Deoxydehydration of Glycerol to Allyl Alcohol over ReO_x-Au/CeO_2 catalyst with H_2

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Abstract: The rhenium oxide catalyst promoted by gold nanoparticles and ceria support (ReO_x-Au/CeO_2) enabled the use of H_2 as a reductant for deoxydehydration (DODH), converting vicinal diols to olefins with higher activity than homogeneous Re catalysts using non-H_2 reductants and with comparable selectivity. In ReO_x-Au/CeO_2 catalyst, about 10 nm Au particles were especially effective for activating H_2 while retaining the C=C bond in DODH products. Glycerol was converted to allyl alcohol in 91% yield, and the TON per Re atom reached 300.

Keywords: heterogeneous catalysis, rhenium oxide, deoxydehydration.

1. Introduction

Because of the finitude of fossil resources, utilization of sustainable substitute resources such as biomass becomes more and more important in production of chemicals. Among the products, unsaturated compounds are difficult to produce but are very attractive since olefinic compounds are especially important platform chemicals which are still produced primarily from petroleum resources.[1-3] One of the most promising reactions is allyl alcohol production from glycerol. Allyl alcohol is a versatile intermediate for various useful chemicals such as agrochemicals, resins, medicines, perfumes, and so on. Glycerol is coproduced by the biodiesel production process from vegetable oils. However, only a few systems of glycerol conversion to allyl alcohol with a cheap reductant were reported. In recent years, deoxydehydration (DODH) which is typically uses Re catalysts and enables one step transformation of vicinal hydroxyl groups into C=C bonds has attracted much attention. It is already reported that direct transformation of biomass derivatives such as sugar alcohols into corresponding DODH products by a homogeneous Re complex catalyst and a secondary alcohol as a reductant. However, application of use of H_2 and heterogeneous catalysts is still under development.

We have recently reported an efficient system of simultaneous removal of vicinal hydroxyl groups such as glycerol to 1-propanol with H_2 and ReO_x-Pd/CeO_2 as the combination of the reductant and a heterogeneous catalyst, respectively.[4,5] The role of Pd is to activate H_2 and to promote the reduction of Re species for DODH; however, Pd is also a very effective hydrogenation catalyst, and olefinic products were not obtained. In order to obtain olefinic products, the component with the promotion of the Re reduction and without hydrogenation activity is necessary. We found that Au particles with an appropriate size are a very effective component, and the ReO_x-Au/CeO_2 catalyst can efficiently convert glycerol to allyl alcohol.[6]

2. Experimental

ReO_x-${}^{imp}M^{0.3}/CeO_2$ catalysts were prepared by sequentially impregnating CeO_2 powder (Daiichi Kigenso Co., Ltd., HS, BET surface area: 84 m^2g^{-1}, after calcination at 873 K for 3 h) with Re and M precursors. The superscript number of M represents the moler ratio of M/Re. ${}^{dp}Au/CeO_2$ catalysts were prepared with the deposition-precipitation method. ReO_x-${}^{dp}Au/CeO_2$ catalysts were prepared by impregnating ${}^{dp}Au/CeO_2$. Active tests were performed in a 190 mL stainless steel autoclave. The standard conditions for the reaction of glycerol were as follows: 0.5 g glycerol, 300 mg catalyst, 0.1 g dodecane (internal standerd), 4 g 1,4-dioxane (solvent), 413 K reaction temperature, 8 MPa initial hydrogen pressure (at reaction temperature) and 2 h reaction time. Products were analyzed using gas chromatograph equipped with FID.

3. Results and discussion

The effect of ReO_x and noble metal supported on CeO_2 for glycerol conversion to allyl alcohol is shown in Table 1. Over the catalysts containing Ru, Rh, Pt, Ir, and Ag as well as Pd, the main product was 1-propanol, which was formed by hydrogenation of allyl alcohol. On the other hand, Au-added catalyst showed very high selectivity to allyl alcohol with comparable activity to other noble-metal-added catalysts. ReO_x/CeO_2 catalyst showed much lower activity, and Au/CeO_2 and CeO_2 alone were inactive for DODH of glycetol. These results indicate that all three components, ReO_x, Au, and CeO_2 are essential for the high selectivity to allyl alcohol with high activity.

