of the mixture of cyclopentene, 1-pentene and 2-pentene, in this paper we tried to (i) discover the optimum condition from the individual oxidations of cyclopentene and 1-pentene and to (ii) identify an interaction between reactants in the cooxidation of the mixture of cyclopentene and 1-pentene.

EXPERIMENTAL

1. Preparation and Characterization of the Catalyst

A V/Mo/P/Al/Ti-mixed oxide catalyst was prepared by the following method reported by Hönicke et al. [1982b].

Step a: In a 2 l beaker, 1,600 ml of water was acidified to pH=1 with 140 ml of 65%-nitric acid and heated to 50 °C. Then, 145.5 g of ammoniummolybdate [(NH₄)₆Mo₇O₂₄·4H₂O] was added and dissolved with stirring. Finally, a mixture of 10.0 g of concentrated phosphoric acid in 50 ml of water was added dropwise. Stirring of the resulting slurry was continued for 2 h. The precipitate was filtered off and dried for 4 h at 120 °C to give 116.78 g of ammoniumphosphomolybdate [(NH₄)₃P(Mo₃O₁₀)₄].

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Step b: In a 1 l beaker, 18.75 g of powdered vanadium pentoxide (V_2O_5) was suspended with stirring in 156.25 ml of water at 70 °C. Then, 41.25 g of powdered oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) was added in small portions to keep the ensuing gas evolution under control. After V_2O_5 was completely dissolved, 41.73 g of $(NH_4)_3P(Mo_3O_{10})_4$, 108.60 g of powdered TiO_2 (anatase) and 26.88 g of powdered $\gamma-Al_2O_3$ were added to the dark blue solution, and water was subsequently evaporated with vigorous stirring until a viscous mass remained. The latter was spread out on a glass plate and dried for 24 h at 170 °C. The resulting dry mass was removed from the plate, crushed and sieved. The fraction, which is a particle size of 1.0-1.5 mm diameters, was heated in a stream of air for 17 h at 400 °C to give a final catalyst.

According to the proportions of the starting materials used, the mass ratio of the sum of the active components V/Mo/P-oxide of the catalyst to the catalyst supports Al/Ti-oxide was calculated by Eq. (1) to be 27.2%. The atomic ratio of the active components V/Mo/P was 41.6 : 53.9 : 4.5 and the mass ratio of the two supports was 80% TiO_2 and 20% $\gamma-Al_2O_3$.

$$\frac{M_V + M_{MO} + M_P}{M_{TiO_2} + M_{\gamma-Al_2O_3}} \cdot 100\% = 27.2\% \quad (1)$$

where, M_V , M_{MO} and M_P : atomic weights of V, Mo and P
 M_{TiO_2} and $M_{\gamma-Al_2O_3}$: weights of TiO_2 and $\gamma-Al_2O_3$.

The specific surface area of the catalyst was 14.87 m^2/g and the specific pore volume was 0.19 cm^3/g . The pore diameters were mainly observed in the range of 0.15 μm and 0.30 μm , and the mean pore diameter was 0.21 μm . The bulk density of the catalyst was 1.20 g/cm^3 .

2. Experimental Procedure

The oxidations of cyclopentene, 1-pentene, and their mixture were carried out in a conventional flow apparatus as shown in Fig. 1 at near atmospheric total pressure. The fixed bed reactor consisted of a quartz tube, having 1.9 cm i.d. and 33 cm of length.

A movable thermocouple immersed in the catalyst bed was used to monitor the reactor temperature controlled at better than ± 0.3 °C along the catalyst bed length. The amount of catalyst used was 3.6 g and the catalyst bed was diluted (1 : 2) with inert quartz particles to avoid adverse thermal effects. Without a catalyst, there were no detectable conversions of hydrocarbons.

The hydrocarbons (i.e., cyclopentene and 1-pentene) were transferred into the saturators which were kept at constant temperatures. To feed these substrates to the reactor, constant flows of nitrogen were sequentially passed through the drying tube, saturators and preheater. In the preheater, hydrocarbons in nitrogen and air were mixed. The mixed stream entered into the reactor with a total oxidation catalyst. The effluent from the reactor was passed through a trap, kept at 0 °C and through a filter into the gas chromatograph equipped with a CarboxenTM 1000 packed column and a thermal conductivity detector (TCD) where the amount of CO_2 was determined by GC analysis. The concentration of the feed in the nitrogen stream was adjusted with the help of the mass flow controller based on the data for CO_2 . When the desired feed concentration was reached, the mixed stream from the preheater was passed through a selective oxidation reactor with a V/Mo/P/Al/Ti-mixed oxide catalyst. For analytical purposes, minor amounts of feed and effluent streams from the reactor were passed through an aluminum block heater to the gas chromatograph equipped with a CP-Sil-5 capillary column and a flame ionization detector (FID) for on-line analysis. The major part of the effluent from the reactor was passed through a series of three traps, which were sequentially kept at 0 °C, -40 °C and -78 °C in order to recover water and the organic oxidation products. The effluent from the third trap was passed through gas chromatograph equipped with a CarboxenTM 1000 packed column and a TCD detector in order to determine the amounts of CO and CO_2 formed.

