Oxidation of Ketones over Metal Oxide Catalysts

I. Catalytic Synthesis of Biacetyl from Methyl Ethyl Ketone

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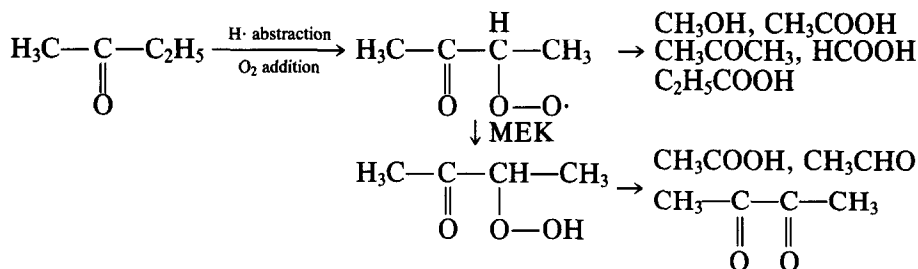Science, Kyushu University, Kasuga-shi, Fukuoka 816, Japan

The gas-phase oxidation of methyl ethyl ketone was studied on metal oxide catalysts in the presence of water vapor. Two types of competitive partial oxidations, i.e., biacetyl formation and oxidative scission reaction leading to acetaldehyde and acetic acid, took place on every oxide studied at 400–500 K. An approximate linear relationship was observed between the selectivity of each reaction and the acid–base property of the oxides; the former reaction was accelerated on the basic oxides such as Co_3O_4, while the latter reaction became predominant on the acidic oxides. As Co_3O_4 was the most effective biacetyl former of single-component oxides, modification of Co_3O_4 was examined to develop more effective catalysts for biacetyl synthesis. Scission reaction took the place of biacetyl formation over a catalyst where Co^{2+} ions were located in Y zeolite by an ion-exchanged method. Scission reaction was suppressed when Co oxide was supported on basic oxides such as MgO or CaO; however, the selectivity to biacetyl was slightly decreased due to the occurrence of a new reaction, acetone formation. The addition of Na_2O or Li_2O to Co_3O_4 was found to improve the selectivity to biacetyl without loss of catalytic activity. The maximum efficiency (13%) in biacetyl formation was attained at a Li content of ca. 7 at.%. © 1984 Academic Press, Inc.

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.
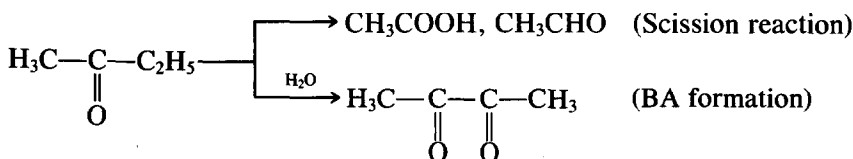
Many investigations of the autoxidation of ketones have been reported. The autoxidation is initiated by the abstraction of an α-hydrogen from reactant ketones followed by the addition of an oxygen molecule to give ketone peroxy radical. This intermediate is then converted into various products in the succeeding reactions. Methyl ethyl ketone (MEK), for example, yields the products (6):

$$H_3C-\underset{\underset{O}{\|}}{C}-C_2H_5 \xrightarrow[O_2\ addition]{H\cdot\ abstraction} H_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O-O\cdot}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 \rightarrow \begin{array}{l} CH_3OH,\ CH_3COOH \\ CH_3COCH_3,\ HCOOH \\ C_2H_5COOH \end{array}$$

$$\downarrow MEK$$

$$H_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O-OH}{|}}{\overset{\overset{}{}}{C}H}-CH_3 \rightarrow \begin{array}{l} CH_3COOH,\ CH_3CHO \\ CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 \end{array}$$

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" (7–10), which is then oxidized to acetic acid (11–13).

