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Oxidation of Propylene with Air in Barrier Discharge in the Presence of Octane

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Abstract—Oxidation of propylene with air in barrier discharge was studied. The effect exerted on the propylene conversion and on the selectivity of propylene oxide formation by replacement of oxygen with air in the course of propylene oxidation was examined.

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Propylene oxide is a valuable raw material for petrochemical and organic synthesis. Today the most efficient synthetic route to propylene oxide is the hydroperoxide procedure ensuring 95-99% yield of propylene oxide in the reaction of hydrogen peroxide with propylene in the presence of a titanium-silicon catalyst [1]. However, both the catalyst and hydrogen peroxide are expensive, which makes it topical to look for cheaper procedures for propylene oxide production. Gas-phase processes attract the greatest attention as being more convenient in implementation. For example, with oxygen and a silver-containing catalyst modified with various additives, 14 wt % conversion of propylene with 34–53 wt % selectivity of propylene oxide formation is attained [2, 3]. With air as oxidant and silver- or gold-containing catalysts, propylene oxide is formed with 18-30 wt % selectivity at 1.5-12 wt % conversion of propylene [4-6]. The other products formed along with propylene oxide are acetaldehyde, propanal, acetone, acrolein, methanol, and ethanol. All the above methods have such drawbacks as the need for preparation and regeneration of catalysts and the use of high temperatures (150-400°C).

As we showed previously [7], in oxidation of propylene with oxygen in barrier discharge (BD) propylene oxide is formed in a yield of approximately 43 wt % [7]. The reaction occurs at atmospheric pressure without catalysts and does not require elevated temperatures. These facts make the plasmachemical procedure for preparing propylene oxide, as alternative to catalytic methods, promising for practical use.

In this study we examined the possibility of using a cheaper oxidant, air, for preparing propylene oxide in BD.

EXPERIMENTAL

Experiments were performed in a flow-through gasdischarge coaxial reactor. The installation and analysis procedure are described elsewhere [8]. Propylene was fed to the reactor at a rate of 5.4 cm³ min⁻¹ (9 vol %), and oxygen, at a rate of 54.6 cm³ min⁻¹ (91 vol %). The total flow rate of the gas mixture was $60 \text{ cm}^3 \text{ min}^{-1}$. The propylene oxidation products were removed from the discharge zone with octane: Octane vapor was fed to the reactor from the vaporizer and was condensed on the cooled wall of the reactor [9]. The liquid hydrocarbon film formed on the wall drained to the receiver together with the dissolved reaction products. The octane flow rate was 0.1 cm³ min⁻¹ (counting on liquid). Experiments were performed at atmospheric pressure. The reactor walls were cooled to 10°C. For more complete trapping of the reaction products, the receiver was cooled to -20°C with a mixture of NaCl and ice. Barrier discharge was excited with a generator of unipolar attenuating pulses. The voltage pulse amplitude was 12.8 kV, and the pulse repetition frequency was 400 Hz. The active power of the discharge was calculated by the procedure described in [10]; it was about 2 W at the discharge burning voltage

of 3.5 kV. An oscillogram of the voltage pulse exciting the discharge and an example of the calculation of the active power and voltage of discharge burning are given in [11]. The reaction products were analyzed on a chromatograph equipped with a thermal conductivity detector. The chromatographic analysis was performed under the following conditions: packed column 3 m long, 3 mm i.d.; sorbent Porapak QS; isothermal mode, 110°C. To identify the reaction products and determine their amounts, we used reference substances.

The data on propylene conversion and composition of reaction products in propylene oxidation with air and oxygen are given in the table.

As seen from the table, the selectivity of the propylene oxide formation with air used as oxidant decreases to 23 wt %. This value, as well as the propylene conversion (7.5 wt %), are comparable with those attained in catalytic oxidation of propylene [4–6]. The products formed by propylene oxidation with air and oxygen have identical compositions.

Cooling of the receiver allowed more complete collection and analysis of the propylene oxidation products, compared to the results given in [7]. We additionally identified acrolein, ethanol, allyl alcohol, and propanal. Similar products are formed in the course of catalytic oxidation of propylene [4–6]. It should be noted that octane also undergoes oxidation. The major products of its oxidation are hydroxy and carbonyl compounds with the same number of C atoms as in the starting compounds. However, the octane conversion is low (less than 1 wt %).

