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Direct Synthesis of Acetic Acid from Synthesis Gas over Rh-Mn-Zr-Li/SiO_2 Catalyst

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The direct synthesis of acetic acid from synthesis gas has been investigated. Acetic acid was produced with more than 63% selectivity over Rh-Mn-Zr-Li/SiO_2 catalyst at 300 °C under 100 kg/cm^2 of synthesis gas (CO/H_2 = 9/1) flow.

Rhodium catalysts are well known to be an excellent catalyst for the formation of C_2-oxygenated compounds, such as ethanol, acetaldehyde, and ethylene glycol, from synthesis gas.[1] An addition of other metal cations to rhodium catalyst shows striking effects on the activity and selectivity. For example, the role of manganese,[2] iron,[3] sodium[4] on supported rhodium catalyst have been extensively studied for these years. An influence of support has been also studied. Rhodium catalyst supported on La_2O_3, Nd_2O_3, or ZrO_2 were reported to produce ethanol selectively from synthesis gas under atmospheric pressure, but the activities remained low.[5] There are few studies which aim at the selective synthesis of acetic acid.

We have been developing the catalyst with selective conversion of synthesis gas into acetic acid. Here, we would like to report the selective synthesis of acetic acid by the combination of the promising catalysts and the favorable reaction conditions. The catalysts were prepared by impregnation method. SiO_2(Davison #57, 9-16mesh) was poured into an aqueous solution containing the required quantities of additive components. Impregnated samples were dried slowly in the air at room temperature for 2 h, followed by air circulation treatment at 80 °C for 20 h.

The catalysts were reduced in a hydrogen stream at 450 °C for 2 h. Reactions were carried out using a flow type reactor under high pressure. The products were analyzed quantitatively by gas chromatography through a warmed gas-line. Acetic acid and acetaldehyde were the main products and in addition to these, small amounts of ethanol, methane, ethylene, propylene, propionaldehyde and other higher products were also formed. Three G.C. columns, chromosorb 101 for oxygenates, active alumina (1% apiezon glease) for hydrocarbons, and active carbon (silicon) for inert gases were used for the analysis of products.

Table 1 shows the effect of additives(A) of singly promoted 2wt%Rh-(A)/SiO_2 catalysts at 320 °C and 50 kg/cm^2 (CO/H_2 = 2/1). These data show that additives are classified into three groups from their roles. Additives, such as LiCl and KCl, were found to be useful to decrease the selectivity of methane, however, the selectivity of higher hydrocarbons(H.C.) increased. On the other hand, additives, such as $CrCl_3$ or $ZrCl_4$ were proved to be effective to decrease the selectivity of higher H.C. compared with other additive groups. Mn and V additives were proved to increase in the rate of reaction.

Triply promoted Rh/SiO_2 catalysts were investigated to develop the high performance catalysts for acetic acid synthesis. A highly active Rh-Mn/SiO_2 catalyst was modified with both $ZrCl_4$ and LiCl. Because, from the data of Table 1, Zr and Li additives are supposed to suppress the formation of higher H.C. and that of methane respectively. The results were shown in Table 2. An addition of $ZrCl_4$ to Rh-Mn/SiO_2 proved to be effective for depressing the selectivity of methane. Moreover, the increase of LiCl amount is more effective for the increase of the acetic acid selectivity. After all, the addition of both $ZrCl_4$ and LiCl on Rh-Mn/SiO_2 catalyst was revealed to be favorable to decrease both the selectivity of methane and that of higher H.C. Consequently, the selectivity of acetic acid was increased extremely.

Syngas reactions over this favorable catalyst were carried out under various reaction conditions and the results were summarized in Table 3. Syngas reactions usually reached steady states within 2 h. The selectivity to acetic acid was 54% after 4 h under the reaction conditions of 290 °C and 100 kg/cm^2 (CO/H_2 = 9/1). There was no remarkable pressure effect on the acetic acid formation at more than 100 kg/cm^2. However, the striking influence of the CO/H_2 ratio on the selectivity to acetic acid over this catalyst at 300 °C and 100 kg/cm^2 was observed as shown in Fig. 1. A high selectivity of acetic acid, as much as 63-65% was obtained by the improved catalyst, Rh-Mn-Zr-Li/SiO_2 under the favorable reaction conditions,

Table 1. Effect of Additives(A) of 2wt%Rh-(A)/SiO_2 Catalysts on Reaction Behavior

Additive[a)] (A)	Temperature / °C	Total activity (CO-mol/g-Rh/h)	Selectivity in carbon efficiency / % AcOH[b)]	AcH[b)]	EtOH[b)]	CH_4	C_2^+(H.C.)
none	320	0.16	15.0	49.2	0.1	22.0	10.0
LiCl	320	0.35	26.3	35.2	2.8	14.3	21.4
KCl	319	0.09	22.0	39.7	0.0	17.9	20.4
$MgCl_2$	305	0.62	17.0	37.0	0.8	19.7	25.6
$CaCl_2$	321	0.21	30.5	21.0	3.0	19.6	25.9
$ZnCL_4$	310	0.56	17.4	14.2	13.3	41.1	14.0
$HfCl_4$	319	0.42	12.0	11.2	11.8	47.0	18.0
$CrCl_3$	320	0.43	11.7	32.7	3.3	38.7	13.6
V_2O_5[c)]	280	0.44	10.2	25.6	7.8	28.3	23.3
$Mn(NO_3)_2$	320	1.47	15.0	45.0	0.6	19.0	19.0

