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SELECTIVE HYDROGENATION OF CARBON MONOXIDE ON SUPPORTED Rh CATALYSTS PREREDUCED IN SITU WITH H_2O AND CO OR H_2

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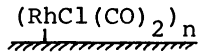
Carbon monoxide was selectively converted to ethylene and propylene(>80 % of C_1-C_6 hydrocarbons produced) at 433-447 K over SiO_2-supported Rh catalysts prereduced in situ with a CO-H_2O mixture, while another Rh catalyst obtained by the pretreatment in situ with a H_2-H_2O mixture yielded ethanol and acetaldehyde at a higher selectivity by a factor of about 100 at 453 K than a usual Rh(0) catalyst reduced with H_2 alone.

The importance of controlling the selectivity in carbon monoxide hydrogenation[1)] prompted us to describe our results in this field. Rh^{III} ions are known to be reduced to Rh^I level with CO in aqueous solution[2)] and Rh_4 or Rh_6 carbonyl clusters are conveniently synthesized from a Rh^I carbonyl compound under CO atmosphere in the presence of water.[3)] The behaviours of $Rh_6(CO)_{16}$ on alumina[4)] and zeolite[5)], such as the reversible decarbonylation-recarbonylation and the fragmentation-clusterization($Rh^0_6 \rightleftharpoons 6\ Rh^I$), have been demonstrated to depend upon the water content of the supports. These results seemed to us to suggest a new way of preparing supported Rh catalysts for the selective CO hydrogenation by reducing supported Rh^{III} ions in the presence of H_2O vapour. We wish to report the selective formations of ethylene and propylene, and ethanol and acetaldehyde from a CO/H_2 gas over the SiO_2-supported Rh catalysts pretreated in situ with H_2O and CO or H_2.

Rh^{III} ions were supported on a silica using a methanol solution of $RhCl_3 \cdot 3H_2O$ (Soekawa Chemicals) without contacting air and moisture in a flow of high purity (99.9995 %) Ar followed by evacuation for 30 min at 293 K and for 1 h at 323 K; the SiO_2 obtained from Snowtex-O(Nissan Kagaku Inc.) was washed with a distilled water, dried at 393 K and heated at 473 K in air. Two types of Rh catalysts were obtained by prereducing the supported Rh^{III} chloride in situ with a CO(200 Torr) - H_2O(20 Torr) mixture or with a H_2(200 Torr) - H_2O(20 Torr) mixture at 363 K for 15 h followed by evacuation for 1 h in a closed circulating system before catalytic reactions.

The supported Rh^{III} ions which exhibited a d-d transition band at 530 nm ($^5T_{2g} \rightarrow {}^5E_g$) indicating an octahedral coordination, were reduced with H_2, stepwisely $Rh^{III} \xrightarrow{328\ K} Rh^{II} \xrightarrow{423\ K} Rh^{I} \xrightarrow{773\ K} Rh^{0}$. The Fischer-Tropsch reactions over these catalysts involving Rh^0, Rh^I or Rh^{II} were carried out in a closed circulating system(200 cm^3) with a liq.N_2 trap. The main product was always methane in the temperature range 413-573 K although the formations of C_2-C_3 hydrocarbons were favoured by the Rh^I catalyst.

The UV absorption band of 530 nm almost disappeared by the CO-H_2O treatment, associated with a colour change from pale brick red to yellow, indicating the formation of a Rh(I) halodicarbonyl species on the SiO_2 surface. Two molecules of HCl evolved per a Rh atom also suggested univalent rhodium. Again the Rh^I species formed was characterized by the twin carbonyl peaks5)6) at 2100 and 2025 cm^{-1}. These twin carbonyls were rapidly eliminated to evolve mainly carbon monoxide at 433 K, no carbonyl peaks being observed during catalytic CO hydrogenation. The catalytic activities gradually decreased during the first ~15 h of reactions and then attained constant activities; the data were taken there. The F-T syntheses over the Rh catalysts prereduced in situ with H_2O and CO are listed in Table 1. The formation of methane was remarkably suppressed, resulting in the high selectivities(85 %) toward C_2-C_3 hydrocarbon formations at 433-447 K, where the C_2-C_3 selectivity(%) is defined as $100[C_2\text{-}C_3]/([C_1\text{-}C_5^+]+[\text{oxygenated compounds}]+[CO_2])$ on carbon base; C_5^+ includes n-pentane, 1- and 2-pentene, n-hexane and hexene isomers (not branched). The olefin fraction in the C_2-C_3 components was 89.1 % (ethylene/propylene=16.5 %/72.6 %). When the catalyst was exposed to air at room temperature followed by reduction with H_2 at 473 K, the catalytic activity decreased but the ethylene/propylene ratio increased to 37.9 %/41.0 %. The structure, environment and chemical nature of active sites of the selective Rh catalyst showing a constant activity are not clear at this stage, but the catalyst precursor for the selective $C_2^=$-$C_3^=$ formations may be a small surface Rh^I cluster,  $(RhCl(CO)_2)_n$.

