# Microstructure and Catalysis in Porous Ag and Ag-Mg Alloys

**Min-Horng Liu,**[a] **Kameoka Satoshi,**[a] **Nishimoto Kazue,**[a] **and An-Pang Tsai,**[a*]
[a]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, 980-8577, Japan*
**Corresponding author: +81-(0)22-217-5723, aptsai@tagen.tohoku.ac.jp*

**Abstract:** Porous Ag leached from $Mg_3Ag$ exhibits outstanding catalytic activity for CO oxidation at relatively low temperature. Structural defects introduced during leaching effectively enhance catalytic activity by increasing active sites. In this study, twin boundary has been certified to be one of the most contributions on catalytic activity in porous Ag though it shows low specific surface area. However, there are still small amounts of residual MgAg which might arise another contribution to high activity of porous Ag. Therefore, the catalytic activities of MgAg and related intermetallics have been further investigated.

**Keywords:** Twin Boundary, Carbon Monoxide Oxidation, Porous Ag.

## 1. Introduction

The porous material, especially porous Au, is supposed to be a promising catalytic material.[1-4] In previous research, the twin boundary (TB) defects in FCC can form closed-packed rows of atoms with the low-coordinated atoms on the stepped {211} surface of porous Au, which are active sites for CO oxidation at low temperatures.[5] It, therefore, introduces several potentials to obtain the catalytically active sites through the leaching and alloy design which are including leaching solution and its concentration; leaching temperature and duration. The present study focuses on porous Ag, which is at the same group in the periodic table of Au; nevertheless, it possesses lower stacking fault energy than Au. Furthermore, the porous Ag with the residual MgAg always exhibits the high catalytic activity for CO oxidation. Consequently, the different kinds of intermetallic compound (IMC) and MgAg alloy have also been discussed. The correlation between catalytic behaviors and microstructure of Ag-Mg alloys will be discussed.

## 2. Experimental (or Theoretical)

The IMC with nominal composition of $Mg_3Ag$ and $Mg_4Ag$ and the MgAg were fabricated by induction furnace under Argon atmosphere. The IMC was hand-crushed and gathered particles under 25 µm mesh. The MgAg was also ground by planetary ball milling at 300 RPM for 40 mins and sieved under 25 µm mesh. Subsequently, the porous Ag was prepared by leaching $Mg_3Ag$ with the different acid aqueous solution, such as Hydrochloric Acid (HCl) and Tatric Acid ($C_4H_6O_6$), etc. Ag-4MgO and Ag-MgO were prepared by a conventional impregnation method as the reference sample. The local and overall chemical compositions were examined by ICP and EDX. The morphology and structure were determined by SEM, XRD, and TEM. The specific surface area was identified by BET theory. The catalytic activity of each sample was evaluated by CO oxidation ($1\%CO+0.5\%O_2$; SV=20000 $h^{-1}$). Finally, the different kinds of experimental data were collected to further analyze catalytic behaviors and discuss the potential contributions for catalytic activity.

## 3. Results and discussion

Firstly, the ligament channel structure can be fabricated after leaching by various types and different concentrations of electrolyte. The complex morphology leads to the higher surface area and provides more active sites for CO oxidation. Compare with commercial Ag, the catalytic activity of porous Ag is significantly improved by leaching process, as shown in Fig. 1. Moreover, the coarsening happened when leaching duration was longer than 24 hrs. However, although the specific surface area decreased due to coarsening, the TB still could be observed even at over-leached porous Ag. For example, the porous Ag leached in 1% HCl without stirring shows relatively low surface area ($4.2\ m^2 \cdot g^{-1}$) but high catalytic activity for CO oxidation. As can be seen from Fig. 2, the existence of stacking disorders, especially TB, can be observed by TEM and estimated Williamson-Hall plot. In Williamson-Hall plot, the broadening of (200) and (400) peaks characterize the density of twinning defects along the <111> direction. The twin is known as a planar defect, which is important on catalysis since penetrating bulk structure; it forms a chain-like intersection with surface around the ligament. In other words, twin defects are likely to appear on the surface. Subsequently, the twin boundaries provide a sequence of atoms with low coordination number (CN) on the surfaces of ligaments, which generate higher catalytic activity of CO oxidation.

