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Baeyer–Villiger Oxidation over HZSM-5 Type Zeolites

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The catalytic performance of various protonated zeolites for the Baeyer–Villiger (BV) oxidation of cyclopentanone to δ-valerolactone with aqueous H_2O_2 as an oxidant was investigated. It was found that highly siliceous HZSM-5 zeolites are active for the oxidation reaction, and that the oxidation reaction is promoted by the Brønsted acid sites in the intracrystallines of zeolites, not on the external surface. The influences of the reaction variables (solvent, temperature, and time) and the crystal size of zeolite on the conversion of cyclopentanone and the yield of δ-valerolactone were also studied.

Although zeolites are generally considered to be excellent sorbents for water vapor, it was recently proven that highly siliceous zeolites are truly hydrophobic.[1] Therefore, highly siliceous zeolites can also exhibit strong acidity in an aqueous solution. Many researchers are interested in applying zeolites to organic reactions in the liquid phase, such as the hydrolysis of ester,[2] the hydration of cyclohexene,[3] the hydration of epoxides,[4] the synthesis of trioxane from formalin,[5] and the ring-opening of 1,2-epoxyalkane with alcohols.[6]

Baeyer–Villiger (BV) oxidation, induced by peroxy acid or a H_2O_2/Lewis acid system, organometallics and metalloenzymes, is an important reaction for synthesizing lactones or esters from ketones. Kaneda et al. have already reported on the heterogeneous BV oxidation of ketones with a combination oxidant of molecular oxygen and aldehydes over a solid base catalyst of hydrotalcites.[7] However, there has been no report related to BV oxidation catalyzed by H-type zeolites. More recently, titanium silicate molecular sieves (TS-1), well known heterogeneous oxidation catalyst using H_2O_2 as an oxidant, have been found to be effective catalysts for the BV oxidation of cyclic and aromatic ketones.[8] In this short paper, we describe our study of the catalytic performance of H-type zeolites, such as H-Mordenite (HM), HY, HZSM-5(Al), and ZSM-5 type metallosilicates (HZSM-5(Fe) and HZSM-5(Ga)), for the Baeyer–Villiger oxidation of cyclopentanone. We also compare the catalytic performance of HZSM-5 with TS-1.

Experimental

The syntheses of HZSM-5(Al), HZSM-5(Fe), and HZSM-5(Ga) were conducted using tetrapropylammonium bromide (TPABr) as an organic crystallization agent according to Ref. 9. The compositions of the synthesis mixtures were $0.1\ \mathrm{TPABr}\cdot 0.05\ Na_2O\cdot 0$—$0.0143\ T_2O_3\cdot SiO_2\cdot 40\ H_2O$ (T = Al, Fe, & Ga). The obtained zeolites were calcined at 500 °C for 24 h in order to remove TPA cations occluded within the framework of zeolite, and protonated in a 0.6 M ($1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$) hydrochloric acid solution at room temperature for 24 h. The identification of zeolites was achieved by X-ray diffraction (XRD, Rigaku RINT 2100). The chemical compositions were measured by X-ray fluorescence using a Philips spectrometer (PW2400). In the following text, the obtained zeolites are assigned to HZSM-5(T)-*r* (T: Al, Fe, Ga; *r*: Si/T ratio).

Water-vapor adsorption isotherms of zeolites were measured at 25 °C using a conventional volumetric apparatus (BELSORP 18); also, the amounts of H_2O adsorbed $[W_0(H_2O)]$ were calculated by analyzing the adsorption isotherms by the Dubinin–Radushkevich (D–R) equation. Prior to adsorption measurements, the powdered zeolite was evacuated at 400 °C for 12 h.

TS-1 was synthesized by published procedures.[10] It was ascertained by XRD, FT-IR, and the catalytic test reaction (the epoxidation of 1-hexene).

A typical oxidation reaction was run using 0.5 g of a catalyst in 0.05 mol of cyclopentanone, 25 ml of a solvent, 0.005 mol of an internal standard (tetradecane) and 25 ml of H_2O_2 (30% aqueous solution) in a round-bottom flask. The reaction mixture was stirred at 20—80 °C for 5—78 h. After the oxidation reaction, zeolites were separated and organic substrates in an aqueous solution of H_2O_2 were extracted using a solvent (i.e. 1,2-dichloroethane). The products were analyzed by GC (Ohkura MODEL-802) and GC-MS (Shimadzu GC-17A-QP5000) using the internal standard (tetradecane). The yield and the selectivity of δ-valerolactone were obtained by the following formula:

$$\mathrm{Yield} = W/(n \times M) \times 100\%;$$
$$\mathrm{Selectivity} = \mathrm{Yield}/X \times 100\%.$$

Here, W is the amount of δ-valerolactone obtained in g; n the mole number of cyclopentanone converted in mol; M the molecular weight of δ-valerolactone in $\mathrm{g\,mol^{-1}}$; and X the conversion of cyclopentanone in %.

