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Carbonylation of *tert*-butyl alcohol over H-zeolites

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Abstract

The Koch-type carbonylation of *tert*-butyl alcohol was studied over H-type zeolites. It was found that the catalytic carbonylation of a large amount of *tert*-butyl alcohol relative to the acidic sites of the H-zeolites in organic solvents requires an elevated temperature and CO pressure, although previous solid state NMR studies have revealed that the transformation of *tert*-butyl alcohol of an amount comparable to the acidic sites into 2,2-dimethylpropanoic acid proceeds just upon the CO co-adsorption in the H-zeolites at room temperature and atmospheric pressure. The catalytic performance of different H-zeolites and the influence of CO pressure, H₂O addition and solvent effects on the carbonylation of *tert*-butyl alcohol have been investigated. H-ZSM-5 gives the highest selectivity for 2,2-dimethylpropanoic acid due to its adequate pore dimensions. The present work indicates the possible industrial application of solid acids as carbonylation catalysts instead of liquid acids for the Koch reaction to produce *tert*-carboxylic acids. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbonylation; Alcohols; Solid acids; Zeolites; Carboxylic acids

1. Introduction

Since the work reported by Koch in 1955, it has been known that *tert*-carboxylic acids can be produced by the reaction of CO with alcohols or with olefins and H₂O in concentrated strong acids (H₂SO₄, BF₃·H₂O, HF) at –20 to 80°C and around 100 atm [1–3]. The discovery of cationic Cu(I), Ag(I), Au(I), Pd(I), Pt(I) and Rh(I) carbonyl catalysts enabled this reaction to proceed at room temperature and atmospheric CO pressure [4–8]. In the industrial application of the Koch-type reaction, however, one of the major problems is the presence of huge amounts of waste acids. Therefore, the use of solid acids as catalysts instead of liquid strong acids is of significant advantage.

There have been only a few reports on the solid acid-catalyzed carbonylation [9–13], although solid acids have been used as catalysts in many reactions [14,15]. In 1984, the carbonylation of methanol into methyl acetate, methyl formate and acetic acid was reported on solid acids, but the reaction had either a very low yield (0.3%) under 100% selectivity or a low selectivity (0.8%) under 34.6% yield with the formation of dimethyl ether being the main non-carbonylating route of the reaction [16].

Recently, Stepanov et al. [17–19] reported the direct NMR observation of the Koch reaction in zeolite H-ZSM-5 at room temperature without application of pressurized conditions. They found that *tert*-butyl alcohol or *iso*-butylene with H₂O is selectively transformed into 2,2-dimethylpropanoic acid at 25°C in high yields when the alcohol and CO or olefin, H₂O and CO of small amounts (approximately equimolar to the acidic sites) were co-adsorbed on H-ZSM-5.

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With respect to a potential industrial application, however, one must investigate the catalytic performance of the Koch-type carbonylation of olefins or alcohols in much larger amounts than the acidic sites of the H-zeolite catalyst.

tert-Butyl alcohol is a suitable reactant for this study since it gives the simplest intermediate, the trimethylcarbenium cation, in strongly acidic media [20–25]. Here, we report the catalytic carbonylation of large amounts of *tert*-butyl alcohol over H-zeolites in organic solvents.

2. Experimental

For the carbonylation of *tert*-butyl alcohol, use was made of the H-type zeolites listed in Table 1 along with their characteristics [26,27]. The zeolite catalysts were calcined at 450°C for 7 h under a dynamic vacuum and sealed off in a glass ampoule before use.

