

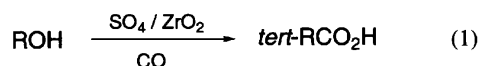
Novel Application of a Solid Super Acid, Sulfated Zirconia, as a Catalyst for Koch Carbonylation Reaction

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(Received October 28, 1999; CL-990918)

A solid superacid, sulfated zirconia, worked well in the Koch reaction. Under optimized conditions, tertiary alcohols were selectively transformed to the corresponding carboxylic acids (34-72%), while primary alcohols were transformed to the corresponding ethers (58-72%).

Direct transformation from alcohols and carbon monoxide to carboxylic acids is a very attractive process in both industrial and synthetic organic chemistry. Although numerous attempts related to the above transformation in strong liquid-acid media, such as concentrated H_2SO_4 , have been reported so far by Koch and other groups,¹ many of them were carried out under extremely severe conditions such as high carbon monoxide pressure and high temperature. We have already reported that Cu(I), Ag(I), Au(I), and Pd(I) carbonyl complexes in concentrated H_2SO_4 showed a high catalytic activity for the carbonylation of alcohols, enabling us to perform this reaction at ambient temperature and pressure.² H_2SO_4 and related strong acids have toxicity, corrosion, and disposal problems. Therefore, from both the industrial and the environmental point of view, this carbonylation process needs to be more environmentally benign by using solid super acids. About twenty years ago, it was reported that sulfated zirconia and related metal oxides showed remarkable strong acidity and had high ability for the isomerization of alkanes.³ Many research groups have investigated their character and structure up to now.⁴ In particular, considerable attention has been paid to the reason for their superacidity. Although sulfated zirconia and related metal oxides showed curiously stronger acidity than other solid acids such as zeolites, Nafion-H, and heteropolyacids, their application was limited to petrochemistry because of their high ability for isomerization and oligomerization of alkanes.³ Very few application studies on synthetic organic chemistry compared with those on other solid acids have been reported so far,⁵ and their potential in this field has not been fully explored. In this paper, as a new application of sulfated zirconia, we describe the carbonylation of *tert*-alcohols with a solid super acid, sulfated zirconia, to form *tert*-carboxylic acids (Eq. (1)). The attempt described here is a novel application of sulfated zirconia to synthetic chemistry which provides a new insight of its catalytic ability.



After the discovery of sulfated zirconia, it was reported that various sulfated metal oxides and modified substrates also exhibited superacidity.⁶ We first investigated their catalytic activity for Koch carbonylation. The reaction was carried out in a stainless steel autoclave at 150 °C with a carbon monoxide (5 MPa: initial charge) atmosphere, using *tert*-butyl alcohol (20

mmol), hexane (50 mL), and ca. 2.0 g of a solid acid catalyst. The obtained results are partly summarized in Table 1. Among all sulfated metal oxides,⁷ zirconia showed the highest activity for this reaction, while other metal oxides, with the exception

Table 1. Yield of carboxylic acids from *tert*-butyl alcohol over various sulfated metal oxides^a

Catalyst	Metal (Starting substrates)	Yield of carboxylic acids ^b / %
$\text{SO}_4 / \text{ZrO}_2$ ^c	Zr (-)	4
$\text{SO}_4 / \text{ZrO}_2$	Zr ($\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$)	13
$\text{SO}_4 / \text{TiO}_2$	Ti ($\text{Ti}(\text{O}i\text{Pr})_4$)	4
$\text{SO}_4 / \text{SnO}_2$	Sn (SnCl_4)	0
$\text{SO}_4 / \text{Al}_2\text{O}_3$	Al (Al_2O_3)	0
$\text{SO}_4 / \text{Fe}_2\text{O}_3$	Fe ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)	0

^aReaction conditions: 120-mL autoclave, *tert*-butyl alcohol (20 mmol), catalyst 2.0 g (the weight before treatment of H_2SO_4), hexane (50 mL), CO (5 MPa: initial charge), 150 °C, 18 h.

^bDetermined by titration with 0.1N NaOH ethanol solution.

^cWako Pure Chemicals Industries, Ltd.

of titania, lacked it. A higher yield of carboxylic acids was obtained by freshly prepared sulfated zirconia.⁸ Then, the solvent effect was investigated under the same condition as above (Table 2). Chlorine-containing solvents, except for carbon tetrachloride, were remarkably effective, while fluorobenzene showed no contribution to this reaction. The solvent effect described above may be understood by either the *in situ* formation of HCl gas or that of superacidic halomethyl cation,⁹ which would be produced from solvent and Lewis acidic sulfated zirconia. Pivalic acid was obtained with moderate selectivity in all solvents, and the polymerization was a main problem under this reaction condition.

