

Highly active and stable performance of catalytic vapor phase Koch-type carbonylation of *tert*-butyl alcohol over H-zeolites

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A high catalytic activity and excellent stability of the vapor phase Koch-type carbonylation of *tert*-butyl alcohol towards 2,2-dimethylpropanoic acid on a H-ZSM-5 catalyst were achieved with a yield as high as 90% without any threat of deactivation in 120 h.

As one of the most important *tert*-carboxylic acids, 2,2-dimethylpropanoic acid has been widely used as a starting material for various agrochemicals, pharmaceuticals, fragrance chemicals, specialty chemicals and polymer additives. Since the work reported by Koch in 1955, it has been known that tertiary carboxylic acids can be produced by the reaction of CO with alcohols or olefins and H₂O in a strong acid medium, such as H₂SO₄, HF or BF₃·H₂O under high CO pressure.^{1–3} The huge amount of acids used for this reaction results in serious corrosion, difficulties in product separation and disposal problems. Although we have found that cationic metal carbonyl catalysts enabled this reaction to proceed at room temperature and atmosphere CO pressure,^{4–8} a strong inorganic liquid acid medium was also inevitably employed. Therefore, the use of more environmentally friendly solid acids as catalysts instead of strong liquid acids would be of significant advantage. There have been only a few reports on solid acid-catalyzed carbonylation, although solid acids have been widely used as catalysts and are indispensable in many reactions.⁹ Until now, no solid acid could catalyze Koch-type carbonylation to produce acceptable yields unless the reaction was carried out at very high pressures and temperatures, assisted by an additional corrosive Lewis acid or operated in multiple steps.¹⁰ Recently, Stepanov *et al.* reported the direct NMR observation of the Koch reaction in zeolite H-ZSM-5 at room temperature without using pressurized conditions.^{11–13} Based on this discovery, we have succeeded in the carbonylation of *tert*-butyl alcohol with CO in the liquid phase over various H-type zeolites,¹⁴ and a selectivity for 2,2-dimethylpropanoic acid as high as 100% was obtained over H-ZSM-5. So far, no studies concerning vapor phase Koch carbonylation have been reported. Obviously, fixed bed reactors offer many advantages such as no use of large amounts of organic solvent, continuity of operation, ease of product work-up and catalyst reusability. We now report the vapor phase carbonylation of *tert*-butyl alcohol with CO over H-zeolites.

The catalytic reaction of the carbonylation of *tert*-butyl alcohol with CO was carried out in a high-pressure fixed-bed continuous-flow stainless steel reactor operated in the down-flow mode. Catalyst (2.0 g; particle size: 0.2–0.35 mm) was placed at the center of the reactor with a pre-heating zone of quartz sand. Prior to the reaction, the catalyst was pretreated in dried air at 450 °C for 3 h. The reactor temperature was then lowered to the reaction temperature under flowing N₂. After thoroughly purging the catalyst with flowing CO, the reaction pressure was maintained at a constant value using a back-pressure regulator in the outlet of the reactor. *tert*-Butyl alcohol was supplied using a microfeeder. The reaction products were analyzed on-line by a gas chromatograph equipped with an FID. A complete C balance was established through internal calibration using pure standards of the main compounds involved in the reaction.

The results of the reaction of *tert*-butyl alcohol with CO over

various H-type zeolites are shown in Table 1. It can be seen that *tert*-butyl alcohol easily reacts on the acid catalysts. All the *tert*-butyl alcohol disappears on the three H-ZSM-5 zeolites with different SiO₂/Al₂O₃ molar ratios, and only a small amount of unreacted alcohol remained on H-Mordenite, H-Beta and H-USY. Isobutene is formed as the main product of the dehydration, and no ethers are formed on all the H-zeolites. Besides isobutene, the dimer (C₈) species are the second by-products, and only traces of the trimer species are detected on H-Mordenite and H-USY. The maximum yield of 2,2-dimethylpropanoic acid is obtained on H-ZSM-5 (50) (SiO₂/Al₂O₃ = 50), and the yield of the main product decreases with increasing SiO₂/Al₂O₃ molar ratio. The yield of 2,2-dimethylpropanoic acid on H-ZSM-5 (50) is much higher than those on the other three H-zeolites with similar SiO₂/Al₂O₃ molar ratios. No significant amounts of higher carboxylic acids are observed in the vapor phase carbonylation, probably due to the short contact time in comparison with that during the liquid phase carbonylation, in which C₉ and C₁₃ carboxylic acids (>40%) along with 2,2-dimethylpropanoic acid were observed on H-Mordenite, H-Beta and H-USY whereas only 2,2-dimethylpropanoic acid was formed on H-ZSM-5.¹⁴

From the reaction mechanism,^{14,15} it seems that the addition of H₂O facilitates the conversion of the *tert*-butyl acylium ion intermediate to 2,2-dimethylpropanoic acid. Only a slight improvement in the yield of 2,2-dimethylpropanoic acid was achieved by the addition of H₂O during the liquid phase carbonylation of *tert*-butyl alcohol on H-ZSM-5,¹⁴ whereas a significant influence of H₂O was observed during the vapor phase carbonylation (Table 2). The addition of an equimolar amount of H₂O into the *tert*-butyl alcohol causes the yield of 2,2-dimethylpropanoic acid to increase from 8.3 to 13.5%. The yield of 2,2-dimethylpropanoic acid reaches the highest value at H₂O/*tert*-butyl alcohol (molar ratio) = 3–5. The yield of 2,2-dimethylpropanoic acid begins to decrease with further H₂O addition, and at the same time, a small amount of unreacted *tert*-butyl alcohol appears. Obviously, the coadsorption of H₂O and the *tert*-butyl acylium ion intermediate on the acidic sites facilitates the formation of 2,2-dimethylpropanoic acid. On the other hand, the addition of H₂O may moderate the acidity of the