A 330-ml stirred stainless steel autoclave enclosed in an electric furnace was used as the batch reactor. The carbonylation of *tert*-butyl alcohol was carried out as follows. The glass ampoule containing 2 g of a pre-treated zeolite catalyst, 20 mmol of *tert*-butyl alcohol, and 50 ml of a solvent were placed in the autoclave. High pressure CO was introduced into the autoclave causing the glass ampoule to break and the pressure was then controlled to the desired value. The initial CO pressure at room temperature was varied in the range of 1–90 atm. The autoclave was heated from room temperature to the desired reaction temperature in 30 min and held at this temperature for 22 h. After the reaction, the products were collected by filtering

out the catalysts and analyzed by GC and NMR and by titration with an ethanol solution of NaOH.

3. Results and discussion

3.1. Reaction of *tert*-butyl alcohol with CO over H-ZSM-5(50)

Fig. 1 shows temperature dependence of the carbonylation of *tert*-butyl alcohol over H-ZSM-5 at 50 atm of CO (initial pressure at room temperature) in chlorobenzene. At room temperature, no carboxylic acids are produced under the current reaction conditions, whereas it was reported that 2,2-dimethylpropanoic acid was formed in 50% yield upon the co-adsorption of *tert*-butyl alcohol and CO on H-ZSM-5 in previous NMR studies [17–19]. The difference appears to originate from the use of a solvent, which is needed for continuing the reaction for a large amount of the reactant. The solvent seems to inhibit the co-adsorption and interaction of CO and the reactant in the H-zeolite channels. *tert*-Butyl alcohol of 74% remains unreacted after the reaction of 22 h at room temperature. *iso*-Butene is formed as the main product of the dehydration, the accurate amount of which could not be determined because of its boiling point being lower than room temperature. No ethers are formed in agreement with the previous observations by Zamaraev and co-workers [28–33]. They have systematically studied the dehydration of C4 alcohols including *tert*-butyl alcohol in H-ZSM-5 and showed that ethers are formed during the dehydration of *n*-butyl and *iso*-butyl alcohols but not

Table 1
H-type zeolites used in this study

Zeolite	Full name	Pore dimensionality ^a	Channel aperture ^a (nm)	SiO ₂ /Al ₂ O ₃ ratio
MFI	ZSM-5	3 ^b	0.53 × 0.56, 0.51 × 0.55	50 ^c , 300 ^d , 1000 ^e
MOR	Mordenite	1	0.65 × 0.70	20 ^e
BEA	Zeolite Beta	3 ^b	0.76 × 0.64, 0.55 × 0.55	25 ^d
FAU	Faujasite	3	0.74	30 (USY ^{d,f})

^a From [26].

^b The pore system consists of two interconnecting channels.

^c Purchased from N.E. Chemcat Corporation.

^d Purchased from Zeolyst International.

^e Offered by Catalysis Society of Japan as reference catalysts.

^f Y-type zeolite.

