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Catalysis Today 74 (2002) 265–269

CATALYSIS TODAY

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# Hydrogenation of 1,3-butadiene and of crotonaldehyde over highly dispersed Au catalysts

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Received 28 September 2001; received in revised form 10 November 2001; accepted 30 November 2001

**Abstract**

When Au is deposited as nano-particles on select metal oxides, it exhibits surprisingly high catalytic activity for many oxidation reactions. Therefore, there is also the possibility to improve the activities of Au catalysts for hydrogenation using the appropriate preparation methods like the gas-phase grafting method (GG) and the deposition precipitation method (DP). In this work, we investigated the hydrogenation of 1,3-butadiene and of crotonaldehyde over Au catalysts prepared by GG and DP and discussed the structure sensitivity of these reactions. From these experiments, it was found that the catalytic activities for the hydrogenation of 1,3-butadiene over Au catalysts was almost structure insensitive in terms of the size effect of Au particles and the influence of metal oxides supports and the crotonaldehyde hydrogenation over Au catalysts was slightly sensitive to the selection of the support in the view point of the product selectivity.

*Keywords:* Gold catalyst; 1,3-Butadiene; Crotonaldehyde; Partial hydrogenation

## 1. Introduction

Although gold had been regarded to be inactive as a catalyst, it drew the attention of some chemists in the 1960s. The first study of the hydrogenation reaction using supported Au catalysts was made by Bond [1–3] using the 1,3-butadiene hydrogenation. They found that the Au/$SiO_2$ catalyst was selective to partial hydrogenation to form butenes. However, these Au catalysts prepared by the impregnation method (hereafter denoted as IMP) were significantly less active than the Pd and Pt catalysts [1,4,14]. Due to the low melting point and poor affinity to oxygen, Au could not be highly dispersed over the metal oxide supports by the IMP method.

Lately, it is found that gold exhibits surprisingly high catalytic activity at low temperatures for many oxidation reactions when it is deposited as nano- particles on select metal oxides by the use of our preparation methods [5–12]. Therefore, it is reasonably expected that the activities of supported Au catalysts could also be appreciably improved for hydrogenation reactions if they were prepared by appropriate preparation methods like the gas-phase grafting method (hereafter denoted as GG), the liquid-phase grafting method (LG), and the deposition precipitation method (DP) [5–7]. Lately, the Au catalysts prepared by co-precipitation with sulfur additives exhibited high activity and selectivity for crotonaldeyde hydrogenation [13]. In this work, we investigated the hydrogenation of 1,3-butadiene and crotonaldehyde over highly dispersed Au catalysts prepared by different methods in order to discuss the size effect of Au particles and the support effect.

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PII: S0920-5861(02)00034-2

## 2. Experimental

The Au catalysts were prepared by GG [5], LG [6], DP [7] and IMP. The metal oxides used as a support were $Al_2O_3$ (JRC-ALO-7), $SiO_2$ (Merck, silica gel 60) $TiO_2$ (Degussa, P-25). As gold precursors, $(CH_3)_2Au(CH_3COCH_2COCH_3)$, abbreviated as $Me_2Au(acac)$, purchased from Tri Chemical Laboratory and $HAuCl_4$ from Kishida Chemicals) were used. Catalytic activity measurements for the hydrogenation of 1,3-butadiene were carried out by use of a fixed-bed flow reactor. A powder sample (500 mg) was placed on a ceramic wool plug in a quartz tube with an inner diameter of 8 mm. After pretreatment of a catalyst sample in a stream of Ar at 523 K for 30 min, the reactant gas (1,3-butadiene 2 vol.% in $H_2$) was passed through the catalytic bed at a flow rate of 67 ml/min ($SV = 8000\,h^{-1}$ ml/g catalyst). Catalytic activity measurements for the hydrogenation of crotonaldehyde were carried out by use of an autoclave (300 ml, stainless steel) under high pressure and under the following conditions: catalyst weight, 20 mg; crotonaldehyde, 2 ml; an initial pressure of hydrogen, 1.0 MPa; temperature, 500 K; time, 4 h. The produced hydrocarbons were detected by a gas chromatograph (SHIMADZU GC-14B) with a flame ionization detector (FID). Hydrogen was detected by a gas chromatograph (SHIMADZU GC-8A) with a thermal conductivity detector (TCD) and a molecular sieve (5A) column (5 m × 3.0 mm) operated at 373 K. The dispersion of the gold particles was examined by TEM (Hitachi H-9000) images and X-ray diffraction. The turnover frequencies (TOFs) were calculated based on the number of gold atoms exposed at the surfaces, which were estimated from the mean diameters and actual loadings of the Au particles. In this calculation, the shape of Au particles was assumed to be hemispherical.

