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CO HYDROGENATION OVER AN AMORPHOUS GOLD-ZIRCONIUM ALLOY

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An amorphous $Au_{25}Zr_{75}$ alloy showed a high catalytic activity for hydrogenation of carbon monoxide. Thus, the rate of methanation was 2.3 μmol s^{-1} g^{-1} under 6.0 MPa at 523 K, being much higher than that over Au/ZrO_2 or ZrO_2. It was found that the alloy was oxidized into metallic gold and ZrO_2 under the reaction conditions.

Several studies have been reported on CO hydrogenation over amorphous alloys, for instance, Fe-Ni-P-B,[1] Ni-Zr,[2] Pd-Zr,[3] and Cu-Zr.[4] In these papers, amorphous alloys are reported to be more active than their crystalline alloys. We found that an amorphous $Au_{25}Zr_{75}$ alloy was oxidized under the reaction conditions and then this oxidized catalyst was very active in methanation. There are a few reports[5,6] on CO hydrogenation over the catalysts containing gold, but in those cases, gold was not a main component of the catalysts. Maehashi et al.[7] reported that the main product of CO hydrogenation over zirconium oxide was methanol at 523 K and isobutene over 623 K. We report here CO hydrogenation over transition metal-zirconium amorphous alloys.

Pure transition metal (Rh, Pd, Os, Ir, Pt, and Au over 99.99%) and zirconium (99.6%) were arc-melted together in an argon atmosphere. From these alloys, amorphous alloy ribbons of 0.01-0.03 mm thick by 0.5-1.5 mm wide were fabricated by a single-roll-type melt quenching method in an argon atmosphere.[1] A supported catalyst (Au/ZrO_2) was prepared by a wet impregnation of commercial zirconium oxide with an aqueous solution of tetrachloroauric(III) acid. Then the catalyst was dried at 393 K for 5 h and calcined at 673 K for 4 h in air. The gold content of thus-prepared catalyst was 2% of zirconium oxide by weight.

0.5 g of the amorphous alloy sample or the supported catalyst was loaded in a tubular reator. The reaction was carried out under 6.0 MPa. The gas mixture of CO, H_2, and Ar ($CO/H_2/Ar=31/64/5$) in a cylinder was used without further purification. The crystalline phase in the catalyst was identified by X-ray diffraction.

Table 1 summarizes the results of the CO hydrogenation reaction over various transition metal-zirconium amorphous alloys after the stationary condition was obtained. CO hardly reacted over amorphous alloys below 600 K except $Au_{25}Zr_{75}$ and $Pd_{25}Zr_{75}$. The main product over $Au_{25}Zr_{75}$ was methane, while that over $Pd_{25}Zr_{75}$ was methanol. However, dimethyl ether was produced over $2\%Au/ZrO_2$ and ZrO_2 at 673 K. The $Au_{25}Zr_{75}$ alloy was more active for CO hydrogenation than the supported catalyst (Au/ZrO_2) or ZrO_2 itself.

The specific surface areas of all the alloys were less than 1 $m^2\ g^{-1}$ in as-quenched state, and unchanged after the reaction except in case of $Au_{25}Zr_{75}$ and $Pd_{25}Zr_{75}$. The surface areas of $Au_{25}Zr_{75}$ and $Pd_{25}Zr_{75}$ after the reaction increased to 35 and 51 $m^2\ g^{-1}$, respectively as shown in Table 1.

It was proved by X-ray diffraction that $Pd_{25}Zr_{75}$ was decomposed into a weakly-bound Pd-Zr-O type complex oxide. A similar phase change has been described previously.[3] $Au_{25}Zr_{75}$ was decomposed into gold and zirconium oxide. This phase change was similar to the decomposition of an amorphous Cu-Zr alloy.[4] However, amorphous phases in the other alloys were maintained though a part of zirconium in the alloys was oxidized.

