# Aerobic oxidation of alcohols over hydrotalcite-supported gold nanoparticles: the promotional effect of transition metal cations

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## Introduction

In the last decade or so, supported gold nanoparticles have attracted considerable attention as promising aerobic alcohol oxidation catalysts owing to their higher selectivity and improved resistance against overoxidation of the metal [1]. The catalytic activity of gold catalysts depends not only on the size of the gold nanoparticles, but also on the nature of the support and, accordingly, the interactions between the gold nanoparticles and the support are also important [2]. Furthermore, the presence of a base is beneficial for the activity of gold catalysts, because it facilitates the initial alcohol dehydrogenation step. However, addition of soluble bases brings notorious problems such as corrosion and waste treatment. Therefore, a promising strategy is to develop solid basic material-supported Au nanoparticle catalysts [3]. Hydrotalcite (HT)-like compounds have the advantage of combining surface basicity and tunable composition [4]. The incorporation of various transition metal cations into the HT structure results in variations of the surface basicity and the nature of the Au-support interactions. Herein, we present a significant promotional effect of transition metal containing HT-supported Au nanoaprticle catalysts on the aerobic oxidation of alcohols.

## Experimental

Transition metal containing HTs were prepared by using the "memory effect" of HT (Mg/Al=2). After calcination at $500^{\circ}$C, the $Mg_2AlO_x$ mixed oxide was rehydrated in aqueous $M^{n+}$ nitrate solution ($M^{n+}$ = $Cr^{3+}$, $Mn^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$). Au was deposited onto the M-HT supports using a modified deposition-precipitation method. The synthesized catalysts were characterized using SEM/EDX, TEM, XRD, Solid $^{27}$Al MAS-NMR, BET, ICP, and temperature-programmed surface reaction (TPSR) of 2-propanol. A typical procedure for the aerobic oxidation of alcohols using the Au/M-HT catalysts was as follows: Au/M-HT (50 mg) was placed in a reaction vessel, followed by the addition of toluene (10 mL), *n*-dodecane (internal standard, 0.2 mmol) and benzyl alcohol (1 mmol), then the mixture was vigorously stirred at 100 $^{o}$C for 0.5 h under $O_2$ (20 mL/min). Reaction products were analyzed by GC-FID (Shimadzu GC-17A, RXI-5MS, 30 m × 0.25 mm) using internal standard technique.

## Results/Discussion

By using the "memory effect" of HT, various M-HT supports keep the layered structure typical for hydrotalcites and have higher surface areas (48 – 90 m$^2$/g) than the Mg$_2$Al-HT

precursor (27 m$^2$/g). The influence of the HT supports on the gold particle size is relatively small with average gold nanoparticle sizes between 2.7 and 3.9 nm. The differences in gold loading and particle size are related to the differences of the surface area, surface basicity and isoelectric point of various HT supports. The surface basicity of Au/M-HT correlated with transition metal cation, with Au/Cu-HT showing the lowest basicity (pH < 8.0 in water).

Interestingly, the catalytic activities of various catalysts show an increase in the order: Au/HT <Au/Cu-HT < Au/Zn-HT < Au/Mn-HT < Au/Co-HT < Au/Fe-HT < Au/Ni-HT < Au/Cr-HT (Fig. 1). Despite its rather low dispersion, Au/Cr-HT has the highest activity (TOF ~ 930 h$^{-1}$), indicating a synergistic effect between gold particles and the Cr-HT support. To confirm this promotional effect of Cr$^{3+}$, a Au/MgCr-HT catalyst without Al was prepared and evaluated in the same reaction. Significantly, Au/MgCr-HT (pH ~ 8.7) shows greatly enhanced activity with TOF ~ 1900 h$^{-1}$, which is respectively 8 and 27 times higher than previously reported state-of-the-art Au/Ga$_3$Al$_3$O$_9$ and Au/TiO$_2$ catalysts. To obtain further insight of the nature of this promotional effect, we adsorbed 2-propanol on the surface of various catalysts and performed TPSR measurement of the desorbed H$_2$ molecules. The TPSR results (in Fig. 2) show that among transition metal-containing Au/M-HT catalysts, Au/MgCr-HT exhibits the highest activity in the 2-propanol dehydrogenation, suggesting the MgCr-HT support not only facilitates the initial O-H band cleavage but also has an effect on the suspected rate limiting β-H elimination over the gold nanoparticles.
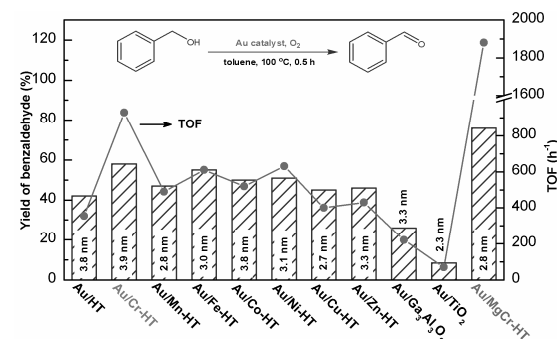


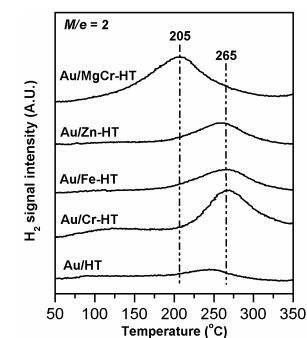Fig. 1 Catalytic performance in benzyl alcohol oxidation.　　Fig. 2 Typical TPSR results.

## References

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