Liquid-phase adsorption experiments of cyclopentanone in ZSM-5 zeolites were carried out at 40 °C using 1,3,5-triisopropylbenzene as a solvent, which is too large to enter the pores of ZSM-5 zeolites.

Results and Discussion

1. Active Site of a Baeyer–Villiger Oxidation Reaction.

The results of the BV oxidation of cyclopentanone (CP) over various hydrogen forms of zeolites are summarized in Table 1. The amounts of H_2O adsorbed $[W_0(H_2O)]$ are also listed. δ-Valerolactone (DV) as the normal BV ox-

Table 1. Baeyer–Villiger Oxidation of Cyclopentanone with Aqueous H_2O_2 as Oxidant over Various Zeolites

No.	Zeolite	Si/T	Crystal size[a)]	$W_0(H_2O)$[b)]	Conv. of CP	Sel. to DV	Yield of DV
			μm	ml(liq) g^{-1}	%	%	%
1	HZSM-5(Al)-34	34	6.6×6.0	0.071	47	32	15
2	HZSM-5(Al)-93	93	5.6×4.3	0.041	45	29	13
3	HZSM-5(Al)-1650	1650	5.3×4.3	0.024	31	29	9
4	TPA–HZSM-5(Al)-35	35	5.2×4.4	—	29	21	6
5	HZSM-5(Fe)-103	103	2.3×1.5	0.032	43	28	12
6	HZSM-5(Ga)-95	95	3.6×2.1	0.033	43	28	12
7	HY	3	0.6×0.6	0.26	29	14	4
8	HM	5	0.2×0.1	0.22	29	17	5
9	None				25	24	6

a) Length×width. b) the amount of H_2O adsorbed. Reaction conditions; cyclopentanone (CP): 0.05 mol, 1,2-dichloroethane: 25 ml, H_2O_2 (30% aq): 25 ml, zeolite: 0.5 g, reaction temperature: 40 °C, reaction time: 5 h.

idation product was obtained in every case. In the case of highly siliceous HZSM-5 zeolites, a relatively high conversion of cyclopentanone and yield of δ-valerolactone were obtained. The conversion of cyclopentanone and the yield of δ-valerolactone increased with decreasing the Si/Al ratio of HZSM-5(Al) zeolite. Both the conversion and the yield over KZSM-5(Al)-34 (K^+ ion exchange: ca. 100%) were much lower than that over HZSM-5(Al)-34. Taking into account the fact that the activity of BV oxidation is very low in the absence of HZSM-5 zeolite, these results strongly indicate that BV oxidation of cyclopentanone is promoted by Brønsted acid sites of HZSM-5 zeolite. The low yield of δ-valerolactone seems to be attributable to the formation of by-products, such as valeric acid, 5-hydroxyvaleric acid (probably) and others (i.e. hydroxy hydroperoxides and their condensation products). The formation of valeric acid indicates the ring-opening reaction of δ-valerolactone. To clarify this, the conversion of δ-valerolactone was carried out under the same reaction condition as the conversion of cyclopentanone. The conversion of δ-valerolactone to valeric acid and other products was 38%. The possibility for the production of hydroxy hydroperoxides and their condensation products is suggested according to Refs. 11 & 12, which have shown that hydrogen peroxide in dilute acid or in neutral solution sometimes converts carbonyl compounds to normal BV oxidation products, but that more frequently hydroxy hydroperoxides and their condensation products are formed.

On the other hand, in the case of HY and HM, whose Si/Al ratios were lower than those of HZSM-5 zeolites, namely, higher numbers of Brønsted acid sites in HY and HM, the BV oxidation reaction hardly occurred. The conversion of cyclopentanone and the yield of δ-valerolactone were almost the same as these in the absence of a zeolite. This result is contradictory to the above conclusion that BV oxidation is promoted by Brønsted acid sites of a zeolite. Taking into account the fact that the amounts of H_2O adsorbed [$W_0(H_2O)$] on HY and HM are much higher than that on HZSM-5(Al), the low activity of HY and HM can account for their high hydrophilicity. Namely, the adsorption of water molecules to Brønsted acid sites is so strong that cyclopentanone can not adsorb to the acid sites. The high hydrophobicity of zeolite enables them to oxidize cyclopentanone with H_2O_2 (30% aq) as the oxidant. This indicates that the hydrophobicity of highly siliceous zeolite is necessary for BV oxidation of cyclopentanone to δ-valerolactone in the presence of water.