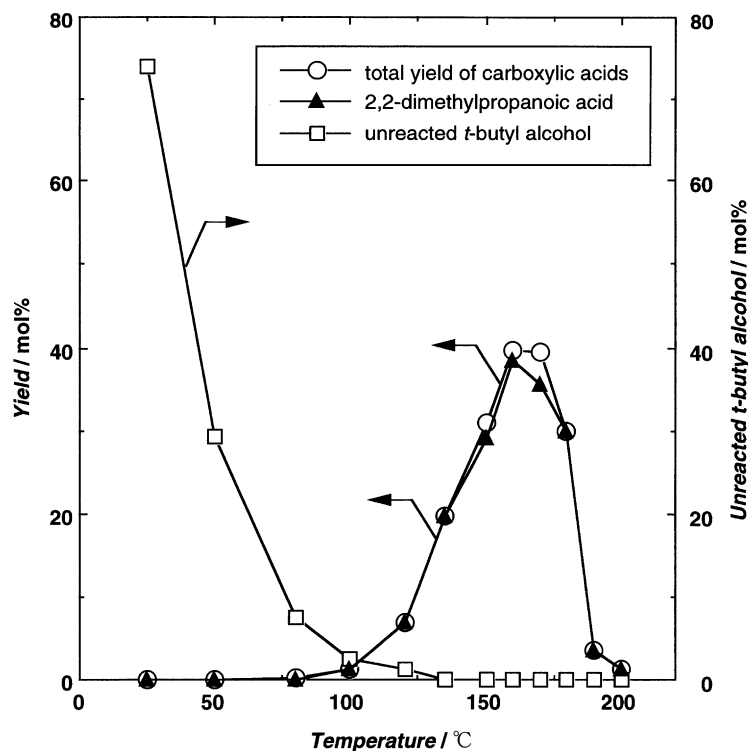


Fig. 1. Carbonylation of *tert*-butyl alcohol over H-ZSM-5(50). Reaction conditions: 20 mmol *tert*-butyl alcohol, 2 g H-ZSM-5(50), 50 ml chlorobenzene, 50 atm CO pressure (initial pressure at room temperature), 22 h reaction time.

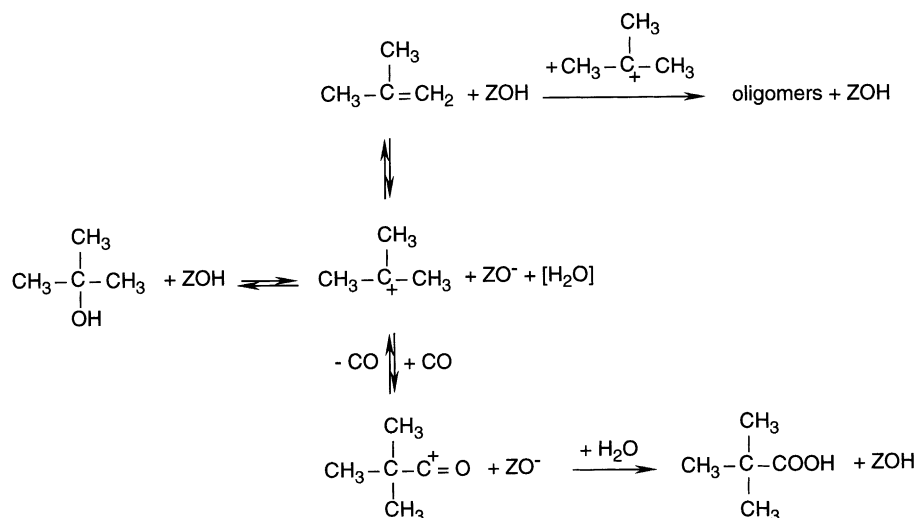
during the dehydration of the *sec*-butyl and *tert*-butyl alcohols.

The conversion of *tert*-butyl alcohol increases with increasing reaction temperature; at 150°C, the *tert*-butyl alcohol completely disappears. With increasing temperature, the dimer (C8) species increase below 140°C, but then begin to decrease, while the trimer species increase above 140°C.

Above 100°C, the carbonylation is significantly enhanced; the total yield of the carboxylic acids reaches the maximum (40%) at 160°C (T_{\max}) and then decreases with increasing temperature. Only traces of the C9 carboxylic acids were detected; the selectivity for 2,2-dimethylpropanoic acid (the ratio of the yield of 2,2-dimethylpropanoic acid to the total yield of carboxylic acids) is nearly 100%.

The overall reactions of *tert*-butyl alcohol with CO over H-ZSM-5 can be described in Scheme 1. This scheme includes the dehydration of *tert*-butyl alco-

hol to form the trimethylcarbenium ion intermediate, which is in equilibria with both *tert*-butyl alcohol and *iso*-butene [23–25]. The secondary reaction between *iso*-butene and the trimethylcarbenium ion intermediate gives the oligomeric species [25]. The reaction of the trimethylcarbenium ion with CO gives rise to the formation of the acylium cation, which reacts with H₂O to form 2,2-dimethylpropanoic acid [17–19]. The reaction of the unsaturated oligomeric species with CO and H₂O produces higher-weight carboxylic acids. At low temperatures, the dehydration of *tert*-butyl alcohol is slow. By raising the temperature, the dehydration is accelerated, accompanied by the enhancement of both oligomerization and carbonylation of the trimethylcarbenium ion intermediate. The observation of the maximum yield of carboxylic acids can be explained in terms of the fast reaction of butene and the trimethylcarbenium ion intermediate, which prevails over the carbonylation of the