$$C_4H_8 \xrightarrow[V_2O_5-MoO_3,\ O_2,\ H_2O]{Oxyhydration}$$

$$H_3C-\underset{\underset{O}{\|}}{C}-C_2H_5 \rightarrow 2CH_3COOH$$
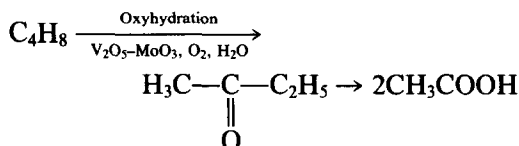
The second stage, i.e., the vapor-phase oxidation of MEK, has been shown to produce scission products or biacetyl (BA), depending on the metal oxide catalyst used (14–16).

$$H_3C-\underset{\underset{O}{\|}}{C}-C_2H_5 \xrightarrow{H_2O} \begin{array}{ll} \rightarrow CH_3COOH,\ CH_3CHO & (Scission\ reaction) \\ \rightarrow H_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 & (BA\ formation) \end{array}$$

It seems very important that BA is obtained directly from MEK in this way. Butter-smelling BA is commonly used for synthetic butter, vinegar, coffee, and other foods (17). So far BA 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 BA (18). Direct catalytic synthesis of BA from MEK, if feasible, will be much superior to the conventional method.

This series of studies has as its aim an investigation of the catalytic properties of transition metal oxides for the vapor-phase oxidation of ketones. The present paper deals with catalytic synthesis of BA over single-metal oxides and some modified catalysts based on cobalt oxide.

EXPERIMENTAL

A. Catalysts

Granules (24–32 mesh) of catalysts were used for experiments.

Oxide catalysts. SnO$_2$ was prepared as follows. The white precipitate obtained by the hydrolysis of SnCl$_2$ · 2H$_2$O was thoroughly washed with distilled water then dried at 333 K for 12 h and 673 K for 4 h.

Fe$_2$O$_3$ and Co$_3$O$_4$ were prepared by the decomposition of Fe(NO$_3$)$_3$ · 9H$_2$O and Co(NO$_3$)$_2$ · 6H$_2$O at 673 K for 4 h.

All of the oxide catalysts were finally calcined at 823 K for 5 h in air.

Metal-ion-exchanged Y zeolites. Linde molecular sieve SK-40 was suspended in distilled water to which an aqueous solution of each metal nitrate (ca. 0.3 M) was added

dropwise for 3 h at ambient temperature while the pH of the suspension was kept not lower than 4.5. After stirring for 1 week, the powder was filtered and then washed with distilled water, dried on a steam bath, and calcined at 673 K for 3 h in air.

Supported and promoted Co₃O₄ catalysts. Supported catalysts were prepared by impregnation of Co(NO₃)₂ · 6H₂O onto MgO and CaO in the aqueous medium followed by calcination at 673 K for 4 h in air. For the preparation of promoted catalysts, diluted aqueous solution of alkali metal hydroxides or alkaline earth nitrates were mixed with the solution of Co(NO₃)₂ · 6H₂O. After drying the solution on a water bath, the resulting precipitate was decomposed to oxides by calcination at 673 K for 4 h.

All of the oxide catalysts were finally calcined at 823 K for 5 h in air.

B. Apparatus and Method

The oxidation reaction was carried out in a conventional flow type reaction system using a 17-mm-i.d. Pyrex glass tubular reactor with a fixed catalyst bed inside. An aqueous solution of MEK was introduced by means of a microliquid feeder to a glass wool bed which was located at the entrance of the reactor and heated at 473 K, where the solution was evaporated and mixed with oxygen and nitrogen. Before every experimental run, prereaction was carried out for 10 h at the temperature where MEK conversion reached about 10% for the stabilization of activity of catalyst.