## 3. Results and discussion

### 3.1. 1,3-Butadiene hydrogenation

By using several preparation methods under a variety of different preparation conditions, we can control the mean diameter and the shapes of the Au particles deposited on a support [10,11,15]. The Au loadings of these catalysts were adjusted to be more or less than 1 wt.%. Fig. 1 shows conversion vs. temperature curves for 1,3-butadiene hydrogenation over $Au/Al_2O_3$ catalyst prepared by GG, LG, DP, and IMP methods. The $Au/Al_2O_3$ catalysts prepared by GG, LG and DP exhibited higher over-all catalytic activities at temperatures of 379–550 K than the

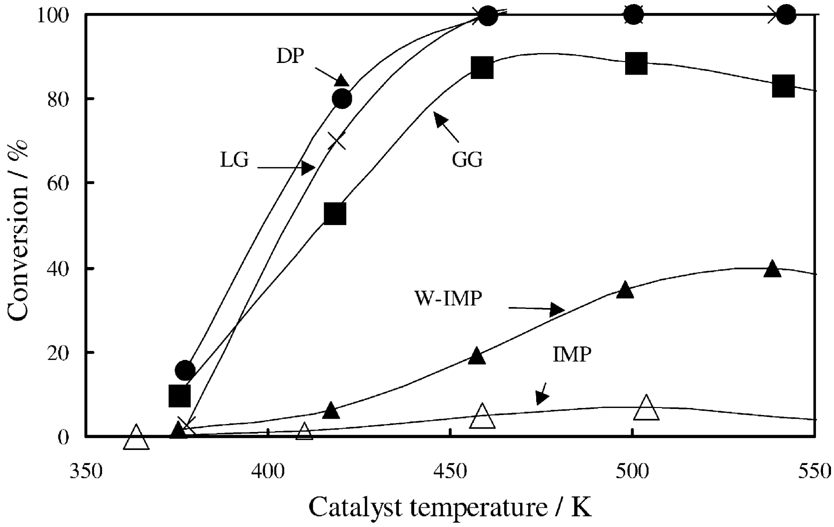

Fig. 1. Conversion vs. temperature curves for 1,3-butadiene hydrogenation over $Au/Al_2O_3$ catalysts prepared by different methods (DP: deposition precipitation, LG: liquid-phase grafting, GG: gas-phase grafting, IMP: impregnation, W-IMP: not washed with hot water).

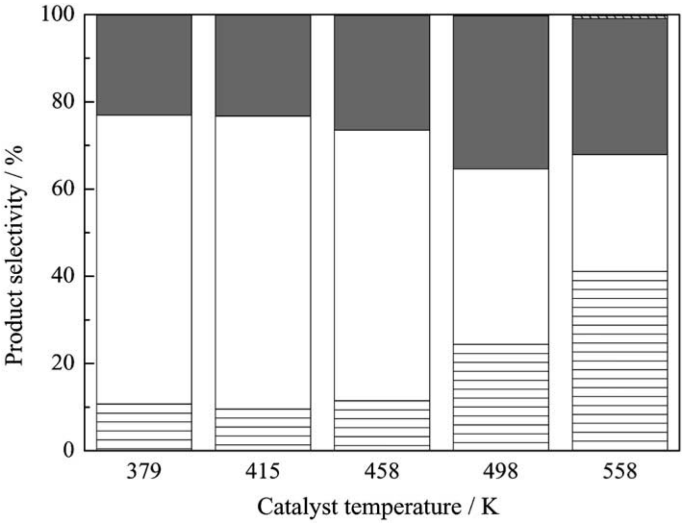

Fig. 2. Product selectivity in 1,3-butadiene hydrogenation over the DP-Au/$Al_2O_3$ catalyst: (☐) 1-butene; (▤) *trans*-2-butene; (▩) *cis*-2-butene.