The adsorption of cyclopentanone on HZSM-5(Al)-34 and TPA–HZSM-5(Al)-35 was measured at 40 °C for 24 h using 1,3,5-triisopropylbenzene (about 0.85 nm) as a solvent. TPA–HZSM-5(Al)-35 was prepared by treating the as-synthesized ZSM-5(Al) with a 0.6 M HCl solution, resulting in the removal of TPA cations on the external surface of the crystal and the formation of Brønsted acid sites on the external surface. The ionic radius of the TPA cation occluded in the zeolitic pore is 0.45 nm. The amount of cyclopentanone adsorbed on TPA–HZSM-5(Al)-35 (0.16 mmol g^{-1}) is considerably smaller than that on HZSM-5(Al)-34 (1.4 mmol g^{-1}). This indicates that the cyclopentanone hardly enters the zeolitic pores of TPA–HZSM-5(Al)-35. In order to clarify that the oxidation reaction proceeds mainly on Brønsted acid sites in the zeolitic pores, not on the external surface, the oxidation reaction was carried out over TPA–HZSM-5(Al)-35. The conversion of cyclopentanone and the yield of δ-valerolactone were very low over TPA–HZSM-5(Al)-35, which only have Brønsted acid sites on the external surface of the crystal (Table 1, No. 4). Therefore, the conclusion that the BV oxidation of cyclopentanone proceeds mainly on Brønsted acid sites in the zeolitic pores can be drawn.

Catalytic reactions were also performed over metallosilicates, HZSM-5(Fe)-103 (Table 1, No. 5) and HZSM-5(Ga)-95 (Table 1, No. 6). HZSM-5(Fe)-103 and HZSM-5(Ga)-95 showed high BV oxidation activity. It is known that the acidities of HZSM-5(Fe) and HZSM-5(Ga) are weaker than that of HZSM-5(Al).[13)] However, no difference in the conversion of cyclopentanone and the yield of δ-valerolactone was observed among these three catalysts. This indicates that the conversion is affected by other factors, such as the crystal size other than the acidity. Thus, our data can not clarify the effect of the acid strength on the conversion and yield correctly at the present time.

2. Effect of Variables in Reaction Condition on Catalytic Performance. The effects of solvents over HZSM-5(Al)-34 were studied on the BV oxidation of cyclopentanone

(Table 2). No clear effect of solvents on the conversion and the yield was observed, except for benzene, which showed a low conversion and yield. This result is consistent with that reported by Priess et al.,[14] which has shown that polar solvents are effective for BV oxidation.

Table 3 shows the results of the oxidation reaction over HZSM-5(Al) with different crystal sizes, which were prepared by changing the alkali concentration in the synthesis mixture for zeolite. The crystal size was measured using scanning electron microscopy. The conversion, selectivity and yield increased with decreasing the crystal size. In the case of a zeolite with a larger crystal size, it is considered that Brønsted acid sites in the inner part of zeolitic pores hardly contribute to the oxidation reaction. In the case of a zeolite with a smaller crystal size, Brønsted acid sites in the vicinity of the opening of zeolitic pores are much more, and promote the oxidation reaction effectively. The reason for the lower selectivity over HZSM-5(Al)-34 with a size of 6.6 (length)×6.0 (width) μm may be considered as follows. Namely, δ-valerolactone having large molecular dimensions converted to the other compound during passing through the longer zeolite pores.

Table 2. Effect of Solvent for Baeyer–Villiger Oxidation of Cyclopentanone

Solvent	Conv. of CP	Sel. to DV	Yield of DV
	%	%	%
CH_2Cl_2	53	28	15
$ClCH_2CH_2Cl$	47	32	15
C_6H_6	38	29	11
$CH_3CO_2C_2H_5$	41	37	15

Reaction conditions; cyclopentanone (CP): 0.05 mol, solvent: 25 ml, H_2O_2 (30% aq): 25 ml, HZSM-5(Al)-34: 0.5 g, reaction temperature: 40 °C, reaction time: 5 h.

