

# Aldol condensation of cyclopentanone and acetone over hydrophobized basic and acid catalysts. Mechanisms and product distribution

Duong Ngo, Tuong Bui, Qiaohua Tan, Daniel Resasco\*  
*School of Chemical, Biological and Materials Engineering*  
*University of Oklahoma, Norman, OK 73019*  
*\* Corresponding author resasco@ou.edu*

## Introduction

In principle, many products can be derived from biomass. However, the great majority of them can only be obtained in relatively low yields and purity, which greatly increases the number of separation steps and their production cost. By contrast, both cyclopentanone (C) and acetone (A) can be produced in high concentrations and high yields; the former by Piancatelli rearrangement of furfural in aqueous phase, the latter via ketonization of acetic acid. Aldol condensation is a desirable C-C bond forming reaction that can generate self- or cross condensation products in the fuel range with a small number of unit operations. A major impediment of aldol condensation is catalyst deactivation. The high activity of strong basic or strong acid catalysts used for this reaction often results in sequential condensation that produces large oligomers that remain on the surface and deactivate the catalyst. In this contribution, we show that by functionalizing the surface with hydrophobic moieties, such as organosilanes, the catalyst stability is greatly enhanced. We compare activity, selectivity and stability of organosilane-functionalized basic catalysts (MgO, SiO<sub>2</sub>/MgO, and B-MgO) and double-functionalized acid catalysts (MCM + sulfonic acid + organosilane). From the observed distribution of products and DFT calculations of energy barriers for possible elementary steps, we evaluate a reaction mechanism that is consistent with the experimental observations.

## Materials and Methods

MgO, TEOS/MgO, and B-MgO high surface area catalysts were prepared by the combustion method. Mesoporous MCM-41 and SBA-15 were used as received. Subsequently, they were functionalized with an organosilane (e.g. OTS) and mercapto-silane, which after oxidation generated sulfonic groups of controlled surface density and distribution. Other acid catalysts included the resin Amberlyst 36 and the faujasite HY30 (Si/Al ratio of 30). The base- and acid-catalyzed condensation reactions of cyclopentanone (C) and acetone (A) were investigated in a Parr reactor at varying T (180-250 C) and P (300-600 psi). The basicity and acidity of the catalysts were quantified by TPD of CO<sub>2</sub> and IPA. The functional groups were quantified by titration, TGA, and FTIR.

## Results and Discussion

Fig. 1 illustrates the much slower catalyst deactivation exhibited by the hydrophobized basic catalyst (OTS/ Si-MgO) compared to the conventional MgO. A very effective way of comparing rates of deactivation in a batch reactor is to plot the evolution of reactant concentration as a function of the product time and catalyst weight (t x W) for two different amounts of catalyst. When there is no deactivation, the curves coincide, but when the catalyst deactivates with time, the curve of the small catalyst weight - longer time for the same (t x W).

We have shown that hydrophobization helps the removal of dimers from the surface to the liquid phase, thus reducing the multiple sequential condensation that produces large molecules, which deactivate the catalyst. Therefore, the kinetics studies were done on the most stable hydrophobized catalysts, basic (MgO-based) and acid catalysts (Bronsted acids).

As shown in Fig. 2, for an equimolar mixture of (C) and (A), the products in which the initially activated molecule is (C) greatly surpass those in which this is (A). That is, the yields of [C]A and [C]C are much higher than those of [A]C and [A]A. This result is not too surprising since the pK<sub>a</sub> of (C) is greater than that of (A). However, what is indeed noteworthy is that the yield of self condensation product [C]C on a basic support is much higher than the cross-condensation [C]A product, while it follows the feed ratio (in this case 1:1) on the acidic supports. In a base-catalyzed aldol condensation, a H from the alpha C with respect to the

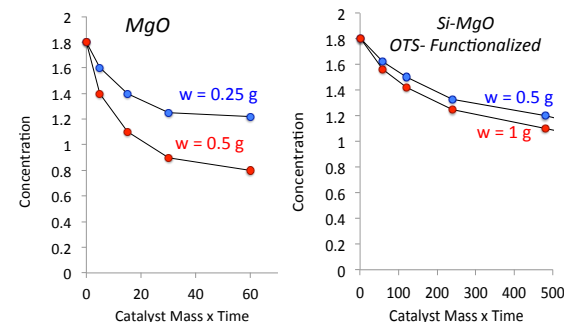


Fig. 1. Comparison of catalyst deactivation during self aldol condensation of cyclopentanone at 150°C and 300 psig – cyclohexane solvent. More separated curves for MgO indicate greater extent of deactivation.

[C] C	[C] A	[A] C	[A] A
Selectivity (%)	Selectivity (%)	Selectivity (%)	Selectivity (%)
Acid Catal: 37	Acid Catal: 33	Acid Catal: 11	Acid Catal: 18
Base Catal: 60	Base Catal: 35	Base Catal: 3	Base Catal: 2

Fig. 2. Product distribution from aldol condensation of cyclopentanone (C) and acetone (A) over acid and basic catalysts.

proposed in the literature, the rate-limiting step in the base-catalyzed reaction were the abstraction of the H<sub>α</sub> one would expect that the ratio of [C]C/[C]A would be that of the surface coverages of C and A. DFT studies show that the heats of adsorption are remarkable similar for the two molecules, assuming similar entropy changes, we expect that the [C]C/[C]A would be about unity. However if the rate limiting step is the reprotonation of the dimer by the surface proton left from the initially activated molecule, the selectivity would greatly depend on the basicity of the substrate being attacked, that is (C) > (A), as experimentally observed.

## Significance

The development of effective and stable catalysts for C-C bond forming reactions will have an important impact in biomass upgrading processes. This study highlights synthesis and testing of functionalized catalysts with excellent performance. In addition, understanding the reaction mechanism that governs the distribution of products and its relationship with the catalyst properties is of crucial significance for further improving the control of selectivity and stability.