Title	Synthesis of unsaturated aldehydes by catalytic vapor phase oxidation of lower olefines : studies on the reactions over arsenic series catalysts
Sub Title	
Author	石川, 敏夫(Ishikawa, Toshio)
Publisher	慶応義塾大学藤原記念工学部
Publication year	1965
Jtitle	Proceedings of the Fujihara Memorial Faculty of Engineering Keio University (慶応義塾大学藤原記念工学部研究報告). Vol.18, No.71 (1965.) ,p.67(3)- 68(4)
JaLC DOI	
Abstract	
Notes	Summaries of Doctor and Master Theses Doctor of Engineering, 1965
Genre	Departmental Bulletin Paper
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=KO50001004-00180071-0003

Synthesis of Unsaturated Aldehydes by Catalytic Vapor Phase Oxidation of Lower Olefines

—Studies on the Reactions over Arsenic Series Catalysts—

Toshio ISHIKAWA*

The author has investigated the catalytic vapor phase oxidation of olefines to unsaturated aldehydes over As series catalysts under the following conditions: Reaction temperature: about 350～500°C, olefine concentration in feed mixtures: above the upper explosion limit of olefine-air system.

Two-components catalysts such as Fe-As, Mn-As and V-As, and some three-components catalysts of the type Mo-X-As have been found effective for acrolein synthesis from propylene. The Fe-As catalyst, atomic ratio of which is As : Fe=1.0 ～1.25, has been found to have high activity for acrolein synthesis at the reaction temperature of about 400°C. The acrolein yield (based on olefine fed) of 13～16% and the selectivity value of about 80% were obtained, when the above mentioned Fe-As catalyst was used with the feed in which propylene concentration was about 13%. Among the Mo-X-As type catalysts investigated, Mo-Ce-As was found to have the best activity for acrolein synthesis.

By using Fe-Li-As catalyst in which the atomic ratio of Li to As was above 1, the stable activity for mathacrolein synthesis from isobutylene was obtained at the suitable reaction temperature. Following results were obtained when the feed mixture, in which the volume ratio of isobutylene to air was 1 : 7～8, was passed over the catalyst Fe-Li-As (atomic ratio=1 : 2 : 2.5) at 470°C and contact time of 1 sec. : O_2-conversion : 90～100%; methacrolein yield : 26～28%; selectivity : about 56%; the atomic ratio of Fe : Li : As became 1 : 2 : 2, when the reaction was continued for 7 hr.

The mechanism of the oxidation of α C-H bond in propylene and isobutylene on the Fe-As series catalyst has been explained as follows: The catalytic oxidation is carried out by a cycle consisting of the following two reactions:

$$2As^{5+}+CH_2=CR\cdot CH_3 \longrightarrow 2As^{3+}+CH_2=CR\cdot CHO \quad (1)$$

$$2As^{3+}+O_2 \longrightarrow 2As^{5+} \quad (2)$$

$$R=H \text{ or } CH_3$$

The reaction (1) is remarkably promoted in the presence of Fe component. This reaction is always accompanied with the formation of CO_2 which is a by-product.

*石 川 敏 夫

The reaction (2) is also promoted by Fe component in the catalyst. It has been also found that the higher the concentration of As^{5+} in the Fe-As series catalyst, the higher the selectivity for unsaturated aldehyde formation