Kinetic studies on diacetyl synthesis over V-containing zeolites

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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 MoO_3- or V_2O_5-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 V_2O_5-based oxides, it was assumed to be an intermediate in the oxidation of MEK to acetic acid [16,17]. Ai found that V_2O_5–P_2O_5 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/V_2O_5 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 sustrates. 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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2. Experimental

2.1. Catalyst preparation

The V-ZSM-5 sample was prepared using the following reactants: TEOS (tetraethylorthosilicate), as the source of silicon and sodium aluminate for Al. TPAOH (tetrapropylammonium hydroxide) as template, following the next steps:

(a) Al source dissolved in water was added to TEOS solution at 0 °C. The clear solution obtained was stirred for 80 min.

(b) The final solution of step (a) converts into a solid co-gel by addition of the corresponding template at room temperature. The xerogel obtained was dried at 110 °C overnight.

(c) The xerogel obtained in step (b) was impregnated with the adequate template solution by wetness impregnation. The incipient wet SiO_2/Al_2O_3 was loaded to a Teflon-lined autoclave and crystallized at 170 °C for 56 h. The final product was filtered, washed with distilled water and dried at 110 °C.

The template was desorbed under N_2 atmosphere (20 ml min^{-1}) from 110 to 520 °C at programmed temperature (10 °C min^{-1}) and then calcined in air at 520 °C for 12 h to obtain NaZSM-5 zeolite. The ammonium form of the catalyst was prepared using NaZSM-5 by ion exchange with 1 M ammonium chloride solution at 80 °C for 40 h. Vanadium-containing zeolite was prepared using NH_4-ZSM-5 by wetness impregnation with aqueous vanadium(IV) oxide sulfate pentahydrate ($O_5SV{\cdot}5H_2O$) solution. Next, the impregnated catalyst was heated under N_2 atmosphere (10 ml min^{-1}) from 110 to 500 °C at programmed temperature (10 °C min^{-1}) and then calcined in air at 500 °C for 10 h to obtain V-ZSM-5. The material have Si/Al $= 17$ and and different vanadium loading.

2.2. Catalytic activity

The standard reactions of oxidation of methyl ethyl ketone (Sintorgan 99%) were conducted in a continuous-flow apparatus at atmospheric pressure. The reactor was made of a quartz tube, 20 cm long and 1 cm i.d., mounted vertically and immersed in an oven. Oxygen and MEK were fed in from the top of the reactor. The effluent from the reactor was led successively into water scrubbers to recover the products of the reaction, the samples were collected at every 20 min. The reaction conditions are indicated in the figures. The yield and selectivity of a particular product were defined as mole percentage yield and selectivity on a carbon-account-for basis.

The reaction products were analyzed by gas chromatography with a capillary AT-Wax column of 30 m and mass spectroscopy using a GC-MS 823.

Table 1
TOF for NaV-ZSM-5 and HV-ZSM-5 samples.

V (%p/p)	TOF (molec. sites^{-1} s^{-1})	
	NaV-ZSM-5	HV-ZSM-5
0.5	0.0161	0.0186
1.5	0.0106	0.0125
2	0.0082	0.0064
3	0.0027	0.0021

3. Results and discussion

3.1. Effect of the content of vanadium in ZSM-5 zeolite

The results of TOF (turnover frequency) for the samples NaV-ZSM-5 and HV-ZSM-5 with different content of vanadium are shown in table 1.

We can observe that the increase in the content of vanadium implies materials with different types of active sites. In figure 1, the yield of products (expressed in molec. sites^{-1} s^{-1}) *versus* TOF was plotted. As we can see, for both catalysts, the dione (diacetyl) would be an instable primary product, acetic acid a secondary product to the expense of the diacetyl and acetaldehyde is produced for the initial scission of MEK, thus is a primary product, and then the HV-Z sample is more active for the scission of C–C of MEK than NaV-Z.

As expected, the conversion and selectivity of the samples increased with vanadium content. However, the increase in the activity is not linearly proportional to the vanadium content of the samples. The higher vanadium in the sample leads to a more extensive secondary oxidation.