conventional Au/$Al_2O_3$ catalyst prepared by IMP (IMP-$Al_2O_3$). The catalytic activity of IMP-$Al_2O_3$ was in a good agreement with that reported by Bond [1–3]. The catalytic activity of IMP-$Al_2O_3$ was improved after hot water washing followed by calcinations again at 523 K (W-IMP-$Al_2O_3$), indicating that Na or/and Cl is poisoning the catalyst for this reaction. All the Au catalysts were very selective in the partial hydrogenation to produce butenes. In Fig. 2, the product selectivities of 1,3-butadiene hydrogenation over Au/$Al_2O_3$ prepared by DP were shown. At temperatures below 478 K, the main product is 1-butene. The yield of 1-butene decreased while the yield of 2-butenes increased with an increase in reaction temperature. Therefore, as the main product, 1-butene is produced by the 1,2-addition of 1,3-butadiene at a lower temperature and *trans*- and *cis*-2-butene are produced competitively in the higher temperature region. The experiments of 1-butene transformations in a $H_2$ stream proved that 1-butene was isomerized to 2-butenes. This isomerization also influenced the product selectivities in the higher temperature region. Table 1 lists the kinetic parameters of 1,3-hydrogenation for Au/$Al_2O_3$ prepared by different methods. Turn over frequencies based on the number of Au atoms exposed to the surface (TOF) of W-IMP-, GG-, LG-, and GP-Au/$Al_2O_3$ were almost the same though the reaction rates at 423 K increased

Table 1
Mean diameter of gold particles and kinetic parameters of 1,3-butadiene hydrogenation at 423 K for Au/$Al_2O_3$ catalysts prepared by different methods and Au/$TiO_2$ and Au/$SiO_2$ catalysts prepared by GG method[a]

| Catalyst | Au loading (wt.%) | $D_{Au}$ (nm) | Reaction rate ($\times 10^{-5}$ l/s g catalyst) | TOF ($\times 10^{-3}$ $s^{-1}$) |
|---|---|---|---|---|
| IMP $Al_2O_3$ | 0.94 | 37 ± 30 | 0.10 | 0.50 |
| W-IMP-$Al_2O_3$ | 0.94 | 37 ± 30 | 0.40 | 2.0 |
| GG-$Al_2O_3$ | 0.87 | 4.9 ± 2.2 | 2.5 | 1.8 |
| LG-$Al_2O_3$ | 0.93 | 3.0 ± 1.2 | 3.2 | 1.2 |
| DP-$Al_2O_3$ | 1.0 | 2.5 ± 0.7 | 3.6 | 1.1 |
| GG-Au/$SiO_2$ | 1.5 | 7.0 + 3.0 | 9.6 | 0.60 |
| GG-Au/$TiO_2$ | 1.0 | 3.5 + 1.3 | 43 | 2.0 |

[a] W-IMP: washed with hot water to remove Na and Cl residues.

Table 2
Product selectivities in 1,3-butadiene hydrogenation over $Au/Al_2O_3$, $Au/SiO_2$ and $Au/TiO_2$

| Sample | Temperature (K) | Conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | 1-Butene | *trans*-2-Butene | *cis*-2-Butene | Butane |
| $Au/Al_2O_3$ | 418 | 53 | 75.0 | 8.2 | 16.8 | 0.0 |
| | 458 | 87.5 | 65.4 | 11.3 | 23.3 | 0.0 |
| $Au/SiO_2$ | 416 | 5.9 | 71.6 | 8.8 | 19.6 | 0.0 |
| | 458 | 38.9 | 72.6 | 9.3 | 18.1 | 0.0 |
| $Au/TiO_2$ | 415 | 68.7 | 70.1 | 6.9 | 23.0 | 0.0 |
| | 456 | 98.0 | 67.2 | 8.2 | 24.3 | 0.3 |

