Studies on the synthesis of diacetyl over oxidation zeolite catalysts

Oscar A. Anunziata, Liliana B. Pierella, Marcos Gómez Costa and Andrea R. Beltramone

CITeQ (Centro de Investigacion y Tecnologia Quimica), Facultad Cordoba, Universidad Tecnologica Nacional, CC36, Suc 16 (5016), Cordoba, Argentina

E-mail: anunziat@sa.frc.utn.edu.ar

Received 1 June 2000; accepted 20 October 2000

Diacetyl (2,3-butanedione) synthesis from methyl ethyl ketone over oxidation zeolites using O_2 as oxidant was studied. Various zeolites with Fe, V and Ti as active sites were employed. VS-1, Ti-NCL, Ti-MCM-41 and FeBEA type materials were synthesized and characterized by BET, FTIR, XRD, pyridine adsorption and template desorption. The detailed study of the effect of reaction temperature, the effect of concentration of oxygen and the addition of water was realized. The most active catalyst was zeolites with V as oxidation center.

KEY WORDS: diacetyl; oxidation; methyl ethyl ketone; VS-1; VZSM-5

1. Introduction

Many lactobacilli produce diacetyl, a desirable aroma in some fermented dairy products. 2,3-butanedione or diacetyl, a flavor compound having a distinct buttery character, accumulates during alcoholic and malolactic fermentation of wine and beer.

Diacetyl is produced by the action of yeast during fermentation. It tastes like butterscotch. Diacetyl may contribute to the flavor of Chardonnay wine irrespective of the occurrence of malolactic fermentation.

During fermentation, in the production of beer, the oxygen is used up almost immediately. One by-product of this aeration is an increased diacetyl production (diacetyl gives beer a butterscotch aroma and flavor).

Diacetyl is responsible of the particular flavor of kefir. Kefir is a refreshing fermented milk with a slightly acidic taste. It is made only from kefir grains or mother cultures prepared from grains, although attempts to produce kefir with pure cultures are in progress. Kefir grains are a complex and specific mixture of bacteria and yeasts held together by a polysaccharide matrix. The lactic acid bacteria and yeast fermentation of milk results in the production of numerous components, including lactic acid, CO_2, a small amount of alcohol, and an array of aromatic molecules, all of which provide kefir with its unique organoleptic properties. Many health benefits related to the consumption of kefir have been observed.

Many aromatic compounds, including diacetyl and acetaldehyde are present in kefir. Diacetyl is produced by *Str. lactis subsp. diacetylactis* and *Leuconostoc sp.* Although kefir is just being discovered in some areas of the world, it has been very popular in the former Soviet Union, Hungary and Poland for many years. In the former Soviet Union, kefir accounts for 70% of the total amount of fermented milk consumed. It is also well known in Sweden, Norway, Finland and Germany, as well as in Greece, Austria, Brazil and Israel. It is currently available in the United States, primarily as an ethnic drink, and is growing in popularity in Japan.

Methyl ethyl ketone (MEK) 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 [1]. 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 [2,3].

Ai et al. found that V_2O_5–P_2O_5 catalysts are effective in the formation of diacetyl; this was predictable from the finding [4] that a considerable amount of diacetyl is formed in the oxidation of n-butenes on V_2O_5–P_2O_5 catalysts.

Diacetyl has been manufactured by the reaction of MEK with ethyl nitrile [5] and used mainly as a perfume.

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 [6], because it has been predicted that such oxides have a high activity for the oxidation of diacetyl, too.

Acidic oxides such as MoO_3 and V_2O_5 produce acetic acid and acetaldehyde with high selectivity, whereas over weakly basic or amphoteric oxides (NiO and Co_3O_4), the formation of 2,3-butanedione predominates [7,8]. The synthesis of 2,3-butanedione and the effect of water on this reaction have been reported, using Cs–K/V_2O_5 as catalyst [9].

