Applied Catalysis A: General 342 (2008) 119–125

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Stability, reutilization, and scalability of activated hydrotalcites in aldol condensation

Sònia Abelló [a], D. Vijaya-Shankar [a], Javier Pérez-Ramírez [a,b,*]

[a] Institute of Chemical Research of Catalonia (ICIQ), Avinguda Països Catalans 16, 43007 Tarragona, Spain
[b] Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluís Companys 23, 08010 Barcelona, Spain

ARTICLE INFO

Article history:
Received 21 December 2007
Received in revised form 11 February 2008
Accepted 4 March 2008
Available online 13 March 2008

Keywords:
C–C bond formation
Solid bases
Aldol condensation
Hydrotalcite
Deactivation
Reutilization
Regeneration
CO_2 poisoning
Scale-up

ABSTRACT

A number of studies have shown that solid bases, among others activated hydrotalcites, are highly efficient catalysts for C–C bond formation reactions. A widely studied case is the aldol condensation of citral and acetone, where rehydrated Mg-Al hydrotalcite shows higher yields to pseudoionone compared to NaOH solutions. Despite this fact, the fine chemical industry still operates with the traditional liquid inorganic bases. This manuscript addresses technical aspects that can explain the limited implementation of activated hydrotalcites in aldol condensations. For this purpose, the catalyst stability in air, its reusability and regenerability after reaction, and the process scalability were investigated. The conciliation of activity data of the fresh hydrotalcite in batch laboratory (ml) and bench (l) reactors with on line ATR analysis is excellent, revealing that the citral–acetone reaction over hydrotalcite can be upscaled. However, the poisoning of the active Brønsted basic centers in the rehydrated hydrotalcite by CO_2 is very fast (50% activity loss after 1 h exposure to ambient). Besides, the catalyst after one run is inactive due to the presence of strongly adsorbed products and requires time-consuming (and not fully complete) regeneration. Basic centers of Lewis nature in calcined hydrotalcites (basically MgO) are more stable, but their activity is very low compared to the rehydrated counterpart. Both the technical disadvantages of current solid bases and the lack of stringent environmental regulations motivate the conservatism of industry to use alkaline solutions.

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1. Introduction

Inorganic bases in solution are traditionally applied in industry as homogeneous catalysts in reactions for the synthesis of fine chemicals, including isomerizations, C–C bond formation, additions, cyclizations, and oxidations [1–3]. High operating costs and serious environmental issues associated with base neutralization, product separation and purification, corrosion, and waste generation motivated substantial efforts toward the development of processes mediated by heterogeneous catalysts. Research in this field during the last decade led to the identification of various solid bases with remarkable activity and selectivity in many of the above reactions [1]. However, these materials have not been widely exploited in large scale, i.e. manufacturers still rely on the traditional alkaline hydroxide and ethoxide solutions.

A well-known example is the aldol condensation of citral and acetone to pseudoionone (PS) (Scheme 1), an important precursor for vitamin A, fragrances, and pharmaceutical products. Industrially, this reaction is catalyzed by NaOH with typical PS yields of 60–80% [4,5]. Different families of solid bases have been found active in this reaction, including alkali-exchanged zeolites (Cs-beta) [6], alkaline-earth metal oxides (MgO, CaO) [7,8], aluminophosphate oxynitrides [9], ion-exchange resins [10,11], and activated Mg-Al hydrotalcites [12–17]. In particular, pseudoionone yields of 100% have been demonstrated over the latter group of materials by optimal treatment of the as-synthesized clay [16] and proper selection of reaction conditions [18].

On the basis of the excellent aldolization performance of activated Mg-Al hydrotalcites in terms of activity and selectivity and taking into account the drawbacks of homogeneous catalysts, one can question why these solid bases have not broadly reached the industrial scene. Of course, the low cost of alkaline hydroxide or ethoxide solutions and the lack of stringent environmental policies are strong reasons to stick to liquid bases. However, the 100% PS yield of rehydrated Mg-Al hydrotalcite reported in lab-tests coupled to the expected reduction in operating costs and waste generation is a good motivation to establish the long-term

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* Corresponding author. Fax: +34 977 920 224.
E-mail address: jperez@iciq.es (J. Pérez-Ramírez).

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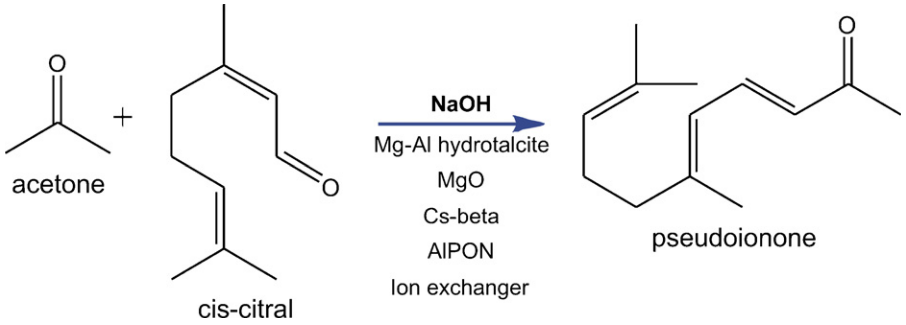
doi:10.1016/j.apcata.2008.03.010



Scheme 1. Base-catalyzed aldol condensation of acetone and *cis*-citral to pseudoionone.

effectiveness of the overall process over the heterogeneous system. Technical aspects that may prevent application of activated hydrotalcites can be related to questions like: is the catalyst preparation reproducible in large scale? How stable is the catalyst upon exposure to air? Can the reaction be effectively upscaled? Is the catalyst reusable? Can it be easily and completely regenerated? To the best of our knowledge, none of these items have been quantitatively addressed in any of the numerous publications dealing with base catalysts and can be important to devise future research strategies in this field.

