

Kinetic studies on diacetyl synthesis over V-containing zeolites

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Received 11 January 2001; accepted 14 May 2001

The gas-phase oxidation of methyl ethyl ketone (MEK) was studied on V-ZSM-5 zeolite in the presence of molecular oxygen. Two types of competitive partial oxidations, *i.e.*, diacetyl formation and oxidative scission reaction leading to acetaldehyde and acetic acid, took place at 200–350 °C. A detailed kinetic study was realized for the oxidation reaction, a linear relationship was observed between the conversion and partial pressure of oxygen, and an activation energy of 16 kcal/mol was encountered. The content of vanadium in the catalyst was also analyzed.

KEY WORDS: kinetics; methyl ethyl ketone; oxidation; diacetyl; V-ZSM-5

1. Introduction

It has been known that the oxidation of ketones gives a wide variety of products in accordance with the oxidizing agents and reaction conditions. When strong oxidizing agents such as potassium permanganate or chromic acid are used, the carbon–carbon bond is split at the α -position relative to the carbonyl group to give carboxylic acids [1,2]. In the case of moderate oxidizing agents, the original carbon skeleton of the reactant is maintained in the products. For example, an acetoxyl group and a hydroxyl group are introduced to the α -position in the oxidation by using mercury and lead acetate [3] and molybdenum peroxide [4], respectively, while an α -diketone is obtained in the oxidation by selenium dioxide [5]. In these reactions, the mechanistic feature is that ketones are isomerized to corresponding enol tautomers prior to the oxidation.

Many investigations of the autooxidation of ketones have been reported. The autooxidation is initiated by the abstraction of an α -hydrogen from reactant ketones followed by the addition of an oxygen molecule to give ketone peroxy radical. This intermediate is then converted into various products in the succeeding reactions.

In contrast with the above oxidation reactions, little is known about the catalytic oxidation of ketones. The authors have revealed that in the catalytic oxidation of butenes to acetic acid over metal oxide catalysts, butenes are first oxidized to the corresponding ketone, MEK, by a so-called oxyhydration mechanism [6–9] which is then oxidized to acetic acid [10,12]. It seems very important that diacetyl is obtained directly from MEK in this way.

Butter-smelling diacetyl is commonly used for synthetic butter, vinegar, coffee, and other foods [13]. So far diacetyl

has been synthesized from MEK by a two stage chemical method: oxidation of MEK to an isonitroso compound followed by the hydrolysis of the isonitroso compound with HCl to diacetyl [14]. Direct catalytic synthesis of diacetyl from MEK, if feasible, will be much superior to the conventional method.

Methyl ethyl ketone is converted very easily to acetic acid and acetaldehyde by an oxidative fission of the central C–C bond with an acidic metal-oxide catalyst, such as a MoO₃- or V₂O₅-based mixed oxide [15]. Besides acetic acid, acetaldehyde, and carbon oxides, diacetyl is obtained in a small amount in the oxidation of MEK. Because of its chemical formula and its high reactivity on V₂O₅-based oxides, it was assumed to be an intermediate in the oxidation of MEK to acetic acid [16,17]. Ai found that V₂O₅-P₂O₅ catalyst are effective in the formation of diacetyl; this was predictable from the finding [18]. Some spinels containing cobalt have been reported to be selective for the formation of diacetyl from MEK when the extent of the reaction is low [19,20].

The synthesis of 2,3-butanedione and the effect of water on this reaction have been reported, using Cs–K/V₂O₅ catalyst [21].

Recently we found that the novel sol–gel process has been an alternative and a simpler method to successfully prepare VS-1 (vanadium silicalite) [22]. This catalyst showed high activity and selectivity in the reactions of hydroxylation, oxifunctionalization and epoxidation of organic substrates. In this study, we focused our attention on the formation of diacetyl from MEK on vanadium-impregnated zeolite, and attempted to determine the kinetic parameters of the reaction and the activation energy.

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