The effluent gas was led into a cold trap kept at ca. 290 K, to condense the products having high boiling points along with water vapor. Both trapped products and the gas that passed through the trap were analized by gas chromatography. The column packings used were PEG No. 1000 (3 m, 313 K) for aldehydes, ketones, and alcohols, silica gel (1.5 m, r.t.) for carbon dioxide, molecular sieves 5A (1.5 m, r.t.) for oxygen, nitrogen, and carbon monoxide, and DOS (2 m,

363 K) for carboxylic acids. The selectivity of a product A is defined as

$$\frac{\text{Moles of MEK converted to A}}{\text{Total moles of MEK consumed}} \times 100 \ (\%)$$

RESULTS AND DISCUSSION

Oxidation of MEK over Single-Metal Oxides

Catalytic properties of some single-metal oxides for the oxidation of MEK were previously reported (*14*). In this study three oxides, i.e., SnO₂, Fe₂O₃, and Co₃O₄, were newly examined to show a more general feature of catalytic activity of single-metal oxides. The results on the three oxides are shown in Table 1. Small amounts of methyl vinyl ketone, propionaldehyde, acetone, acrolein, and propionic and acrylic acids were also formed but are not included in the table. Oxidative scission of MEK took place predominantly over SnO₂; the selectivity to scission products (acetaldehyde and acetic acid) went up to over 70% at 473 K, while the selectivity to BA reached no more than 15% over the temperatures examined. Fe₂O₃ was less active in MEK conversion and less selective for both BA formation and scission reaction than SnO₂.

The activity of Co₃O₄ was so high as to come after V₂O₅ (*14*) and oxidation of MEK proceeded at a measurable rate even at 403 K. Co₃O₄ has been known to be the most active of transition metal oxides for the complete oxidation of hydrocarbons (*19, 20*). MEK oxidation over Co₃O₄ was fairly selective. BA formation surpassed scission reaction at the temperatures below 433 K. The selectivity to BA decreased monotonously with increasing temperature from 48% at 403 K to 18% at 473 K.

Combining the present results with those reported previously (*14*), one may classify metal oxides into the following three categories on the basis of MEK oxidation taking place at low temperatures:

Category A: BA formation is predominant, Co₃O₄ and NiO.

Category B: both scission reaction and

TABLE 1

Methyl Ethyl Ketone Oxidation over Single-Metal Oxides

Catalyst	Temperature (K)	Conversion (%)	Selectivity (%)				
			$(CH_3CO)_2$	CH_3CHO	CH_3COOH	CO	CO_2
SnO_2	473	11.8	13.3	35.9	36.3	—	7.4
	493	12.9	14.6	22.2	38.5	—	13.3
	513	18.8	11.0	22.5	26.7	8.5	16.9
	533	31.0	5.6	20.5	21.2	10.5	27.4
Fe_2O_3	473	2.4	11.5	46.3	8.8	—	30.7
	493	4.7	6.7	30.4	12.3	—	45.0
	513	12.9	0.5	27.7	35.1	—	34.7
	533	21.5	0.8	8.6	19.0	—	69.1
Co_3O_4	403	1.96	47.7	13.4	18.3	—	16.8
	433	13.3	34.3	7.3	20.0	1.2	36.0
	453	23.8	27.2	5.4	22.6	2.7	40.6
	473	39.0	17.6	5.5	20.0	5.1	50.3

Note. Catalyst: 2.489 g; Feed gas composition: 1.16 mol% EMK, 32.9 mol% each of N_2, O_2, and H_2O; $W/F = 4.27$ s · g-cat./cm³.

BA formation take place, ZnO, CuO, TiO_2, Bi_2O_3, Fe_2O_3, SiO_2, and SnO_2.

Category C: scission reaction is predominant, V_2O_5, MoO_3, WO_3, U_3O_8, and Cr_2O_3.

