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Direct Synthesis of Ethyl Acetate from Ethanol Carried Out under Pressure

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Direct synthesis of ethyl acetate from ethanol over a Cu–Zn–Zr–Al–O catalyst was investigated under pressured conditions between 473 and 533 K. Both the selectivity to ethyl acetate and the space-time yield of ethyl acetate increase with increasing reaction pressure, whereas ethanol conversion decreases. The highest space-time yield of ethyl acetate is attained at a reaction pressure of about 0.8 MPa with maximum selectivity of 93 wt%. During the process, ethanol is first dehydrogenated to acetaldehyde and is then coupled with another ethanol molecule to form hemiacetal, which is further dehydrogenated to ethyl acetate. The concentration of by-products such as 1-butanol and butanone, which form after the aldol addition of acetaldehyde, decreases with increasing reaction pressure. Since the equilibrium of the dehydrogenation of ethanol to acetaldehyde shifts to an ethanol-rich composition at high pressure, the decrease in the partial pressure of acetaldehyde explains the suppression of the by-products formed through acetaldol. © 2002 Elsevier Science (USA)

Key Words: **ethyl acetate; ethanol; pressured condition.**

INTRODUCTION

Ethyl acetate is an environmentally friendly organic solvent used in paint and adhesive, thus eliminating the use of aromatic compounds, in the working environment. Ethyl acetate can be produced industrially in three ways (1): the Fischer esterification process (2–4), the Tishchenko reaction of acetaldehyde (5, 6), and the addition of acetic acid to ethylene (7–10). The conventional processes, however, have some disadvantages. Both conventional esterification and the addition of acetic acid to ethylene require stock tanks and apparatuses for plural feedstocks; the use of acetic acid causes corrosion of the apparatuses. Acetaldehyde is only available in a petrochemical industrial area and is difficult to handle because of its toxicity. Therefore, a novel process for the production of ethyl acetate is desirable.

The dehydrogenative dimerization of ethanol to ethyl acetate is a simple, noncorrosive, and less-toxic process, requiring only an ethanol feedstock. There are several pioneering studies of the dehydrogenative dimerization of ethanol using Cu-based catalysts (11–19). However, these studies have not answered questions of economy, especially in terms of selectivity to ethyl acetate and space-time yield (STY) of ethyl acetate under atmospheric pressure. In 1999, Kvaerner Process Technology announced the development of a process of dehydrogenative dimerization of ethanol to ethyl acetate (20), which operates under pressure (21). The process requires a copper catalyst and results in about 30 to 40% ethanol conversion and about 95% ethyl acetate selectivity with liquid hourly space velocity (LHSV) $= 1.0\ \mathrm{h}^{-1}$ at 496 K and 2.86 MPa (21). Although it has high selectivity to ethyl acetate, the STY of ethyl acetate is not yet satisfactory.

To improve the STY of ethyl acetate, we must consider the reaction mechanism of ethyl acetate formation and other by-products. Elementary reactions in the process are divided into three types: (a) reactions preferred by high pressure, (b) reactions preferred by low pressure, and (c) reactions that do not depend on pressure. The dehydrogenative dimerization of ethanol to ethyl acetate is a combination of dehydrogenation, which is preferred by low pressure, and dimerization, which is preferred by high pressure. Furthermore, most of the by-products are formed through elementary reactions which are preferred both by high and low pressure. The reaction rate is also important in manufacturing processes. It is advantageous that the rate of formation of ethyl acetate is accelerated at high pressure by the increase in intermolecular collision frequency together with the formation of by-products.

We recently reported an effective catalyst system, Cu–Zn–Zr–Al–O, for the dehydrogenative dimerization of ethanol at ambient pressure (22). The present study clarifies the efficiency of the high-pressure process using the Cu–Zn–Zr–Al–O catalyst, that is, the effect of reaction pressure on the total reaction rate of ethyl acetate as well as on the product selectivity. We also discuss the reaction mechanism of ethyl acetate formation from ethanol.

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EXPERIMENTAL

Catalyst Sample

The Cu–Zn–Zr–Al–O catalyst was prepared by conventional coprecipitation using the corresponding nitrates and a sodium hydroxide solution (about 3 mol dm^{-3}) as the precipitant. The atomic ratio of Cu/Zn/Zr/Al was fixed at 12 : 1 : 2 : 4. After precipitation, the precipitate was stored at room temperature for 18 h and was then washed with deionized water. The resulting precipitate was dried at 353 K for 10 h followed by calcination in a N_2 flow at 773 K for 3 h. The specific surface area calculated using the BET method for N_2 adsorption at 77 K was 99.7 m^2 g^{-1}, and the Cu surface area measured by TPR titration of Cu oxidized by N_2O (23) was 38.7 m^2 g^{-1}.

Catalytic Reaction

Dehydrogenative dimerization of ethanol was carried out at a reaction pressure between 0.1 and 1.0 MPa using a conventional fixed-bed down-flow stainless steel reactor. Prior to the catalytic reaction, the catalyst was reduced in a flow of H_2–N_2 ($H_2/N_2 = 10 : 90$) at 100 cm^3 min^{-1} at temperatures of up to 443 K. The carrier gas was then switched to N_2 and the sample was heated at a prescribed reaction temperature. The ethanol reactant was introduced into the reactor at a temperature between 473 and 533 K at $W/F = 0.018$–7.9 h, where W and F are catalyst weight [kg] and flow rate of ethanol [kg h^{-1}], respectively. N_2 carrier gas (30 cm^3 min^{-1}) was used at 0.1 MPa, whereas no carrier gas was used at >0.1 MPa. The partial pressures of inlet ethanol in the reaction operated at 0.1 MPa are 0.072 and 0.091 MPa at W/F of 3.16 and 1.58 h, respectively. The reactant was heated and vaporized in the preheating zone in front of the catalyst bed. The products were recovered by cooling at 195 K. The effluent was collected periodically and analyzed by gas chromatography (Shimadzu GC-14A) using a capillary column (G-100, Kagakuhin Kensa Kyokai) with toluene as the internal standard. The water content in the effluent was determined using a Karl-Fischer moisture meter. The gaseous products, such as H_2 and CO_2, that did not condense at 195 K were collected in a plastic bag and analyzed by gas chromatography (Shimadzu GC-9A) in a packed column (active carbon).