It is also seen from the table that the propylene conversion with air as oxidant decreases by a factor of only 1.7 relative to the reaction with oxygen (from 12.9 to 7.5 wt %), whereas the oxygen content of the gas phase decreases by a factor of 4.8. In this connection, it was interesting to examine in more detail how the concentrations of nitrogen and oxygen affect the propylene oxidation.

Figure 1 shows the dependence of the propylene conversion on the nitrogen content of the oxygennitrogen mixture, with the propylene concentration in the starting mixture kept constant, 9 vol %.

Linear correlation is observed between the propylene conversion and nitrogen concentration in the starting mixture. As in the experiments with air, a decrease in the propylene conversion is not proportional to a decrease in the oxygen concentration in the starting mixture. Propylene conversion X and selectivity S of product formation in propylene oxidation with oxygen and air

Product	<i>S</i> , wt %	
	oxygen	air
Propylene oxide	45.00	22.71
Propanal	26.51	23.61
Acetone	3.20	21.76
Acrolein	1.70	8.72
Allyl alcohol	1.27	4.57
Methanol	8.31	6.68
Ethanol	2.32	1.04
Acetaldehyde	9.69	7.60
Unidentified	2.00	3.31
<i>X</i> , wt %	12.9	7.5

According to the existing views on the mechanism of hydrocarbon oxidation in BD, the reaction products are mainly formed in the reaction of propylene with atomic oxygen generated from molecular oxygen under the action of electron impact [12–14]:

$$O_2 + e \to 2O + e, \tag{1}$$

$$C_3H_6 + O \rightarrow \text{products.}$$
 (2)

The lack of proportionality between a decrease in the propylene conversion and a decrease in the oxygen concentration in the starting mixture may be due to generation of an additional amount of atomic oxygen in the reaction of molecular oxygen with an electronically excited nitrogen molecule [10]:

$$N_2 + e \rightarrow N_2^* (A^3 \Sigma_u^+, C^3 \Pi_u) + e, \qquad (3)$$



Fig. 1. Propylene conversion *X* as a function of the nitrogen concentration *c* in oxygen–nitrogen mixtures.



Fig. 2. Relative distribution E of BD electron energy over excitation levels of molecules of the starting mixture in relation to the nitrogen concentration c in oxygen–nitrogen mixtures. Levels: (1) electronic of oxygen, (2) vibration of nitrogen, and (3) electronic of nitrogen. The populations of the vibration and electronic excitation levels of propylene are about 12 and 7%, respectively.

$$N_2^* + O_2 \to 2O + N_2.$$
 (4)

Similar effect was observed in generation of ozone from air [10].

This assumption is confirmed by the results of calculations of the relative electron energy distribution in BD (%) over excitation levels of molecules of the starting mixture (Fig. 2). The calculations were performed using Bolsig program [15] for the field intensity in the discharge gap of the reactor of 100 T, which corresponds to the amplitude of high-voltage pulses of 12.8 kV. The initial data on the differential cross sections of electron scattering on nitrogen and oxygen molecules were taken from the database of the program. Data on differential cross sections of electron scattering on propylene molecule are available from [16, 17], except the cross sections of excitation of electronic transitions. In this case, we used instead the data for propane molecule [18–20].

Figure 2 shows that, with an increase in the nitrogen concentration in the starting mixture, the BD electron energy loss for the excitation of the electronic levels of oxygen decreases, and for the excitation of the electronic levels of nitrogen it, on the contrary, increases. Hence, a significant part of atomic oxygen at a nitrogen concentration in the starting mixture of 78 vol % (model of air) can be formed by reactions (3) and (4). The BD electron energy loss for the excitation of the vibration levels of the ground electronic state of the nitrogen molecule also increases. Apparently, the above factors also affect the selectivity of formation of



Fig. 3. Selectivity S of formation of (1) propylene oxide, (2) propanal, and (3) acetone as a function of the nitrogen concentration c in oxygen–nitrogen mixtures.

propylene oxidation products on replacement of oxygen with air.

Figure 3 shows how the selectivity of formation of propylene oxide, propanal, and acetone depends on the nitrogen concentration in the starting mixture. As can be seen, for the formation of propylene oxide the trend is opposite compared to acetone. This fact suggests that the formation of propylene oxide and acetone is interrelated and that these products may be formed from a common intermediate. Apparently, further transformations of this intermediate depend on the BD electron energy distribution over the excitation levels of molecules of the starting mixture. At the same time, the selectivity of the propanal formation only slightly depends on the nitrogen concentration in the starting mixture. The similar composition of products in propylene oxidation with both air and oxygen suggests a common reaction mechanism.