3.2. Effect of the partial pressure of oxygen

The experiments were performed as described in section 2. A Na–V-ZSM-5 sample with 0.5% p/p of vanadium was used. Only the partial pressure of oxygen changed: 0.6, 0.75 and 0.9 atm, respectively. Figure 2, where the conversion of MEK *vs.* W/F is displayed for the three different partial pressures of oxygen, shows a linear increase in the initial reaction rate with increasing partial pressure of oxygen, which means that the MEK oxidation is of first order in oxidant concentration. The maximum conversion was proportional to the partial pressure of oxygen.

From the reported influences on the measured reaction rates of the partial pressure of oxygen, it can be concluded that the overall reaction rate for the oxidation of MEK can be described by the following equation:

$$\gamma = kP_{O_2}. \tag{1}$$

According to this, the following relation between the relative conversion X and the contact time W/F can be derived:

$$\ln(1-X) = -k\frac{W}{F}. \tag{2}$$

According to the first-order rate equation, the values of $\ln(1-X)$ are plotted against the nominal contact time, W/F

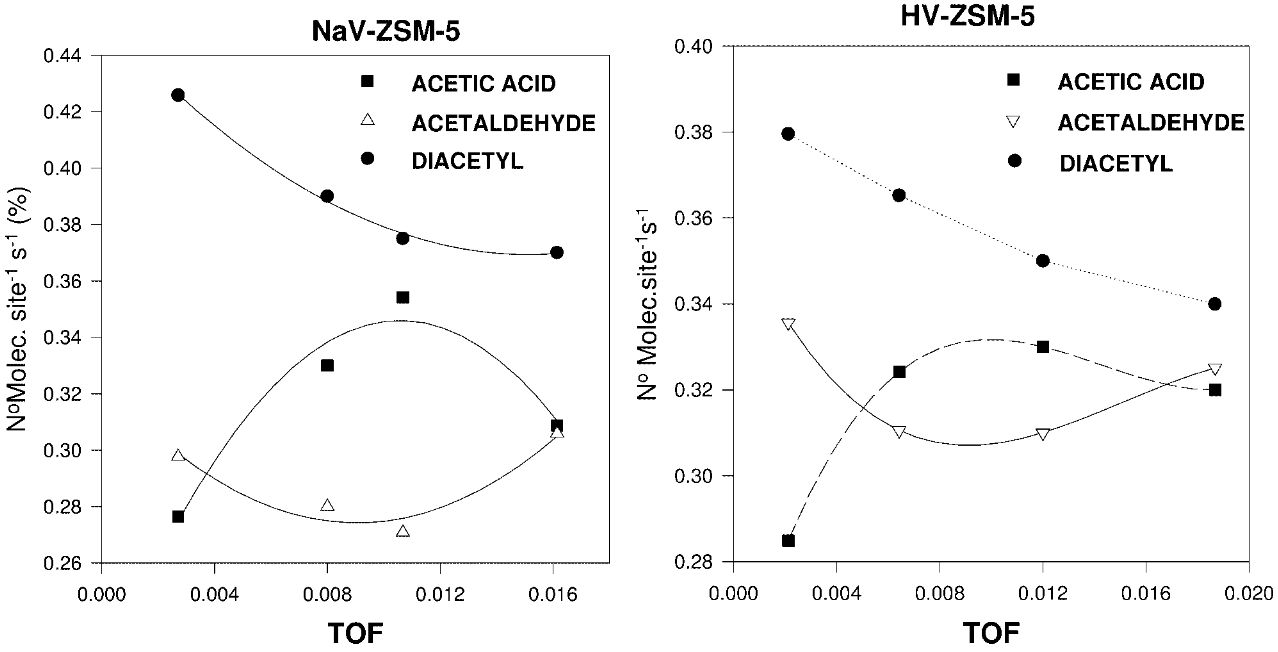

Figure 1. Yield of products (molec. sites^{-1} s^{-1}) *vs.* TOF over NaV-ZSM-5 and HV-ZSM-5. Reaction conditions: $P_{O_2} = 0.75$ atm, $T = 250\,^{\circ}C$, $W/F = 24\ g_{cat}\,h\,mol^{-1}$.