RESULTS

Figure 1 shows the conversion of ethanol over the Cu–Zn–Zr–Al–O catalyst at temperatures between 473 and 513 K and the equilibrium conversion calculated for the dehydrogenation of ethanol to ethyl acetate as a function of reaction pressure. We did not observe a decrease in the catalytic activity during the process time. At each temperature, the observed conversion of ethanol and the equilibrium conversion decrease with increasing reaction pressure. Since the reaction rate is low at the low temperature of 473 K, the actual conversion of ethanol is lower than the equilibrium conversion. Nevertheless, the actual ethanol conversion above 493 K is greater than the equilibrium conversion. Since the produced acetaldehyde is further converted to other by-products, such as butanone and butanol, at high temperatures, the actual conversion is greater than the equilibrium conversion of ethanol to ethyl acetate.

Table 1 lists typical product distributions in the reaction of the dehydrogenative dimerization of ethanol over the Cu–Zn–Zr–Al–O catalyst at different reaction pressures. In the reaction, total mass in the effluent liquid and gas is balanced to the mass of inlet ethanol. A wide variety of products, such as ethyl acetate, acetaldehyde, butanone, propanone, 2-pentanone, 1-butanol, ethyl butyrate, butyl acetate, water, and a small number of unidentified products, were found in the effluent. Both at 473 and 513 K, the selectivity to ethyl acetate increases with increasing reaction pressure. The selectivity of by-products decreases with increasing reaction pressure. In particular, we observed a considerable suppression of the formation of acetaldehyde and butanone at higher pressure. This significant suppression leads to a high ethyl acetate selectivity of 92.6 wt%. In addition, a trace amount of butanal was formed during this reaction, whereas no 2-butenal is detected. It is reported that butanal is formed from acetaldehyde over acetaldol (16, 17). It is reasonable that 2-butenal and butanal are hydrogenated to 1-butanol as soon as they are formed over the catalyst.

In the analysis of gaseous products, hydrogen and carbon dioxide were observed: more than 99 mol% of the gaseous products was hydrogen with a small amount of CO_2. CO_2 is probably produced from the decomposition of acetaldol

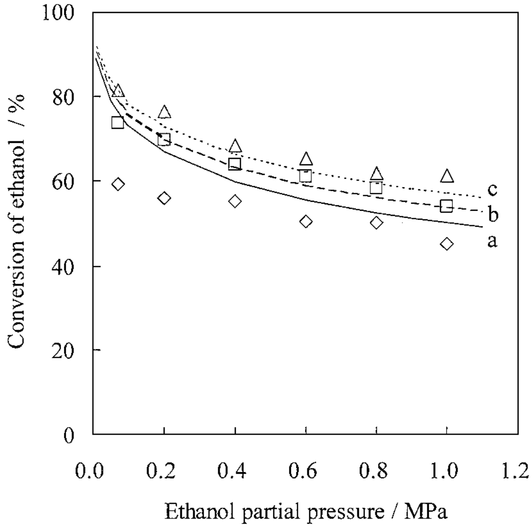


FIG. 1. Changes in conversion with ethanol partial pressure ($W/F = 3.16$ h). Reaction temperature: ◇, 473; □, 493; △, 513 K; lines represent equilibrium conversion of ethanol calculated at (a) 473, (b) 493, and (c) 513 K.

TABLE 1

Catalytic Results over Cu–Zn–Zr–Al–O Catalyst for the Reaction of Ethanol

			Selectivity (wt%)										
Temp. (K)	Press. (MPa)	X[a] (%)	AcOEt	AcH	MEK	AcMe	2PN	1BO	EB	BE	H_2O	H_2	Others
473	0.1	60.3	84.8	3.6	3.7	0.5	0.1	0.2	0.6	0.3	1.1	4.2	0.9
	0.2	57.1	89.2	2.1	2.0	0.3	0.0	0.2	0.5	0.2	0.5	4.2	0.9
	0.4	56.4	92.1	1.0	0.9	0.1	0.0	0.2	0.5	0.2	0.2	4.2	0.8
	0.6	51.6	91.3	1.0	0.7	0.1	0.0	0.2	0.5	0.2	0.1	4.2	1.8
	0.8	51.4	92.9	0.8	0.5	0.1	0.0	0.2	0.3	0.1	0.1	4.2	1.0
	1.0	46.3	91.6	0.7	0.3	0.1	0.0	0.1	0.2	0.1	0.9	4.2	1.9
513	0.1	82.1	75.9	3.8	5.8	2.2	0.4	0.6	1.1	0.9	1.9	4.2	3.2
	0.2	77.2	78.0	2.9	4.3	1.5	0.3	1.1	2.0	1.7	1.6	4.2	2.4
	0.4	69.3	81.5	1.6	3.3	1.1	0.3	0.8	0.9	0.6	1.8	4.2	4.1
	0.6	66.4	82.6	1.6	2.7	0.9	0.2	1.1	1.4	0.8	1.5	4.2	3.1
	0.8	62.9	84.2	1.3	2.2	0.7	0.2	0.9	1.0	0.5	1.5	4.2	3.4
	1.0	62.4	83.5	1.1	1.6	0.3	0.1	0.5	0.6	0.3	2.1	4.2	5.8

Note. AcOEt, ethyl acetate; AcH, acetaldehyde; MEK, butanone; AcMe, propanone; 2PN, 2-pentanone; 1BO, 1-butanol; EB, ethyl butyrate; BE, butyl acetate. Others indicates a small number of unidentified products.

