

# Al doped ZnO support for methanol reforming: modified electronic structure and interaction with the active site

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## Introduction

The Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst for methanol production/reforming is a well-established catalyst but the exact interaction mechanism between the metallic phase and the surface of the mixed oxide had not been understood in detail. Considering the potential importance of such catalyst in a hydrogen-based economy - methanol is a promising lightweight H<sub>2</sub>-carrier molecule [1] - it is important to understand the nature of the active site and optimize its performance to the specific application. In this contribution we want to elucidate the importance of Al doping for the properties of the ZnO substrate. It was recently shown that for extremely low Al content (in the range 2-4 mol%) the Al<sup>3+</sup> ions are preferentially located in the zincite lattice, whereas for higher Al content a segregation of Al-rich phases (ZnAl<sub>2</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>) is observed [2]. The typical industrial catalyst ranges between 15 and 20 mol% Al.

## Materials and Methods

The ZnO/Al<sub>2</sub>O<sub>3</sub> support was prepared with Al contents ranging from 0–45 mol% by coprecipitation analogous to Cu-containing systems as described in previous contributions [3]. The support was then characterized under several different working conditions: in reducing environments (H<sub>2</sub> @ 250°C), followed by exposure to CO<sub>2</sub>. These different catalysts were deeply characterized by XRD, <sup>27</sup>Al-MAS-NMR, UV-VIS and FTIR spectroscopy, NEXAFS of the O-K, Al-K and Zn-L3 edges and environmental XPS of the valence band and of several Al, Zn and O core levels, to study the structural, electronic and surface properties of the materials.

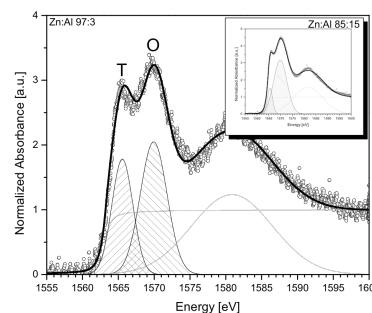
## Results and Discussion

The Al doped ZnO with low Al content presents a different electronic structure than the same support with a high amount of Al. The band gap energy varies according to table 1. The range 2-4 mol% is characterized by a minimum of band gap, which is correlated to the amount of Al atoms in the ZnO lattice and might be due to the creation of interband states. To verify this hypothesis we studied the aluminum K-edge NEXAFS spectra (shown in figure 1). The edge transitions represents the 1s→3p transitions inside the Al atom. The 2 features at 1565 and 1570 eV can be ascribed to aluminum in tetrahedral and octahedral coordination [4]. The amount of T-Al in the 3 mol% sample is sensibly higher than in the 15 mol% (shown in the inset), that is dominated by the O-Al. This latter one is typical of α-Al<sub>2</sub>O<sub>3</sub> while the former can be ascribed as substitution of Al in the ZnO HCP framework. Indeed the 15 mol% Al sample presents some forms of alumina segregation.

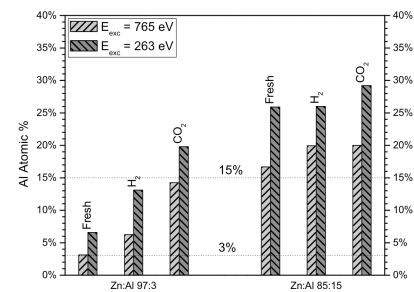
**Table 1** Band gap energies for different Zn:Al molar ratios

Zn:Al	100:0	98:2	96:4	92:8	85:15	70:30	55:45
Energy (eV)	3.13	3.06	3.08	3.12	3.16	3.19	3.26

This different electronic structure can also lead to different properties and behavior of the material under operational conditions. By mean of environmental XPS at different excitations energies we measured the surface and near-surface composition of the material looking at the Zn3p – Al2p photoemission lines in the range 100-70 eV B.E. We can see from figure 2 that the low Al content sample shows a pronounced migration of the Al on the surface during reduction and also in contact with CO<sub>2</sub>, during the simulated reaction conditions. This evolution is extremely pronounced and is not observed in higher Al content samples. These results are consistent with a modification of the band gap energy under these conditions (not shown here). Partial surface reduction of ZnO may attract more Al to the surface and can be assumed as the driving force for formation of this newly reconstructed material, which also interacts strongly with the gas phase reactants like CO<sub>2</sub>. This suggests that a similar support can actually participate actively in the catalysis or modify the properties of the metal (Cu) that sits on it. Again all these properties are not observed in high Al content supports, which do not modify themselves during the reaction.



**Figure 1.** NEXAFS Al-K edge showing Tetrahedral and Octahedral Al coordination 1s→3p transitions.



**Figure 2.** Al atomic % calculated from XPS spectra of the Zn3p and Al2p photoemission regions.

## Significance

ZnO supports with low Al content present novel electronic properties, which is related to Al doping. These results suggest that Al participates actively in the reducibility of the support resulting in different behavior under reaction conditions compared to pure ZnO or Al-rich samples with segregated Al phases. Thus the Zn:Al ratio represents a practical way to tune the performance of the resulting metal-containing catalyst.

## References

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