

## A Novel Efficient Au-Ag Alloy Catalyst System: Preparation, Activity, and Characterization

### Beamline

01C1 Extended X-ray Absorption Fine Structure beamline

17C Extended X-ray Absorption Fine Structure beamline

### Authors

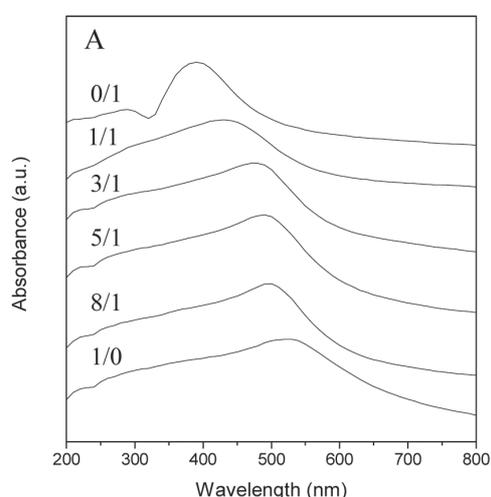
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*We present a novel efficient catalyst, Au-Ag alloy nanoparticles supported on mesoporous aluminosilicate. The catalysts were applied to low temperature CO oxidation reaction. We demonstrate such Au-Ag alloy particles with an average particle size of about 20~30 nm exhibit exceptionally high activity for CO oxidation at low temperatures. Moreover, the activity varies with the Au/Ag molar ratios, and attains the highest CO conversion when Au/Ag is 3/1. UV-Vis and EXAFS confirm the Au-Ag alloy formation. EPR results show there exist  $O_2^-$  species on the catalyst surface, the signal for  $O_2^-$  species becomes the strongest at Au/Ag = 3/1.*

Supported gold catalysts have been extensively investigated in the low temperature CO oxidation since Haruta's pioneering work. It has been found that the catalytic activity of gold is remarkably sensitive to the size of the gold particle, the preparation methods, and the nature of support. An alternative way to modify the gold-based catalysts is to search a second metal that can form an alloy with gold and exhibits stronger affinity with  $O_2$  than gold. For two different metal atoms in intimate proximity to each other, such as in an alloy, the activated  $O_2$  can easily react with the activated CO at neighboring gold atom to give the product  $CO_2$ . Au-Ag alloy nanoparticles supported on mesoporous aluminosilicate were prepared by a one-pot synthesis method using hexadecyl-trimethyl-ammonium bromide (CTAB) both as a stabilizing agent for nanoparticles and as a template for the formation of mesoporous structure. The alloy catalyst exhibited exceptionally high activity in low temperature (250 K) CO oxidation. While either monometallic Au@MCM-41 or Ag@MCM-41 shows no activity at this temperature, the Au-Ag alloy system shows a strongly synergistic effect in high catalytic activity.

In this work, we prepared a series of Au-Ag alloy catalysts supported on MCM-41 to study the variations of catalytic activities with respect to reaction temperature and catalyst composition. Many characterization techniques were employed to study the catalyst system, including nitrogen adsorption, XRD, XPS, EXAFS, UV-Vis, and EPR spectroscopies.

To synthesize the gold-silver alloy nanoparticles supported on mesoporous aluminosilicate (denoted as AuAg@MCM) in one pot, a proper amount of  $H AuCl_4$  (Aldrich) and  $AgNO_3$  (Acros) was added into an aqueous solution of quaternary ammonium surfactant. Then,  $NaBH_4$  solution was added drop-wise, and a dark-red solution was formed. After that, the Au-Ag alloy nanopar-



**Fig. 1:** UV-Vis absorption spectra of Au-Ag@MCM with different Au/Ag ratio

ticles solution was directly poured into a sodium alumino-silicate solution with pH value adjusted to about 9.0 and a red-colored precipitate formed immediately. The gel solution was then transferred to an autoclave to undergo hydrothermal reaction at 100 °C for 6 hours. After filtration, washing, drying and 560 °C-calcination in air the AuAg@MCM was obtained. Prior to characterization and activity measurement, the catalysts were reduced in 10% H<sub>2</sub>/N<sub>2</sub> at 600 °C for 1h.