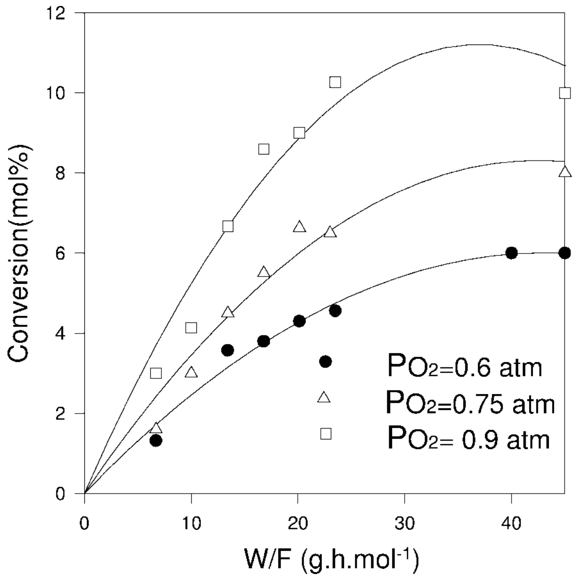

Figure 2. Conversion of MEK *vs.* W/F at different partial pressures of oxygen, $T = 200\,^{\circ}C$.

($g_{cat}\,h\,mol^{-1}$), where X represents the fraction of the converted MEK. From the slope of this curve the value of the first-order rate constant k can be obtained, which can be used to characterize the catalyst activity.

The first-order dependence on P_{O_2} is consistent with the participation of molecular oxygen, so we suggest that molecular oxygen O_2^- is the active species reacting with MEK. This feature is different from that observed in oxidations over acidic catalysts at higher temperatures [23–27]. However, a good proportional relation was observed in the oxidation of *n*-butenes to acetic acid at temperatures below 250 °C [28]. The participation of molecular oxygen was also assumed in the oxidation of MEK on cobalt-based oxides by Yamazoe *et al.* [19]. This led us to consider that the first-order dependency is a feature observed commonly in oxidative C–C fission performed at low temperatures.

As O_2^- rather than lattice oxygen is important in the partial oxidation of MEK, we suggest that the metal supported catalyst can have its surface reduced in the reaction atmosphere to form lower-valent cations such as V_4^+, wich can act as adsorption sites for O_2^- species. It is suggested that O_2^- is formed on the surface of V_4^+ sites and reacts with MEK.

At this point, we should perhaps pay attention to the oxygen species reacting with MEK. The similarity between the gas-phase and the liquid-phase oxidation of MEK strongly suggests the molecular oxygen, probably O_2^- in this case, participates in the gas-phase oxidation to form a peroxide type intermediate resembling the one assumed in the liquid-phase oxidation. There are facts supporting the participation of molecular oxygen. First the reactions concerned are favored at lower temperatures compared with other typical reactions of hydrocarbon oxidation.

The rate-determining step is considered to be the reaction of the conjugated complex and the O_2^- species that forms a peroxide species or an hydroperoxide, according to the first-order kinetics on oxygen. However, it should be noted that the ability of the above peroxide-like reactions to occur is to be ascribed both to the easiness of C–H bond fission at the secondary C–H bonds adjacent to the carbonyl group and to the strong power of the catalyst for hydrogen abstraction.

The promotion effect is considered to result from the increase of surface V_4^+ ions which can accommodate the O_2^- species.

In the case of the intermediate derived from MEK, the negative charge will be distributed for the most part on the carbonyl group and the central carbon–carbon bond by the electron-repelling effect of the methyl group, thus making difficult the nucleophilic attack by active oxygen on these parts. This may explain why the carbon skeleton of the reactant can be preserved in the products over vanadium catalysts.

3.3. Effect of the temperature of the reaction

The influence of reaction temperature on the oxidation of MEK is shown in figure 3. In this figure the conversion *vs.* W/F is plotted for reactions conducted at 200, 250 and 350 °C. The contact time was varied by changing the amounts of catalyst (100, 150, 200, 250, 300, and 350 mg), while fixing the total flow rate as 1.34 $\mathrm{ml\,h^{-1}}$ (at 25 °C). From these curves, the value of k for each temperature can be obtained by application of equation (2), where k is the slope of each plot (figure 4).