Scheme 1.

trimethylcarbenium ion above T_{\max} . The high selectivity for 2,2-dimethylpropanoic acid in the carbonylation products, very close to 100%, is most probably due to the pore dimensions of H-ZSM-5 being rather similar to the dimensions of the C4–C5 molecules; these pore dimensions seem disadvantageous to the carbonylation of larger oligomeric molecules.

3.2. Effects of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and pore structure of H-zeolite on catalytic behavior

Table 2 shows the results of the reaction of *tert*-butyl alcohol with CO (50 atm, initial pressure at room temperature) over H-ZSM-5 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and over H-zeolites with different pore structures in chlorobenzene. For H-ZSM-5, the increase in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, corresponding to the decrease in the acidic sites, slows the dehydration of *tert*-butyl alcohol, and the oligomerization and the carbonylation of the trimethylcarbenium ion intermediate. Unreacted *tert*-butyl alcohol increases from 74 to 95% by changing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 50 to 1000 at room temperature. The maximum total yield of the carboxylic acids shifts to higher temperatures with lower values, while the selectivity for 2,2-dimethylpropanoic acid is maintained at 100%.

H-MOR has larger pore sizes than H-ZSM-5 as shown in Table 1 [26,27]. Over H-MOR(20), the unre-

acted *tert*-butyl alcohol at room temperature is 68.4%, slightly lower than that for H-ZSM-5(50). At 100°C, the total yield of the carboxylic acids is 16.9%, much higher than 1.2% for H-ZSM-5(50). The maximum total yield of the carboxylic acids appears at 140°C, lower than the T_{\max} (160°C) for H-ZSM-5(50), due to the fast oligomerization over H-MOR(20). Large amounts of the C9 and C13 carboxylic acids are observed and the selectivity for 2,2-dimethylpropanoic acid is much lower than that (100%) for H-ZSM-5(50). These observations can be understood in terms of the larger pore sizes of H-MOR, which is advantageous for the oligomerization of the trimethylcarbenium ion intermediate and for the carbonylation of the large oligomeric molecules. At 200°C, only a small amount of carbonylation products are formed.

H-BEA(25) and H-USY(30) have larger pore sizes [26,27]. At 25°C, fast dehydration occurs over H-BEA(25) and H-USY(30), resulting in the small amounts of the unreacted *tert*-butyl alcohol of 23.5 and 38.0%, respectively. The maximum total yield of the carboxylic acids appears at lower temperatures, 130 and 120°C, for H-BEA(25) and H-USY(30), respectively, suggesting a fast oligomerization. The selectivity for 2,2-dimethylpropanoic acid for both of the zeolites are also much lower than that (100%) for H-ZSM-5, due to their large pore sizes.

Table 2
Carbonylation of *tert*-butyl alcohol over a variety of H-zeolites^a

Zeolite	Temperature (°C)	Unreacted <i>tert</i> -butyl alcohol (%)	Total yield of acids (%)	Selectivity ^b for 2,2-dimethylpropanoic acid (%)
H-ZSM-5(50)	25	74.0	0	
	100	2.4	1.2	100
	160 ^c	0	39.6	97
	200	0	1.2	100
H-ZSM-5(300)	25	90.5	0	
	100	4.1	0	
	200 ^c	0	10.8	100
	230	0	6.8	100
H-ZSM-5(1000)	25	95.0	0	
	100	7.0	0	
	160	1.1	2.5	100
	200	1.0	9.4	100
H-MOR(20)	25	68.4	0	
	100	0	16.9	16
	140 ^c	0	38.1	54
	200	0	0.5	
H-BEA(25)	25	23.5	0	
	100	0	29.0	22
	130 ^c	0	33.6	49
	170	0	0	
H-USY(30)	25	38.0	0	
	100	0	27.2	23
	120 ^c	0	34.8	44
	180	0	0	

^a Reaction conditions: 20 mmol *tert*-butyl alcohol, 2 g zeolite, 50 ml chlorobenzene, 50 atm CO pressure (initial pressure at room temperature), 22 h reaction time.