The presence of transition metals in the framework of a zeolite lattice can impart oxidation activity, which can be combined with shape selective properties of the molecular sieves. Vanadium-incorporated molecular sieves are a new class of materials, which can also catalyze various oxidation reactions selectively.

Recently we found that the novel sol–gel process has been an alternative and a simpler method to successfully prepare VS-1 (vanadium silicalite) [10]. This catalyst showed high

1011-372X/01/0100-0127$19.50/0

activity and selectivity in the hydroxylation of benzene to phenol, oxyfunctionalization of n-hexane and epoxidation of 1-hexene to epoxi derivatives; VS-1 converted toluene to benzaldehyde with high selectivity (80%) [10].

In this study, we focused our attention on the formation of diacetyl from MEK on vanadium silicalite, and attempted to clarify the effects of catalysts and reaction variables.

2. Experimental

2.1. Catalyst preparation

2.1.1. Ti-NCL-1, Ti-MCM-41 and Fe-BEA

Ti-NCL-1 (Si/Ti = 33), Ti-MCM-41 (Si/Ti = 41) and Fe-BEA (Si/Fe = 18) were prepared following the procedure shown in our previous work [10].

2.1.2. VS-1

The VS-1 sample was prepared using the following reactants: TEOS, as source of silicon, vanadium(IV) oxide sulfate pentahydrate ($O_5SV{\cdot}5H_2O$) for vanadium and TPAOH as template. Xerogel of SiO_2/V_nO_m solid was used as raw material, following the next steps: Step (a), vanadium source in water was added to TEOS solution at 0 °C. The clear solution obtained was stirred for 45 min. Step (b), the final solution of step (a) was converted into a solid co-gel by addition of the corresponding template at room temperature. The xerogel obtained was dried at 110 °C overnight. Step (c), the xerogel obtained in step (b) was impregnated with the adequate template solution by wetness impregnation. The incipient wet SiO_2/V_nO_m was charged in a Teflon-lined autoclave and crystallized at 180 °C for 30 h. The final product was filtered, washed with distilled water, dried at 110 °C and calcined at 500 °C for 12 h. VS-1 type material has Si/V ratio = 24.

2.1.3. V-ZSM-5

The sample was prepared using the following reactants: TEOS (tetraethylorthosilicate), as the source of silicon, and sodium aluminate for Al and TPAOH (tetrapropylammonium hydroxide) as template, following the next steps: Step (a), Al source dissolved in water was added to TEOS solution at 0 °C. The clear solution obtained was stirred for 80 min. Step (b), the final solution of step (a) was converted into a solid co-gel by addition of the corresponding template at room temperature. The xerogel obtained was dried at 110 °C overnight. Step (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) from 110 to 520 °C at programmed temperature (10 °C/min) 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) from 110 to 500 °C at programmed temperature (10 °C/min) and then calcined in air at 500 °C for 10 h to obtain V-ZSM-5. The material has Si/Al = 17 and 1 wt% vanadium loading.

2.2. Catalysts characterization

The catalyst were characterized by powder XRD patterns with applications of synchrotron radiation obtained in the Laboratorio Nacional de Lus Synchrotron, LNLS/CNPq, Campinas SP, Brazil. BET surface area determinations were carried out with an ASAP 2000 equipment. Infrared analysis of the samples was performed on a JASCO 5300 spectrometer in the lattice vibration region using a KBr 0.05% wafer technique. Pyridine adsorption experiments were carried out in a thermostatted cell with CaF_2 windows connected to a vacuum line, and using a self-supporting wafer. TPD data of the template from VS-1, Ti-NCL and FeBEA samples were collected with an INSTRELEC programmer, which admits to change the heat slope. The slope was 10–20 °C/min and the nitrogen flow was 20 ml/min. Desorbed products were analyzed using a FID detector.

2.3. 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; at the end of 1 h, the content of the scrubbers was collected. The reaction conditions are indicated in table 1. 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.