[a] Conversion of ethanol; $W/F = 3.16$ h.

to propanone. The amount of hydrogen produced corresponded to the sum of the derivatives from the dehydrogenation. Since hydrogen and water were observed as inorganic products, dehydrogenation and dehydration surely proceed over the catalysts.

Figure 2 shows the changes in the selectivity to ethyl acetate with reaction pressure together with the sum of the selectivities to acetaldol derivatives. Here, the acetaldol derivatives include butanal, 1-butanol, ethyl butyrate, butyl acetate, butanone, propanone, and 2-pentanone. At an ambient pressure of 0.1 MPa, the maximum selectivity to ethyl acetate was 85.0 wt% at the low temperature of 473 K. At each reaction temperature, the selectivity to ethyl acetate greatly increased with increasing reaction pressure, and reached a plateau at around 0.4 MPa at 473 K. At higher temperatures, a much higher pressure is needed to improve the ethyl acetate selectivity. At all temperatures, the sum of the selectivities to acetaldol derivatives decreased with increasing reaction pressure.

Figure 3 shows the changes in the STY of ethyl acetate and the selectivity to ethyl acetate with *W/F* at 1.0 MPa. The STY decreased with increasing *W/F* and increased with increasing reaction temperature. The maximum STY exceeded 20 mol h^{-1} kg_{cat}^{-1} at 533 K. At all temperatures, the selectivity to ethyl acetate increased with increasing *W/F* and reached a maximum at $W/F =$ ca. 0.5–1.0 h. This

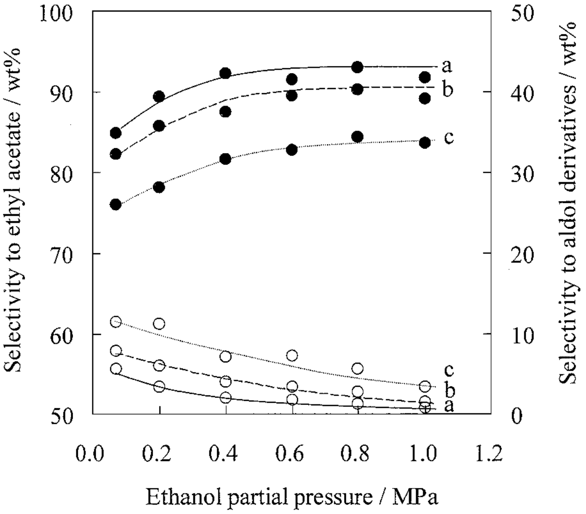


FIG. 2. Changes in the selectivity to ethyl acetate (●) and aldol derivatives (○) with ethanol partial pressure. Reaction temperature: (a) 473, (b) 493, (c) 513 K; $W/F = 3.16$ h.

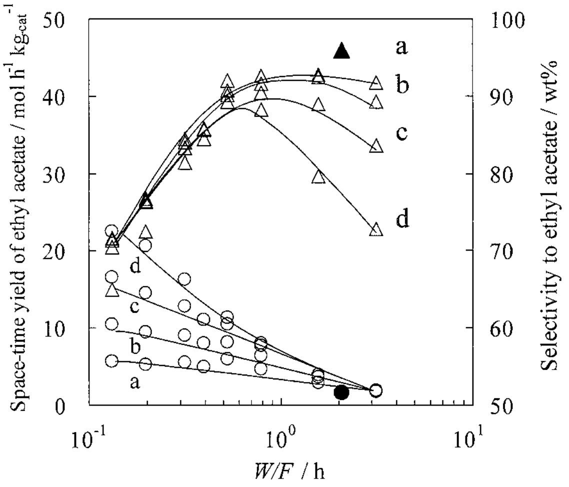


FIG. 3. Changes in STY of ethyl acetate (○) and selectivity to ethyl acetate (△) with *W/F*. Reaction temperature: (a) 473, (b) 493, (c) 513, (d) 533 K; pressure, 1.0 MPa. Reference data:(●) STY, (▲) selectivity, (498 K 2.7 M Pa; Ref. 21).

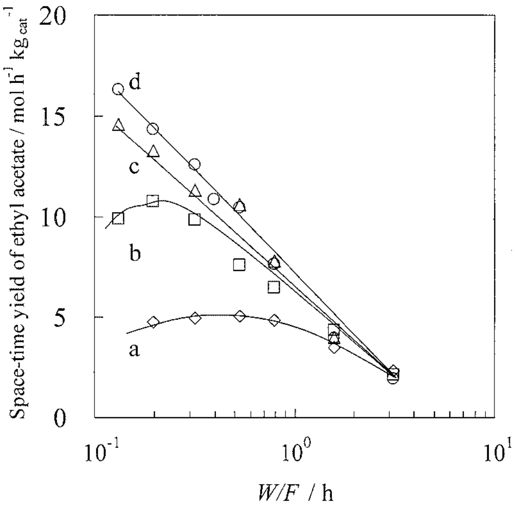


FIG. 4. Changes in STY of ethyl acetate with *W/F* at 513 K. Reaction pressure: (a) 0.1, (b) 0.4, (c) 0.8, (d) 1.0 MPa.

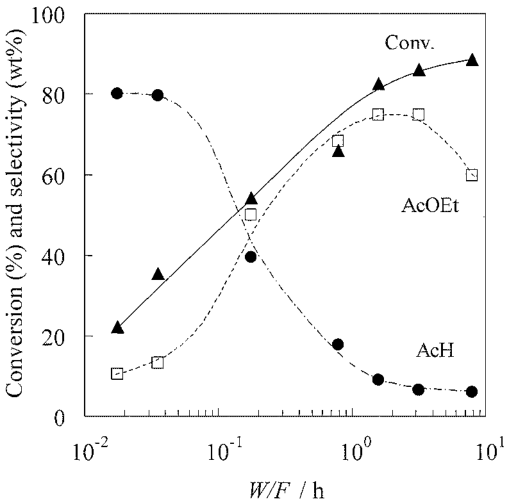


FIG. 5. Changes in conversion and selectivity with *W/F* at 533 K and 0.1 MPa: (▲) ethanol conversion, (□) ethyl acetate selectivity, (●) acetaldehyde selectivity.

demonstrates that a high STY of ethyl acetate with high selectivity to ethyl acetate can be achieved over the present Cu–Zn–Zr–Al–O catalyst; 92.6 wt% selectivity was obtained at 493 K, 1.0 MPa, and $W/F = 0.53$ h with STY of 8 mol h^{-1} kg^{-1}, compared with a reference STY of 2.8 mol h^{-1} kg$_{\text{cat}}^{-1}$, which was calculated assuming a catalyst bulk density of 1.68 g cm^{-3}, as reported for a CuO-based catalyst at 498 K and 2.7 MPa (21).

