Carbonylation of alcohols over Nafion-H, a solid perfluoroalkanesulfonic acid resin catalyst

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Abstract

Nafion-H was used as a solid acid catalyst for the Koch-type carbonylation of alcohols. The carbonylation of a variety of primary, secondary and tertiary alcohols in various solvents such as hexane, cyclohexane, dichloromethane and chlorobenzene produces the corresponding tertiary carboxylic acids in high yields. For example, the conversions of 2-methyl-2-propanol, 1-pentanol and 1-adamantanol to carboxylic acids are 62.5, 64.6 and 76.9%, respectively, at 433 K and 9 MPa CO. The optimum temperature for this reaction is between 433 and 443 K. A high CO pressure is advantageous for the carbonylation. Only small amounts of ethers were observed for the primary alcohols under CO pressure and without water removal, in contrast with the previous report that primary alcohols are converted to ethers over Nafion-H in quantitative yields when CO is absent and water is removed by azeotropic distillation. © 2002 Elsevier Science B.V. All rights reserved.

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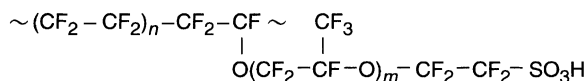
1. Introduction

A simple and efficient synthetic method for tertiary carboxylic acids is of industrial importance. Koch first reported that tertiary carboxylic acids can be produced by the reaction of CO with alcohols or with olefins and H_2O in concentrated strong acids (H_2SO_4, $BF_3 \cdot H_2O$, HF) at 253–353 K and around 10 MPa [1–3]. We have found that Cu(I), Ag(I), Au(I), Pd(I), Pt(I) and Rh(I) carbonyl cations cause the Koch-type reaction to proceed at room temperature and atmospheric CO pressure [4–9]. However, in the industrial application of the Koch reaction, there are problems such as the corrosion of the equipment, a complicated separation procedure for the products and the disposal of huge

amounts of waste acids due to the use of strong acids. Therefore, the use of solid acid catalysts instead of strong liquid acids is of significant advantage.

There have been only a few reports on the solid acid-catalyzed carbonylation, although solid acids have been used as catalysts and are indispensable in many reactions [10]. In 1984, the carbonylation of methanol into methyl acetate, methyl formate and acetic acid was reported on solid acids, but the reaction exhibited either a very low yield (0.3%) under 100% selectivity or a low selectivity (0.8%) with a 34.6% yield with the formation of dimethyl ether via the non-carbonylating route [11]. The carbonylation of formaldehyde has been studied over ion exchange resin catalysts including Nafion-H, Dianion, Amberlyst, and Dowex [12]. Recently, we reported the carbonylation of alcohols over H-zeolites [13] and sulfated zirconia [14]. For the carbonylation of

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$\sim(CF_2-CF_2)_n-CF_2-CF\sim\quad CF_3$

$\qquad\qquad\qquad\quad |\qquad\qquad |$

$\qquad\qquad\qquad O(CF_2-CF-O)_m-CF_2-CF_2-SO_3H$

Scheme 1.

2-methyl-2-propanol over H-zeolites, H-ZSM-5 gives the highest selectivity for 2-2-dimethylpropanoic acid due to its adequate pore dimensions [13]. With the sulfated zirconia catalyst, tertiary carboxylic acids were obtained from tertiary alcohols in good yields, whereas only ethers were formed from primary alcohols [14].

The Nafion-H catalyst, a perfluoroalkanesulfonic acid resin first synthesized by DuPont chemists, has the general chemical formula as shown in Scheme 1, where the value of m can be as low as 1 and the value of n ranges between 6 and 13 [15]. It has hydrophobic (–CF_2-CF_2-) and hydrophilic (–SO_3H) regions in its structure and its superacidity is due to the electron withdrawing effect of the perfluoroalkyl backbone to which the sulfonic acid group is attached. The estimated Hammett (H_0) value for Nafion-H is comparable to that of 96–100% sulfuric acid ($H_0 = -12.0$) [16].

Nafion-H has been used as a catalyst for various reactions such as transalkylation (Friedel–Crafts reaction), ether synthesis, esterification, the condensation of ketones, and pinacol-pinacolone and Fries rearrangements [16]. There have been few reports on the carbonylation over Nafion-H, however. In this paper, we report the carbonylation of a variety of primary, secondary and tertiary alcohols with CO over the Nafion-H catalyst, which produces tertiary carboxylic acids in high yields.

