

## Nature of Active Sites in MgO catalysts for the Synthesis of Flavanone

José A Cortés-Concepción, Zheng Liu, Florian Patcas and Michael Amiridis\*  
University of South Carolina, Department of Chemical Engineering, Columbia, SC 29208  
(United States)

\*amiridis@engr.sc.edu

### Introduction

Flavanone is an important intermediate in numerous pharmaceutical syntheses. The heterogeneous synthesis of flavanone has been established as an alternative to the homogeneous one, with significant environmental advantages [1-4]. Our previous work has focused on kinetic and mechanistic studies of this reaction over MgO[3, 4]. However, the nature of the active sites and the catalytic role of the surface are subjects of controversy in the literature and still remain an open question.

In the current study we are addressing the nature of the MgO active sites involved in the synthesis of flavanone. The adopted research strategy includes the controlled modification of a base considered MgO catalyst by both decreasing and increasing of its basicity. To decrease the basicity of MgO, different anions ( $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ , and  $\text{Cl}^-$ ) were used. In contrast, lithium ( $\text{Li}^+$ ) was introduced to increase the basicity of MgO. The resulting catalysts were characterized by  $\text{CO}_2$  temperature programmed desorption (TPD) and  $\text{CO}_2$  Fourier transmission infrared (FTIR) measurements. The catalysis activity for the heterogeneous synthesis of flavanone was also measured and the results were correlated to the characterization information obtained.

### Materials and Methods

For the anion-modified samples MgO was calcined at 773 K for 4 h. Samples were impregnated with 0.3 mmol charge equivalents of anion per g of catalyst using 0.1 M solutions of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HCl}$ , or  $\text{NH}_4\text{F}$ . For the Li-modified samples, MgO was impregnated with aqueous solutions of lithium nitrate, used as the precursor. Samples were calcined in air at 1023 K for 4 h.

$\text{CO}_2$  TPD measurements were conducted in a conventional flow apparatus, the  $\text{CO}_2$  evolved was converted through a methanation catalyst to methane which was monitored using a FID detector. Activity measurements were conducted in a batch reactor system. The reactor was initially charged with 150 ml of a mixture containing 1.5 M benzaldehyde and 1.5 M 2'-hydroxyacetophenone in DMSO. Samples were removed from the reactor periodically during the course of the reaction and subsequently analyzed in a gas chromatograph off-line.

### Results and Discussion

Table 1 summarizes the results for  $\text{CO}_2$  TPD measurements and initial reaction rates of the anion-modified samples. The TPD patterns indicate the presence of three kinds of sites with different basicity considered weak, medium and strong. Almost all "weak" basic sites disappear upon treatment of MgO with the anions used in this study. In contrast, no considerable differences are observed for the "strong" basicity with the exception of the chloride-treated sample. A gradual effect is observed on the sites of "medium" basic strength depending on the anion used. The amount of "medium", strength basic sites in the anion-modified MgO samples correlates with the observed catalytic activity for the Claisen-Schmidt condensation reaction.

Increasing basicity has generally a beneficial effect on the catalytic activity. Figure 1 shows the conversion vs. time curves, for pure MgO in comparison with a F-modified (i.e., less basic) catalyst and a Li-modified (i.e., more basic) catalyst. An increase in the initial reaction rates was observed for low loadings of lithium (0.1 and 0.5 wt%). However, high loadings of lithium (>0.5 wt%) yielded lower initial reaction rates than bulk MgO. A significant decrease of surface area was observed upon the introduction of lithium into MgO and was more pronounced for samples of high Li loadings. This effect has been attributed to particle agglomeration, as well as formation of unreactive carbonates that block the active sites.

Table 1. Basicity Measurements and initial reaction rates for anion-modified MgO samples.

Samples	Initial reaction rate $\times 10^4$ (mol/g/s)	Basicity (mmol of desorbed $\text{CO}_2/\text{g}$ )			
		Total	Weak (298-420 K)	Medium (420-650 K)	Strong (650-1050 K)
MgO	6.5	0.440	0.119	0.181	0.140
$\text{PO}_4^{3-}/\text{MgO}$	5.5	0.289	0.012	0.141	0.136
$\text{SO}_4^{2-}/\text{MgO}$	3.2	0.232	0.003	0.095	0.134
F/MgO	2.9	0.198	0.013	0.065	0.120
Cl/MgO	1.8	0.027	0.006	0.012	0.009

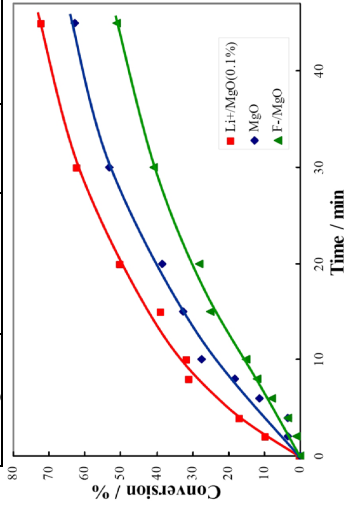


Figure 1. Conversion as a function of reaction time for pure and modified MgO samples.

### Significance

The current work leads to a better understanding of the nature of the active sites of MgO catalysts used for the synthesis of flavanone.

### References

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