An Arrhenius plot of the first-order reaction rate constant obtained from this conversion curves is shown in the figure 5, and from this graph an activation energy can be derived for the oxidation of MEK.

As we can see in figure 3, about 10% of the MEK is converted at a low temperature of 200 °C, while the conversion increases with a futher elevation of temperature. This led us to examine the temperature dependency of the reaction. As figure 4 shows, relatively good linear relationships were obtained for each temperature, suggesting the validity of the first-order approximation. Then the values of the first-order rate constant estimated from the initial slopes in figure 4 were plotted according to the Arrhenius equation. A reasonably straight line was obtained. The apparent activation energy calculated was $E_a = 16\ \mathrm{kcal\,mol^{-1}}$.

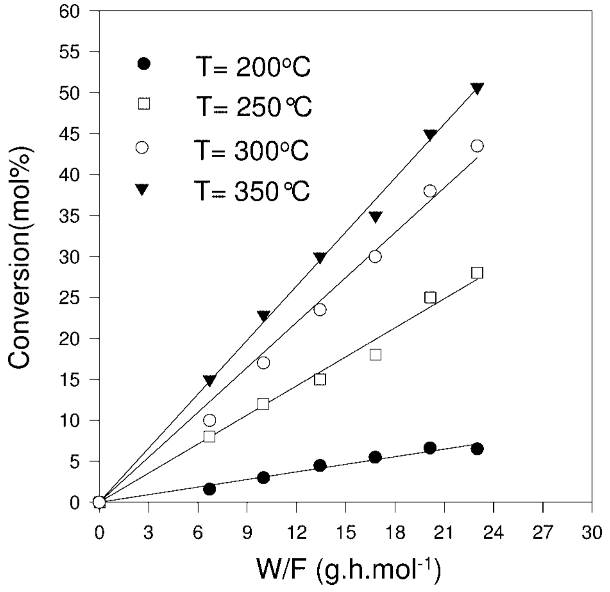

Figure 3. Conversion of MEK *vs.* W/F at different reaction temperatures, $P_{O_2} = 0.75$ atm.

The apparent activation energies in mild oxidations with V_2O_5-based oxides range from 12 to 30 $\mathrm{kcal\,mol^{-1}}$ [29], for example, apparent activation energies of 17.5 [23] and 20 $\mathrm{kcal\,mol^{-1}}$ [24] were observed in the oxidation of *n*-butenes to maleic anhydride on V_2O_5–P_2O_5 catalysts. On the other hand, an apparent activation energy of 9.8 $\mathrm{kcal\,mol^{-1}}$ was observed in the oxidation of *n*-butenes to acetic acid [28].

3.4. Selectivity of V-ZSM-5 catalyst

The product selectivity of V-ZSM-5 zeolite as a fuction of MEK conversion is shown in figure 6.

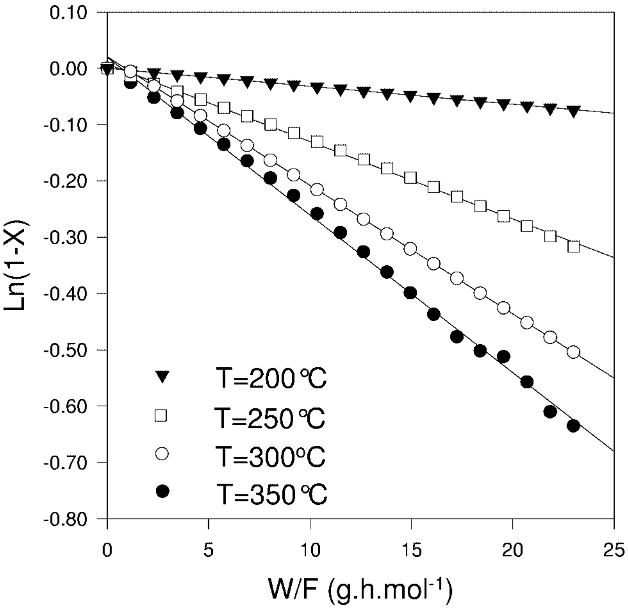

Figure 4. First-order relation between relative conversion X and W/F.