One can point out a marked tendency that the scission reaction proceeds over acidic oxides (Category C) while BA formation is observed only on basic oxides (Category A). The effects of the acid–base properties of oxides on the selectivities of both reactions are clearly seen in Fig. 1 where the selectivities at 473 K are plotted versus the electronegativity (χ_i) of the metal ions (21). Apparently, the selectivity to BA and the scission products decreases and increases, respectively, as χ_i increases. In other words, acid–base properties of oxides are one of the most important factors governing the selectivity of partial oxidation of MEK.

Cathela *et al.* studied the oxidation and the ammoxidation of MEK over acidic Bi–Mo oxide and observed the principal formation of scission products in the oxidation with air and of acetnitrile and acetic acid in the ammoxidation (22). This supports the present conclusions.

According to ir spectrometric investiga-

tions, acetone and MEK are adsorbed associatively onto a SiO_2 surface (23, 24), while acetone is adsorbed dissociatively onto MgO (25, 26), NiO (25, 26), and ZnO (27)
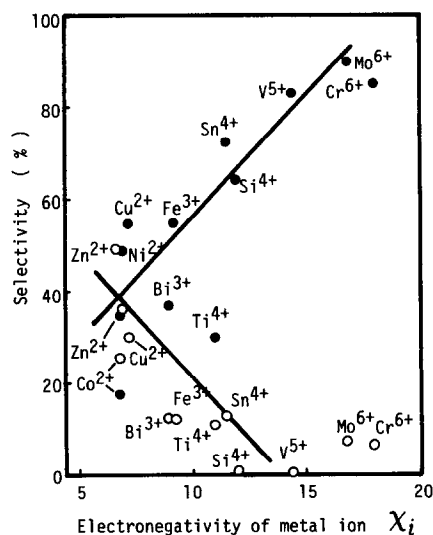

FIG. 1. The effect of electronegativity of the oxides on the selectivity in the oxidation of MEK. O, BA formation; ●, scission reaction. Reaction temperature: 473 K. Other reaction conditions are the same as shown in Table 1. χ_i was calculated by $\chi_i = \chi_0 + (\Sigma I_i)$, where χ_0 and I_i are electronegativity of metals and *i*th ionization potential of metals, respectively (21).

TABLE 2

Methyl Ethyl Ketone Oxidation over Metal-Ion-Exchanged Y Zeolites

Catalyst	Temperature (K)	Conversion (%)	Selectivity (%)				
			$(CH_3CO)_2$	CH_3CHO	CH_3COOH	CO	CO_2
Co(66)–Y	438	2.6	17.1	41.7	7.2	—	28.3
	480	14.7	0.7	11.0	50.1	3.6	32.0
Cu(70)–Y	441	15.5	1.3	4.7	33.0	2.6	55.6
	460	33.7	0.6	2.8	16.9	4.3	73.9
Ni(92)–Y	441	2.4	3.5	45.3	12.5	—	35.9
	460	10.5	2.2	20.1	51.0	2.5	23.6
	480	22.5	0.7	12.3	61.0	3.1	20.9

Note. Catalyst: 1 g, The numbers in parentheses denote the degree of ion exchange, 1 cm^3 SiC (16 mesh) was added; Feed gas composition: 1.64 mol% EMK, 13.8 mol% O_2, 27 mol% H_2O, 51.8 mol% N_2; $W/F = 0.90$ s · g-cat./cm^3.

to form surface species similar to enolate. Whichever types of adsorption may occur, the intermediate formed on basic oxides will be to varying degrees negatively charged. 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 basic oxide catalysts.

The Oxidation of MEK over Metal-Ion-Exchanged Y Zeolite

Catalytic performances of Y zeolites exchanged with Co(II), Cu(II), and Ni(II) ions for MEK oxidation are summarized in Table 2. Comparison of the performance data with those of the corresponding oxides in Table 1 shows that zeolite catalysts tend to depress BA formation even at low MEK conversion levels while enhancing the scission reaction. This trend may be caused by the native acidic property of Y zeolite. The highest selectivity to complete oxidation over Cu–Y would result from the abundance of adsorbed oxygen on that catalyst (*28*).