3. Analyses

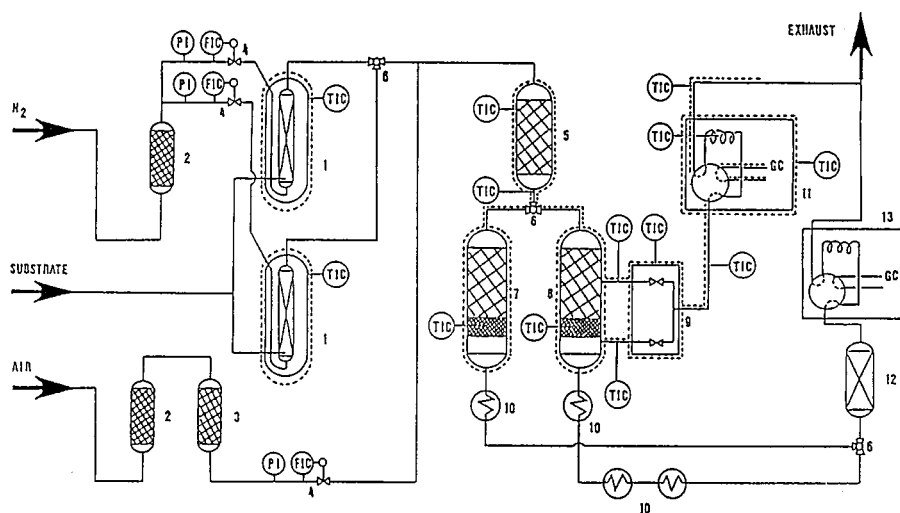


Fig. 1. Schematic diagram of the apparatus for the oxidation.

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|-----------------------------|------------------------------------|--|
| 1. Saturator | 6. Three way cock | 11. Gas chromatograph equipped with FID detector |
| 2. Drying tube (bluegel) | 7. Reactor for total oxidation | 12. Filter |
| 3. Drying tube (P_2O_5) | 8. Reactor for selective oxidation | 13. Gas chromatograph equipped with TCD detector |
| 4. Mass flow controller | 9. Aluminum block heater | |
| 5. Preheater | 10. Cooling traps | |

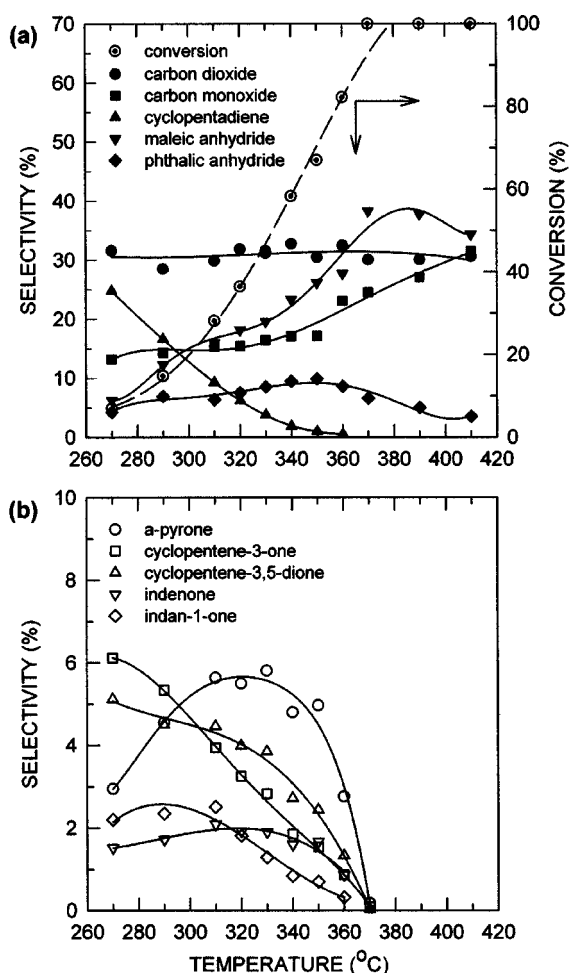


Fig. 2. Conversion and selectivities for selected organic products in the oxidation of cyclopentene. Experimental conditions: 0.4 vol% of cyclopentene; a GHSV of 20,000 h⁻¹.

For the analyses of organic oxidation products, a Hewlett-Packard type 5890A gas chromatograph, equipped with a 25 m × 150 μm fused silica capillary column coated with CP-Sil-5 and a FID detector, was used. The carrier gas was nitrogen with a flow of 0.3 ml/min, the program used was 10 min at 30 °C, followed by 6 °C/min up to 90 °C and 10 °C/min up to 200 °C. For the analyses of CO and CO₂, a Hewlett-Packard type 5890A gas chromatograph, equipped with a 10 ft × 1/8 inch CarboxenTM 1000 packed column and a TCD detector, was used. The carrier gas was helium with a flow of 20 ml/min, the program used was 7 min at 35 °C, followed by 10 °C/min up to 200 °C and then maintained at 200 °C for 20 min. The peaks for CO and CO₂ appeared at the retention times of 5.75 min and 17.37 min, respectively. The organic products condensed in the traps were analyzed by GC- and GC/MS-methods. The GC/MS analyses were carried out on a Hewlett-Packard system 5985B equipped with a 50 m × 200 μm fused silica capillary column coated with 5% phenyl-methyl-silicon. The conditions were: 30 °C for 10 min, 6 °C/min up to 90 °C, and then 10 °C/min up to 250 °C.

