## BASE-ACID MECHANISM FOR THE CITRAL/ACETONE REACTION ON MgyAlOx OXIDES

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## Introduction

The liquid-phase aldol condensation of citral with acetone (DMK) is catalyzed by diluted bases and forms selectively pseudoionones (PS), but the process entails concerns related to toxicity, corrosion, and disposal of spent base materials. New industrial strategies for PS synthesis demand then the replacement of liquid bases by solid catalysts. The citral/DMK reaction has been studied on Mg-Al mixed oxides (Mg<sub>v</sub>AlO<sub>x</sub>), but knowledge regarding the role played by the  $Mg_vAlO_x$  chemical composition to fulfill the requirements of acid/base site density and strength for promoting the selective PS formation at high rates, is lacking. The optimum Mg<sub>v</sub>AlO<sub>x</sub> composition should improve the citral/DMK crossaldol condensation rate at expenses of the DMK self condensation reaction. Here, we have carried out a detailed study of the citral/DMK reaction on MgO, Al<sub>2</sub>O<sub>3</sub>, and Mg<sub>v</sub>AlO<sub>x</sub> with Mg/Al molar ratios of 0.11-3. The structural, textural and acid/base properties of the samples were determined by using a variety of experimental techniques and then correlated with the catalyst performance for citral/DMK reaction.

## **Results and Discussion**

The initial conversion rates of DMK  $(r_{DMK}^0)$  and citral  $(r_{Cit}^0)$  on Mg<sub>y</sub>AlO<sub>x</sub> depended on the sample composition, following opposite trends:  $r_{DMK}^0$  increases while  $r_{Cit}^0$  diminishes with the Al content. A linear plot was obtained when  $r_{PS}^0$  was represented as a function of the density of strong base sites  $(O^2)$ . Thus, the PS synthesis was particularly promoted on MgO and MgO-rich Mg<sub>y</sub>AlO<sub>x</sub> samples, probably because these samples contain a much large number of strongly basic  $O^2$ - sites, which are able to detach the  $\alpha$ -proton from the acetone molecule and to form a carbanion intermediate

in the rate-determining step (Figure 1). The parallel DAA formation from the self-



the selfcondensation of acetone takes place also on strong base sites, sharing the carbanion intermediate with the

pseudoionone formation mechanism [1]. However, we obtained here a good linear correlation between  $r_{DAA}^0$  and the total surface acid site density. Taken into account that the IR spectra of adsorbed pyridine showed that Mg<sub>y</sub>AlO<sub>x</sub> samples contain mainly Lewis acidity, the DMK interaction with the solid surface would involve essentially Al<sup>3+</sup> acid sites, which are more electronegative than Mg<sup>2+</sup> cations. Lewis Al<sup>3+</sup> sites would activate the DMK molecule in equilibrium with the enol tautomer via the oxygen of the C=O group generating an electrophilic carbonyl intermediate (Figure 2). Then, the enol form that is <u>nucleophilic</u> at the  $\alpha$ -carbon, attacks the electrophilic carbonyl carbon leading to DAA. The abundance of surface Al<sup>3+</sup> sites accounts for the high DAA formation rates observed on Al<sub>2</sub>O<sub>3</sub> and Al-rich Mg<sub>y</sub>AlO<sub>x</sub> samples. In contrast, the cross condensation of citral with DMK was not promoted on acid sites. Probably, the interaction of the electrodonors

**Figure 2:** Acid mechanism of DAA formation on  $Al_2O_3$ and Al-rich  $Mg_vAlO_x$  samples



groups of the citral molecule (C=C and C=O) $Al^{3+}$ with acid sites is strong enough to prevent the reaction of the

adsorbed aldehyde with the DMK intermediate at measurable rates. This is consistent with the fact that the citral/DMK cross aldolization on Mg-Al catalysts is negative order with respect to citral which reflects the stronger adsorption of citral in comparison to acetone.

## References

1. V.K. Díez, C.R. Apesteguía, J.I. Di Cosimo, J. Catal. 240 (2006) 235.