The Oxidation of MEK over Supported Co Oxide Catalysts

Cobalt oxide, Co_3O_4, was the most active and selective catalyst of the single-metal oxides tested for BA formation as shown previously. It was also stated that BA formation was favored on basic oxide catalysts. In this and the next sections, we investigate the possibilities of improving the catalytic properties of Co_3O_4 by supporting it on basic oxides or by adding basic oxides to it. The results of MEK oxidation over the Co oxide catalysts supported on MgO and CaO are listed in Table 3. It is remarkable that compared with the corresponding data on unsupported Co_3O_4 catalyst (Table 1), the formation of scission products was suppressed while BA selectivity showed higher values at low MEK conversions. This trend is understood as resulting from the increased basic properties of the supported catalysts. A more characteristic feature of the supported catalysts was the generous formation of acetone. In one case, acetone selectivity exceeded 50%. Although acetone can be found in the products of autoxidation of MEK, its selectivity is not as high as observed in this study (*29*). The fact that the generous formation of acetone was observed only on the supported catalysts strongly suggests that the reaction

TABLE 3

Methyl Ethyl Ketone Oxidation over Supported Cobalt Oxide Catalysts

Catalyst	Temperature (K)	Conversion (%)	Selectivity (%)					
			$(CH_3CO)_2$	CH_3CHO	CH_3COOH	CH_3COCH_3	CO	CO_2
$Co_3O_4(5\ wt\%)/MgO$	453	1.1	65.4	15.4	—	19.2	—	—
	553	8.9	24.9	19.2	—	55.0	—	—
	603	23.7	16.1	21.9	—	19.9	14.9	27.3
	653	31.1	4.8	11.6	—	10.7	8.7	64.3
$Co_3O_4(1\ wt\%)/MgO$	503	3.0	36.0	16.9	6.6	27.9	—	12.5
	563	13.4	13.4	7.4	8.2	29.1	—	41.9
	613	48.6	2.1	7.7	2.1	24.1	—	61.9
$Co_3O_4(5\ wt\%)/CaO$	503	1.1	52.2	13.0	—	34.8	—	—
	563	8.0	21.4	11.8	—	45.8	—	21.0
	593	31.4	7.4	8.4	—	20.0	—	48.0

Note. Feed gas composition: 1.04 mol% MEK, 33.0 mol% each of N_2, O_2, and H_2O; $W/F = 0.89$ s · g-cat./cm³.

proceeded on the supports. It has been well known that acetone is formed from thermal decomposition of metal acetates. In the present case acetone plausibly originates from acetate ions adsorbed on the basic supports.

$$2CH_3COO^-_{ads} \rightarrow CH_3COCH_3 + CO_2 + O^{2-}$$
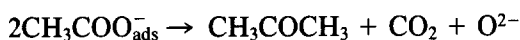
Possibilities of acetone formation through other paths cannot be ruled out. In any case, acetone formation makes the supported Co oxides inefficient for BA formation.

The Oxidation of MEK over Modified CO_3O_4 Catalysts

Modification of Co_3O_4 by the addition of basic oxides was investigated in expectation of the selective inhibition of scission reaction.

Modification by alkali metal oxides: Oxidation data over the modified catalysts are shown in Figs. 2 and 3. The data over Co_3O_4 under the same reaction conditions is also shown in Fig. 4 for comparison, where higher BA selectivities were attained than in Table 1 mainly because of a smaller W/F. The excellent agreement of the MEK conversions between Figs. 2 and 4 indicates