2. Experimental

For the carbonylation of alcohols, commercial Nafion NR-50 (beads, 7–9 mesh, Aldrich) in the H form (ion exchange capacity: ca. $0.8\,meq\,g^{-1}$; equivalent weight: 1250) was used as the catalyst. The commercial alcohol and solvent reagents were used without further purification. A 120 ml stirred stainless steel autoclave enclosed in an electric furnace was used as the batch reactor. As a general procedure, 2.0 g of Nafion-H beads without pretreatment,

20 mmol of an alcohol, and 50 ml of a solvent were placed in the autoclave. CO was introduced into the autoclave and its pressure was raised to the desired value. The initial CO pressure at room temperature was varied in the range of 0.1–9 MPa. The autoclave was heated to the desired temperature in 30 min and held at this temperature for 22 h. After the reaction, the products were collected by filtering off the catalyst and then analyzed by GC, GC–MS and NMR and by titration with an ethanol solution of NaOH.

3. Results and discussion

3.1. Carbonylation of 2-methyl-2-propanol over Nafion-H

Fig. 1 shows the temperature dependence of the carbonylation of 2-methyl-2-propanol over Nafion-H at 5 MPa CO (initial pressure at room temperature) in chlorobenzene. At room temperature, no carboxylic acids are produced and 2-methyl-2-propanol of 76% remains unreacted after the reaction of 22 h. Isobutene 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. The conversion of 2-methyl-2-propanol increases with increasing reaction temperature; at 383 K, 2-methyl-2-propanol completely disappears. 2,2-Dimethylpropanoic acid is formed in a yield of 2.1%, while in the dehydration products the dimer (C_8) species are increased. The rapid dehydration of 2-methyl-2-propanol has also been reported for sulfonic acid resins such as Nafion-H [17], Amberlyst 15 and Dowex 50W [18]. The carbonylation is significantly enhanced at higher temperatures; the total yield of the carboxylic acids reaches the maximum at 443 K (T_{max}) and then decreases with increasing temperature. The value of total yield at T_{max} is 51.2%, corresponding to a turnover number of ca. 7 as the ion exchange capacity of the Nafion-H catalyst used is ca. $0.8\,meq\,g^{-1}$. Besides 2,2-dimethylpropanoic acid, higher-weight carboxylic acids including the C_9 carboxylic acids are also obtained. Similar temperature dependence of the total yield has been observed for the carbonylation of 2-methyl-2-propanol over thermally stable H-zeolites [13]; the appearance of maximum was explained in terms of the fast
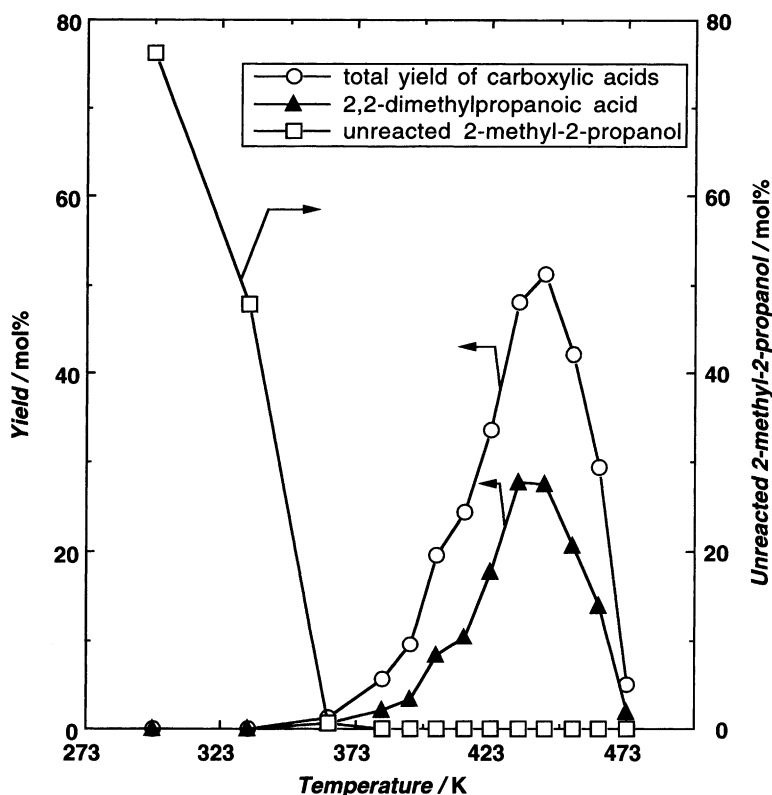
Fig. 1. Temperature dependence of the carbonylation of 2-methyl-2-propanol over Nafion-H. Reaction conditions: 2.0 g Nafion-H, 20 mmol 2-methyl-2-propanol, 50 ml chlorobenzene, 5 MPa CO pressure (initial pressure at room temperature), 22 h reaction time.