^b $100 \times (\text{yield of 2,2-dimethylpropanoic acid} / \text{total yield of carboxylic acids})$.

^c T_{max} , the temperature where the maximum total yield of the carboxylic acids appears.

In brief summary, the carbonylation of *tert*-butyl alcohol over H-ZSM-5 selectively gives rise to the formation of 2,2-dimethylpropanoic acid because the dimensions of the channels in H-ZSM-5 are rather similar to the dimensions of the C4–C5 molecules which are disadvantageous to the carbonylation of larger oligomeric molecules. Over the H-MOR, H-BEA and H-Y zeolites, the carbonylation of large oligomeric molecules proceeds to form higher carboxylic acids, resulting in the low selectivity for 2,2-dimethylpropanoic acid.

3.3. Influence of H₂O addition, CO pressure and solvent effects

Table 3 shows the influence of H₂O addition and CO pressure on the carbonylation of *tert*-butyl alcohol over

H-ZSM-5(50) at 160°C. At 50 atm (initial CO pressure at room temperature), H₂O addition of upto 20 mmol into the starting materials (20 mmol of *tert*-butyl alcohol, 2 g of zeolite, and 50 ml of chlorobenzene) causes the yield of 2,2-dimethylpropanoic acid to increase from 38.5 to 46.0%. As shown in Scheme 1, the trimethylcarbenium ion intermediate is in equilibria with the *tert*-butyl acylium ion intermediate and *iso*-butene. The formation of 2,2-dimethylpropanoic acid needs H₂O to react with the *tert*-butyl acylium ion intermediate, while the reaction of the trimethylcarbenium ion intermediate with butene gives rise to the formation of oligomeric products. Although the dehydration of *tert*-butyl alcohol is accompanied by the formation of equimolar amount of H₂O, the addition of an adequate amount of H₂O seems to facilitate the conversion of the *tert*-butyl acylium ion

Table 3
Influence of H₂O addition and CO pressure on the carbonylation of *tert*-butyl alcohol over H-ZSM-5(50)^a

CO pressure ^b (atm)	H ₂ O ^c (mmol)	Yield of 2,2-dimethylpropanoic acid (%)
50	0	38.5
50	5	43.4
50	10	44.3
50	20	46.0
50	40	43.6
50	150	31.3
50	200	15.8
50	1000	3.7
1	20	0.3
10	20	11.3
30	20	28.4
70	20	54.8
80	20	55.4
90	20	60.6

^a Reaction conditions: 20 mmol *tert*-butyl alcohol, 2 g H-ZSM-5(50), 50 ml chlorobenzene, 160°C, 22 h.

^b Initial pressure at room temperature.

^c Added along with *tert*-butyl alcohol and chlorobenzene.

intermediate to 2,2-dimethylpropanoic acid. Another effect from the H₂O addition is probably the decrease in the acidity of the acidic sites, and therefore, the depression of oligomerization, which causes the overall reactions to shift to the carbonylation. Further H₂O addition causes the total yield of the carboxylic acids to decrease, indicating that the proper acidity of the acidic sites is required for the carbonylation.