that the addition of Na_2O or Li_2O has no influence on the activity of Co_3O_4. As for the effect on selectivity, the addition of these oxides reduced both the scission reaction and the complete oxidation, while high BA selectivities were retained up to higher temperatures, especially in the case of Co_3O_4–Li_2O, where 61% BA selectivity was attained compared with 25% over Co_3O_4 at 503 K. The addition of K_2O or Rb_2O brought about negative effects on BA formation as shown in Fig. 3, although it was somewhat effective to depress the scis-
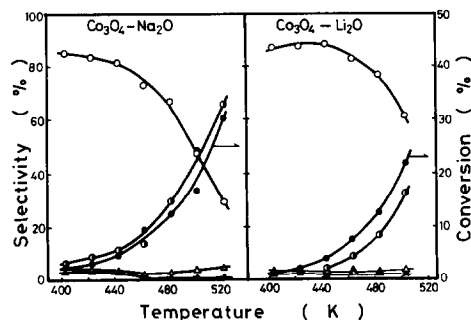

FIG. 2. The oxidation of MEK over Co_3O_4 promoted by Na_2O and Li_2O. Catalyst: 5 at.% Na_2O or Li_2O, 3.0 g. $W/F = 2.65$ (s · g-cat./cm³). Symbols: ●, MEK conversion; ○, BA; △, acetaldehyde; ▲, acetic acid; ◑, carbon oxides.
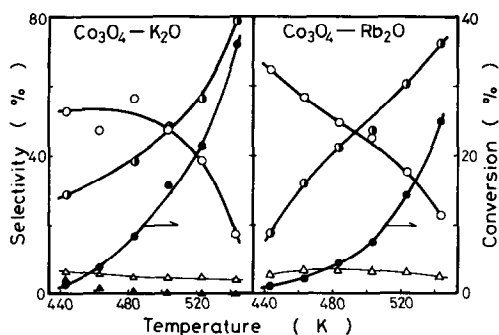
FIG. 3. The oxidation of MEK over Co_3O_4 promoted by K_2O and Rb_2O. Catalyst composition: 5 at.% K_2O or Rb_2O. Reaction conditions and symbols are the same as in Fig. 2.
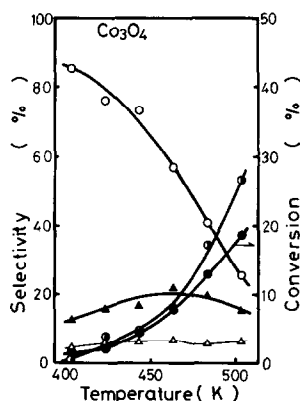
FIG. 4. The oxidation of MEK over Co_3O_4. Reaction conditions and symbols are the same as in Fig. 2.

sion reaction and successive complete oxidation at higher temperatures. Thus, only Na_2O and Li_2O are effective to improve BA formation.

Modification by alkaline earth oxides: Diverse effects were observed by the addition of alkaline earth oxides (Fig. 5). The activity was increased drastically by combining BeO with Co_3O_4. BA formation was suppressed to less than 10% selectivity through 373–463 K, while the scission reaction was largely promoted. These effects are thought to come from the acidic property of BeO which belongs to a group of amphoteric oxides. In the cases of the other alkaline earth oxides, both BA formation

and the scission reaction were discouraged and only complete oxidation was accelerated. The addition of alkaline earth oxides is thus undesirable for BA formation.

The Effects of Composition in Co_3O_4–Li_2O System

As clarified in the previous sections, Li_2O was the most effective promoter of Co_3O_4. BA selectivities over this catalyst system were plotted in Fig. 6 as a function of Li content at several temperatures. BA selectivity increased with increasing Li content up to 7%, above which the effect became almost saturated. The contents of Li also affected the specific rates and spe-
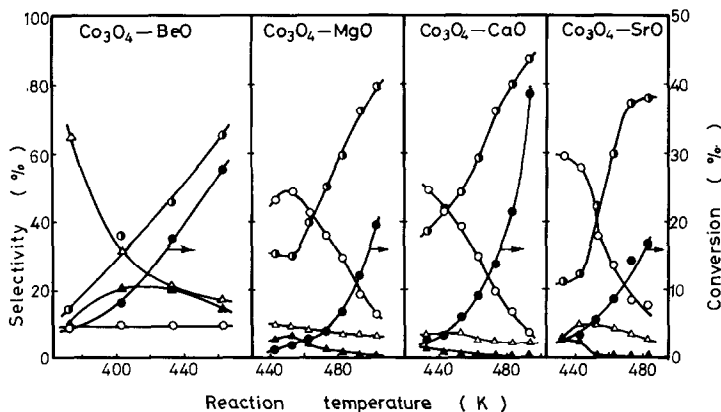