Figure 4 shows the changes in the STY of ethyl acetate at 513 K with *W/F*. The STY increased with increasing reaction pressure. The STY reached maxima at the low pressures of 0.1 and 0.4 MPa and a linear decrease with increasing *W/F* at high pressures. This indicates that the maximum in STY shifts to lower *W/F* with increasing reaction pressure.

Figure 5 shows the changes in ethanol conversion, ethyl acetate selectivity, and acetaldehyde selectivity with *W/F*. Over the Cu–Zn–Zr–Al–O catalyst at 533 K and 0.1 MPa, the ethanol conversion increased with increasing *W/F*, while the acetaldehyde selectivity decreased. At low *W/F*, acetaldehyde was preferentially formed and ethyl acetate increased with increasing ethanol conversion with *W/F*. The ethyl acetate selectivity reached a maximum at $W/F = 1$–2 h. Since by-products are produced at $W/F > 2$ h, the ethyl acetate selectivity decreased.

Table 2 lists the reaction results of acetaldehyde, ethanol, and 1,3-butandiol as the feedstock over the Cu–Zn–Zr–Al–O catalyst under different conditions. In a reaction of acetaldehyde in a flow of N_2 hardly any converted to ethyl acetate and a small amount of acetaldol derivatives such as 2-butenal and butanal were observed. In contrast, the reaction of acetaldehyde in an H_2 flow was accompanied by the formation of ethyl acetate as a major product. Hydrogenated products such as ethanol and 1-butanol were also observed in an H_2 flow. However, hardly any 2-butenal was detected in the presence of H_2 (Table 2). The product distribution in an H_2 flow is similar to that observed in the reaction of ethanol in an N_2 flow. In the reaction of an equimolar mixture of acetaldehyde and ethanol

TABLE 2

Reaction of Other Feedstocks over Cu–Zn–Zr–Al–O Catalyst

		Composition of products (wt%)												
Feedstock	Carrier gas	EtOH	AcH	13BD	AcOEt	MEK	AcMe	CA	BA	1BO	2PN	EB	BE	Others
AcH	N_2	2.1	83.0	0	3.3	0.3	1.6	3.3	3.9	0.1	0.3	0.7	0.3	1.1
AcH	H_2	16.9	10.6	0	46.8	2.9	5.0	0	0.6	1.6	1.9	4.1	4.1	5.5
EtOH	N_2	38.5	5.6	0	39.0	4.7	0.7	0	0	0.5	0.2	0.8	0.5	9.5
AcH + EtOH	N_2	30.7	14.8	0	31.1	6.3	1.4	0	0	1.8	0.5	1.8	1.9	9.7
13BD	N_2	5.4	4.9	0	1.2	47.4	4.1	0	0	4.4	0.3	1.3	1.0	30.0
13BD	H_2	7.4	3.1	trace	1.2	44.4	4.1	0	0	4.6	0.2	1.0	1.0	33.0

Note. Reaction temperature, 493 K; pressure, 0.1 MPa; $W/F = 1.58$ h; carrier gas flow rate = 30 cm^3 min^{-1}. 13BD, 1,3-butanediol; MEK, butanone; AcMe, propanone; AcH, acetaldehyde; EtOH, ethanol; AcOEt, ethyl acetate; CA, 2-butenal; BA, butanal; 1BO, 1-butanol; 2PN, 2-pentanone; EB, ethyl butyrate; BE, butyl acetate. Others indicates water, hydrogen, and unidentified liquid products.