The degree of total conversion of substrates (U), the degree of conversion of cyclopentene (U_1) and the degree of conversion of 1-pentene (U_2) were calculated according to Eqs. (2), (3)

and (4), respectively.

$$U = \frac{(A_{1f} + A_{2f}) - (A_{1p} + A_{2p})}{(A_{1f} + A_{2f})} \cdot 100\% \quad (2)$$

$$U_1 = \frac{A_{1f} - A_{1p}}{A_{1f}} \quad (3)$$

$$U_2 = \frac{A_{2f} - A_{2p}}{A_{2f}} \quad (4)$$

where, A_{1f} and A_{2f} : the peak areas of cyclopentene and 1-pentene in the feed stream

A_{1p} and A_{2p} : the peak areas of cyclopentene and 1-pentene in the effluent stream.

The selectivities of oxidation products, defined as mole percentage selectivities on a carbon account for basis, were calculated by Eqs. (5), (6), (7) and (8). The response factors f_i and f_j were estimated by using a method suggested by Ackman [1964, 1968]. The correctness of use of the response factors was identified by the values which were determined by injecting authentic samples of obtained products and by comparison of the peak integration values.

$$S_{CO_x} = \frac{Y_{CO_x}}{C_i \cdot Y_{HC}} \cdot U/100 \cdot 100\% \quad (5)$$

$$S_{org.} = 100\% - (S_{CO} + S_{CO_2}) \quad (6)$$

$$S_i = S_{org.} \cdot X_i \quad (7)$$

$$X_i = \frac{A_i \cdot f_i}{\sum A_j \cdot f_j} \quad (8)$$

where, S_{CO_x} : the selectivities of CO_x (i.e. CO and CO₂)

$S_{org.}$: the selectivity for the sum of all organic products

S_i : the selectivity of an individual organic product i

Y_{CO_x} : the volume percentages of CO_x

Y_{HC} : the concentration of the substrate in the feed gas

C_i : the number of carbon atoms of the substrate

X_i : the molar ratio of component i

A_i and A_j : the peak areas of components i and j

f_i and f_j : the response factors of the components i and j .

RESULTS AND DISCUSSION

1. Identification of Reaction Products

The oxidation reactions of cyclopentene, 1-pentene and their mixture were carried out by using a concentration of 0.4 vol% of the respective hydrocarbons, 3.6 g (3 ml) of catalyst and a constant space velocity of 20,000 h⁻¹. The organic oxidation products were characterized on the basis of the identity of their gas-chromatographic retention times with those of authentic samples and/or based on their mass spectra which were obtained by GC/MS analyses.

At high degrees of conversion above 99% only a few organic products were obtained, as evidenced by gas chromatograms which were obtained by on-line analyses. The single major product was MA, obtained both from cyclopentene and from 1-pentene as starting material. The second product formed from

either substrates was PA. However, starting from 1-pentene, PA was formed in considerably lower proportion than starting from cyclopentene. In addition to MA and PA, the oxidation of 1-pentene afforded also citraconic anhydride (CA).

At low and intermediate degrees of conversion a considerable number of products were obtained. From the oxidation of cyclopentene a total of 20 organic products were detected. They were identified as acetaldehyde, acrolein, furan, cyclopentadiene, acetic acid, benzene, acrylic acid, 3-pentene-2-one, cyclopentanone, MA, cyclopentene-3-one, cyclopentene-3,5-dione, 5-methylene-2-furanone, α -pyrone, benzaldehyde, indenone, indan-1-one, PA, bicyclo(2,2,1)hept-5-ene-2,3-dicarboxic anhydride, cumarine, 9-fluorenone. From the oxidation of 1-pentene a total of 25 organic products were detected. They were identified as formaldehyde, propylene, acetaldehyde, acrolein, acetone, trans-2-pentene, cis-2-pentene, acetic acid, benzene, 2-pentanone, 3-pentanone, acrylic acid, 3-pentene-2-one, MA, cyclopentene-3-one, cyclopentene-3,5-dione, 5-methylene-2-furanone, CA, α -pyrone, indenone, indan-1-one, PA, 3-methyl-phthalic anhydride, cumarine, 9-fluorenone. That is, oxidation of 1-pentene gave a greater variety of products than oxidation of cyclopentene. Independent from the starting material, there were three types of products formed, namely,

(a) C_1 - C_3 -products which result from the cleavage of the original C_5 -carbon skeleton and which can not be converted into the target product MA or PA,

(b) acyclic and monocyclic oxygenated C_4 - C_5 -products which could be precursors for MA, and

(c) bicyclic oxygenated products which could be precursors for PA.

2. Individual Oxidations

2-1. Oxidation of Cyclopentene

The effect of the reaction temperature upon the conversion and upon the product selectivities in the oxidation of cyclopentene was studied by raising the temperature from 270 °C to 410 °C. The changes in the conversion of cyclopentene and in the selectivities of reaction products are shown in Fig. 2a and b. The conversion increased with increasing temperatures and reached ca. 100% at 370 °C. The selectivity for CO_2 was almost constant at about 30% in the entire range of temperatures. It was observed that the selectivity for CO very weakly increased at below 350 °C, while it considerably increased above the temperature with the increase of temperature. It may be considered that the results from the over-oxidation of other organic oxidation products besides MA. Organic oxidation products in the oxidation of cyclopentene were identified as a total 20 numbers including MA and PA as the above mentioned. The selectivity for MA reached a maximum of 38.8% at 370 °C; the selectivity for PA passed through a maximum of 9.9% at 350 °C. Besides, cyclopentadiene, cyclopentene-3-one, cyclopentene-3,5-dione, α -pyrone, indenone and indan-1-one, potential intermediates for the formation of MA and PA, showed relatively lower selectivities. The selectivities for cyclopentadiene, cyclopentene-3-one and cyclopentene-3,5-dione decreased continuously, while those for α -pyrone, indenone and indan-1-one passed through maxima with increasing the temperature. However, they were no