CONCLUSIONS

(1) The selectivity of the formation of propylene oxide in air, compared to oxygen, decreases from 45 to 23 wt %, and the propylene conversion decreases from 12.9 to 7.5 wt %.

(2) Preparation of propylene oxide by propylene oxidation with air in barrier discharge reactors can be considered in the future as a procedure for commercial production of propylene oxide, alternative to the catalytic procedure. OXIDATION OF PROPYLENE WITH AIR IN BARRIER DISCHARGE

 Nijhuis, A.T., Makkee, M., Moulijn, J.A., and Weckhuysen, B.M., *Ind. Eng. Chem. Res.*, 2006, vol. 45, pp. 3447–3459.

REFERENCES

- 2. US Patent 5698719.
- Jin, G., Lu, G., Guo, Y., et al., *Catal. Lett.*, 2003, vol. 87, nos. 3–4, pp. 249–252.
- Suoa, Z., Jina, M., Lub, J., et al., J. Natural Gas Chem., 2008, vol. 17, no. 2, pp. 184–190.
- Luo, M., Lu, J., and Li, C., *Catal. Lett.*, 2003, vol. 86, nos. 1–3, pp. 43–49.
- 6. Lu, J., Luo, M., Lei, H., and Li, C., *Appl. Catal. A: General*, 2002, vol. 237, nos. 1–2, pp. 11–19.
- Kudryashov, S.V., Ryabov, A.Yu., Sirotkina, E.E., and Shchegoleva, G.S., *Zh. Prikl. Khim.*, 2004, vol. 77, no. 11, pp. 1922–1924.
- Kudryashov, S.V., Ryabov, A.Yu., Sirotkina, E.E., and Shchegoleva, G.S., *Khim. Vys. Energ.*, 2000, vol. 34, no. 2, pp. 145–148.
- Kudryashov, S.V., Ryabov, A.Yu., Sirotkina, E.E., and Shchegoleva, G.S., *Khim. Vys. Energ.*, 2003, vol. 37, no. 3, pp. 220–222.
- Samoilovich, V.G., Gibalov, V.I., and Kozlov, K.V., *Fizicheskaya khimiya bar'ernogo razryada* (Physical Chemistry of Barrier Discharge), Moscow: Mosk. Gos. Univ., 1989.
- Kudryashov, S.V., Ryabov, A.Yu., Shchegoleva, G.S., et al., *Izv. Tomsk. Politekh. Univ.*, 2006, vol. 309, no. 6, pp. 92–96.
- 12. Hirokami, S. and Cvetanovic, R., J. Am. Chem. Soc., 1974, vol. 96, no. 12, pp. 3738–3746.

- Tanner, D. and Kandanarachchi, P., J. Org. Chem., 1998, vol. 63, no. 14, pp. 4587–4593.
- 14. Zhao, H., Bian, W., and Liu, K.A., J. Phys. Chem. A, 2006, vol. 110, pp. 7858–7866.
- Morgan, W.L., Kinema Software BOLSIG, www.siglokinema.com: BOLSIG: User-Friendly Boltzmann Solver from the SIGLO Series, 1994, URL: http://www.siglokinema.com/program/bolwin.exe (addressing date February 15, 2010).
- Bettega, M.H.F., Winstead, C., Lima, M.A.P., and McKoy, V., Abstracts of Papers, *Int. Symp. on Electron–Molecule Collisions and Swarms*, Campinas, SP (Brazil), July 27–30, 2005, p. 80.
- Kim, Y.-K., Irikura, K.K., Rudd, M.E., et al., Electron-Impact Cross Sections for Ionization and Excitation, www.nist.gov: National Institute of Standards and Technology's Web Site, 2009, URL: http:// physics.nist.gov/cgi-bin/Ionization/bebcsdwnload?C3H6 (addressing date February 21, 2010).
- 18. Mertz, R. and Linder, F., J. Phys. B: At., Mol. Opt. Phys., 2003, vol. 36, pp. 2921–2941.
- 19. Slovetskii, D.N., in *Khimiya plazmy* (Plasma Chemistry), Moscow: Energoizdat, 1981, issue 8, pp. 189–230.
- Kim, Y.-K., Irikura, K.K., Rudd, M.E., et al., Electron-Impact Cross Sections for Ionization and Excitation, www.nist.gov: National Institute of Standards and Technology's Web Site, 2009, URL: Electron-Impact Cross-Sections for Ionization and Excitation. http:// physics.nist.gov/cgi-bin/Ionization/table.pl?ionization= C3H8 (addressing date February 21, 2010).