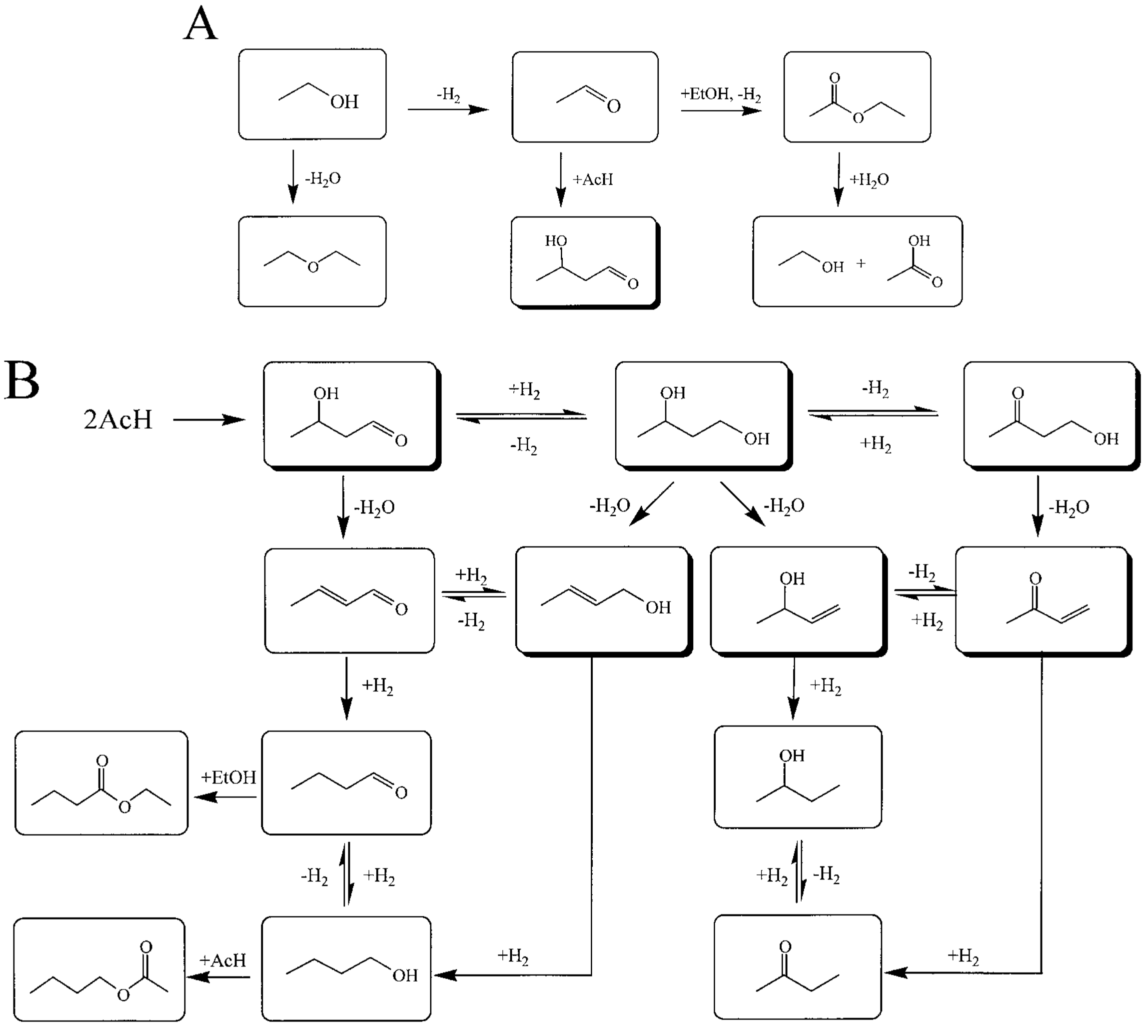
in an N_2 flow, the product distribution is also similar to that observed in the reaction of ethanol. Butanone is the major product of the 1,3-butanediol reaction and small amounts of acetaldehyde, 1-butanol, ethanol, propanone, and ethyl acetate were detected. Furthermore, in the 1,3-butanediol reactions with N_2 and H_2 as carrier gases, the water detected in the effluent was 15.0 and 17.0 wt%, respectively.

DISCUSSION

1. Reaction Mechanism

First, we propose a total products map of ethanol conversion over the Cu–Zn–Zr–Al–O catalyst (Scheme 1). We must consider each elementary reaction and the dependence of its equilibrium on pressure for each of the routes and discuss the total reaction mechanism. The elementary reactions are divided into three types: reactions preferred by high pressure, reactions preferred by low pressure, and reactions that do not depend on pressure (Table 3). A large number of elementary reactions are pressure-sensitive (Tables 3A and 3B).

It is obvious that pressure affects the catalytic reaction; i.e., the ethanol conversion (Fig. 1) and product distribution (Table 1). High-pressure operation suppresses both the ethanol conversion and the formation of by-products such as butanone and 1-butanol, derived from acetaldol, which can be rationalized by the decrease in the partial pressure of acetaldehyde caused by a shift in equilibrium among ethanol, acetaldehyde, and hydrogen at high pressure. Consequently, a high selectivity to ethyl acetate is achieved by suppressing the acetaldehyde partial pressure in the initial elementary reaction rather than by suppressing each elementary reaction for the by-products. The following discussion deals with the elementary reactions.



SCHEME 1. Possible reaction routes over Cu–Zn–Zr–Al–O catalyst: (A) routes to major products, (B) routes to acetaldehyde derivatives. Materials shown in squares with no shadow represent the products detected in this work, whereas substrates shown in squares with shadows are undetected products.

TABLE 3A

High-Pressure Preferable Elementary Reactions

a-1.	$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$ acetaldehyde ethanol	Hydrogenation (b-1)
a-2.	$CH_3CHO + CH_3CH_2OH \rightarrow CH_3CH(OH)OC_2H_5$ acetaldehyde ethanol hemiacetal	Hemiacetal formation
a-3.	$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$ acetaldehyde acetaldol	Aldol addition (b-3)
a-4.	$CH_3CH{=}CHCHO + H_2 \rightarrow CH_3(CH_2)_2CHO$ 2-butenal butanal	Hydrogenation
a-5.	$CH_3(CH_2)_2CHO + H_2 \rightarrow CH_3(CH_2)_3OH$ butanal 1-butanol	Hydrogenation (b-5)
a-6.	$CH_3CH(OH)CH_2CHO + H_2 \rightarrow CH_3CH(OH)CH_2CH_2(OH)$ acetaldol 1,3-butanediol	Hydrogenation (b-6)
a-7.	$CH_3CH(OH)CH{=}CH_2 + H_2 \rightarrow CH_3CH(OH)CH_2CH_3$ 3-hydroxy-1-butene 2-butanol	Hydrogenation
a-8.	$CH_3COCH_2CH_3 + H_2 \rightarrow CH_3CH(OH)CH_2CH_3$ butanone 2-butanol	Hydrogenation (b-8)
a-9.	$CH_3CH(OH)CH_2CHO + O_{(S)} \rightarrow CH_3CH(OH)CH_2COO_{(S)}$ acetaldol carboxylate adsorbed	Oxidation
a-10.	$CH_3COCH_3 + H_2 \rightarrow CH_3CH(OH)CH_3$ propanone 2-propanol	Hydrogenation (b-10)
a-11.	$CH_3COCH_3 + CH_3CHO \rightarrow CH_3COCH_2CH(OH)CH_3$ propanone acetaldehyde 4-hydroxy-2-pentanone	Aldol addition (b-11)
a-12.	$CH_3COCH{=}CHCH_3 + H_2 \rightarrow CH_3CO(CH_2)_2CH_3$ 3-pentene-2-one 2-pentanone	Hydrogenation
a-13.	$CH_3(CH_2)_2CHO + CH_3CH_2OH \rightarrow C_3H_7CH(OH)OC_2H_5$ butanal ethanol hemiacetal	Hemiacetal formation
a-14.	$CH_3CHO + CH_3(CH_2)_2CH_2OH \rightarrow CH_3CH(OH)OC_4H_9$ acetaldehyde butanol hemiacetal	Hemiacetal formation

Note. Reaction numbers in parentheses indicate the number of the reverse reaction shown in Table 3B.

