Multifunctional Heterogeneous Catalysts for Cascade Reactions in the Preparation of Fragrances

Maria J. Climent, Avelino Corma*, Sara Iborra, Maria Mifsud and Alexandra Velty
Instituto de Tecnología Química (UPV-CSIC), Avda. Los Naranjos s/n, 46022 Valencia(Spain)

**acorma@itq.upv.es*

Introduction

In the late 1980s Sheldon [1] proposed the concept of the E (environmental) Factor for assessing the environmental impact of manufacturing processes, which is defined as the mass ratio of waste to desired product (Kg waste/Kg product). The ideal E Factor is zero while a higher E Factor means the production of high amount of waste and therefore larger negative environmental impact. Catalysis play an important role in reducing or eliminating waste in chemical processes, particularly in the production of Fine Chemicals, where the E Factor values are specially higher, however, the eventual success in green chemistry is the combination of various catalytic steps into one-pot catalytic cascade process [2]. The fact that the same catalyst catalyzes different processes in a single reaction vessel without intermediate product recovery, decrease not only operating time but reduce considerably the amount of waste produced. Heterogeneous multifunctional catalysts besides the typical advantages of solids catalysts, they include the easy creation of catalytically active centers on solid surfaces.

The 4-(4-methoxyphenyl)-butan-2-one (**2**) (Scheme 1), is an odorous fine chemical with raspberry scent approved by FDA for food use. We have prepared **2** through a cascade process which involves the condensation of 4-methoxybenzaldehyde with acetone under hydrogen atmosphere using heterogeneous trifunctional acid-base metal catalysts based on Pd supported on nanocrystalline MgO (PdMgO), and Al-Mg mixed oxide (PdHTc) and a hydrated Al-Mg mixed oxide (PdHTr). MgO and Al-Mg mixed oxides present Lewis basicity associated to O^{2-} sites while the adjacent metal cation (Mg^{+2} or Al^{+3}) can acts as weak Lewis acid sites. In addition, hydration of the Al-Mg mixed oxide leads to the substitution of Lewis by Bronsted basic sites[3]. Thus, on the catalysts tested coexists three catalytic sites: basic (Lewis or Bronsted) and Lewis acid sites for the aldol and subsequent dehydration steps (giving the compound **1**), while the metal acts as hydrogenating site. The E Factor of this cascade process is calculated and compared with the E factor of the conventional homogeneous process as well as with those obtained in the homogeneous and heterogeneous catalyzed Heck reaction.

Materials and Methods

MgO sample was purchased from NanoScale Materials Inc, and the Mg-Al mixed oxides was prepared according to ref [4]. Pd catalysts at 1 wt% loading were obtained by contacting the metal oxide samples with a toluene solution of palladium acetylacetonate. After calcinations of the solid in nitrogen flow at 550 ^{o}C, reduction of the Pd(II) was performed in a flow of H_2/N_2 (90/10) at 450 ^{o}C. The PdHTc sample was hydrated at room temperature by direct addition of CO_2 free water (36 wt%) before their use, and was labeled as PdHTr. Reactions were performed in a glass reactor by mixing 4-anisaldehyde (3.8 mmol), acetone (37 mmol) with 38 wt% of catalyst respect to anisaldehyde at 75 ^{o}C and 5 bar H_2 pressure.

Results and Discussion

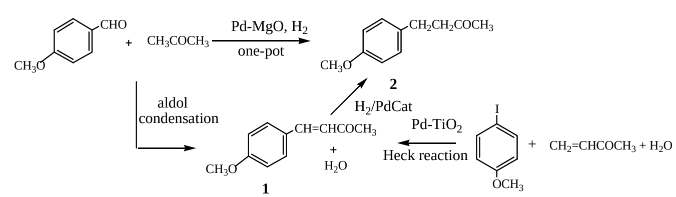
Table 1 show that PdMgO and PdHTr exhibit excellent activity and selectivity for the compound **2**. However, PdMgO results the most active catalyst, which is attributed to their nanocristalline nature (average particle size 3nm). The catalyst allows obtaining the raspberry scent with exceptional yield under very mild reaction conditions. Moreover the catalyst can be reused without loss of activity.

Table 1. Results for the synthesis of **2** using different multifunctional catalysts.

Catalysts	r^o 10^4 ($mmolmin^{-1}g^{-1}$)	Conversion (%)	Yield 1 (%)	Yield 2 (%)	Selectivity 2 (%)
PdMgO	12	100	-	100	100
PdHTc	5.00	89	27	62	68
PdHTr	9,70	95	-	95	100

r^o rate of disappearance of 4-anisaldehyde.

The E factor of the process using PdMgO was calculated by subtracting the mass of the desired product (**2**) from the total mass of raw materials, divided by the mass of product out. This gives an E Factor value = 0.01 Kg/Kg which correspond to the water formed in the condensation reaction. However, the homogeneous process gives a E Factor of 9.5 Kg/Kg. Evaluation of the E Factor in the synthesis of **2** through the Heck reaction (Scheme 1) using an heterogeneous catalyst (Pd-TiO_2) and a homogeneous catalyst ($Pd(C_3H_5Cl)_2$) was also performed giving E Factors of 2.53 and 4.09 Kg/Kg respectively.



Scheme 1

Significance

We have demonstrated that compound **2** can be prepared selectively through a cascade process with high yield using multifunctional nanocristalline PdMgO catalyst, giving minimum amount of waste, and showing that this is a new environmental friendly alternative route for the synthesis of raspberry scent.

References

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