Selective Hydrogenation of Unsaturated Carbonyl Compounds over an Oxidized Gold–Zirconium Alloy

M. Shibata,[a] N. Kawata,[a] T. Masumoto,[b] and H. Kimura[b]

[a] *Central Research Laboratories, Idemitsu Kosan Co., Ltd., 1280 Kamiizumi, Sodegaura, Kimitsu-gun, Chiba 299-02, Japan*
[b] *Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan*

An oxidized amorphous Au–Zr alloy showed high selectivities for partial hydrogenation of unsaturated carbonyl compounds to unsaturated alcohols, contrasting with their low catalytic activity in the hydrogenation of unsaturated to saturated alcohols; the active sites of this catalyst are modified gold rather than impurities since the amounts of impurities present were too small (<80 p.p.m.) to show hydrogenation activity.

We have reported that an amorphous gold–zirconium alloy showed a high catalytic activity for CO hydrogenation,[1] the alloy changing into metallic gold and ZrO_2 during the reaction, and resulting in the formation of active sites. Reports on hydrogenation catalysts containing gold are limited,[2—4] and so it was of interest to study the nature of the active site of the gold–zirconium alloy for hydrogenation. We now report studies on the selective hydrogenation of various unsaturated carbonyl compounds over an oxidized gold–zirconium alloy.

A master alloy, which contained 30 atom% of gold, was prepared by arc-melting zirconium (99.6%) and gold (99.99%) together in an argon atmosphere. From this master alloy, an amorphous alloy ribbon 0.01—0.03 mm thick and 0.5—1.5 mm wide was fabricated by the single-roll type melt quenching method under argon.

The alloy ribbon (0.5—1 g) was cut into 1—2 mm lengths, loaded into a Pyrex tube, and then oxidized in flowing nitrogen–water (0.04 : 1) at 573 K for 10 h. *X*-Ray diffraction of the sample showed that it contained metallic gold and monoclinic ZrO_2, and we designate it AuZr(O). Its specific surface area was 30 m^2/g.

For comparison, a supported gold catalyst was prepared by

Table 1. Hydrogenation of but-2-enal, 2-methylprop-2-enal, and but-3-en-2-one over AuZr(O) using a pulse reactor. Conditions as in the text.

Reactant	T/K	Conversion /mol%	Selectivity/mol%			
			Enol	-al	-ol	Hydrocarbon
But-2-enal	383	8.4	57.1	38.1	4.8	0.0
	393	10.1	59.4	37.6	3.0	0.0
	413	16.0	58.1	36.9	5.0	0.0
2-Methylprop-2-enal	363	8.3	47.2	42.9	6.7	0.0
	373	9.8	44.9	45.0	6.8	0.0
	383	13.6	42.2	46.4	6.9	0.0
But-3-en-2-one	363	6.3	9.6	90.4	0.0	0.0
	373	9.8	9.5	90.5	0.0	0.0
	383	14.6	8.3	91.0	0.0	0.0

Table 2. Hydrogenation of but-2-enal, but-2-en-1-ol, butanal, and butan-1-ol over AuZr(O) using a pulse reactor. Conditions as in the text.

Reactant	T/K	Composition of effluent gas/mol% (selectivity/mol%)				
		But-2-enal	But-2-en-1-ol	Butanal	Butan-1-ol	Hydrocarbon
But-2-enal	383	91.6	4.8(57.1)	3.2(38.1)	0.4(4.8)	0.0
	393	89.9	6.0(59.4)	3.8(37.6)	0.3(3.0)	0.0
	413	84.0	9.3(58.1)	5.9(36.9)	0.8(5.0)	0.0
But-2-en-1-ol	383		100.0	0.0	0.0	0.0
	393		98.9	0.3(27.3)	0.8(72.7)	0.0
	413		96.9	0.8(25.8)	0.8(25.8)	0.3(25.0)
Butanal	383			96.8	3.2(100)	
	393			94.0	3.2(100)	
	413			93.6	6.4(100)	
Butan-1-ol	383				100.0	
	393				100.0	
	413				100.0	

conventional impregnation of commercial ZrO_2 pellets (Strem Chemicals Inc.) with an aqueous solution of $H_2AuCl_4 \cdot nH_2O$, followed by drying and calcining at 673 K for 4 h. This sample, which we designate Au/ZrO_2, contained 2 wt% of gold.