1.1. Formation of ethyl acetate. Figure 5 strongly suggests that the formation of ethyl acetate proceeds stepwise via acetaldehyde, which is an intermediate. It is obvious that the dehydrogenation step is not a rate-determining step in the formation of ethyl acetate from ethanol, because the product distribution in the reaction of acetaldehyde in H_2 flow is similar to that observed in the reaction of ethanol (Table 2).

Two possible routes of ethyl acetate formation from ethanol are proposed. Route 1, the Tishchenko reaction, consists of dehydrogenation followed by coupling of acetaldehyde:

$$2C_2H_5OH \rightarrow 2CH_3CHO \rightarrow CH_3COOC_2H_5. \qquad [1]$$

Route 2 consists of dehydrogenation followed by addition of ethanol to acetaldehyde:

$$\begin{aligned} &2C_2H_5OH \rightarrow CH_3CHO + C_2H_5OH \\ &\qquad \rightarrow CH_3CH(OH)OC_2H_5 \rightarrow CH_3COOC_2H_5. \qquad [2] \end{aligned}$$

The result of the reaction of acetaldehyde in an inert carrier gas of N_2 over the Cu–Zn–Zr–Al–O catalyst (Table 2) differs from that of route 1 via the Tishchenko reaction. Furthermore, Takeshita *et al.* did not use the Tishchenko route over a reduced copper catalyst, because propanal did not condense to give the corresponding ester (15). Takezawa and Iwasa proposed route 2, the nucleophilic addition of either ethanol or surface ethoxide to acetaldehyde to form a hemiacetal, followed by dehydrogenation to ethyl acetate over a supported copper catalyst (Cu/SiO_2; 16). Takeshita also proposed the same route over a reduced copper catalyst (19). The results in Table 2 indicate that a hydrogenated acetaldehyde, e.g., ethanol, is needed for the formation of an intermediate in ethyl acetate production. Thus, we conclude that route 2 is the probable route for the formation of ethyl acetate over the present system of Cu–Zn–Zr–Al–O rather than the Tishchenko reaction. The stepwise reactions via hemiacetal (route 2) consist of a reaction a-2 (listed in Table 3), which is preferred by high pressure, and reactions b-1 and b-2, which are preferred by low pressure.

1.2. Butanone and propanone. The by-products of the ethanol reaction are divided into two groups: some arise from acetaldol, formed by the aldol addition of

TABLE 3B

Low-Pressure Preferable Elementary Reactions

b-1.	$CH_3CH_2OH \rightarrow CH_3CHO + H_2$ ethanol acetaldehyde	Dehydrogenation (a-1)
b-2.	$CH_3CH(OH)OC_2H_5 \rightarrow CH_3COOC_2H_5 + H_2$ hemiacetal ethyl acetate	Dehydrogenation
b-3.	$CH_3CH(OH)CH_2CHO \rightarrow 2CH_3CHO$ acetaldol acetaldehyde	Reverse aldol addition (a-3)
b-4.	$CH_3CH(OH)CH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$ acetaldol 2-butenal	Dehydration
b-5.	$CH_3(CH_2)_3OH \rightarrow CH_3(CH_2)_2CHO + H_2$ 1-butanol butanal	Dehydrogenation (a-5)
b-6.	$CH_3CH(OH)CH_2CH_2(OH) \rightarrow CH_3CH(OH)CH_2CHO + H_2$ 1,3-butanediol acetaldol	Dehydrogenation (a-6)
b-7.	$CH_3CH(OH)CH_2CH_2(OH) \rightarrow CH_3CH(OH)CH{=}CH_2 + H_2O$ 1,3-butanediol 3-hydroxy-1-butene	Dehydration
b-8.	$CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3 + H_2$ 2-butanol butanone	Dehydrogenation (a-8)
b-9.	$CH_3CH(OH)CH_2COO_{(S)} \rightarrow CH_3COCH_3 + H_2 + CO_2$ carboxylate adsorbed propanone	Ketonization
b-10.	$CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 + H_2$ 2-propanol propanone	Dehydrogenation (a-10)
b-11.	$CH_3COCH_2CH(OH)CH_3 \rightarrow CH_3COCH_3 + CH_3CHO$ 4-hydroxy-2-pentanone propanone acetaldehyde	Reverse aldol addition (a-11)
b-12.	$CH_3COCH_2CH(OH)CH_3 \rightarrow CH_3COCH{=}CHCH_3 + H_2O$ 4-hydroxy-2-pentanone 2-penten-4-one	Dehydration
b-13.	$CH_3(CH_2)_2CH(OH)OC_2H_5 \rightarrow C_3H_7COOC_2H_5 + H_2$ hemiacetal ethyl butyrate	Dehydrogenation
b-14.	$CH_3CH(OH)OC_4H_9 \rightarrow CH_3COOC_4H_9 + H_2$ hemiacetal butyl acetate	Dehydrogenation

Note. Reaction numbers in parentheses indicate the number of the reverse reaction shown in Table 3A.

acetaldehyde, and others do not form this way. Elliot and Pennella proposed a reaction mechanism for butanone and propanone formation over $Cu/ZnO/Al_2O_3$ (17). According to their mechanism (Eqs. [3]–[5]), butanone forms from acetaldol (Eq. [3]) accompanied by the formation of lattice oxygen, represented as $O_{(S)}$ in Eq. [4] where the subscript (S) represents a surface-adsorbed species. They also described how lattice oxygen was consumed by propanone formation (Eq. [5]). Although the lattice oxygen was needed to explain the formation of propanone (Eq. [5]), the generation of the lattice oxygen described in Eq. [4] is invalid. The first part of Eq. [4] must contain several elemental reactions such as hydrogenation, dehydration, and the decomposition of water. The generation of the lattice oxygen may be consistent with the decomposition of water: $H_2O \rightarrow H_2 + O_{(S)}$. If the $O_{(S)}$ derives from water, then we accept the mechanism. Furthermore, ketonization of esters to form a symmetric ketone, as proposed by Wrzyszcz *et al.* (24), is not possible because propanone decreased with increasing concentration of ethyl acetate at high pressure (Table 1).