Table 2. Solvent effect on the carbonylation of *tert*-butyl alcohol^a

Solvent	Yield of carboxylic acids / %		Selectivity ^d / %
	Total ^b	Pivalic acid ^c	
Hexane	13	5.8	45
Benzene	19	11.0	58
Chlorobenzene	35	16.0	46
Fluorobenzene	4	2.8	70
Dichloromethane	47	23.7	50
CCl_4	11	6.1	55

^aReaction conditions: 120-mL autoclave, *tert*-butyl alcohol (20 mmol), $\text{SO}_4 / \text{ZrO}_2$ 2.0 g (the weight before treatment of 1N H_2SO_4), solvents (50 mL), CO (5 MPa: initial charge), 150 °C, 18 h.

^bTitration yield of total carboxylic acids. ^cGC yields.

^d $100 \times (\text{yield of pivalic acid} / \text{yield of total carboxylic acids})$.

We also studied the effect of temperature and pressure of carbon monoxide, finding that the reaction at 150 °C under 5 MPa pressure of CO was the most favorable for the high-yield preparation of *tert*-carboxylic acids. Although high CO pressure is generally advantageous for Koch carbonylation, the comparatively reduced character of sulfated metal oxides¹⁰ might not accept the above generality.

Then, we carried out the carbonylation of various alcohols under a well-defined condition (Table 3). Interestingly, primary alcohols selectively gave the corresponding ethers in good yield,¹¹ and no carboxylic acid was obtained at all (entries 1-3). In comparison with the liquid-acid process, in which primary alcohols are easily converted to the corresponding *tert*-carboxylic acids,¹ sulfated zirconia turned out to have poor ability for the carbonylation of primary alcohols, because it would be poisoned to some extent by the starting substrates. In the case of secondary alcohols, the complex mixture, which did not contain neither carboxylic acids nor ethers, was obtained. The higher yield was observed at the series with lower amounts (5 mmol) of tertiary alcohols (entries 6-9) and higher selectivity of pivalic acid was also observed (entry 6). Thus, reaction with *tert*-butyl alcohol, 1-adamantanol, 3-methyl-3-pentanol, and 2-methyl-2-butanol gave the corresponding carboxylic acids in a yield above 60%,¹² and the generality for various tertiary alcohols was demonstrated. In addition, the used sulfated zirconia could be easily recycled by calcination again, and the reformed catalysts showed almost the same results as the new ones (entry 6). Although the above results demonstrate that sulfated zirconia has some limitations for carbonylation, it is disclosed that it can effectively convert tertiary

alcohol to *tert*-carboxylic acid and has a promising potential as a solid catalyst for ether formation from primary alcohols.

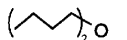
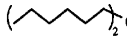
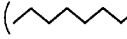









In conclusion, we have demonstrated a convenient method for the preparation of *tert*-carboxylic acid by sulfated zirconia and reported a newly discovered possibility of using sulfated zirconia in synthetic organic chemistry.

We thank Professor K. Arata for helpful suggestions.

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- In the case of tertiary alcohols, starting substrates were not recovered at all.

Table 3. Results of carbonylation of various alcohols by sulfated zirconia^a

Entry	Subs.	Main Product	Yield	
			Main product / % (mmol)	Total carboxylic acids / %
1	1-Butanol		62 (6.2) ^c	—
2	1-Hexanol		72 (7.2) ^d	—
3	1-Octanol		58 (5.8) ^d	—
4	2-Hexanol	—	—	—
5		—	—	—
6 ^b			52 ^{c,e} (2.6)	67 ^f , 69 ^{f,g}
7 ^b			72 ^d (3.6)	79 ^f
8 ^b			34 ^{c,h} (1.7)	71 ^f
9 ^b			47 ^{c,i} (2.4)	76 ^f

^aReaction conditions: 120-mL autoclave, substrates (20 mmol), SO₄/ZrO₂ 2.0 g (the weight before treatment of 1N H₂SO₄), hexane (50 mL), CO (5 MPa: initial charge), 150 °C, 18 h. ^bSubstrates (5 mmol) in CH₂Cl₂. ^cGC yields. ^dIsolated yields. ^e2,2-Dimethylbutyric acid (0.2 mmol) was also obtained. ^fTitration yields. ^gCarried out by the recycled catalyst. ^h2-Ethyl-2-methylbutyric acid (0.75 mmol), 2,2-dimethylbutyric acid (0.33 mmol), and pivalic acid (0.21 mmol) were also obtained. ⁱ2,2-Dimethyl-*n*-valeric acid (0.34 mmol), 2-ethyl-2-methylbutyric acid (0.16 mmol), and pivalic acid (0.67 mmol) were also obtained.