



MAX-PLANCK-GESELLSCHAFT



## Comparison of gold and silver species supported and incorporated into mordenites

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### Introduction

The unique properties of zeolites including transition metal ions within the zeolite framework or cavities have opened new possibilities for many applications including catalysis. The transition metal ions incorporated in zeolites are considered to be highly dispersed at the atomic level and well defined, existing in a specific structure of the zeolite framework. This phenomenon is of great significance in the design of highly dispersed transition metal. Fundamental understanding of the coordination structure and electronic state of the active species is important in the design and development of applicable catalysts having high activity and selectivity [1].

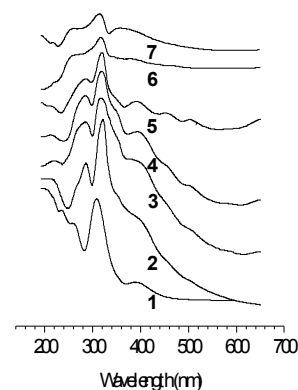
UV-Visible spectroscopy could be very informative to clarify the nature of active species in the case of Ag, Au and Cu incorporated into zeolites. Optical properties of these metals are well studied but these results are not intensively applied to characterization of catalysts [2]. However the formation of different Ag species including clusters was investigated in mordenite by UV-Visible reflectance spectroscopy [3].

In this work investigation for gold and the comparison of the optical spectra of gold and silver species in mordenites had been performed.

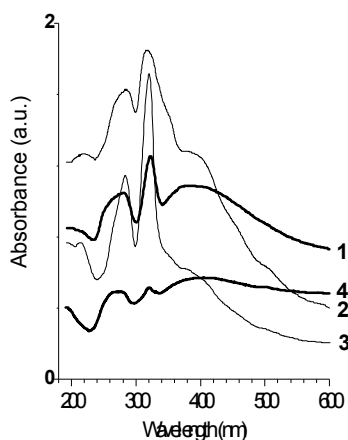
### Catalysts preparation and characterization

Mordenites in protonated form with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio (MR) from 10 (M10) to 206 (M206) supplied by TOSOH corporation (Tokyo, Japan) were used for the ion exchange of the gold and silver cations. Metal containing samples were obtained by ion exchange in aqueous solution of

AgNO<sub>3</sub> [3] and of [Au(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>3</sub>. The last complex was prepared by reaction of HAuCl<sub>4</sub> with NH<sub>4</sub>OH and NH<sub>4</sub>NO<sub>3</sub> [4]. After ion exchange the samples were dried and reduced by H<sub>2</sub> at different temperatures during 4 and 2.5 hs for Ag and Au samples, respectively. The silver content measured using X-ray Fluorescence Spectrometer SEA 2010 was 0.4-2.3 wt. %. The gold content evaluated by energy dispersive spectroscopy was within 0.5-2 wt. %. UV-Visible diffuse reflectance spectra were measured at room temperature on a CARY 300 SCAN (VARIAN) spectrophotometer with a standard diffuse reflectance unit. The spectra are presented after subtraction of spectrum of pure zeolite from the spectra of metal containing samples.



**Fig. 1.** UV-Visible spectra of Ag M15 reduced by hydrogen at: 1-25°C, 2-50°C, 3 -100°C, 4- 200°C, 5-300°C, 6-400°C, 7-500°C (curves were translated in vertical direction for clear observation).