FIG. 5. The oxidation of MEK over Co_3O_4 promoted by alkaline earth oxides. Catalyst composition: 5 at.% alkaline earth oxide. Reaction conditions and symbols are the same as in Fig. 2.
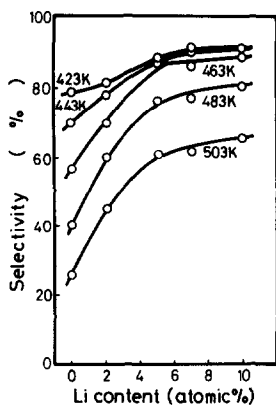
FIG. 6. The effect of Li content on the BA selectivity. Reaction conditions and symbols are the same as in Fig. 2.

FIG. 8. The effect of W/F on the selectivity. Catalyst: Co_3O_4–Li_2O (5 at.% Li_2O). Symbols are the same as in Fig. 2.

cific surface area of Co_3O_4–Li_2O system as shown in Fig. 7. The specific rate had the maximum value at 7% Li both for MEK consumption and for BA formation, while specific surface area was reduced to about one-half the value of Co_3O_4 by the addition of Li_2O by 7–10 at.%. These results suggest that 7–10 at.% Li content is optimum for BA formation.

It has been known that there are many binary oxide compounds containing cobalt with spinel or perovskite structure and also many oxide compounds between cobalt and alkali metals or alkaline earth metals, for example, $LiCoO_2$, $Ca_3Co_2O_6$, $Ca_3Co_4O_9$, $Mg_2Co_2O_4$, and so on (30). However, the X-ray powder diffraction patterns of Co_3O_4 and Co_3O_4–Li_2O catalysts used here exhib-

ited only the reflections characteristic of Co_3O_4 of spinel structure. Therefore, Li oxide may exist in the grain boundary of Co_3O_4 crystallites. It is thought that the basic character of Co_3O_4 may require a relatively high concentration of Li such as 7–10 at.% to show a remarkable effect on BA formation.

The Effect of W/F on BA Formation

Figure 8 shows the variation of selectivities as a function of W/F over Co_3O_4–Li_2O catalyst. BA selectivity decreased gradually with increasing W/F because of successive oxidation of BA. The value of BA selectivity at $W/F = 0$ estimated by extrapolation is 65–90% at 443–503 K. Similarly, the selectivity to carbon oxides is 15–30% at 483–503 K. This indicates that a part of MEK was oxidized to carbon oxides directly as a simultaneous reaction competing with BA formation even on the Co_3O_4 catalyst promoted by Li_2O.
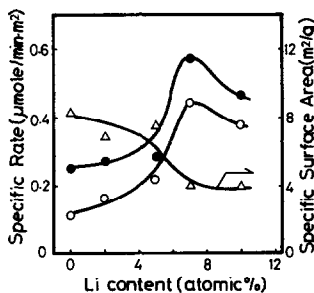
FIG. 7. The effects of Li content on the specific surface area and specific rates. ●, MEK consumption; ○, BA formation.
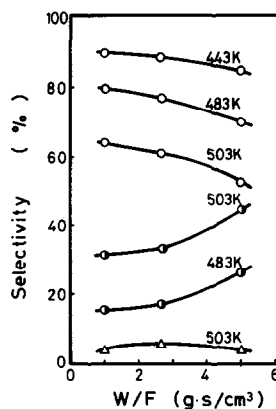
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