3. Results and discussion

A preliminary catalyst-screening test revealed that the best results for the formation of diacetyl are obtained with the VS-1 catalyst. The Fe-Beta sample is active but the selectivity is poor. Thus the oxidation of MEK was studied with the VS-1 catalyst. The results are shown in table 1.

The major products (>97%) were diacetyl, acetic acid and acetaldehyde, the minor products were unidentified.

Table 1
MEK conversion and selectivity to diacetyl using O_2, over zeolites at different reaction conditions and at 250 °C.

Catalyst	Partial pressure of O_2 (atm)	W/F (g h/mol)	Conversion (mol%)	Selectivity to diacetyl (mol%)
Ti-MCM-41	0.56	12	3.0	25.0
Ti-NCL-1	0.56	12	2.5	32.0
Fe-Beta	0.56	12	5.6	29.5
Fe-Beta	0.56	24	7.9	26.8
Fe-Beta	0.77	24	40.5	4.0
VS-1	0.56	24	15.2	57.7
VS-1	0.77	24	20.6	45.8
VS-1	0.77	20	18.3	45.0

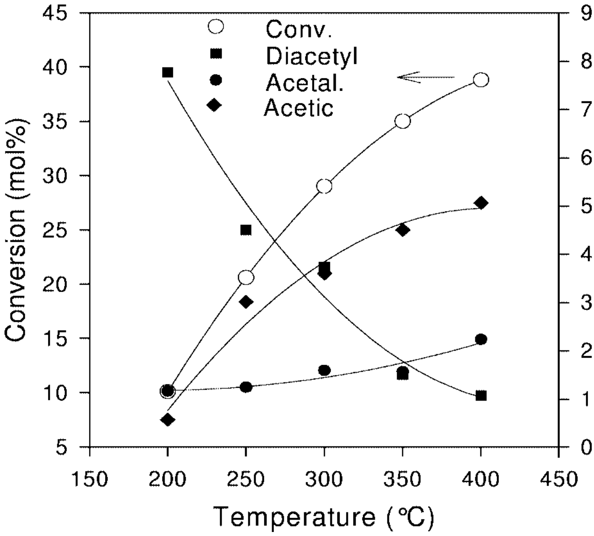

Figure 1. Conversion of MEK and selectivity at different temperatures over VS-1. Reaction conditions: $P_{O_2} = 0.77$ atm and $W/F = 24$ g h/mol.

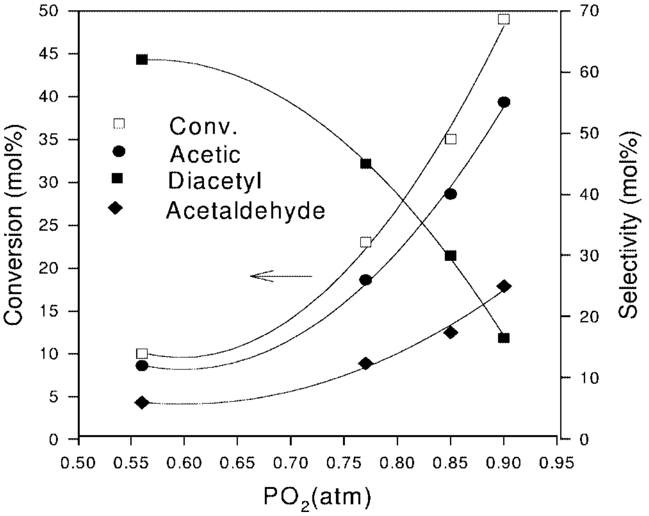

Figure 2. Effect of the partial pressure of oxygen on the conversion and selectivity over VS-1. Reaction conditions: $T = 250\,°C$ and $W/F = 24$ g h/mol.

3.1. Effect of the reaction temperature

The changes in the conversion of MEK, the selectivities to diacetyl, and of the sum of acetic acid and acetaldehyde selectivities, were studied by changing the reaction temperature. The results are shown in figure 1.

The selectivity to diacetyl is about 80 mol% at MEK conversion of up to 10 mol%, but it falls with a further increase in the conversion. The yield of diacetyl reaches 9.5 mol% at 270 °C.