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO \qquad [3]$$

$$\begin{aligned} CH_3CH(OH)CH_2CHO + H_2 &\rightarrow CH_3CH(OH)CH_2CH_3 + O_{(S)} \\ &\rightarrow CH_3COCH_2CH_3 + H_2 \qquad [4] \end{aligned}$$

$$\begin{aligned} CH_3CH(OH)CH_2CHO + O_{(S)} &\rightarrow CH_3CH(OH)CH_2COO_{(S)} \\ &\rightarrow CH_3COCH_3 + CO_2 + H_2. \qquad [5] \end{aligned}$$

On the other hand, Chung *et al.* investigated the reaction of 1,3-butanediol over Cu/ZnO catalyst (25). They reported that butanone and butanal formed from 1,3-butanediol. Butanone is the major product in the reaction of 1,3-butanediol over the present Cu–Zn–Zr–Al–O catalyst (Table 2). Since the hydrogenation is fast, as shown in the

TABLE 3C

Pressure-Independent Elementary Reactions

c-1.	$2CH_3CH_2OH \rightarrow C_2H_5OC_2H_5 + H_2O$ ethanol diethyl ether	Dehydration
c-2.	$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ ethyl acetate acetic acid ethanol	Hydrolysis (reversible)

acetaldehyde-in-H_2 reaction (Table 2), 1,3-butanediol must be formed during the hydrogenation of acetaldol. Because acetaldehyde, ethanol, and propanone were observed in the reaction of 1,3-butanediol, even propanone must form through acetaldol. Both hydrogenation and dehydrogenation, in addition to the reverse aldol addition, can proceed smoothly over the present catalyst. These results indicate that 1,3-butanediol, the hydrogenated acetaldol, is a possible intermediate of the major by-product butanone. The following reaction sequence described in Eq. [6] consists of the elementary reactions a-6, b-7, a-7, and b-8 listed in Table 3:

$$\begin{aligned}&CH_3CH(OH)CH_2CHO + H_2\\ &\quad\rightarrow CH_3CH(OH)CH_2CH_2OH\\ &\quad\rightarrow CH_3CH(OH)CH{=}CH_2 + H_2O\\ &\quad\rightarrow CH_3CH(OH)CH_2CH_3(-H_2)\\ &\quad\rightarrow CH_3COCH_2CH_3 + H_2. \qquad [6]\end{aligned}$$

1.3.1-Butanol. A series of the reactions b-4, a-4, and a-5 (Table 3) originates from the aldol addition of acetaldehyde. Acetaldol, 2-butenal, and butanal should have formed as intermediates of 1-butanol. 2-Butenal and butanal are observed in the reaction of acetaldehyde (Table 2), whereas they were barely detected in the ethanol reaction. They would be rapidly hydrogenated on the catalyst forming butanal and 1-butanol, respectively. Takezawa and Iwasa (16) and Elliot and Pennella (17) support the mechanism. On the other hand, Iwasa and Takezawa also described that butanal did not form on KOH-treated Cu/Al_2O_3 (18). It is also reported that hardly any butanal and 1-butanol formed over pure Cu (18, 19). Therefore, the aldol addition probably occurs either on an acid site or on acid–base concerted sites formed on the metal–oxide support.

Since both the dehydrogenation of alcohols and the reverse hydrogenation of carbonyl compounds are rapid in the total reactions, the irreversible dehydration of alcohols determines the by-products' distribution. In Table 2, the product distributions, with the exception of ethyl acetate, are roughly the same as in the reactions of 1,3-butanediol, ethanol, ethanol and acetaldehyde, and acetaldehyde and H_2. 1,3-Butanediol is an intermediate of 1-butanol, as shown in Scheme 1.

1.4.2-Pentanone. It is very probable that 2-pentanone forms through aldol condensation of acetaldehyde and propanone followed by dehydration and hydrogenation. These are speculations, because no intermediate was detected in the present work. The formation route of 2-pantanone consists of the elementary reactions a-11, a-12, and b-12 (Table 3).

1.5. Ethyl butyrate and butyl acetate. Butanal and 1-butanol can be other sources of esters. Ethyl butyrate and butyl acetate form through a mechanism similar to route 2 for the formation of ethyl acetate by means of hemiacetal formation. These routes consist of the elementary reactions a-13, a-14, b-13, and b-14 (Table 3).

1.6. Diethyl ether and acetic acid. By-products that do not form through acetaldol are diethyl ether and acetic acid. Diethyl ether forms in the intermolecular dehydration of ethanol. This reaction is pressure-independent (c-1 in Table 3C).

Cu/Al_2O_3 catalyzes the formation of dimethyl ether as well as methyl formate in the reaction of methanol (26). The formation of dimethyl ether is probably due to the surface acidity of alumina. The formation of less diethyl ether over Cu–Zn–Zr–Al–O indicates that the surface acidity of the Cu–Zn–Zr–Al–O catalyst is relatively low. The combination of aluminum oxide with Zn and Zr oxides probably reduces the acidity of alumina.