A high CO pressure is also advantageous for the Koch-type carbonylation over H-type zeolites as observed in acidic solutions [1–3]. Under 1 atm of CO (initial pressure at room temperature), only a very small amount of 2,2-dimethylpropanoic acid (0.3%) is formed from *tert*-butyl alcohol over H-ZSM-5(50) in chlorobenzene at 160°C (see Table 3). By increasing the initial CO pressure to 90 atm (room temperature), the total yield of carboxylic acids increases to over 60% with the selectivity for 2,2-dimethylpropanoic acid kept at nearly 100%. Higher yields are expected to be obtained at higher CO pressures.

The solvent effects were also investigated for the carbonylation of *tert*-butyl alcohol over H-ZSM-5(50) (Fig. 2). The maximum total yield of the carboxylic acids appears at 150°C with a value of 35% when hexane or benzene is used as the solvent, whereas it appears at 160°C with a value of 39.6% in chloroben-

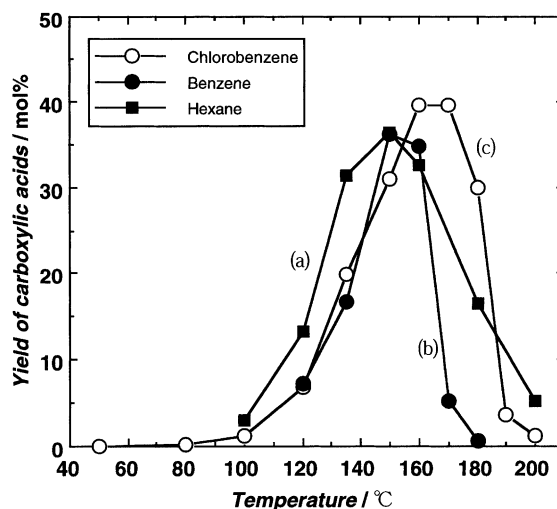


Fig. 2. Carbonylation of *tert*-butyl alcohol over H-ZSM-5(50) in (a) *n*-hexane, (b) benzene and (c) chlorobenzene. Reaction conditions: 20 mmol *tert*-butyl alcohol, 2 g H-ZSM-5(50), 50 ml solvent, 50 atm CO pressure (initial pressure at room temperature), 22 h reaction time.

zene. The differences can probably be understood in terms of the polarity of the solvents. Polar solvents such as chlorobenzene interact with the acidic sites in the H-zeolites more strongly than the non-polar solvents such as benzene and hexane [15]. The oligomerization seems to be slower, and therefore, the conversion to carbonylation products is relatively higher in chlorobenzene than in hexane and benzene. The selectivity for 2,2-dimethylpropanoic acid is found to be nearly 100% in all of the solvents.

As already described, the CO pressure is advantageous for the carbonylation of *tert*-butyl alcohol over H-ZSM-5. The H₂O addition and the change in the solvent polarity can slightly modify the catalytic performance. The selectivity for 2,2-dimethylpropanoic acid (nearly 100%) over H-ZSM-5 is not dependent on the CO pressure, H₂O addition and solvent, but seems to be mainly determined by the pore dimensions.

4. Conclusions

The Koch-type carbonylation of *tert*-butyl alcohol with CO over H-type zeolites was investigated. The catalytic transformation of a large amount of *tert*-butyl alcohol relative to the acidic sites of the H-zeolites into

2,2-dimethylpropanoic acid in organic solvents needs an elevated temperature and high CO pressure. A high selectivity for 2,2-dimethylpropanoic acid (100%) is obtained over H-ZSM-5 because of its suitable pore dimensions, while higher carboxylic acids are also formed over H-Y, H-MOR and H-BEA, the zeolites having larger pores. A high CO pressure is advantageous for the carbonylation of *tert*-butyl alcohol in H-zeolites as in strong acids. The catalytic performance can be slightly modified by changing the solvent polarity or by the H₂O addition. The present work indicates the possible industrial application of solid acids as catalysts instead of liquid acids for the Koch reaction and, especially, indicates that the selective synthesis of the desired carboxylic acids may be achieved by choosing H-zeolites with suitable pore structures.

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