The selectivity to acetaldehyde increases only a little and the selectivity to acetic acid tends to increase, at the expense of a decrease in the selectivity to diacetyl, with an increase in the conversion.

3.2. Effect of the concentration of oxygen

The initial concentration of oxygen was varied. The change in the MEK conversion at 250 °C is shown in figure 2. The conversion increases almost proportionally to the oxygen concentration.

Figure 2 shows the selectivities to each product obtained from the reaction. From a comparison with the results obtained varying the temperature, it was found that the formation of acetic acid is enhanced with a decrease in the formation of diacetyl, and that the consecutive decomposition of diacetyl is enhanced, with an increase in the oxygen concentration.

An oxygen dependency similar to that observed in the oxidation of MEK seems to be a common feature observed in oxidation with an acidic catalyst. Possibly the surface of the catalyst is far from being saturated with oxygen because of its low affinity for oxygen. This may be the reason why these oxidations are usually performed in the presence of an excess of oxygen. The oxygen dependency does not necessarily prove the participation of molecular oxygen in the reaction, but in view of the high extent of reaction achieved at a low temperature, the participation of molecular oxygen seems to be very probable.

3.3. Comparison of the performances of V/catalysts and effect of the addition of water in the feed

A comparison of the activity of VS-1 with vanadium-impregnated ZSM-5 (V-ZSM-5) in the oxidation of MEK is given in table 2.

The vanadium catalysts show a higher selectivity for diacetyl formation than all the other catalysts tested.

Table 2
MEK conversion and selectivity to diacetyl, acetic acid and acetaldehyde over VS-1 and V-ZSM-5 zeolites. $T = 200\,^\circ\mathrm{C}$, $P_{\mathrm{O}_2} = 0.77$ atm, $W/F = 24$ g h/mol.

Catalyst	Partial pressure of water (atm)	Conversion (mol%)	Selectivity (mol%)		
			Diacetyl	Acetic acid	Acetaldehyde
VS-1	0	11.0	80.0	7.5	11.0
V-ZSM-5	0	26.6	36.0	34.0	26.0
V-ZSM-5	0.3	39.3	33.14	34.6	29.0
V-ZSM-5	0.5	43.2	31.3	35.7	29.4
V-ZSM-5	0.73	31.0	37.0	31.0	28.0

The activity and the selectivity of these catalysts vary markedly depending on the differences in the mode of preparation. The best results are obtained with the vanadium-impregnated ZSM-5 catalyst.

The reaction was carried out at 200 °C in the presence of water vapor in the range from zero to 0.73 atm of partial pressure in the feed, using V-ZSM-5 as catalyst. Changes in the MEK conversion and selectivities to each product are shown in table 2.

According with the results V-ZSM-5 shows high activity for this reaction.

With an increase in the amount of water vapor, the overall MEK conversion increases at pressures below 0.6 atm, but it ceases to increase as the pressure rises to more than 0.73 atm.

These results suggest that the addition of water vapor directs the reaction to the oxidative C–C fission, but it does not promote the decomposition of diacetyl.

Kung et al. reported that the change in the activity of the catalyst can be correlated with the amount of surface carbonaceous species, thus the water enhances the activity of the catalyst by reducing the formation of surface carbonaceous species. They suggest that the enhancement of activity by water is not due to the generation of additional Brønsted sites; instead it can be suggested that Brønsted acidity may be responsible for polymerization of surface intermediates that poison the catalyst. Thus the following scenario can explain the effect of water. Increasing water partial pressure in the feed results in additional Brønsted acidity on the catalyst surface. The increase in Brønsted acidity could lead to increased carbonaceous deposits as suggested above. The relative rates of the two reactions, i.e., removal of the carbonaceous deposits by reaction with water and formation of those species due to increased surface Brønsted acidity, determine the effect of water on the acidity. The observed increase in activity with increased water partial pressure then signifies that the reaction of water with surface carbonaceous deposits or their precursors is faster than their rate of formation. That is true to partial pressure of water up to 0.6 atm, then the activity decreases.