Acetic acid forms by hydrolysis of ethyl acetate (c-2 in Table 3C). This pathway requires water, i.e., the water concentration in the ethanol feedstock affects the selectivity to acetic acid (data not shown). The selectivity to acetic acid increases with increasing water content in the ethanol feedstock. Thus, a higher concentration of water in the reactor causes a high selectivity to acetic acid, whereas acetic acid is hardly detected in the reactions carried out under pressure in our study.

2. *Optimum Conditions in Pressured Reaction*

We explained that the reaction pressure greatly affected product selectivity. The initial reaction of ethanol dehydrogenation is preferred by low pressure (b-1 in Table 3B). Nevertheless, the effective production of ethyl acetate occurs under high pressure. The high-pressure operation has two effects on the reaction: (1) the effect on the equilibrium of the dehydrogenation of ethanol, where the product, acetaldehyde, forms in the reaction preferred by low pressure, and (2) the effect of prolonging contact time at high pressure. In the formation of ethyl acetate from ethanol, the stepwise reaction requires a prolonged contact time, whereas much longer contact times cause by-products to form (Fig. 5). When acetaldehyde has a high partial pressure in the reactor, an acetaldehyde molecule reacts with another acetaldehyde molecule to form acetaldol through aldol addition. Therefore, by-products other than ethyl acetate hardly form at high pressure.

An optimum W/F is about 0.5 h in a practical operation at 1.0 MPa because of the relatively high STY of ethyl acetate together with the highest selectivity to ethyl acetate and tolerably low selectivity to butanone. Thus, Figs. 3 and 4 indicate the most suitable operating conditions for the effective production of ethyl acetate.

CONCLUSIONS

The dehydrogenative dimerization of ethanol over a Cu–Zn–Zr–Al–O catalyst was investigated under pressure. The product distribution is greatly affected by the reaction pressure. The high-pressure operation suppresses both ethanol conversion and the formation of by-products derived from acetaldol. A selectivity to ethyl acetate of 92.6 wt%, which corresponds to 96 mol% based on ethanol, is achieved over the catalyst at 493 K, 1.0 MPa, and $W/F = 0.53\,\mathrm{h}$, while the STY of ethyl acetate exceeds $8\ \mathrm{mol\ h^{-1}\ kg_{cat}^{-1}}$.

Ethyl acetate probably formed stepwise from ethanol. Initially ethanol was dehydrogenated to acetaldehyde, followed by nucleophilic addition of ethanol to acetaldehyde to form a hemiacetal, and finally the hemiacetal was dehydrogenated to ethyl acetate. Most of the by-products form via the acetaldol, which is formed from two molecules of acetaldehyde through aldol addition. A long residence time and high concentration of acetaldehyde in the reactor lead to the formation of acetaldol, resulting in a decrease in ethyl acetate selectivity.

REFERENCES

1. Wessermel, K., and Arpe, H. J., "Industrielle Organische Chemie. Bedeutende Vor- und zweischenprodukte" 4th Ed., VCH, Weinheim, 1994.
2. Monick, J. A., *Alcohol* **19**, 45 (1968).
3. McMurry, J., *in* "Organic Chemistry," 5th Ed., p. 855. (2000) Brooks/Cole.
4. "KIRK-OTHMER Encyclopedia of Chemical Technology." 4th Ed., Wiley, New York, 1994.
5. March, J., "Advanced Organic Chemistry, Reactions, Mechanism, and Structure." 4th Ed., Wiley, New York, 1992.
6. Ogata, Y., and Kawasaki, A., *Tetrahedron* **26**, 929 (1969).
7. Sato, T., and Hagiwara, T., Tokuyama Sekiyu Kagaku, K. K., JP 11140017 (1999).
8. Gregory, R., Smith, D. J. H., and Westlake, D. J., *Clay Miner.* **18**, 431 (1983).
9. Sano, K., Nishiyama, M., Suzuki, T., Wakabayashi, S., and Miyahara, K., Showa Denko, K. K., EP 0562139 (1993).
10. Atkins, M. P., and Sharma, B., BP Chemicals, EP 0757027 (1997).
11. Deschamps, J., *Compt. Rend.* 1285 (1953).
12. Kunugi, T., Matsuura, T., and Kono, T., *Kagaku Kougyozasshi* (Japanese) **71**, 1517 (1968).
13. Nakamura, S., and Kawamoto, K., *Bull. Chem. Soc. Jpn.* **44**, 1072 (1971).
14. Kawamoto, K., and Nishimura, Y., *Bull. Chem. Soc. Jpn.* **44**, 819 (1971).
15. Takeshita, K., Nakamura, S., and Kawamoto, K., *Bull. Chem. Soc. Jpn.* **51**, 2622 (1978).
16. Takezawa, N., and Iwasa, N., *Shokubai* (Japanese) **30**, 148 (1988).
17. Elliot, D. J., and Pennella, F., *J. Catal.* **119**, 359 (1989).
18. Iwasa, N., and Takezawa, N., *Bull. Chem. Soc. Jpn.* **64**, 2619 (1991).
19. Takeshita, K., *J. Sci. Hiroshima Univ. A* **54**, 99 (1990).
20. *Eur. Chem. News*, February 26, 1 (1999).
21. Fawcett, C. R., Tuck, M. W. M., Rathmell, C., and Colley, S. W., Kvaerner Process Tech., Ltd., EP 0990638 (2000).
22. Inui, K., Kurabayashi, T., and Takahashi, T., Chisso Petrochemical Corp., WO 00/53314 (2000).
23. Sato, S., Takahashi, R., Sodesawa, T., Yuma, K., and Obata, Y., *J. Catal.* **196**, 195 (2000).
24. Wrzyszcz, J., Grabowska, H., Klimkiewicz, R., and Syper, L., *Catal. Lett.* **54**, 55 (1998).
25. Chung, M.-J., Moon, D.-J., Kim, H.-S., Park, K.-Y., and Ihm, S.-K., *J. Mol. Catal. A* **113**, 507 (1996).
26. Sato, S., Iijima, M., Nakayama, T., Sodesawa, T., and Nozaki, F., *J. Catal.* **169**, 447 (1997).