Table 1. Reduction of glycerol over various catalysts[a]

Entry	Catalyst	Conv. [%]	Selectivity [%]						
			Allyl alcohol	1-Propanol	1,2-Propanediol	1,3-Propanediol	Propanal	Hydrocarbon	Others
1	$ReO_x\text{-}^{imp}Ru^{0.3}/CeO_2$	23	1	92	2	<1	2	1	2
2	$ReO_x\text{-}^{imp}Rh^{0.3}/CeO_2$	14	<1	93	4	1	<1	1	1
3	$ReO_x\text{-}^{imp}Pd^{0.3}/CeO_2$	23	<1	83	16	<1	<1	<1	1
4	$ReO_x\text{-}^{imp}Pt^{0.3}/CeO_2$	24	<1	95	3	<1	<1	1	1
5	$ReO_x\text{-}^{imp}Ir^{0.3}/CeO_2$	19	6	83	3	<1	1	3	5
6	$ReO_x\text{-}^{imp}Ag^{0.3}/CeO_2$	27	17	70	1	<1	9	<1	2
7	$ReO_x\text{-}^{imp}Au^{0.3}/CeO_2$	19	99	1	<1	<1	1	<1	<1
8[b]	$ReO_x\text{-}^{imp}Au^{0.3}/CeO_2$	25	96	2	1	<1	1	<1	<1
9	ReO_x/CeO_2	2	87	<1	<1	<1	6	<1	7
10	$^{dp}Au/CeO_2$[c]	3	2	2	90	<1	3	<1	4
11	CeO_2	<1	-	-	-	-	-	-	-

[a] Glycerol (0.5 g), 1,4-dioxane (4 g), W_{cat} =0.3 g (1 wt% Re, M/Re = 0.3 mol·mol^{-1}), P_{H_2} = 8 MPa, T = 413 K, t = 2 h. [b] 4th use. [c] 0.32 wt% Au.

It is known that the size of Au particle dramatically affects the performance of various Au-catalyzed reactions. Smaller Au nanoparticles are known to be generally more active, and such smaller Au nanoparticles can be prepared by the deposition-precipitation method.[7] Table 2 shows the effect of Au particle size on the reduction of glycerol over ReO_x-Au/CeO_2 catalysts. The reaction results at short reaction time showed slightly higher conversion of glycerol over $ReO_x\text{-}^{dp}Au/^{0.3}CeO_2$ than over $ReO_x\text{-}^{imp}Au^{0.6}/CeO_2$ and $ReO_x\text{-}^{imp}Au^{0.3}/CeO_2$, while the selectivity to allyl alcohol was similarly high. However, at longer reaction time, $ReO_x\text{-}^{imp}Au^{0.3}/CeO_2$ maintained high selectivity to allyl alcohol, but $ReO_x\text{-}^{dp}Au/^{0.3}CeO_2$ catalyst exhibited serious progress of subsequent hydrogenation to 1-propanol before complete conversion of glycerol. Therefore, ReO_x-Au/CeO_2 catalyst with suitable Au particle size (~10 nm) is the best catalyst for the production of allyl alcohol from glycerol.

Table 2. Effect of Au particle size on the reduction of glycerol over ReO_x-Au/CeO_2 catalysts[a]

Entry	Catalyst	Au/Re [mol·mol^{-1}]	d_{XRD}[b] [nm]	t [h]	Conv. [%]	Selectivity [%]					
						Allyl alcohol	1-Propanol	1,2-Propanediol	Propanal	Hydrocarbon	Others
1	$ReO_x\text{-}^{imp}Au^{0.6}/CeO_2$	0.6	25	2	22	94	2	<1	1	<1	3
2[c]				24	63	83	11	1	2	<1	3
3	$ReO_x\text{-}^{imp}Au^{0.3}/CeO_2$	0.3	12	2	19	99	1	<1	1	<1	<1
4[c]				24	57	95	3	<1	1	<1	1
5	$ReO_x\text{-}^{dp}Au^{0.3}/CeO_2$	0.3	3	2	34	93	5	1	1	<1	<1
6[c]				24	72	62	30	5	1	1	1

[a] Glycerol (0.5 g), 1,4-dioxane (4 g), W_{cat} = 0.3 g (1 wt% Re), P_{H_2} = 8 MPa, T = 413 K. [b] The size of Au particles determined by XRD patterns. [c] Conversion and selectivity values are the average ones of three runs with different lots of catalysts.

4. Conclusions

We have discovered that the Au promoter has a very specific function for utilization of H_2 as reductant in heterogeneously Re-catalyzed DODH. The heterogeneous ReO_x-Au/CeO_2 catalyst produced allyl alcohol by one step from glycerol with high selectivity. The Au particles with ~10 nm size were especially effective for retaining the C=C bond in allyl alcohol.

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