oligomerization reaction in the high temperature region. Olah et al. have shown that Nafion-H catalyst is stable at temperatures up to 483 K while above this temperature the catalytic activity is irreversibly decreased due to its limited thermal stability [16,17]. For investigating the thermal stability of Nafion for the carbonylation of 2-methyl-2-propanol, a Nafion-H catalyst that had been used at 473 K for 22 h was reused at 433 K, which exhibited no significant decrease in the total yield of carboxylic acids and the selectivity of 2,2-dimethylpropanoic acid in comparison with the fresh Nafion-H catalyst. This fact implies that not the thermal instability of Nafion-H but the fast oligomerization accounts for the decrease in the total yield with increasing temperature above T_{max}, as observed for thermally stable H-zeolites [13]. In addition, the observation indicates that the Nafion-H catalyst is reusable for the carbonylation of alcohols at temperatures below 473 K.

The overall reactions of 2-methyl-2-propanol with CO over Nafion-H can be described in Scheme 2. This scheme includes the dehydration of 2-methyl-2-propanol to form the trimethylcarbenium ion intermediate, which is in equilibrium with both 2-methyl-2-propanol and isobutene. The secondary reaction between isobutene and the trimethylcarbenium ion intermediate gives the dimer (C_8) and the oligomeric species. The reaction of the trimethylcarbenium ion with CO gives rise to the formation of the acylium cation, which reacts with H_2O to form 2,2-dimethylpropanoic acid. The reaction of the unsaturated oligomeric species with CO and H_2O produces higher-weight carboxylic acids. At low temperatures, the carbonylation of the trimethylcarbenium ion intermediate is slow. By raising the temperature, the carbonylation is accelerated, accompanied by an oligomerization enhancement. The observation of the maximum yield of the carboxylic acids can
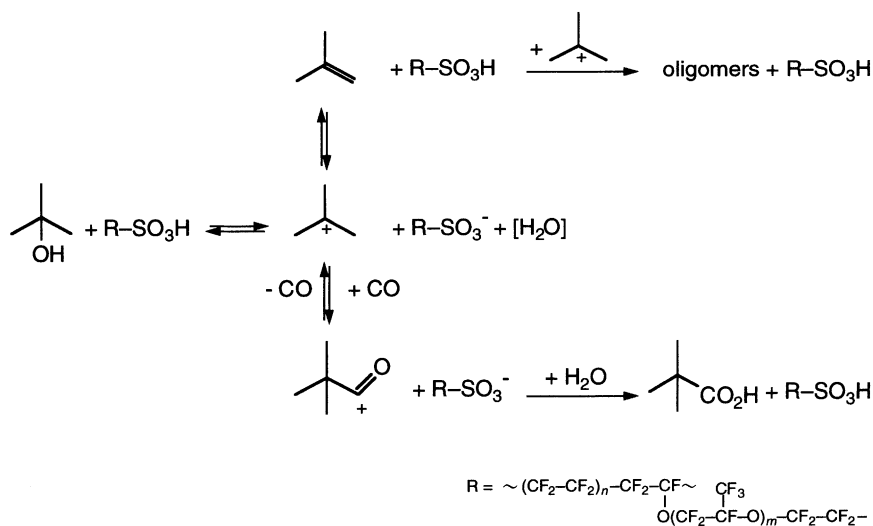
Scheme 2.

be explained in terms of the fast oligomerization reaction, which prevails over the carbonylation of the trimethylcarbenium ion above T_{max}.

A small amount of C_6 and C_7 carboxylic acids are also obtained as by-products, in particular, at high temperatures, which may be formed via dimerization and fragmentation of the carbenium ion intermediates as observed in strong liquid acids [19,20]. No ethers can be detected in contrast to the observation by Olah et al. that primary alcohols quantitatively gave ethers over Nafion-H [21]. An S_N2-type reaction mechanism has been proposed for the formation of ethers which involves the in situ formation of an oxonium ion, where Nafion-H converts the hydroxyl group of the alcohol into a better leaving group by protonation, and the ether is then formed by the nucleophilic attack of the alcohol on the oxonium ion in a bimolecular reaction (S_N2 type) [21]. Therefore, steric reasons may account for the absence of ethers in the reaction of 2-methyl-2-propanol over Nafion-H. In chlorobenzene, a small amount (3.6% at 433 K) of chlorobenzene alkylation products are formed via the Friedel–Crafts reaction [17,22].