Table 1 Carbonylation of *tert*-butyl alcohol over various H-type zeolites^a

Catalyst ^b	Conversion of <i>tert</i> -butyl alcohol (%)	Yield of 2,2-dimethylpropanoic acid (%)
H-ZSM-5 (50) ^c	100	8.3
H-ZSM-5 (300) ^d	100	2.4
H-ZSM-5 (1000) ^e	100	0.3
H-Mordenite (20) ^e	94.0	4.1
H-Beta (25) ^d	96.8	3.7
H-USY (30) ^d	98.2	1.9

^a Reaction conditions: catalyst = 2.0 g, reaction temp. = 200 °C, WHSV of *tert*-butyl alcohol = 0.10 h⁻¹, CO stream = 0.8 MPa, 30 ml min⁻¹.

^b SiO₂/Al₂O₃ molar ratio in parentheses. ^c Purchased from N. E. Chemcat Corporation. ^d Purchased from Zeolyst International. ^e Offered by Catalysis Society of Japan as reference catalysts.

Table 2 Influence of H₂O addition on the carbonylation of *tert*-butyl alcohol over H-ZSM5 (50)^a

H ₂ O/ <i>tert</i> -butyl alcohol (molar ratio)	Conversion of <i>tert</i> -butyl alcohol (%)	Yield of 2,2-dimethylpropanoic acid (%)
0	100	8.3
1.0	100	13.5
2.0	100	16.3
3.0	100	18.9
5.0	100	18.8
10.0	99.6	14.2
50.0	97.2	4.5

^a Reaction conditions: catalyst = 2.0 g, reaction temp. = 200 °C, WHSV of *tert*-butyl alcohol = 0.10 h⁻¹, CO stream = 0.8 MPa, 30 ml min⁻¹.

acidic sites on the catalyst and, therefore, depress the oligomerization.

A high CO pressure is also advantageous for Koch-type carbonylation. Table 3 shows the effect of reaction pressure on the carbonylation of *tert*-butyl alcohol over H-ZSM-5 (50). At 0.1 MPa CO, only a small amount of 2,2-dimethylpropanoic acid is formed. By raising the CO pressure, the yield of 2,2-dimethylpropanoic acid dramatically increased with a yield as high as 90.8% at 9.0 MPa CO. This value is much higher than the highest yield (about 60%) for liquid phase carbonylation on the H-ZSM-5 catalyst at the same CO pressure. Fig. 1 shows the time-on-stream (TOS) dependence of the yield of 2,2-dimethylpropanoic acid over H-ZSM-5 (50). Obviously, the yield of 2,2-dimethylpropanoic acid remains constant during the TOS for 120 h. No threat of deactivation is observed. In addition, no significant change in the color of the catalyst was observed after 120 h reaction, indicating nearly no coke built up on the catalyst after so long on stream.

Table 3 Effect of CO pressure on the carbonylation of *tert*-butyl alcohol over H-ZSM5 (50)^a

CO pressure (MPa)	Conversion of <i>tert</i> -butyl alcohol (%)	Yield (%) ^b			
		2,2-Dimethylpropanoic acid	Isobutene + ULP	Dimer (C8) species + UMP	Trimer species + UHP
0.1	100	2.3	75.6	22.1	0
0.8	100	18.9	47.6	33.5	0
3.0	100	39.8	27.6	32.1	0.6
5.0	100	74.2	11.7	12.7	1.5
6.5	100	82.8	6.3	7.4	3.4
9.0	100	90.8	3.2	3.7	2.3

^a Reaction conditions: catalyst = 2.0 g, reaction temp. = 200 °C, H₂O/*tert*-butyl alcohol (molar ratio) = 3.0, WHSV of *tert*-butyl alcohol = 0.10 h⁻¹, CO stream = 30 ml min⁻¹. ^b By-products consist mainly of isobutene, dimer (C8) species and trimer species together with traces of unidentified low-weight (ULP), medium-weight (UMP) and high-weight (UHP) products.

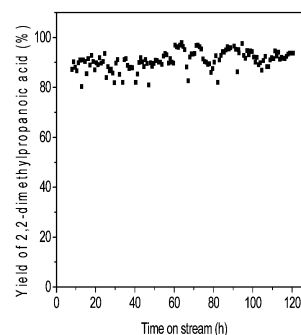


Fig. 1 Time-on-stream (TOS) dependence of the yield of 2,2-dimethylpropanoic acid catalyzed by the H-ZSM-5 (50) catalyst. (Reaction conditions: catalyst = 2.0 g, reaction temp. = 200 °C, H₂O/*tert*-butyl alcohol (molar ratio) = 3.0, WHSV of *tert*-butyl alcohol = 0.10 h⁻¹, CO stream = 9.0 MPa, 30 ml min⁻¹.)

In summary, we have successfully demonstrated for the first time that the H-ZSM-5 catalyst exhibits a very high and stable catalytic performance for the vapor phase Koch-type carbonylation of *tert*-butyl alcohol to produce 2,2-dimethylpropanoic acid. This catalytic system is more efficient and environmentally friendly in comparison to any known liquid phase carbonylation, and we believe that this advantage may extend to other alcohols or olefins as well as being of practical application.

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