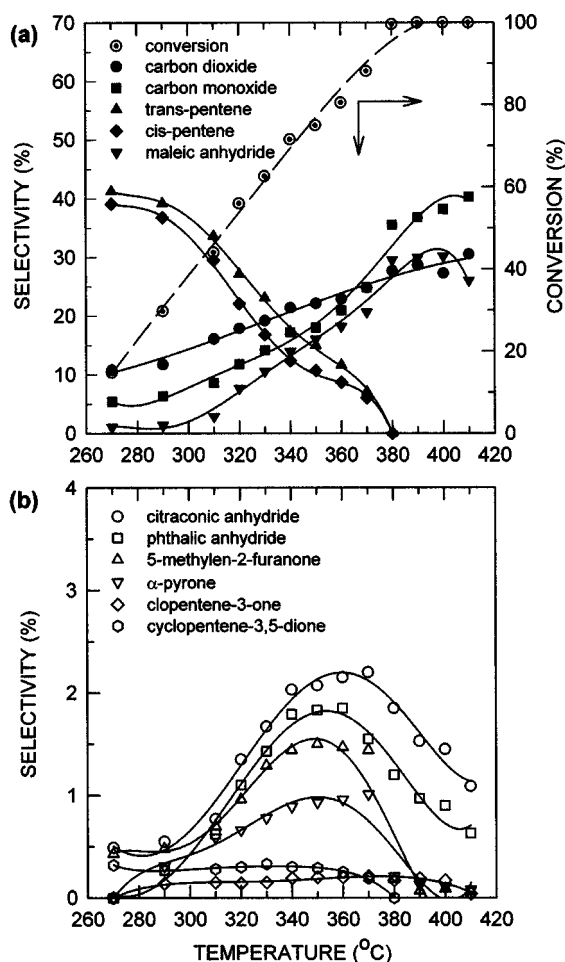


Fig. 3. Conversion and selectivities for selected organic products in the oxidation of 1-pentene. Experimental conditions: 0.4 vol% of 1-pentene; a GHSV of 20,000 h^{-1} .

longer formed at temperatures above 370 °C reaching complete and almost complete conversion.

2-2. Oxidation of 1-Pentene

The effect of the reaction temperature upon the conversion and upon product selectivities in the oxidation of 1-pentene was also studied by raising the temperature from 270 °C to 410 °C. Fig. 3a shows that below a reaction temperature of 380 °C the conversion increased almost steadily up to nearly 100%. Both selectivities for CO and CO_2 continuously increased with increasing the temperature, but the proportion of the increase for the selectivity of CO more greatly appeared compared with that for the selectivity of CO_2 .

Organic oxidation products in the oxidation of 1-pentene were identified as a total 25 numbers including MA, PA and CA. The main results obtained are shown in Fig. 3a and b. High selectivities for trans- and cis-2-pentene, which were isomerization products of 1-pentene, can be observed at lower temperature. With increasing the temperature, however, the selectivities for the isomerization products decreased, and they disappeared at the above temperature of 380 °C. The selectivity for the major product MA increased remarkably with increasing the temperature up to a maximum value of 30.2% at 400 °C. The selectivities

for CA and PA as the by-products passed through maximum values, viz. 2.3% for CA at 370 °C and 1.8% for PA at 350 °C. The potential intermediate products on the way from 1-pentene to MA, viz. α -pyrone, cyclopentene-3-one, cyclopentene-3,5-dione and 5-methylene-2-furanone were formed in considerably lower selectivities than the other products mentioned above. The selectivities of all of these minor products passed through maxima with increasing conversion levels. It is in line with the contention that they are intermediate products. Besides, the formation of acetaldehyde and acetic acid which resulted from the cleavage of the original C₅-carbon skeleton could be observed.

3. Cooxidation of the Mixture of Cyclopentene and 1-Pentene

The cooxidation of the mixture of cyclopentene and 1-pentene was studied by using a concentration of 0.4 vol% of the hydrocarbons and 3.6 g of catalyst. Two sets of experiments were carried out. According to the results in individual oxidations, the maximum yield of MA as desired product was obtained at complete or almost complete conversion of substrates. The yield of CA as undesired product decreased as the reaction temperature increased. Therefore, in the first set, a reaction temperature of 390 °C and a GHSV of 20,000 h⁻¹ were chosen as the optimized reaction condition, and the interaction between cyclopentene and 1-pentene was investigated at ca. 100% of conversion. In the second set, the interaction was also investigated at low degrees of conversion. For the decrease of conversion the reaction temperature was decreased, while a GHSV of 20,000 h⁻¹ was kept constant.

On the other hand, to identify the interaction between substrates in the cooxidation, it is necessary to calculate the theoretical selectivities and conversions if no interactions occur. Therefore, the following assumptions are made:

(1) The adsorption probability of a reactant molecule on the catalyst surface in the cooxidation is equal to that in their individual oxidations.

(2) The conversions of cyclopentene and 1-pentene in the mixture are equal to those in their individual oxidations.