Table 1 shows the pressure dependence of the carbonylation of 2-methyl-2-propanol over Nafion-H at 433 K in chlorobenzene. A high CO pressure is also advantageous for the Koch-type carbonylation over Nafion-H as observed in strong acid solutions [1–3]

and observed for H-zeolites [13]. At 0.1 MPa CO (initial pressure at room temperature), no significant amounts of carboxylic acids are formed. By increasing the initial CO pressure to 9 MPa (room temperature), the total yield of the carboxylic acids increases to over 60% and the selectivity of 2,2-dimethylpropanoic acid in the products increases to a value as high as 85%. The increase of selectivity of 2,2-dimethylpropanoic

Table 1
CO pressure dependence of the carbonylation of 2-methyl-2-propanol over Nafion-H[a]

CO pressure[b] (MPa)	Yield (%)	
	2,2-Dimethylpropanoic acid	Total carboxylic acids
0.1	0	0.1
0.5	2.7	7.5
1	9.2	23.9
2	15.0	32.6
3	20.3	38.3
4	24.5	42.0
5	27.8	48.0
6	30.2	56.1
7	38.1	56.8
8	41.5	59.5
9	53.4	62.5

[a] Reaction conditions: 2.0 g Nafion-H, 20 mmol 2-methyl-2-propanol, 50 ml chlorobenzene, 433 K, 22 h reaction time.
[b] Initial pressure at room temperature.

Table 2

Influence of solvent on the carbonylation of 2-methyl-2-propanol over Nafion-H[a]

Solvent	Temperature (K)	Total yield of carboxylic acids (%)
Dichloromethane	413	21.9
	433	50.3
	453	35.5
Chlorobenzene	413	24.4
	433	48.0
	453	42.2
Hexane	413	21.4
	433	44.4
	453	34.0
Cyclohexane	413	17.7
	433	39.1
	453	26.9

[a] Reaction conditions: 2.0 g Nafion-H, 20 mmol 2-methyl-2-propanol, 50 ml solvent, 5 MPa CO pressure (initial pressure at room temperature), 22 h reaction time.

acid with increasing CO pressure results from the enhancement of the carbonylation of the trimethylcarbenium ion prior to the dimerization or oligomerization that gives higher-weight carbonylation products. A higher yield and selectivity of 2,2-dimethylpropanoic acid are expected to be obtained at higher CO pressures.

The solvent effects were also investigated for the carbonylation of 2-methyl-2-propanol over Nafion-H (Table 2). The maximum total yields of the carboxylic acids are slightly higher in the polar solvents such as dichloromethane (50.3%) and chlorobenzene (48.0%)

than those in the nonpolar solvents such as hexane (44.4%) and cyclohexane (39.1%) at 433 K and 5 MPa CO (initial pressure at room temperature). The influence of the solvent polarity on the carbonylation of 2-methyl-2-propanol over Nafion-H, however, is much smaller than that observed by Lange for the carbonylation of di-isobutylmethanol [23]. It was reported that at 423 K and 8 MPa CO the carbonylation of di-isobutylmethanol over Nafion-H gave the corresponding branched carboxylic acid in 39% yield in the polar solvent heptanoic acid, while the yield of the carboxylic acid was as low as 1% in the nonpolar solvent dodecane.

3.2. Carbonylation of a variety of alcohols over Nafion-H

Table 3 summarizes the results of the carbonylation for a variety of alcohols over Nafion-H at 433 K and 9 MPa CO (initial pressure at room temperature). In addition to the carbonylation of 2-methyl-2-propanol as described above, primary and secondary alcohols such as 1-pentanol, 2-pentanol, 1-hexanol and 1-octanol also react with CO to give the corresponding tertiary carboxylic acids, which have been distinctly identified by ^{13}C NMR and GC–MS, in yields as high as 64.6, 52.6, 57.9 and 57.4%, respectively, in the solvent hexane. So far, there have been few examples for the carbonylation of primary and secondary alcohols over solid acid catalysts. The conversion of primary and secondary alcohols to tertiary carboxylic acids indicates the isomerization of the carbenium

Table 3

Carbonylation of a variety of alcohols over Nafion-H[a]