The hydrogenation of unsaturated compounds (but-2-enal, 2-methylprop-2-enal, and but-3-en-2-one (chemical grade without further purification), was carried out using a conventional pulse reactor, under the following conditions: pulse size: 1 µl; weight of catalyst: 100 mg; flow rate of carrier gas (H_2): 20 ml/min. The hydrogenation of but-2-enal was carried out using an autoclave (250 ml, stainless steel) under high pressure, under the following conditions: catalyst weight [AuZr(O)]: 0.1 g; 5 ml of but-2-enal (61.4 mmol) diluted with 45 ml of ethanol; initial pressure of hydrogen: 1.0 MPa; temperature: 373 K; time: 4 h. Without a catalyst, a small amount of but-2-enal was converted into butan-1-ol, and so the conversion was calculated by deducting the amount converted into butan-1-ol in the blank test from the total conversion of but-2-enal.

Table 1 summarizes results for the hydrogenation of unsaturated carbonyl compounds over AuZr(O) using the pulse reactor; AuZr(O) was extremely active. In contrast, Au/ZrO_2 showed little activity; the conversion of but-2-enal was 3%, with almost complete selectivity for formation of butanal, even at 573 K. In the hydrogenation of but-2-enal, the C=O bond was more easily hydrogenated than the C=C bond over AuZr(O), whereas in the hydrogenation of but-3-en-2-one the C=C bond was more easily hydrogenated. In the hydrogenation of 2-methylprop-2-enal, an intermediate (C=C *vs.* C=O) reactivity pattern was observed. These results suggest that the difference between the reactivity of the C=O and C=C bonds arises from changes in electron density on the C=O and C=C bonds and/or steric hindrance by methyl substitution of the C=C–C=O structure. It should be noted that the hydrogenation of both C=O and C=C bonds was rarely observed.

Table 2 summarizes results for the hydrogenation of but-2-enal, but-2-en-1-ol, butanal, and butan-1-ol over AuZr(O) using the pulse reactor. The C=O bond was hydrogenated in preference to the C=C bond in the conjugated C=C–C=O structures over AuZr(O), but the activity for hydrogenation of compounds which have only one double bond (C=O or C=C) was low. Little hydrogenolysis occurred over AuZr(O) under these conditions.

The product of hydrogenation of but-2-enal using an autoclave was solely but-2-en-1-ol at 13.5% conversion, except for a trace of butan-1-ol, under 1.0 MPa of hydrogen.

Unsaturated carbonyl compounds are normally preferentially hydrogenated to the saturated carbonyl compounds in the first stage. Over palladium, for example, the reaction stops spontaneously when the saturated carbonyl compound is formed. This preference for C=C bond hydrogenation may be due to the lower energy of the C=C (615 kJ/mol) than the C=O bond (715 kJ/mol).[5] The preferential hydrogenation of the C=O bond is thus a unique property of AuZr(O).

It has to be emphasized that the high activity of AuZr(O) for hydrogenation is rather surprising considering the low activity of metallic gold. One might be tempted to argue that traces of other metals, rather than gold, are responsible for the observed activity. However, the effect is so large that a considerable amount of impurities would be required to cause the observed activity. Careful analysis of the catalyst using inductively coupled plasma and *X*-ray fluorescence techniques did not reveal any significant metal impurity except for iron (80 p.p.m.). In addition, the AuZr(O) was totally inactive for ethane hydrogenolysis up to 700 K, which indicates the absence of group VIII metal impurities such as rhodium, palladium, or iridium. XPS measurement for the AuZr(O) did not reveal metallic Zr, indicating that no Au–Zr alloy survived the oxidation procedure. Therefore, there would be little possibility that residual alloy showed some catalytic activity.

In conclusion, a unique interaction between gold and zirconium oxide in the AuZr(O) catalyst could, under certain conditions, modify its physicochemical properties, resulting in unique catalytic activity for hydrogenation. The nature of the active site of AuZr(O) and the hydrogenation mechanism are under investigation.

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