(3) The fraction of a component in the mixture, which is converted to a product *i* is equal as that in the individual oxidation of the component.

Using these assumptions, the conversion of the mixture (U_{mix}) and selectivity to a product *i* (S_i) were calculated according to Eqs. (9) and (10), respectively.

$$U_{mix} = U_1^* \cdot f_1 + U_2^* \cdot (1 - f_1) \quad (9)$$

$$S_i = \frac{U_1^* \cdot S_{i,1}^* \cdot f_1 + U_2^* \cdot S_{i,2}^* \cdot (1 - f_1)}{U_1^* \cdot f_1 + U_2^* \cdot (1 - f_1)} \quad (10)$$

The data marked with an asterisk(*) are those obtained by the individual oxidations of the two components. f_1 is the fraction of component 1 in the mixture. The conversions U_1^* and U_2^* and the selectivities $S_{i,1}^*$ and $S_{i,2}^*$ have to be determined experimentally in the individual oxidations of the two components.

3-1. Cooxidation at ca. 100% Conversion

Changes in product selectivities were studied by varying the

mixing ratio of cyclopentene and 1-pentene. In this set, all values of theoretical and experimental conversion (U_1^* , U_2^* , and U_{mix}) were 100%. Therefore, Eq. (10) was simply rearranged to Eq. (11).

$$S_i = S_{i,1}^* \cdot f_1 + S_{i,2}^* \cdot (1 - f_1) \quad (11)$$

The yields of organic products other than MA, PA and CA were almost negligible. Accordingly, changes in selectivities to MA, PA and CA according to the mixing ratios of cyclopentene and 1-pentene were mainly observed. The selectivity to MA plotted over the fraction of cyclopentene is shown in Fig. 4. The dashed line represents the calculated selectivities and the filled circles are the experimental data. There were only a few differences between the calculated and experimental data, which were within the ex-

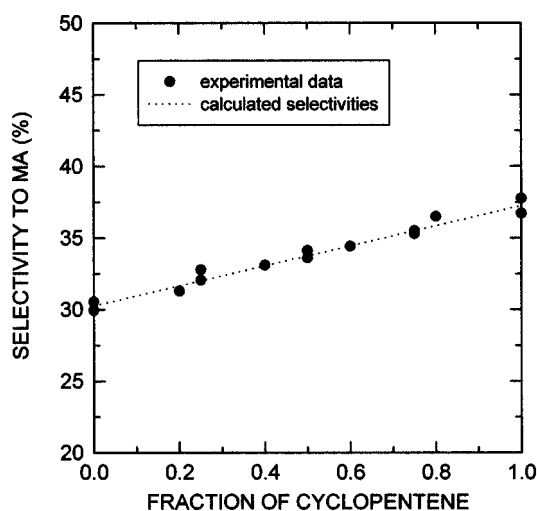


Fig. 4. Selectivity to MA vs. the fraction of cyclopentene in the cooxidation of mixed 1-pentene and cyclopentene at 390 °C. Experimental conditions: 0.4 vol% hydrocarbon; a GHSV of 20,000 h⁻¹.

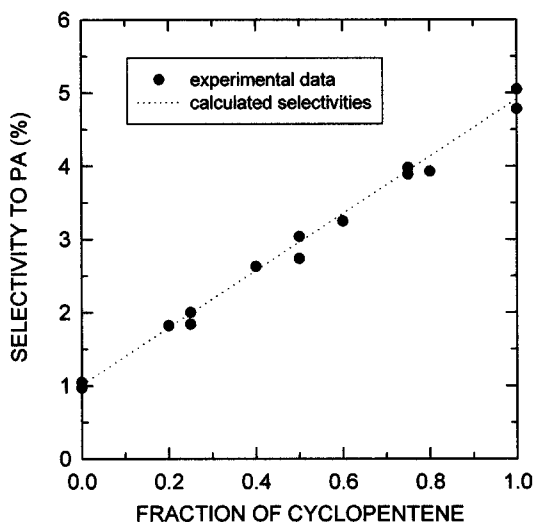


Fig. 5. Selectivity to PA vs. the fraction of cyclopentene in the cooxidation of mixed 1-pentene and cyclopentene at 390 °C. Experimental conditions: 0.4 vol% hydrocarbon; a GHSV of 20,000 h⁻¹.

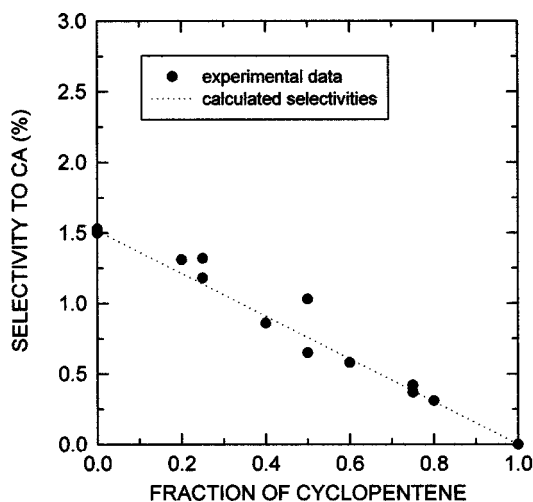


Fig. 6. Selectivity to CA vs. the fraction of cyclopentene in the cooxidation of mixed 1-pentene and cyclopentene at 390 °C. Experimental conditions: 0.4 vol% hydrocarbon; a GHSV of 20,000 h⁻¹.