Figures 1a and 1b show the effect of the reaction temperature on the conversion of cyclopentanone and the yield of δ-valerolactone over HZSM-5(Al)-34 (crystal size: 6.6×6.0 μm) and HZSM-5(Al)-31 (crystal size: 2.6×2.6 μm), respectively. The conversion of cyclopentanone increased with the reaction temperature over these two zeolites. The selectivity to δ-valerolactone showed a maximum at 70 °C over HZSM-5(Al)-34, while it decreased with the reaction temperature over HZSM-5(Al)-31. This result indicates that the selectivity decreases when the conversion becomes higher than some value. Although the yield showed a maximum over these two zeolites, the maximum yield over HZSM-5(Al)-31 was higher than that over HZSM-5(Al)-34.

Figures 2a and 2b show the effect of the reaction time over HZSM-5(Al)-34 (crystal size: 6.6×6.0 μm) and HZSM-5(Al)-31 (crystal size: 2.6×2.6 μm). The conversion always increased with the reaction time over these two zeolites, while the yield passed through a maximum at 48 and 10 h, respectively. The selectivity to δ-valerolactone showed a maximum at 36 h over HZSM-5(Al)-34, while it decreased with the reaction time over HZSM-5(Al)-31. This result is at-

Table 3. Effect of the Crystal Size for Baeyer–Villiger Oxidation of Cyclopentanone

No.	Zeolite	Si/Al	Crystal size$^{\text{a)}}$	$W_0(H_2O)^{\text{b)}}$	Conv. of CP	Sel. to DV	Yield of DV
			μm	ml(liq) g^{-1}	%	%	%
1	HZSM-5(Al)-31	31	2.6×2.6	0.073	51	51	26
2	HZSM-5(Al)-34	34	6.6×6.0	0.071	47	32	15

a) Length×width. b) the amount of H_2O adsorbed. Reaction conditions; cyclopentanone (CP): 0.05 mol, 1,2-dichloroethane: 25 ml, H_2O_2 (30% aq): 25 ml, HZSM-5(Al): 0.5 g, reaction temperature: 40 °C, reaction time: 5 h.

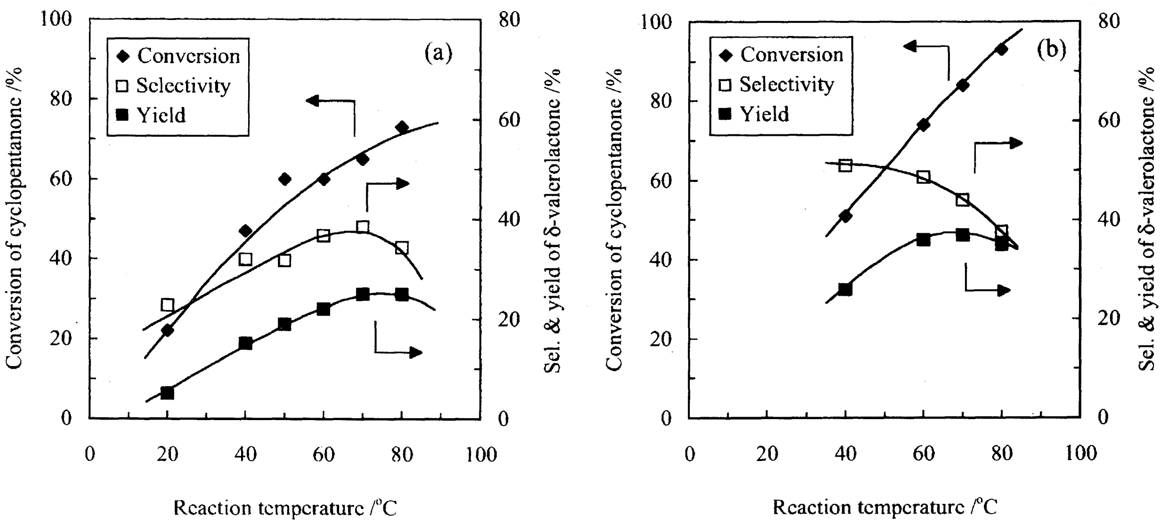

Fig. 1. Effect of reaction temperature on catalytic performance of (a) HZSM-5(Al)-34 and (b) HZSM-5(Al)-31. Reaction conditions; cyclopentanone: 0.05 mol, 1,2-dichloroethane: 25 ml, H_2O_2 (30% aq): 25 ml, HZSM-5(Al): 0.5 g, reaction time: 5 h.