Table 1. Results of CO hydrogenation under the total pressure of 6.0 MPa ($CO/H_2/Ar=31/64/5$) at the flow rate of 2.1 l h^{-1} under the stationary state and the surface area after the reaction

Catalyst	T/K	CO %conv.	CO base selectivity/%						Surface area
			CH_4	C_{2+}H.C.	MeOH	DME[a]	C_{2+}OH	CO_2	$m^2\ g^{-1}$
$Rh_{25}Zr_{75}$	670	8.7	85.8	7.9	2.5	2.1	1.7	0.0	<1
$Pd_{25}Zr_{75}$	478	21.2	15.0	0.9	79.0	1.1	0.1	3.9	36
$Os_{25}Zr_{75}$	653	2.5	66.7	19.5	13.8	0.0	0.0	0.0	<1
$Ir_{25}Zr_{75}$	653	3.8	51.9	30.4	13.6	0.0	4.1	0.0	<1
$Pt_{25}Zr_{75}$	663	2.6	61.7	9.2	29.1	0.0	0.0	0.0	<1
$Au_{25}Zr_{75}$	523	33.0	49.5	0.1	3.0	0.3	0.0	47.1	51
Au/ZrO_2	673	8.5	14.4	8.0	5.4	42.7	5.0	24.5	40
ZrO_2	672	10.4	10.7	11.5	6.3	36.4	5.4	31.0	40

a) Dimethyl ether.

Figure 1 shows the change of the activity over $Au_{25}Zr_{75}$ at various temperatures. Table 2 summarized the conversions and selectivities after the stationary condition was obtained at various temperatures and the surface areas after the reaction. The activity sharply increased with running time over 511 K. It gradually increased at 498 K, but scarecely increased under 486 K. However, the CO conversion of 4.3% was obtained even at 473 K after the stationary condition was obtained at 523 K. X-ray diffraction proved that spent alloys partly oxidized into gold and zirconium oxide and the surface area slightly increased, even if the reaction temperature was lower than 486 K. The nature of the active site and the reaction mechanism of the methanation is under investigation.

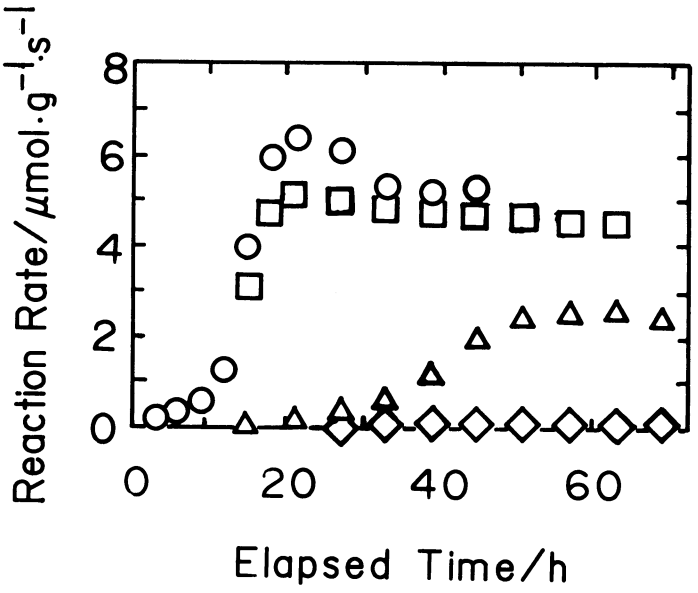

Fig. 1. Change in the activity over $Au_{25}Zr_{75}$ under 6.0 MPa at various temperatures
○; 523 K, □; 511 K, △; 498 K, ◇; 486 K.

Table 2. Results of CO hydrogenation reaction[a] over $Au_{25}Zr_{75}$ at various temperatures and the surface area after the reaction

T/K	CO %conv.	CO base selectivity/%					Surface area
		CH_4	C_{2+}H.C.	MeOH	DME[b]	CO_2	$m^2\ g^{-1}$
473	0.3	61.3	0.0	0.0	0.0	38.7	9
	4.3[c]	47.8	0.0	6.8	0.5	44.9	
486	0.9	57.7	0.0	1.5	0.6	40.2	31
	7.4[c]	48.1	0.1	4.6	0.3	46.9	
503	15.0	47.7	0.1	5.2	0.5	46.5	-
	13.4[c]	48.1	0.1	4.8	0.4	46.6	
511	27.8	48.3	0.1	3.9	0.4	47.3	49
	25.8[c]	48.2	0.1	4.3	0.4	47.0	
523	33.0	49.3	0.1	3.0	0.3	47.3	51

a) Reaction conditions: see Table 1. b) Dimethyl ether. c) Stabilized at 523 K.

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