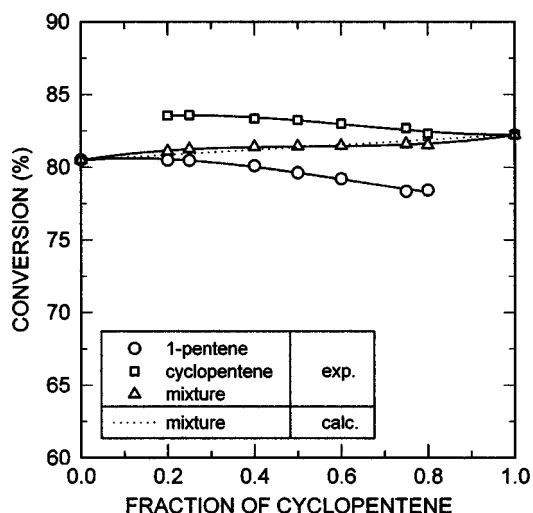


Fig. 7. Conversions vs. the fraction of cyclopentene in the cooxidation of mixed 1-pentene and cyclopentene at 360 °C. Experimental conditions: 0.4 vol% hydrocarbon; a GHSV of 20,000 h⁻¹.

perimental error. Accordingly, increasing and inhibiting effects concerning the selectivity to MA are not found. The selectivities to PA and CA plotted over the fraction of cyclopentene are shown in Figs. 5 and 6, respectively. There were also a few differences between the calculated and experimental data, and hence increasing and inhibiting effects concerning the selectivities to PA and CA were also not found. Accordingly, interactions between 1-pentene and cyclopentene were not observed in the cooxidation at ca. 100% conversion.

3-2. Cooxidation at Low Degrees of Conversion

There is a structural difference between cyclopentene and 1-pentene, because the former is a cyclic monoolefin and the latter is a linear monoolefin. So, it is considered that minor differences of reaction phenomena due to the structural difference of reactants exist during the cooxidation on the catalyst. Cooxidation at low degrees of conversion, however, required to identify the effect due to the structural difference of those because any interaction was not found in the cooxidation at ca. 100% conversion. The cooxidations of the mixture of cyclopentene and 1-pentene at low degrees of conversion were studied by varying the reaction temperature and the mixing ratio. The theoretical conversion of the mixture and theoretical selectivities were calculated according to Eqs. (9) and (10).

While comparing the experimental data with the calculated values in the cooxidation at 380 °C and 360 °C, also no differences were observed. The results in the cooxidation at 360 °C as representative are shown in Figs. 7 and 8.

However, the cooxidation at 340 °C indicated specific results as shown in Fig. 9. The conversion of 1-pentene and that of cyclopentene showed obviously a different behavior: in the case of 1-pentene, increasing cyclopentene content in the mixture yielded a decreasing conversion of 1-pentene until a constant level of conversion of about 60% was reached at a cyclopentene fraction of 0.75, and in the case of cyclopentene, increasing 1-pentene content in the mixture yielded an increasing conversion of 1-pentene until a constant level of conversion of about 72%

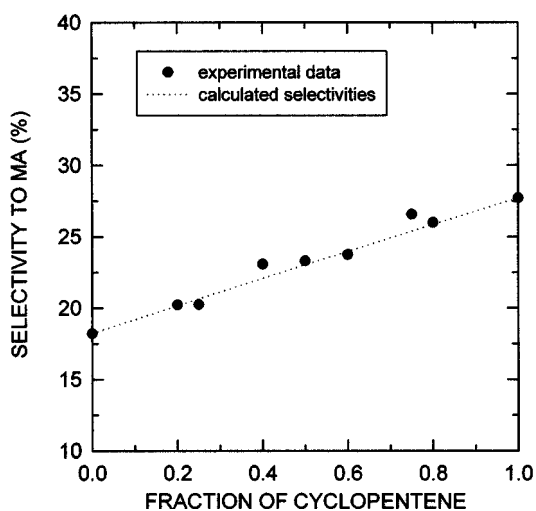


Fig. 8. Selectivity to MA vs. the fraction of cyclopentene in the cooxidation of mixed 1-pentene and cyclopentene at 360 °C. Experimental conditions: 0.4 vol% hydrocarbon; a GHSV of 20,000 h⁻¹.

was reached at a cyclopentene fraction of 0.25. The former was lower than the conversion of 72% obtained by the individual oxidation of 1-pentene, and the latter was higher than the conversion of 58% obtained by the individual oxidation of cyclopentene. These interactions also influenced the selectivities. Fig. 10 showed the selectivity to the main product, MA, as a function of cyclopentene fraction. The experimental selectivities were found higher than the calculated selectivities for all compositions of the mixture. The highest deviation between experimental and calculated data was found at nearly equimolar mixture. To confirm the interaction, the cooxidation at 320 °C was examined at various compositions of 1-pentene and cyclopentene. The interaction between reactions observed at 320 °C was similar to that at 340 °C. Consequently, the conversion of 1-pentene was inhibited by the

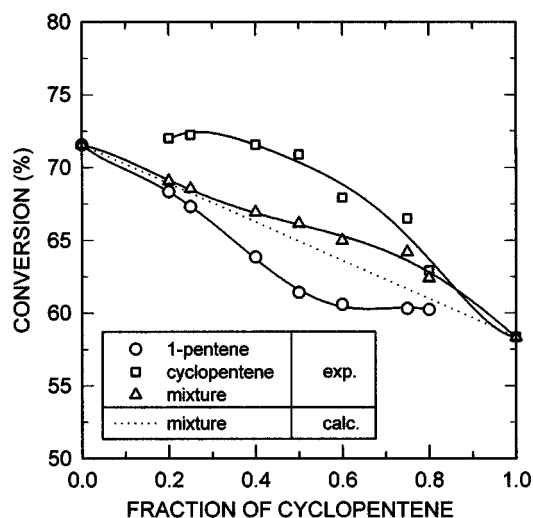


Fig. 9. Conversions vs. the fraction of cyclopentene in the cooxidation of mixed 1-pentene and cyclopentene at 340 °C. Experimental conditions: 0.4 vol% hydrocarbon; a GHSV of 20,000 h⁻¹.

