NANOSTRUCTURED GOLD SUPPORTED CATALYSTS: RELATION BETWEEN STRUCTURE AND HYDROGEN CATALYTIC ACTIVITY*

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Six supported gold catalysts: Au/Al2O3, Au/TiO2, Au/CeO2, Au/ZrO2, Au/Fe2O3 and Au/SiO2 were prepared by deposition-precipitation and impregnation methods, respectively. All catalysts were characterized in order to determine total surface area and gold nanoparticle size using BET method and X-ray diffraction. Catalytic activity was tested in H2/D2 isotopic exchange reaction in transient conditions. This method provide also information about hydrogen spill-over from metal to support. It was found that preparation method and support nature have a big influence over the gold nanoparticle size. There is a good correlation between particle size, microstrain and fault probability – small crystallite size imply large values for microstrain and fault probability. Catalytic activity is influenced both by gold nanoparticle size and support nature which prove the strong interaction between metal particle and oxide and sustain X-ray data regarding the disorder of metal network in these gold/oxide systems. Occurrence of hydrogen spill-over is a good indication for capability of gold nanoparticle to chemisorb and dissociate the hydrogen molecule.

Key words: gold supported catalysts, X-ray diffraction, hydrogen spill-over, H/D isotopic exchange.

1. INTRODUCTION

The position of gold in catalysis drastically changed at the end of the 1980s, when Haruta and coworkers were able to prepare small gold particles supported on oxides and discovered that these catalysts were active in CO oxidation at low temperatures [1]. The focus on oxidation reaction masked the capability of gold in hydrogenation reaction, even though there are promising first examples of possible applications [2]. Gold has been more recently tested again in hydrogenation reaction and it also seems a very promising catalyst for this type of reactions due to its very good selectivity in C=C and C=O bond hydrogenation [3,4].


The catalysts active in hydrogenation reaction are active in H/D isotopic exchange, too. We have tested the catalytic activity of gold supported catalyst in H/D isotopic exchange reaction in transient conditions.

2. EXPERIMENTAL

2.1. CATALYST PREPARATION

The gold catalysts were prepared by deposition – precipitation with urea (DP) and impregnation (IMP) methods. The oxidic supports used to prepare gold catalysts were: SiO$_2$, Al$_2$O$_3$, TiO$_2$, CeO$_2$, ZrO$_2$, Fe$_2$O$_3$. All the catalysts were prepared by DP method, except Au/SiO$_2$ prepared by IMP. The supports were prepared by us.

For the catalysts preparation by DP with urea, 3g of oxide support was added to 75ml of aqueous solution containing HAuCl$_4$ (2x10$^{-2}$M) and 1g urea. The initial pH was 2. The suspension was thermostated at 80°C and vigorously stirred for 16h. Urea decomposition lead to a gradual rise of pH. The final pH was 9. The solid was filtered and washed with distilled water. The operation was repeated 3-4 times, until no residual Cl$^{-}$ was detected in washing water.

For Au/SiO$_2$ a solution containing 0.3g HAuCl$_4$ x 3H$_2$O in 4,5 ml distilled water was added to a 3g SiO$_2$ and kept at room temperature for 24h.

All samples were dried in oven at 100°C for 16h, and calcineted in air at 300°C for 3h.

The target loading of gold for catalysts were 5%wt.

2.2. CATALYST CHARACTERIZATION

Total surface areas of catalysts were measured by BET method using Kr adsorption at liquid nitrogen temperature.

The grain size were determined by X-ray methods. The X-ray (111), (200), (220) and (311) diffraction data of gold catalysts were collected using a horizontal powder diffractometer in Bragg-Brentano (BB) geometry with Ni filtered CuK$_{α}$ radiation, $\lambda$ = 1.54178 Å, at room temperature on DRON 2 setup connected with PC, containing a large spectra library. The typical experimental conditions were: 60 sec. for each step, initial angle 2θ = 10°, step 0.02° respectively and each profile was measured on 3500 points. The diffraction profiles were measured with a scintillation detector, single channel pulse-height discrimination and standard associated counting circuit.

Data processing is based on Warren-Averbach and Charlson approximations. X-ray line profiles (XRLP) and their Fourier transform were approximated with the generalized Fermi functions (GFF) [5,6] (Fig. 2).
2.3. H/D EXCHANGE REACTION STUDY

The catalyst samples were studied in transient conditions in a typical reaction system for H/D isotopic exchange studies [7]. It consist in a gas supply unit and a differential-bed-plug-flow reactor, followed by a quadrupole mass spectrometer QMS (Fig. 1).

![Fig. 1 – H/D exchange reaction set-up.](image)

The catalyst samples were studied in transient conditions in a typical reaction system for H/D isotopic exchange studies [7]. It consist in a gas supply unit and a differential-bed-plug-flow reactor, followed by a quadrupole mass spectrometer QMS (Fig. 1).

The input feed stream is composed by an effluent gas (Argon) and one of the hydrogen isotopes, H or D, at a time. The out species from reactor were monitored by QMS, with a constant inner pressure of 5x10⁻⁶ torr. The gases used in all experiments are of ultrahigh purity (min 99,9%vol).

![Fig. 2 – XRD Spectra of Au/ZrO₂.](image)

1g of each catalyst samples was placed into the column reactor and was measured in isothermal conditions at 6 temperature between 20°C–300°C.