On the other hand the conventional catalyst made by an impregnation method using aqueous $RhCl_3$ solution in air did not exhibit such a selectivity by similar CO-H_2O pretreatments as given in Table 1 although the effect of the pretreatment

Table 1 Selectivities of the "In Situ-Prereduced" Rh Catalysts and the Impregnation Catalyst in Carbon Monoxide Hydrogenation(catalysts=1 g, CO/H_2= 1/4 (total P.=250 Torr, 433 & 453 K) or 1/2 (total P.=300 Torr, 493 & 523 K)

catalysts	pretreatments	Rh O.N.[a]	Rh wt%	T/K	conv.[b] %	selec./%[c] H.C.	selec./%[c] Ox.C	olefin fraction[d]	H.C. distributions/% C_1	C_2	$C_2^=$	C_3	$C_3^=$	C_4	$C_4^=$	C_5^+[j]	Ox.C. distributions/% E	A	EA[e]
Rh/SiO_2	H_2	0	5	523	64.7	99.5	0.4	25.4	86.2	4.6	0.0	3.9	0.6	1.4	2.0	1.3	36.1	39.4	9.6
Rh/SiO_2	H_2	1	1	433	2.7	89.1	6.8	74.8	63.6	5.3	7.0	1.9	9.7	1.5	7.8	3.2	20.3	63.4	1.5
Rh/SiO_2	CO	1	4	453	0.5	96.8	0.0	86.3	45.8	2.9	13.1	3.2	25.8	1.3	7.9	0.0	0.0	0.0	0.0
Rh/SiO_2[f]	$CO-H_2O$	-	1	433	3.5*	93.9	4.3	81.4	37.7	8.2	28.6	2.2	8.4	1.0	12.1	1.8	2.2	86.3	11.5
Rh/SiO_2	$CO-H_2O$	1	5	433	2.5*	93.5	4.0	87.8	5.3	4.2	15.0	5.7	65.9	0.8	1.2	1.9	3.9	78.1	18.0
Rh/SiO_2	$CO-H_2O$	1	5	447	3.0*	94.3	3.0	88.0	5.6	6.4	14.3	3.5	65.9	1.3	2.6	0.4	5.9	79.1	13.8
Rh/SiO_2	$CO-H_2O$[g]	1	5	433	0.75*	90.6	2.9	78.5	6.8	8.9	34.2	10.2	37.0	0.8	2.0	0.0	0.0	84.3	15.7
Rh/SiO_2	H_2-H_2O	1.6	4	453	12.0*	68.0	31.5	72.5	79.6	4.0	6.0	1.1	4.5	0.4	2.1	2.5	41.7	45.8	3.6
Rh/SiO_2	H_2-H_2O	1.6	4	493	13.3	89.4	10.2	78.7	71.4	3.7	4.3	1.3	10.7	0.4	6.1	2.1	69.0	19.9	4.2
Rh_2/SiO_2[h]	none	1	5	433	9.2	94.9	4.6	75.9	48.9	6.6	9.4	3.8	17.3	1.1	7.3	5.6	2.0	88.4	0.0
Rh_6/SiO_2[i]	none	0	3	453	1.3	93.6	4.2	89.4	83.9	0.9	2.8	0.6	7.3	0.2	4.1	0.1	8.4	87.0	0.0

a oxidation numbers of Rh ions in catalyst precursors. b carbon base conversions(%) per 1 h(5 h for *) per 1 g of catalysts = $100([C_1-C_5^+]+[\text{oxygenated compounds}]+[CO_2])/[CO]_0$. c selectivities(%) to hydrocarbons = $100[C_1-C_5^+]/([C_1-C_5^+]+[\text{oxygenated compounds}]+[CO_2])$. selectivities(%) to oxygenated compounds such as ethanol, acetaldehyde, ethyl acetate, methanol, etc.,= $100[\text{oxygenated compounds}]/([C_1-C_5^+]+[\text{oxygenated compounds}]+[CO_2])$. d olefin fractions(%) in the $C_2-C_5^+$ components.

e E, ethanol; A, acetaldehyde; EA, ethyl acetate. Acetic acid was not produced . f conventional impregnation catalysts.

g sample, exposed to air followed by reduction with H_2. h supported $Rh_2Cl_2(CO)_4$. i supported $Rh_6(CO)_{16}$. j n-pentane, 1- and 2-pentene, n-hexane and hexene isomers(not branched).

on the product distribution was observed; the $C_2^=$-$C_3^=$ components were 37 % of whole hydrocarbons produced. The supported Rh^{III} ions were reduced to Rh^I dicarbonyl species by treating with CO alone coinciding with the literatures$^{6)}$, but this surface species was catalytically unselective. Also $Rh_2Cl_2(CO)_4$ and $Rh_6(CO)_{16}$ supported on SiO_2 yielded ethylene and propylene as minor products.

The supported Rh(III) chloride was converted to another selective catalyst by prereduction in situ with a mixture of H_2 and H_2O. It was found in Table 1 that the Rh catalyst yielded oxygenated compounds at the selectivity of 31.5 % at 453 K under a reduced pressure. The C_2 fraction like ethanol and acetaldehyde was 87.5 % $(100([C_2H_5OH]+[CH_3CHO])/([C_2H_5OH]+[CH_3CHO]+[CH_3COOC_2H_5]+[CH_3OH]))$. A usual SiO_2-supported Rh^0 catalyst which was prepared by reducing the supported Rh^{III} ions with H_2 alone gave no significant amounts of C_2-oxygenated compounds(0.3 % in selectivity) under similar reaction conditions. Thus the supported Rh catalyst obtained by the novel preparation method produced ethanol and acetaldehyde at a higher selectivity by a factor of about 100 than the usual Rh^0 catalyst.

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