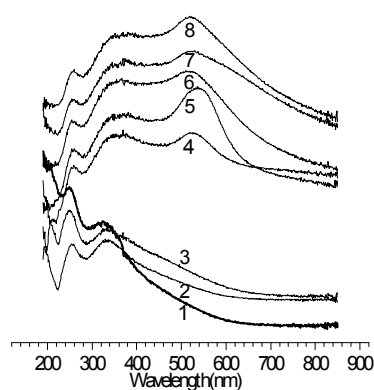


**Fig. 2.** UV-Visible spectra of Ag samples reduced at 100°C with various MR: 1-Ag M10, 2-Ag M15, 3-Ag M20, 4-Ag M 206.

### Results and discussion

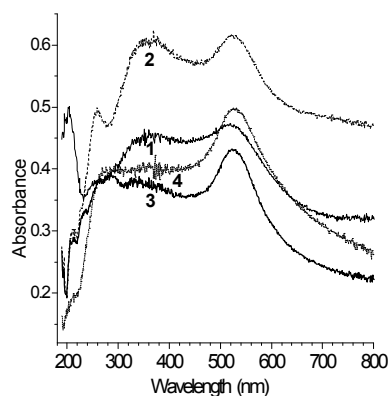
The diffuse reflectance spectra of Ag-mordenites with various  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios registered immediately after sample reduction are represented in the Figs. 1 and 2. For all samples the absorption bands at 320 and 285 nm (typical for absorption of neutral  $\text{Ag}_8$  and charged  $\text{Ag}_8^-$  clusters, respectively) with shoulder at 265 nm ( $\text{Ag}_4^{2+}$  clusters) were observed in UV region. Identical positions of peaks indicate that mordenites stabilize selectively the same silver cluster types independently on  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio. In the spectra of all studied samples, peaks in the wavelength regions 370-400 nm and higher than 400 nm were also observed (Fig. 2). These peaks were assigned to quasi-metal colloidal particles and larger silver particles, respectively [3].

UV-Visible spectra of Au samples are presented on Figs. 3 and 4. The spectra of Au samples show three characteristic



**Fig. 3.** UV-Visible spectra of Au/M15 samples 1- no reduced, 2- reduced at: 25°C, 3- 50°C, 4- 100°C, 5-200°C, 6- 300°C, 7-400°C, 8-500°C (curves were translated in vertical direction for clear observation).

absorption bands. The absorption band at 195 nm was assigned to the gold cations  $\text{Au}^+$  [5]. It implies that precursor  $[\text{Au}(\text{NH}_3)_4]^{3+}$  complex was at least partially reduced to  $\text{Au}^+$

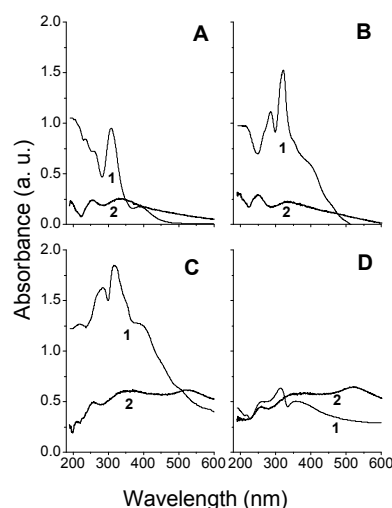


**Fig. 4.** UV-Visible spectra of samples reduced at 100°C: 1- Au M10 (1), Au M15 (2), Au M24 (3), Au M206 (4).

just after ion exchange. The reliable interpretation of two other absorption bands in the regions 250-260 and 320-340 nm we could not find in literature. In reference [2] it was suggested that the absorption bands in this spectra region could be due to the gold clusters. It should be noticed that relative intensity of absorption bands in the region of clusters correlates with the concentration of Brønsted acid centres in mordenites measured in [3] (Fig. 4).

The maximum at  $\lambda=530$  nm in the spectra presented in Figs. 3 and 4 is attributed to the surface plasmon resonance for Au nanoparticles [5] located on external surface of zeolite microcrystals. Increase of reduction temperature (Fig. 3) leads to decrease of relative intensity of the peak assigned to cations and to rise of relative intensity of the plasmon resonance of nanoparticles. Thus, with increase of reduction temperature the contribution of gold cations decreases and the features of reduced species are developed.

The spectra of silver and gold supported samples are illustrated in Fig. 5. The peaks at 250 and 320 nm assigned preliminary to gold clusters are much broader than those for silver clusters that can be due to the set of clusters in the silver samples is more uniform than in gold samples. In the spectra for both metals the absorbance at  $> 400$  nm assigned to the nanoparticles grows significantly after reduction at the temperatures  $\geq 100^\circ\text{C}$ .



**Fig. 5.** UV-Visible spectra of 1-Ag M15 and 2- Au/M15 reduced at: A- 25°C, B- 50°C, C- 100°C, D- 500°C.

Thus, UV-Visible data show the presence of silver and gold species in the supported mordenites in similar spectra region. The reduction treatment increases the amount of reduced species for both metals. The contribution of species attributed to clusters can be varied with variation of reduc-

tion temperature and with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio for both Ag and Au. The revealed difference between Ag and Au samples is suggested to be due to uniform set of Ag clusters and not uniform set of Au clusters.

## References

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