Herein we have studied technical aspects that can result critical for industrial implementation of solid bases, taking the citral–acetone condensation over rehydrated hydrotalcites as case study. Aspects related to stability, reusability, regenerability, and scalability were systematically investigated by means of catalytic tests in lab and bench-scale reactors as well as characterization of the samples.

2. Experimental

2.1. Catalyst preparation

Mg-Al hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$) was prepared by coprecipitation at pH 10 using the in-line dispersion-precipitation (ILDP) method (Fig. 1, left) detailed elsewhere [19]. The resulting slurry was aged in a mechanically stirred vessel at 298 K for 12 h, followed by filtration, washing, and drying at 353 K for 12 h. The solid was calcined in static air at 723 K for 15 h at 10 K min^{-1}, followed by liquid-phase reconstruction [16]. For this purpose, the calcined sample was immersed in decarbonated water at room temperature for 1 h, leading to meixnerite ($Mg_6Al_2(OH)_{18}{\cdot}4H_2O$). Extreme care was taken to avoid contact of the rehydrated hydrotalcite with air using inert gas atmosphere in all operations during preparation, processing, storage, and use of the solid. Along the manuscript, the as-synthesized, calcined, and rehydrated hydrotalcites are denoted as HT-as, HT-ca, and HT-rh, respectively.

2.2. Catalyst characterization

The chemical composition of the as-synthesized hydrotalcite was determined by AAS (Hitachi Z-8200) and ICP-OES (PerkinElmer Plasma 400). Powder X-ray diffraction patterns were acquired in transmission on a D8 Brucker-Nonius Advance Series $2\theta/2\theta$ powder diffraction system using Cu Kα radiation. Data were collected in the 2θ range of 5–70° with an angular step of 0.016° and a counting time of 10.4 s per step. Thermogravimetric analysis (TGA) was carried out in a Mettler Toledo TGA/SDTA851e microbalance equipped with a 34-positions sample robot and 70 μl α-alumina crucibles. Analyses were performed in dry air flow of 50 ml STP min^{-1}, ramping the temperature from 298 to 1173 K at 5 K min^{-1}. Transmission electron microscopy (TEM) was carried out in a JEOL JEM-1011 microscope operated at 80 kV and equipped with a SIS Megaview III CCD camera. A few droplets of the sample suspended in ethanol were placed on a carbon-coated copper grid followed by evaporation at ambient conditions. N_2 adsorption–desorption isotherms at 77 K were measured on a Quantachrome Autosorb 1-MP analyzer. Before analysis, the samples were degassed in vacuum at 393 K for 16 h. Temperature-programmed desorption of CO_2 was measured in a Thermo TPDRO 1100 unit. Before TPD experiments, the sample (50 mg) was pretreated at 353 K with 3.5 vol.% CO_2 in He flow (20 ml STP min^{-1}) for 1 h, followed by removal of weakly adsorbed CO_2 at 373 K, and ramping in He (20 ml STP min^{-1}) from 373 to 1173 K at 10 K min^{-1}. A SuperCRC^{TM} microcalorimeter from Omnical was used to determine the heat evolved upon contacting citral (Aldrich, 95%) and acetone (Aldrich, 99%) with the catalysts. Ca. 50 mg of solid was introduced in a glass vial sealed with a septum and located inside a Teflon reactor under Ar atmosphere. The reactor was heated at 313 K and the reactant was dosed by means of a syringe. The catalyst mass was 16% of the mass of citral or acetone injected. An empty vial loaded with the same reactant amount was used as the reference. Both vials were magnetically stirred and the heat flow was recorded at intervals of 3 s during

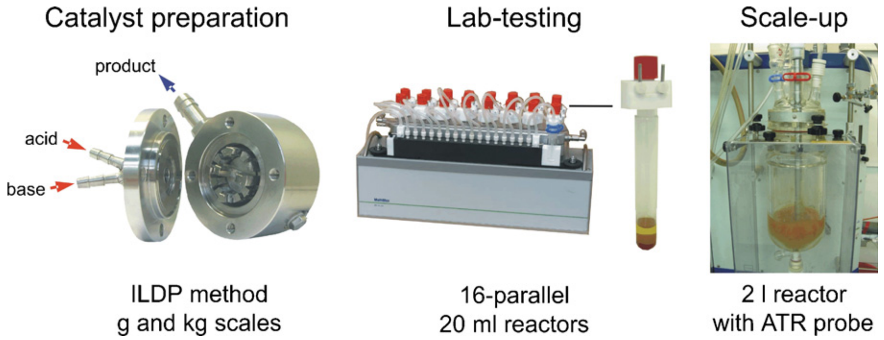


Fig. 1. Platforms used for preparation of hydrotalcite by the ILDP method [19], parallel catalyst testing [18], and reactor scale-up.

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