with a decrease in the mean diameter of Au particles. It appears that the size effect of the gold particles is not significant on the 1,3-butadiene hydrogenation. This feature is completely different from that of CO oxidation [5–11], which exhibits a remarkable dependency on the size of the Au particles. At present, it was presumed that $H_2$ was activated at the exposed surface of Au particles while $O_2$ was mainly activated at the perimeter between the deposited Au particles and the support surface. Therefore, the total amount of the exposed surface area of Au particles was monotonously increased with a decrease of the size of Au particles although the perimeter of Au particles was remarkably increased with a decrease of the size of Au particles. Consequently, it could presume that the over-all catalytic activity of the hydrogenation over Au catalysts was monotonously increased with a decrease of the size of Au particles.

Table 1 also shows the catalytic performances of $Au/SiO_2$ and $Au/TiO_2$ in 1,3-butadiene hydrogenation. At 423 K, TOF of $Au/SiO_2$ was a little smaller than those of the $Au/TiO_2$ and $Au/Al_2O_3$ catalysts. As shown in Table 2, the product selectivities are more or less similar over the three catalysts, that there is no significant effect of the support metal oxides on the product selectivity in 1,3-butadiene hydrogenation. Accordingly, it can be concluded that 1,3-butadiene hydrogenation over Au catalysts is almost structure insensitive in terms of the size effect of Au particles and the influence of metal oxides supports.

### 3.2. Crotonaldehyde hydrogenation

In order to examine the selective hydrogenation of C=C and/or C=O bonds, the crotonaldehyde hydrogenation over Au catalysts was investigated. Highly dispersed Au catalysts exhibited higher over-all catalytic activities for crotonaldehyde hydrogenation at 500 K. As shown in Table 3, they were selective in the partial hydrogenation and produced buthyladehyde. Although the main product was buthylaldehyde, the product selectivity to crotyl alcohol over $Au/TiO_2$ was about 25% and was different from those over $Au/Al_2O_3$ and $Au/SiO_2$. The higher selectivities over the $TiO_2$ support were also observed over the other noble metal catalysts [14]. However, the TOFs of the crotonaldehyde hydrogenation over the Au catalysts obtained were similar. Therefore, it could be concluded that crotonaldehyde hydrogenation over Au catalysts was slightly sensitive to the selection of the support only for the product selectivity.

Table 3
Mean diameter and loadings of gold particles and the product selectivities in crotonaldehyde hydrogenation over $Au/TiO_2$, $Au/Al_2O_3$ and $Au/SiO_2$ catalysts at 500 K

| Sample | Loading (wt.%) | $D_{Au}$ (nm) | Conversion (%) | Selectivity (%) | | | TOF ($s^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | | | $C_3H_7CHO$ | $C_3H_7OH$ | $C_4H_9OH$ | |
| DP-$Au/TiO_2$ | 0.96 | 3.4 ± 0.7 | 29.6 | 75.6 | 24.4 | 0.00 | 1.8 |
| DP-$Au/Al_2O_3$ | 0.48 | 4.6 ± 1.6 | 12.9 | 96.5 | 3.50 | 0.00 | 1.2 |
| GG-$Au/SiO_2$ | 0.86 | 5.3 ± 2.4 | 3.34 | 91.0 | 9.00 | 0.00 | 0.23 |

These Au catalysts were compared with Pt and Pd catalysts prepared by IMP under the same experimental condition. The highly dispersed Au catalyst, like Au/$TiO_2$ presents a relatively equivalent catalytic activity with Pt catalysts in the viewpoint of the conversion. Finally, the obtained order of the catalytic activity was as follows: $Pd > Pt \geq Au$.

## 4. Conclusions

Highly dispersed Au catalysts were prepared by DP, GG and LG methods using $Al_2O_3$, $SiO_2$ and $TiO_2$ as supports. They exhibited higher over-all catalytic activities than the Au catalysts prepared by IMP and good selectivities in the partial hydrogenation of 1,3-butadiene and crotonaldehyde. While the 1,3-butadiene hydrogenation over Au catalysts was almost insensitive to the size of Au particles and the selection of the support, the crotonaldehyde hydrogenation over Au catalysts was slightly sensitive to the selection of the support for the C=O activation of crotonaldehyde.

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