Both Au and Ag, as well as Au-Ag alloy, have characteristic UV-Vis absorption peaks due to their surface plasma resonance. Figure 1 shows the UV-Vis spectra of the catalysts with various Au/Ag ratios. For the monometallic Au@MCM and Ag@MCM, the absorption bands with maximum at 525 nm and 394 nm were observed respectively, which are consistent with the reported values in literature. All the Au-Ag bimetallic catalysts exhibit absorption peaks located between the absorption bands for pure Au and pure Ag, and the absorption peaks red-shift with an increase of Au/Ag molar ratios. In all the investigated Au-Ag bimetallic catalysts, only one absorption peak was observed, which is an indication of Au-Ag alloy formation.

In order to confirm the Au-Ag alloy formation on the mesoporous support, we employed EXAFS technique to determine the atom type and number of nearest atoms around Au, and the results are listed in Table 1. The coordination numbers (CN) of Au-Au and Au-Ag reflect the particle size and the degree of alloy formation. Clearly, the total CN for all the investigated catalysts is near 12 of bulk Au or Ag, indicating the formation of relatively large particles. On the other hand, the ratio of CN for Au-Au and CN for Au-Ag is very close to the nominal Au/Ag ratio, confirming the Au-Ag alloy formation.

In this work, EPR spectra were recorded for catalysts with different Au/Ag ratio in order to detect the existence of O<sub>2</sub><sup>-</sup> and to explore the effect of Au/Ag ratio on the intensity of O<sub>2</sub><sup>-</sup> signal. The EPR results are illustrated in Fig. 2. The signals at g = 2.008 can be assigned to O<sub>2</sub><sup>-</sup> radicals. The variation in EPR signal amplitude of the samples is mainly caused by the different Au/Ag ratios. The O<sub>2</sub><sup>-</sup> EPR signal intensity follows the order: 3/1 (Au/Ag) > 5/1 > 8/1 > 1/1.

**Fig. 2:** EPR spectra of Au-Ag@MCM samples at 84K. The samples were reduced with H<sub>2</sub>, and then exposed to air.

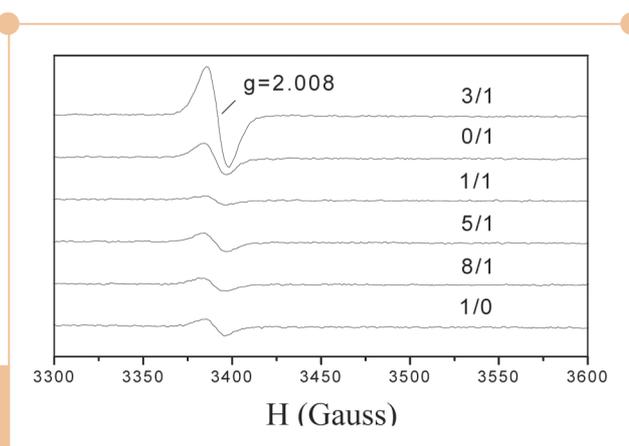
**Table 1:** Au L<sub>III</sub>-edge EXAFS analysis of the Au-Ag@MCM catalysts after reduction.