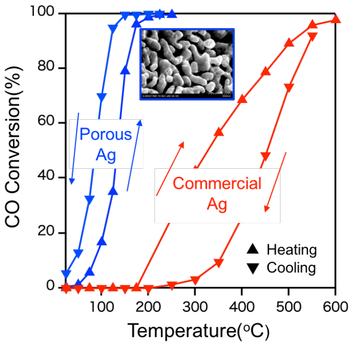

**Fig. 1.** Catalyst testing of porous Ag.

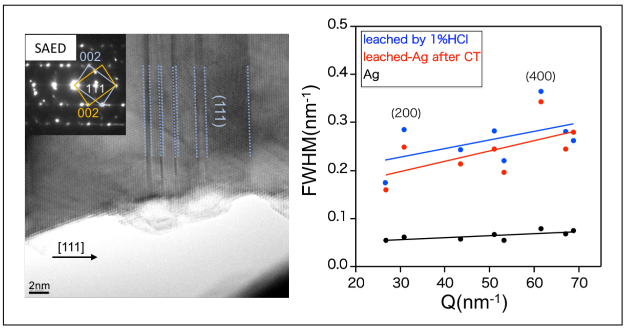

**Fig. 2.**TEM and Williamson-Hall plot of porous Ag leached in 1%HCl without stirring.

In the IMC and MgAg, the composition of Ag at surface is changing during the catalyst testing at high temperature. The gathering oxides of Mg and Ag which might also contribute to the higher and steady catalytic activity after heating period are substantially discovered on the surface, as shown in Fig. 3. The catalytic activity is suspected to be improved by the influence of the oxides, such as charge-transfer process or chemisorption at interfaces. Additionally, MgAg, fabricated by planetary ball milling, possesses high surface area, which leads to the better catalytic behavior in comparison with other IMCs.

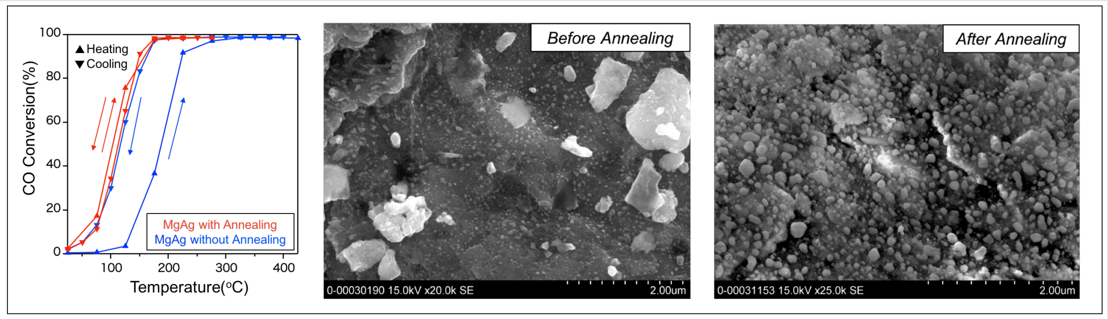

**Fig. 3.** The catalytic activity of MgAg and the change in morphology before and after annealing.

## 4. Conclusions

The porous Ag revealed high catalytic activity for CO oxidation because its complex morphology provided more active sites for CO reaction. Meanwhile, TB on porous Ag was also observed, which was supposed to be a key factor showing high catalytic activity even though the sample showed low surface area. The high catalytic activity of over-leached porous Ag at CO oxidation was correlated with the existence of structural defects, including mainly TBs. Furthermore, in the IMC and MgAg, the catalytic activity becomes stable after heating. The oxides dispersed on the surface could be observed in each sample, which might be a factor improving catalytic behavior.

## References

1. A. Wittstock, V. Zielasek, J. Biener, C. M. Friend, and M. Bäumer, Science 327, 319322 (2010).
2. Z. Li-Tuo, W. Yu-Lei, G. He-Qing, and Q. Lei, Chin. J. Anal. Chem. 41(1), 137–144 (2013).
3. D. Li, Y. Zhu, H. Wang, and Y. Ding, Sci. Rep. 3, 3015 (2013).
4. J. Biener, M. M. Biener, R. J. Madix, and C. M. Friend, ACS Catal. 5, 6263–6270 (2015).
5. M. Krajčí, S. Kameoka, A.P. Tsai, J. Chem. Phys. 145, 084703 (2016).