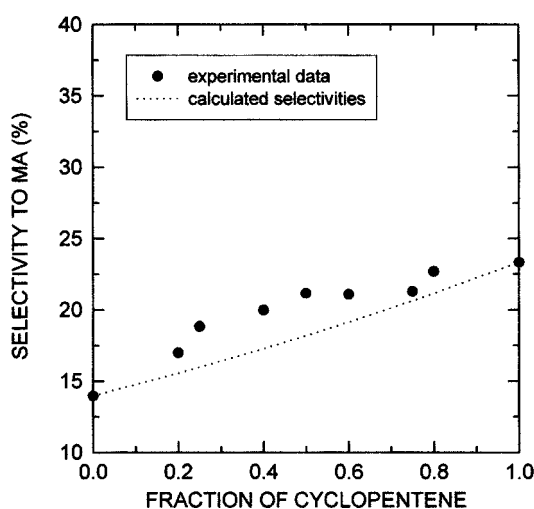


Fig. 10. Selectivity to MA vs. the fraction of cyclopentene in the cooxidation of mixed 1-pentene and cyclopentene at 340 °C. Experimental conditions: 0.4 vol% hydrocarbon; a GHSV of 20,000 h⁻¹.

existence of cyclopentene, while the conversion of cyclopentene was promoted by the existence of 1-pentene in the cooxidation below 360 °C. In these conditions, it was observed that the selectivities to MA, a major desired product, were also higher than the calculated selectivities. It may be considered as the mixed effect due to the decreased conversion of 1-pentene and the increased conversion of cyclopentene.

In this connection, we would like to explain the behavior of reactants in terms of the reaction mechanism. It was found that the oxidation of cyclopentene on a V/Mo/P/Al/Ti-mixed oxides catalyst indeed afforded the mixtures of MA and PA as main products. The formation of the latter, in particular, has been focused on as a new type of heterogeneous mechanism of oxidation from the fundamental point of view, since it is one of the

few examples of a selective oxidation reaction with the formation of products with higher C atom numbers than the starting material [Hönicke et al., 1984; Centi et al., 1987, 1989, 1990a]. It was proposed that PA from the oxidation of cyclopentene could be formed by a series of reaction steps via bicyclo[2,2,1]hept-5-en-2,3-dicarboxylic anhydride from Diels-Alder reaction between MA and cyclopentadiene and via tricyclic anhydride from Diels-Alder reaction of MA and α -pyrone [Hönicke et al., 1984]. On the other hand, it was also assumed that the most probable mechanism of PA formation from the oxidation of linear C₅-olefin is a series of reaction steps via a Diels-Alder-like reaction between MA and a pentadiene [Miura et al., 1992]. Fig. 2 and Fig. 3 show that PA can be formed more easily from cyclopentene rather than 1-pentene. Therefore, the addition of cyclopentene in the gas phase should favor PA synthesis according to a Diels-Alder mechanism with intermediates. However, the cooxidation experiments at ca. 100% conversion do not provide evidence on this question as shown in Fig. 4 and Fig. 5. In fact, the addition of cyclopentene to 1-pentene does not affect the formation of the two anhydrides. This result suggests indirectly that one reactant is not participating in a reaction mechanism for the syntheses of anhydrides from the other reactant. Additionally, it seems quite possible that the synthetic reaction of PA does not involve a gas phase Diels-Alder reaction, but rather a surface Diels-Alder-like reaction between two adsorbed species as suggested by Centi et al. [1990b]. In line with these thoughts, the higher reactivity of cyclopentene shown in the cooxidation at low degrees of conversion may be attributed to the slightly stronger adsorption of cyclopentene as compared with 1-pentene.

CONCLUSIONS

In the first part, the individual oxidations of cyclopentene and 1-pentene with air have been carried out on a V/Mo/P/Al/Ti-mixed oxide catalyst in a fixed bed integral reactor. At the high levels of conversion, maleic anhydride was in each case the single major organic product along with phthalic anhydride as the main byproduct. The highest selectivities for maleic anhydride, ca. 39% from cyclopentene and ca. 30% from 1-pentene, were obtained at complete or almost complete conversion.

In the second part, the cooxidation of the mixture of cyclopentene and 1-pentene with air has been carried out on the same catalyst. The interactions between reactants were not found in the cooxidation at ca. 100% conversion selected as optimized condition, which indicates that two reactants can be simultaneously utilized at one oxidation unit process. In contrast, the cooxidation at low degrees of conversion gave such interaction. The conversion of 1-pentene was inhibited by the existence of cyclopentene, while that of cyclopentene was promoted by the existence of 1-pentene during the cooxidation. In these conditions, it was observed that the selectivities to MA, a major desired product, were higher than the calculated selectivities, which may be considered as the mixed effect due to the decreased conversion of 1-pentene and the increased conversion of cyclopentene. Accordingly, the interaction which existed in the cooxidations at low degrees of conversion was only related to the slightly stronger adsorption of cyclopentene as compared with 1-pentene.