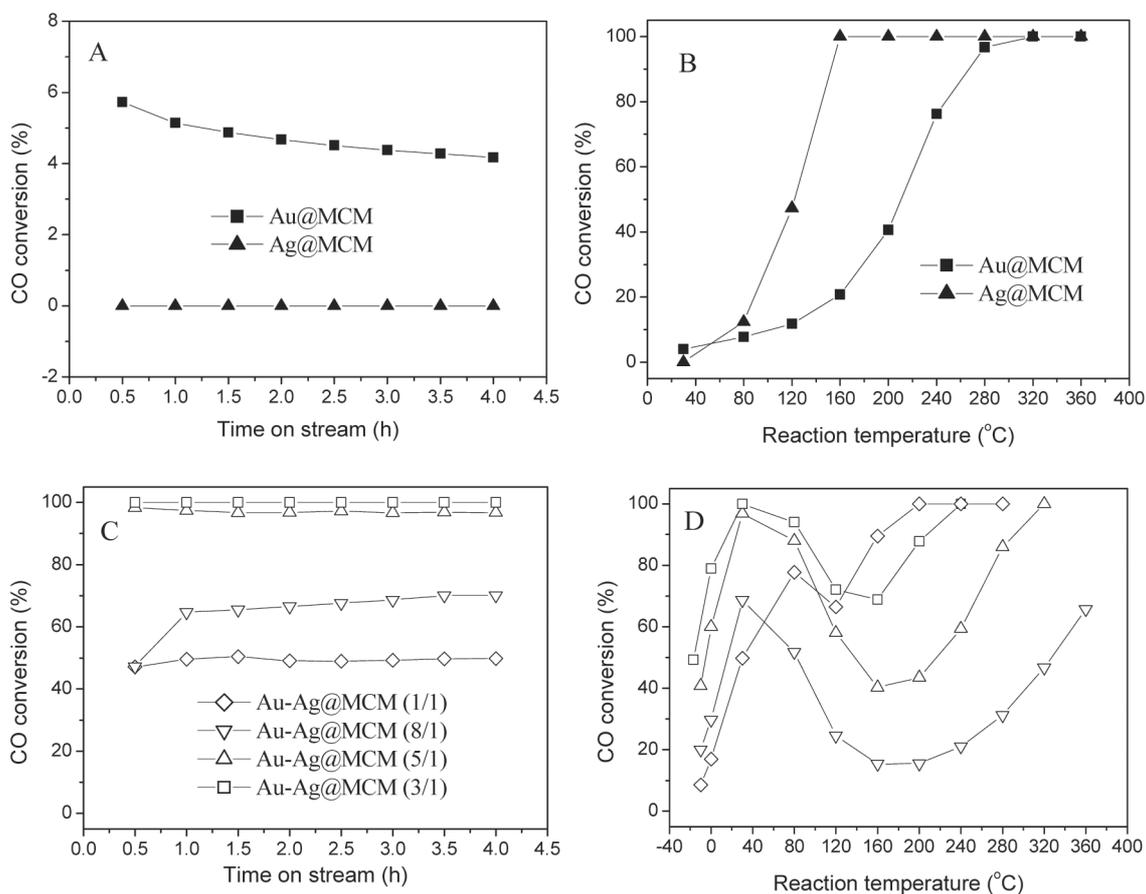
Au/Ag <sup>a</sup>	Shell	R (Å)	C.N.
1/0	Au-Au	2.858 ± 0.002	10.9 ± 0.5
5/1	Au-Au	2.860 ± 0.008	9.1 ± 1.3
	Au-Ag	2.858 ± 0.024	1.7 ± 1.0
3/1	Au-Au	2.851 ± 0.008	8.0 ± 1.2
	Au-Ag	2.865 ± 0.018	2.9 ± 1.0
1/1	Au-Au	2.860	5.6 ± 0.6
	Au-Ag	2.862 ± 0.002	4.6 ± 0.5

<sup>a</sup> The molar ratio of gold to silver

Figure 3 shows the catalytic performance with different Au/Ag ratio. Au@MCM had a very low activity at room temperature. In contrast, all the Au-Ag alloy catalysts gave a much higher activity than the monometallic catalysts, showing a strongly synergistic effect between Au and Ag. The catalyst with Au/Ag ratio of 3/1 has the highest activity on which CO is completely converted at room temperature.

In this work, Au-Ag alloy nanoparticles on mesoporous support were prepared by a novel one-step method. Although thus formed alloy particles are relatively large, they exhibited exceptionally high activity for CO oxidation at low temperature. Compared with monometallic Au or Ag catalysts, the alloy catalysts show an unusual activity profile with the reaction temperature, and the presence of excess hydrogen in feed gas deactivated them significantly. In this alloy system, Ag played a key role for oxygen activation, and Au helps this activation process by decreasing the activation energy for molecular adsorption of oxygen, showing a strongly synergistic effect between Au and Ag.





**Fig. 3:** Catalytic profiles of (A) Au@MCM and (B) Au-Ag@MCM (Au/Ag = 3/1) in the presence of rich hydrogen. The reaction gas composition: 1% CO, 4% O<sub>2</sub>, and He balance.

## Experimental Station

X-ray Absorption Spectroscopy end station

## References and Publications

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