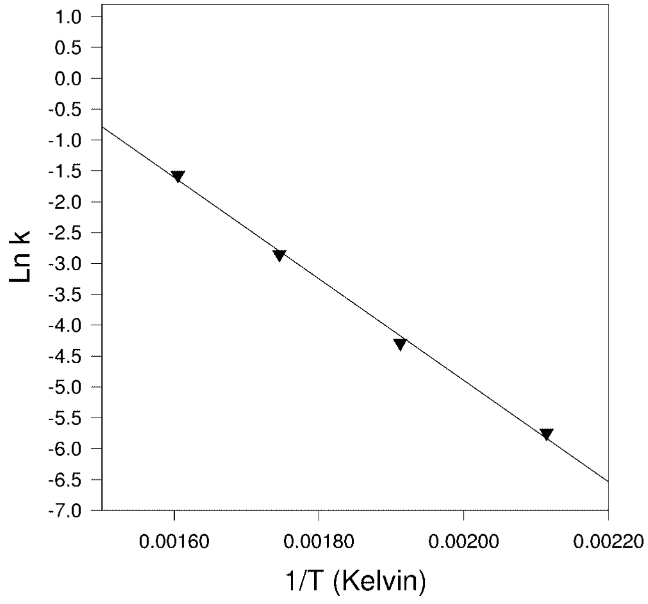

Figure 5. Arrhenius plot of the first-order rate constant for the oxidation of MEK.

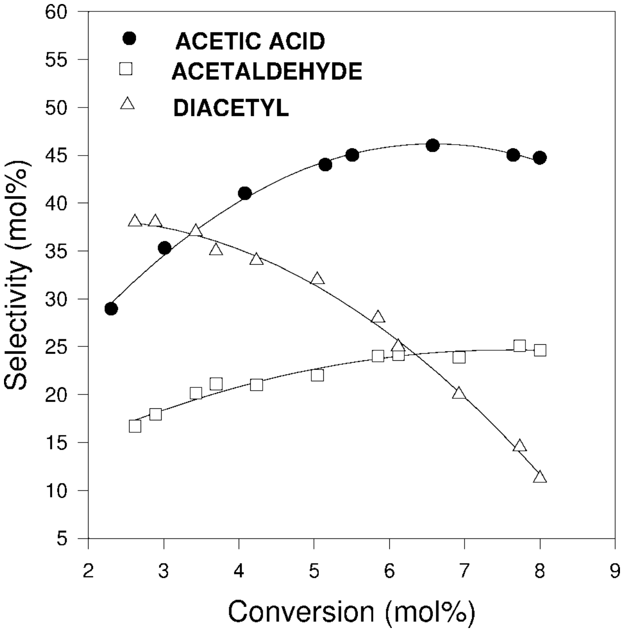

Figure 6. Selectivity *vs.* conversion of MEK, $P_{O_2} = 0.75$ atm, $T = 200\,°C$.

The diacetyl formation becomes less selective with increasing conversion, being replaced by the formation of AcOH at first and then by complete oxidation.

An examination of the product distribution shows that the activation of the carbon atom at the second position is preferred to others on vanadium silicates. Similar activities for TS-1 and TS-2 in the oxidation of n-hexane, but with no activation of the primary carbon have been reported. Investigation of the oxidation kinetics revealed that the ratio of (aldehyde + acetic acid) to diacetyl increased with conversion, as figure 6 shows. This suggests that the acid is a secondary product from the corresponding primary diacetyl.

4. Conclusion

According to the kinetics data, the MEK conversion is nearly proportional to the concentration of oxygen even at higher concentration levels and at a low temperature.

The apparent activation energy obtained is 16 kcal mol^{-1}. In view of the value of the activation energy and the high extent of the reaction achieved at a low temperature, the participation of molecular oxygen seems to be very probable.

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