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REFERENCES

- Ackman, R. G., "Fundamental Groups in the Response of Flame Ionization Detectors to Oxygenated Aliphatic Hydrocarbons," *J. of Gas Chromatography*, **4**, 173 (1964).
- Ackman, R. G., "The Flame Ionization Detector, Further Comments on Molecular Breakdown and Fundamental Group Responses," *J. of Gas Chromatography*, **6**, 497 (1968).
- Böckler, R., Cordes, G. and Smolen, H., "Development of a Petrochemical Process from Laboratory Scale Tests to a Commercial Plant," *Chem.-Ing.-Tech.*, **62**, 447 (1990).
- Butt, N. S. and Fish, A., "The Vanadium-Pentoxide-Catalyzed Oxidation of Pentenes: II. Straight-Chain Pentenes," *J. Catal.*, **5**, 494 (1966).
- Centi, G., Burattini, M. and Trifiró, F., "Oxi-condensation of n-Pentane to Phthalic Anhydride," *Appl. Catal.*, **32**, 353 (1987).
- Centi, G., Nieto, J. L., Iapalucci, C., Brückman, K. and Serwicka, E. M., "Selective Oxidation of n-Pentane on 12-Molybdovanadophosphoric Acids," *Appl. Catal.*, **46**, 197 (1989).
- Centi, G., Golinelli, G. and Busca, G., "Modification of the Surface Pathways in Alkane Oxidation by Selective Doping of Brønsted Acid Sites of Vanadyl Pyrophosphate," *J. Phys. Chem.*, **94**, 6813 (1990a).
- Centi, G., Nieto, J. L., Pinelli, D., Trifiró, F. and Ungarelli, F., "Synthesis of Phthalic and Maleic Anhydrides from n-Pentane: Reactivity of Possible Intermediates and Co-feeding Experiments," *New Developments in Selective Oxidation*, Centi, G. and Trifiró, F., eds., Elsevier Science Publishers B. V., Amsterdam, 635 (1990b).
- Griesbaum, K. and Hönicke, D., "Möglichkeiten zur Chemischen Nutzung von Olefinischen Kohlenwasserstoffen der C₅-Fraktionen von Naphtha-Steamcrackern," *Erdöl, Erdgas, Kohle*, **102**, 366 (1986).
- Herwig, J., Schlepplinghoff, B. and Schulwitz, S., "New Low Energy Process for MTBE and TAME," *Hydrocarbon Processing*, (6), 86 (1984).
- Hönicke, D. and Griesbaum, K., "Katalysierte Selektivoxidation von Cyclopenten," *Chem. Ing. Tech.*, **54**, 497 (1982a).
- Hönicke, D. and Griesbaum, K., "A Catalyst for the Selective Oxidation of Chlorinated Dienes to Chlorinated Anhydrides," *Appl. Catal.*, **2**, 177 (1982b).
- Hönicke, D., Bühner, R. and Newrzella, A., "Zur Chemischen Verwendung von Nebenprodukten des Steamcrackers: Selektivoxidation von Cyclopenten und Cyclopentadien," *Erdöl und Kohle, Erdgas, Petrochem.*, **37**, 569 (1984).
- Hönicke, D., Griesbaum, K., Augenstein, R. and Yang, Y., "Heterogen Katalysierte Selektivoxidation von n-Pentenen und n-Pentadien," *Chem. Ing. Tech.*, **59**, 222 (1987).
- Jun, K. W., Chang, Y. K., Jung, S. J. and Lee, K. W., "Oxidation of Cyclopentadiene over Vanadium Oxide and Its Mixed Oxides," *Korean J. Chem. Eng.*, **3**, 135 (1986).
- Jun, K. W. and Lee, K. W., "The Effect of Silver Addition on Catalytic Properties of Vanadia Catalyst for Oxidation of Cyclopentadiene," *Korean J. Chem. Eng.*, **8**, 67 (1991).
- Kim, J. S., Park, N. C. and Kim, Y. C., "Synthesis of Maleic Anhydride over Mixed Oxide Catalyst(I)-Catalytic Oxidation of Cyclopentadiene over V-Mo-P Catalyst," *HWAHAK KONGHAK*, **26**, 149 (1988).
- Lange, P. M., Martinola, F. and Oeckl, S., "Use Bifunctional Catalysts for MTBE, TAME and MIBK," *Hydrocarbon Processing*, (12), 51 (1985).
- Miura, M., Schultheis, K. and Griesbaum, K., "Heterogeneously Catalyzed Gas Phase Oxidation of 1,3-Pentadiene-Cyclodimers and of Related Substances," *Appl. Catal. A*, **87**, 241 (1992).
- Schlepplinghoff, B. and Schulwitz, B., "Wege zur Erzeugung von Hochoktanigen Komponenten aus Petrochemischen Produktströmen," *Erdöl und Kohle, Erdgas, Petrochemie*, **38**, 209 (1985).
- Wittcoff, H. A. and Reuben, B. G., "Industrial Organic Chemicals," John Wiley & Sons, Inc., New York (1996).