Alcohol	Main product	Yield (%)	
		Main product	Total carboxylic acids
2-Methyl-2-propanol[b]	2,2-Dimethylpropanoic acid	53.4	62.5
1-Pentanol	2,2-Dimethylbutanoic acid	48.2	64.6
2-Pentanol	2,2-Dimethylbutanoic acid	40.4	52.6
1-Hexanol	2,2-Dimethylpentanoic acid	25.8	57.9
	2-Methyl-2-ethylbutanoic acid	22.8	
1-Octanol	2,2-Dimethylheptanoic acid	26.8	57.4
	2-Methyl-2-ethylhexanoic acid	21.6	
1-Adamantanol[b]	1-Adamantanecarboxylic acid	76.8	76.9

[a] Reaction conditions: 2.0 g Nafion-H, 20 mmol alcohol, 50 ml hexane, 433 K, 9 MPa CO pressure (initial pressure at room temperature), 22 h reaction time.

[b] 50 ml chlorobenzene instead of hexane as the solvent.

ion intermediates to form tertiary carbenium ions prior to the carbonylation over Nafion-H. The optimum temperature for the reaction is between 433 and 443 K. No starting substrates remain unreacted. Besides the major products of the corresponding carboxylic acids having one more carbon atom than the starting materials, tertiary carboxylic acids having more than one extra carbon atom are obtained as minor products, which may be formed via dimerization and fragmentation of the carbenium ion intermediates over Nafion-H as observed in strong liquid acids [19,20]. No significant amounts of primary or secondary carboxylic acids are formed as observed in strong liquid acids, in contrast to the NMR observation by Stepanov et al. that in H-ZSM-5, the reaction of 1-octene with CO and H_2O results in acids of the $C_8H_{17}COOH$ and $C_{16}H_{33}COOH$ families with predominantly linear hydrocarbon chains although the carbonylation of 2-methyl-2-propanol, isobutyl alcohol and isobutene produces 2,2-dimethylpropanoic acid with high selectivity [24]. The reason for the predominant formation of linear carboxylic acids from 1-octene over H-ZSM-5 was considered to be that 1-octene molecule is too large for the bulky tertiary carbenium ions to be formed and carbonylated in the narrow pores of H-ZSM-5 [24], whereas the pores of Nafion-H are sufficiently large for the carbenium ions formed from the primary and secondary alcohols used in this work to isomerize to tertiary carbenium ions and to be subsequently carbonylated to give tertiary carboxylic acids.

Only small amounts of ethers ($<2\%$) are formed from the primary alcohols and no ethers are observed for the secondary alcohols. In contrast, over the sulfated zirconia catalyst, no carboxylic acids but high yields of ethers were formed from primary alcohols and neither carboxylic acids nor ethers from secondary alcohols [14]. It was reported by Olah et al. that over Nafion-H, primary alcohols gave the corresponding ethers in quantitative yields while secondary alcohols, except for the cyclic alcohols, gave only traces of ethers [21]. The removal of water formed in the reaction by azeotropic distillation was found to be necessary for achieving a high conversion to the ethers. The low conversions of the primary alcohols to the corresponding ethers in this study may be due to the effects of water, which was not removed during the reaction, and/or, to a certain extent, originate from the carbony-

lation of the alcohols with CO prior to the etherification. The absence of ethers for secondary alcohols may be mainly due to steric reasons, which are disadvantageous for the S_N2-type etherification, as observed for 2-methyl-2-propanol.

No carboxylic acids are obtained from lower alcohols such as methanol, ethanol and 2-propanol. Small amounts ($<3\%$) of alkylation products of chlorobenzene are formed from the low alcohols via the Friedel–Crafts reaction in the solvent chlorobenzene instead of hexane [17,22]. From 1-adamantanol, 1-adamantane carboxylic acid is formed in a yield as high as 76.8%. In chlorobenzene, adamantylchlorobenzene is formed as a by-product in a yield of 15% via the Friedel–Crafts reaction with the solvent, and a small amount of adamantane is also observed.

4. Conclusions

The Koch-type carbonylation of alcohols with CO over Nafion-H, a solid perfluoroalkanesulfonic acid resin catalyst, was investigated. Tertiary carboxylic acids are obtained in high yields from not only tertiary but also primary and secondary alcohols. The optimum temperature for this reaction is between 433 and 443 K. A high CO pressure is advantageous for the carbonylation. The catalytic performance can be slightly modified by changing the solvent polarity. The present study indicates the potential industrial application of solid acids instead of strong liquid acids as catalysts for the Koch-type reaction to selectively synthesize tertiary carboxylic acids.

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