Selective Formation of Acetic Acid from Syngas in the Presence of H₂O over Zirconium Hydroxide

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Acetic acid was selectively synthesized from syngas using zirconium hydroxide catalysts without precious metals.

The direct synthesis of acetic acid from syngas has been investigated using precious metals such as rhodium.^{1–3} In this letter, the selective formation of acetic acid from syngas in the presence of H_2O over zirconium hydroxide catalysts without precious metals is described.

Catalysts were prepared by precipitating metal hydroxide from the addition of an aqueous solution of 5% ammonia to an aqueous solution of metal nitrate, washing with distilled water, and drying the hydroxide at 403 K for overnight. The zirconium hydroxides with different activity were prepared by controlling pH in the hydrolysis solution. The filtration follwed by washing was repeated three times. The CO hydrogenation was carried out in a conventional flow system with 2.0 g of catalyst at 573 K and an atmospheric pressure with a flow rate of 100 mL min⁻¹ (CO/H₂/N₂ = 2/2/1). The products were collected in ethanol trap cooled at Dry Ice temperature of 233 K and determined by GC equipped with Adsorb P-1 column.

As we have already reported, the precipitation of zirconium hydroxide at lower pH, followed by calcination at 723 K, results in the lower activity for CO hydrogenation reaction to form isobutene as a main product at 673 K.⁴ However, the reaction at 573 K with zirconium hydroxide before calcination gave the perfectly different results. Table 1 shows the results for CO hydrogenation over some zirconium hydroxides along with some metal oxide catalysts. Zr(3) is most effective for the formation of acetone and methyl acetate. Zr(4) is most effective for the formation of acetic acid. The preparation at the higher pH leads to the less active catalyst. Yittrium hydroxide is most active among the hydroxides of La, Ce, and Y, yielding large amount of methyl acetate along with methanol, acetic acid, and ketones. The activity for the formation of these compounds disappears within the initial few-hour reaction, although the formation of CO_2 is observed.

On the other hand, the fact that the calcination of Zr(4) at 723 K causes the disappearance of the catalytic activity as shown in Table 1 suggests that the deactivation by the long reaction is due to the consumption of hydroxy species or water on the surface and, therefore, the continuous feeding of H₂O leads to the steady catalytic reaction. Figure 1 shows the time-on-stream of CO hydrogenation in the presence over Zr(4) catalyst. The products were collected for every 8 h, i.e., 0–8, 10–18, 20–28, 30–38, and 40–48 h, and the reaction time plotted in Figure 1 is the average in the collected time. H₂O was fed by bubbling the reaction gas into water trap cooled with ice. The content of H₂O was about 0.5%. The increase of the content to 1.0% resulted in the increase of CO₂ and the remarkable

Table 1. Product formation from syngas over some oxidecatalysts for initial 8 h at 573 K

Ion ^a of	Area/	Product yield ^{b)/} CO-base µmol					
M _x (OH) _y	m^2g^{-1}	MeOH	AcH	Me ₂ CO	AcOH	MA	DIK
Zr(3)	0.2	45	20	295	130	133	114
Zr(4)	0.2	14	24	90	320	+	+
Zr(6)	2.5	47	17	198	64	11	215
Zr(8)	65	1	+	39	1	3	102
$Zr(4)^{c)}$	40	+	0	0	0	0	0
La(9)	15	+	+	+	1	+	+
Ce(9)	54	10	1	7	4	6	169
Y(9)	32	102	30	60	61	375	105

^aParentheses stand for pH values in the precipitation of the hydroxides. The hydroxides of La, Ce, and Y were precipitated at pH=9.0, because the solution of lower pH gave no precipitate. ^bHydrocarbons and higher alcohols such as ethanol were not detected. Small amounts of methyl ethyl ketone, methyl isopropyl ketone, diethyl ketone, and ethyl isopropyl ketone were detected, depending on the catalysts. AcH: acetaldehyde, AcOH: acetic acid, MeOAc: methyl acetate, and DIK: diisopropyl ketone. ^cThe catalyst was calcined at 723 K.

decrease of the organic products. It is clear that the presence of H_2O leads to much longer catalyst life, indicating that the supply of H_2O is indispensable to the catalytic formation of acetic acid. The other effect of H_2O is the retardation of formation of methanol, acetaldehyde, and ketones, leading to the higher selectivity to acetic acid. The stable catalyst life is shown in no color change of the catalyst after 48 h-reaction. The selectivity (about 90%) to acetic acid is much higher and the yield of acetic acid is lower in almost 10 times than reported best results (about 65%) carried out at 1 MPa and 523 K with Ph/Na Y-A catalyst.³

XRD analysis of catalysts showed only broad spectra. It is due to no calcination of the catalysts. The avoidance of deactivation by the presence of H_2O would suggest that the catalyst activity is dependent on the water or hydroxy content on the catalyst. TG measurement showed that there are three temperature ranges of weight loss from 300 to 773 K, 300–400, 450–600, and above 700 K. The weight loss between 300 and 400 K is due to the desorption of physically adsorbed H_2O . Since the calcination at 723 K resulted in the deactivation of Zr(4), the weight loss above 700 K should be excluded. Thus,



Fugure 1. Formation rate of products from CO and H_2 in the presence of H_2O and selectivity to acetic acid over zirconium hydroxide. \diamondsuit : methanol. \bigcirc : acetic acid. \bigtriangleup : acetone. \Box : diisobutyl ketone. \bigcirc : selectivity to acetic acid.



Figure 2. Dependence of amounts of acetic acid, methyl acetate, and ketones on the weight loss between 450 and 600 K with some hydroxide catalysts. \bigcirc : acetic acid. \bigcirc : methyl acetate. \diamondsuit : ketones.

the hydroxy or water shown in the weight loss in 450–600 K is likely to participate in the deactivation of catalyst. Figure 2 shows the relation of the amount of products in Table 1 to the amount of weight loss in 450–600 K. The catalyst with much weight loss forms a large amount of acetic acid, while the amount of ketones seems to be independent of the weight loss. Water desorbed at 450–600 K could come from hydroxy species and the desorption would not cause immediate change of structure to ZrO₂, because feeding H₂O recovers the catalytic activity. It is reported that zirconium hydroxide prepared in the acidic conditions has the anion excgange ability and the preparation above pH = 6.2 results in the large decrease of the ability.⁵

Thus, the high activity of Zr(4) would correspond to this ability. Y(9) catalyst shows the high activity for the formation of methyl acetate. This may be due to the high yield of methanol as shown in Table 1. Thus, high content of water or hydroxyl brings the high yield of acetic and retards the formation of acetaldehyde. Acetone could be formed along with CO_2 from 2 moles of acetic acid (ketonization reaction) and the higher ketones could be produced from acetone by the aldol condensation with formaldehyde, although we have no direct evidence at presnt.

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