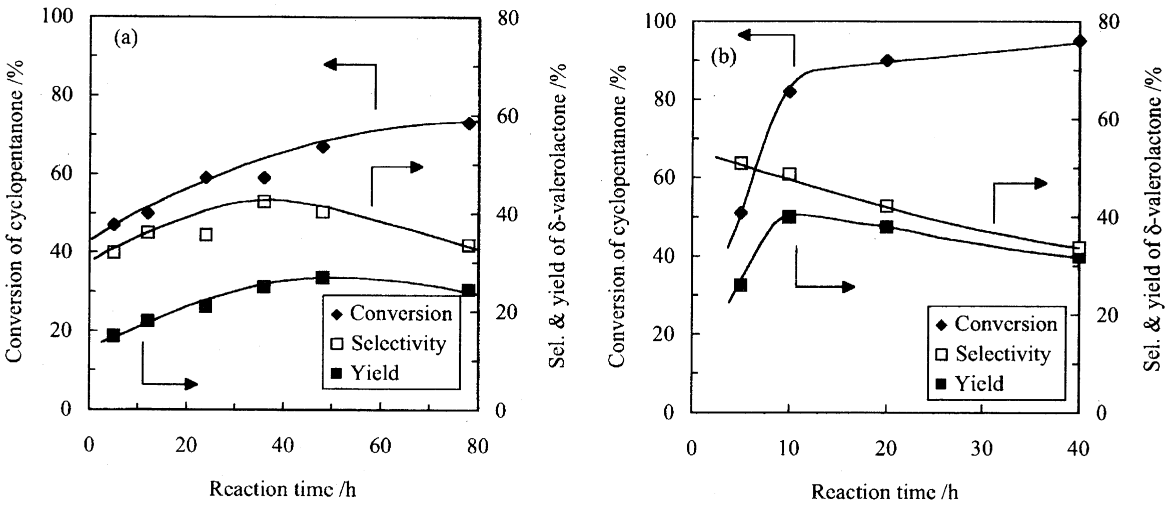

Fig. 2. Effect of reaction time on catalytic performance of (a) HZSM-5(Al)-34 and (b) HZSM-5(Al)-31. Reaction conditions; cyclopentanone: 0.05 mol, 1,2-dichloroethane: 25 ml, H_2O_2 (30% aq): 25 ml, HZSM-5(Al): 0.5 g, reaction temperature: 40 °C.

tributable to the conversion of δ-valerolactone into other byproducts (i.e. valeric acid and 5-hydroxyvaleric acid) after a long reaction time.

3. Comparison of HZSM-5 with TS-1. At first, the prepared TS-1 was characterized. The FT-IR spectrum of TS-1 showed an adsorption band at 960 cm^{-1}. This band is attributed to Ti species incorporated in the zeolite framework, namely, a stretching mode of a $[SiO_4]$ unit bonded to a Ti^{4+} ions in the $[SiO_4]$ structure.[15] To check the quality of TS-1, the oxidation ability was tested by an oxidation reaction of 1-hexene to 1,2-epoxyhexane with H_2O_2 (30% aq). The TS-1 showed high activity (conversion: 67%, yield: 16%).

Next, the BV oxidation ability of TS-1 was investigated. TS-1 exhibited activity for the BV oxidation (conversion: 35%, yield: 10%). It has been considered that TS-1 exhibits Brønsted acidity in the presence of aqueous H_2O_2, due to the formation of a titanium peroxo species (Ti–O–O···H) which is stabilized by a protic solvent, like water.[8] It is considered that this stabilized titanium peroxo species promotes the BV oxidation of cyclopentanone. However, both the conversion of cyclopentanone and the yield of δ-valerolactone over TS-1 were lower than that over HZSM-5(Al)-34 (Table 1, No.1). This indicates that the ability of HZSM-5 for the BV oxidation of cyclopentanone in the presence of water is superior to that of TS-1.

Conclusions

The Baeyer–Villiger oxidation of cyclopentanone was carried out over various zeolites using an aqueous H_2O_2 solution as the oxidant. It was found (1) that the hydrophobicity of zeolite plays an important role in the BV oxidation, (2) that highly siliceous HZSM-5 zeolite is an efficient catalyst for the oxidation reaction, (3) that the oxidation reaction proceeds mainly on Brønsted acid sites in the zeolitic pores, and (4) that the oxidation activity of HZSM-5 is higher than that of TS-1.

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