Reaction conditions; Catalyst charge: 30 ml(ca. 12 g),Reaction Temp.: 320 °C,
Reaction pressure: 50 kg/cm^2, Flow rate: 100 Nl/h, Syngas ratio(CO/H_2):2/1.
a): The atomic ratio of additive to Rh (A/Rh) is 1/3.
b): AcOH=CH_3COOH, AcH=CH_3CHO, EtOH=C_2H_5OH, C_2+(H.C.)=higher hydrocarbons
c): prepared by dissolving V_2O_5 in aqueous solution of $(COOH)_2$,Rh:V=1:2/3

Table 2. Reaction Behavior of Triply Promoted 3wt%Rh-Mn-Zr-Li/SiO_2 Catalysts

Component (M/Rh)[a)] (atomic ratio)	Temp /°C	Total activity (CO-mol/g-Rh/h)	Selectivity in carbon efficiency/ % AcOH	AcH	EtOH	CH_4	C_2^+(H.C.)
$MnCl_2$(1/3)	280	1.06	36.1	31.1	1.9	13.7	12.3
$MnCl_2$(1/3)-$ZrCl_4$(1/8)	300	1.38	39.5	30.7	3.6	15.4	8.5
$MnCl_2$(1/3)-LiCl(1/3)	300	1.67	48.8	27.6	1.6	8.5	8.9
$MnCl_2$(1/3)-$ZrCl_4$(1/8)-LiCl(1/3)	300	1.66	46.6	29.7	3.2	10.4	6.3
$MnCl_2$(1/3)-$ZrCl_4$(1/8)-LiCl(2/3)	300	1.53	53.2	28.2	2.5	8.1	4.4

Reaction conditions; Catalyst charge: 10 ml(ca. 4 g), Reaction temp.: 300 °C,
Reaction pressure: 100 kg/cm^2, Flow rate: 100 Nl/h, Syngas ratio(CO/H_2): 2/1.
a): The number in a parenthesis is the atomic ratio of additives to Rh.

Table 3. Influences of Reaction Conditions on Syngas Reaction over 3wt%Rh-Mn-Zr-Li/SiO_2 Catalyst

Total pressure / kg/cm^2	Temperature / °C	AcOH STY g/l-cat/h	T.A.[a)]	Selectivity in carbon efficiency /% AcOH	AcH	EtOH	CH_4	C_2^+(H.C.)
100	270	78	0.43	50.2	26.3	1.4	6.4	8.8
100	290	213	1.10	53.7	26.2	2.2	7.1	5.9
100	320	483	2.76	48.7	28.2	2.5	10.6	3.2
50	300	263	1.56	46.8	28.2	3.8	8.4	6.1
125	300	286	1.57	51.9	27.7	3.5	8.9	3.9

Reaction conditions; Catalyst charge: 10 ml(ca. 4 g), Flow rate: 100 Nl/h,
Syngas ratio(CO/H_2) : 2/1.
Catalyst: Rh:Mn:Zr:Li = 1:1/3:1/8:2/3 in atomic ratio.
a): Total activity (CO-mol/g-Rh/h)

300 °C, 100 kg/cm^2, and CO/H_2 = 9/1. The roles of additives on Rh-Mn-Zr-Li/SiO_2 catalyst are now being investigated and will be discussed in the future.

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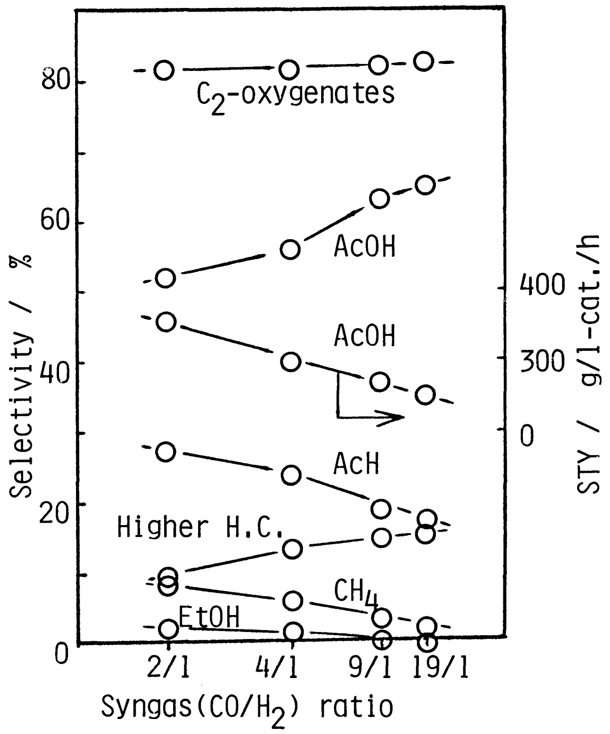

Fig. 1. Influence of Syngas Ratio on Reaction Behavior over 3wt%Rh-Mn-Zr-Li/SiO_2
Reaction conditions; Pressure: 100 kg/cm^2, Temperature: 300 °C, Flow rate: 100 Nl/h. Rh:Mn:Zr:Li = 1:1/3:1/8:2/3 in atomic ratio

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