Relative to the case of no water in the feed, the presence of water increased the selectivity to scission products but the selectivity to 2,3-butanedione was invariable.

The following peroxide mechanism can be proposed: the secondary C–H bonds in MEK are weakened due to the conjugation with the carbonyl group, so the adsorption of MEK causes a hydrogen abstraction at this position, resulting in the formation of a conjugated complex, the hydrogen atom is abstracted by the diradical V_4^+–O–O$^\bullet$. Gaseous oxygen is adsorbed in a peroxide species, O_2^-. The reaction of the conjugated complex and the O_2^- forms a peroxide species or an hydroperoxide. Then, the peroxide species or hydroperoxide proceeds via two parallel pathways, the fission of the O–O bond and adjacent C–H bond leads to the formation of diacetyl. The fission of the O–O bond and the adjacent C–C bond leads to the formation of acetic acid and acetaldehyde.

The ability of the above peroxide-like reactions to occur is to be ascribed both to the ease 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, which may be related to the action of Lewis acid sites present in the VS-1 and V-ZSM-5 catalysts.

In addition, this reaction was performed in presence of $\mathrm{H_2O_2}$/MEK $= 6$ and $W/F = 20$ g h/mol over VS-1 obtaining low conversion (7% at 200 °C) but high selectivity to diacetyl (60 mol%).

4. Conclusion

VS-1 and V-ZSM-5 catalysts prepared by a sol–gel method were found to be effective for the synthesis of diacetyl in the vapor-phase oxidation of methyl ethyl ketone. The conversion of MEK increased with an increase of temperature and concentration of oxygen. The selectivity to diacetyl decreased markedly with a further increase in the conversion, the selectivity for the oxidative C–C fission to form acetic acid and acetaldehyde decreased with an increase in the conversion.

The addition of water vapor to the feed results in an increase in the conversion of MEK. The promoting action of water is usually observed in oxidations performed at lower temperatures, regardless of the participation of water in the reaction. The effect on the selectivity is much more important. The water plays a role in directing the reaction solely to the oxidative C–C fission, not in promoting the decomposition of diacetyl. It seems likely that Brønsted acid is connected with the selectivity.

From a comparison of the results shown in tables 1 and 2 it is evident that the good performance of the VS-1 and V-ZSM-5 catalysts is in part to be ascribed to their low catalytic activity for the decomposition of diacetyl.

Acknowledgement

To CONICET-PIA-No. 6963/96-99. To CONICOR-grant No. 4458/97-2000. OAA and LBP, CONICET Researcher; ARB CONICOR Doctoral Fellowship.

References

[1] M. Ai, P. Boutry and R. Montarnal, Bull. Soc. Chim. Fr. (1970) 2275.
[2] T. Yamashita, S. Ninagawa and T. Kato, Bull. Jpn. Pet. Inst. 18 (1976) 167.
[3] T. Yamashita, Y. Matsuzawa and S. Ninagawa, Bull. Jpn. Pet. Inst. 19 (1977) 109.
[4] M. Ai, J. Catal. 89 (1984) 413.
[5] W.L. Semon, in: *Organic Synthesis*, Vol. 2 (Wiley, New York, 1943) p. 204.
[6] N. Yamazoe, M. Noguchi and T. Seiyama, Nippon Kagaku Kaishi (1983) 470.
[7] Y. Takita, K. Nita, T. Maheara, N. Yamazoe and T. Seiyama, J. Catal. 50 (1977) 364.
[8] Y. Takita, F. Hori, N. Yamazoe and T. Seiyama, Bull. Chem. Soc. Jpn. 60 (1987) 2757.
[9] I. Jahan and H.H. Kung, Ind. Chem. Res. 31 (1992) 2329.
[10] O.A. Anunziata, L.B. Pierella and A.R. Beltramone, Stud. Surf. Sci. Catal. 125 (1999) 523.