When the reactor temperature was stabled at the desired value, a hydrogen stream was pass through the reactor for 5min. Then the H₂ stream was changed with an argon stream, which washed the catalyst surface until the QMS did not detect any signal for mass 2 (H₂). At this moment the D₂ stream was admitted through the reactor. Simultaneously the MS diagrams corresponding for the 2 (H₂),
3(HD), 4(D2) masses were recorded with the scanning speed of 1 mass unit in 0.1 min. The experiments were coded with initial letter of gases (e.g. the experiment is coded HAD when the passing gases are hydrogen-argon-deuterium).

When all catalyst surfaces was covered with deuterium, the D2 stream was replaced with H2 stream, and the similar MS diagram was recorded (the DH experiment). The same ways were performed for the other two symmetrical experiments coded HD and DAH, respectively.

3. RESULTS AND DISCUSSIONS

The preparation methods of gold supported catalysts seems to be very specific regarding the gold catalyst activity in H/D exchange reaction. These catalysts preparation methods influence not only the metal and support structure, but the catalytic activity too.

We have obtained the following global structure parameters: crystallite size, microstrain and faults probability. Only the XRLP with a good S/N ratio were processed. In the case of multiple lines for one spectrum we were able to determine the crystallite morphology. The obtained parameters are listed in the Table 1.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Line</th>
<th>D_{eq} (nm)</th>
<th>Microstrain × 10^5</th>
<th>SFP [%]</th>
<th>S_t (m^2/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/SiO2 (DP)</td>
<td>(111)</td>
<td>18</td>
<td>0.419</td>
<td>0.7</td>
<td>209</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>9</td>
<td>1.51</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(220)</td>
<td>11</td>
<td>1.21</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>Au/SiO2 (IMP)</td>
<td>(111)</td>
<td>21</td>
<td>0.395</td>
<td>0.79</td>
<td>261</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>15</td>
<td>0.741</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(220)</td>
<td>11</td>
<td>1.10</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Au/Al2O3</td>
<td>(311)</td>
<td>2.7</td>
<td>15.3</td>
<td>0.57</td>
<td>176</td>
</tr>
<tr>
<td>Au/CeO2</td>
<td>(111)</td>
<td>3.2</td>
<td>11.289</td>
<td>0</td>
<td>67</td>
</tr>
<tr>
<td>Au/Fe2O3</td>
<td>(111)</td>
<td>13</td>
<td>0.907</td>
<td>0.9</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>5</td>
<td>5.870</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Au/ZrO2</td>
<td>(111)</td>
<td>25</td>
<td>0.216</td>
<td>0.7</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>15</td>
<td>0.525</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Au/TiO2</td>
<td>(200)</td>
<td>3.3</td>
<td>6.385</td>
<td>3.03</td>
<td>46</td>
</tr>
</tbody>
</table>

We can observe the good correlation between these parameters (i.e. small crystallite sizes imply large values for the microstrain and the faults probability).

It can see that the S_t and D_{eq} are strongly dependent of the support nature. For the Au/Al2O3, Au/CeO2, Au/TiO2, the gold particles are about 3nm and for Au/Fe2O3, Au/SiO2 (DP), Au/SiO2 (IMP), Au/ZrO2 there values are rising up to 24 nm.
The activity for all this catalysts was put into evidence in the H/D isotopic exchange reaction by our transient method. It is well known that the first step in the reaction implied hydrogen is dissociative hydrogen chemisorption on metal surface. This chemisorbed hydrogen move over the metal – oxide interface, react with OH groups on the oxide surface and return to metal surface to be desorbed. If we can measure the hydrogen spillover on gold catalyst (Fig. 3) it proves that the Au/oxide is active for hydrogen involved reactions. By the kinetic transient method it is possible to measure the whole quantities of hydrogen isotopes which spillover from metal to support and reverse.

![MS diagram](image_url)

**Au/Al₂O₃ HAD 300°C**

![MS diagram](image_url)

**Au/TiO₂ DH 200°C**

Fig. 3 – MS diagrams.
It was observed that only some catalysts present catalytic activity into the temperature range of 20-300°C (Table 2).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>d_{eff} (nm)</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/SiO₂ DP</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>Au/SiO₂ IMP</td>
<td>21</td>
<td>200</td>
</tr>
<tr>
<td>Au/Al₂O₃</td>
<td>2.7</td>
<td>150</td>
</tr>
<tr>
<td>Au/CeO₂</td>
<td>3.2</td>
<td>250</td>
</tr>
<tr>
<td>Au/Fe₂O₃</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>Au/ZrO₂</td>
<td>25</td>
<td>150</td>
</tr>
<tr>
<td>Au/TiO₂</td>
<td>3.3</td>
<td>150</td>
</tr>
</tbody>
</table>

The 3rd column of Table 2 contains the starting temperature of H/D isotopic exchange reaction. The influence of catalyst preparation method is relevant in the case of Au/SiO₂ where only one catalyst is active. The gold particle size seems to be not crucial for gold catalyst activity in this reaction. The catalytic activity is more influenced by the support nature.

4. CONCLUSIONS

1. The gold support catalysts have catalytic activity in H/D isotopic exchange reaction.
2. The gold particle size is dependent on the preparation method and support nature.
3. The hydrogen catalytic activity is not determined by gold particle size and it is strongly influenced by the support nature of catalysts.
4. The fact that hydrogen spill over can be measured on Au/support catalysts prove the dissociative chemisorption of H₂ on gold catalysts.

REFERENCES