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Aerosol route to nanostructured WO_3-SiO_2-Al_2O_3 metathesis catalysts: Toward higher propene yield

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ABSTRACT

Aerosol processing is presented as a powerful new method to yield in one step highly efficient olefin metathesis catalysts. Combined with sol–gel chemistry, evaporation induced self-assembly and polyanions, it allows a fine tuning of the dispersion of WO_x species and the generation of acidic matrices which are key parameters controlling the formation of active metathesis sites. These spray dried catalysts are characterized by N_2-physisorption, XRD, TEM, NH_3-TPD, TPO, TPR, ICP-AES and systematically compared to relevant reference catalysts prepared by impregnation methods on different carriers (silica, alumina and silica–alumina). Tested in the industrially relevant cross-metathesis of ethene and 2-butene to propene, the new catalyst outcompetes reference catalysts, reaching 68 $\mathrm{mmol_{propene}\,g^{-1}\,h^{-1}}$ at 250 °C. By-products formed by isomerization reactions remain very low and high propene yields (39%) are reached.

1. Introduction

The metathesis of light olefins is a widely studied reaction due not only to its academic interest [1,2] but also to its massive industrial importance [3]. The metathesis reaction technology indeed affords the adjustment of petrochemical products in the refinery as a function of market demand. Nowadays, the highly demanded propene is produced on-site via the cross-metathesis of ethene and butene in a process called "Olefin Conversion Technology", licensed by Lummus Technology.

Supported transition metal oxides, including Mo [4–6], Re [7–9] and W [10,11] are the typical catalysts for metathesis reactions. Recently, tungsten hydride catalysts prepared by surface organometallic chemistry was reported as a promising alternative [12,13]. Silica-supported tungsten oxide is however the catalyst that is currently applied industrially for heterogeneous gas phase light olefin conversion. It is generally accepted [3,14], that the driving catalytic step in metathesis is the formation of the metallocyclobutane intermediate by interaction of an olefin with a surface metallocarbene complex which was formed by the reaction between an olefin and dispersed tungsten oxide species. Therefore, the dispersion of the supported phase and the nature of the interaction between the carrier and active species are the most significant parameters that govern the metathesis rate. Usually, WO_x-catalysts are prepared by simple impregnation of ammonium metatungstate on silica, alumina or mixed Si–Al followed by drying and calcination. In such two-step preparation methods the challenge is two-fold.

Firstly, a well-balanced acidity is central for (i) the successful anchoring of WO_x during the catalyst preparation and (ii) the fast reaction propagation during the catalytic cycle. Alumina-supported tungsten oxide exhibits strong acid sites promoting high surface dispersion but also inducing side-reactions like isomerization. Silica-supported tungsten oxide is usually preferred since amorphous SiO_2 alone is barely acidic. The disadvantage here is that WO_x species sinter easily because their interactions with the support are weak and this leads to the formation of species that are

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too reducible and thus inactive. Thus several authors have studied mixed Si–Al materials as supports. For example, Huang et al. studied physically mixed $WO_3/Al_2O_3/HY$ in metathesis of ethene and 2-butene. They stated that during calcination the bulk WO_3-phase becomes better dispersed first into microcrystallites and further, via chemical transformation thanks to the mixed support structure, to monomeric surface tungstate species which are identified as the active species in the metathesis reaction [15]. Another pertinent strategy [16] is to modify an alumina support by grafting silica onto it in order to mitigate the acidity and thus the dispersion and reducibility of impregnated WO_x species.

Secondly, impregnation methods offer limited opportunities in terms of textures. Whether the support is a commercial one or prepared on purpose with tailored texture, it is difficult to ensure that the active phase gets truly dispersed on the entire available surface and down to the bottom of the pores [17]. Instead it is frequent to observe WO_3 aggregates at the outer surface of the support particles [18]. This being said, it is known that dispersion of the metal site is critical to high activity, i.e. isolated metal sites have high activity and good selectivity whereas polymeric MO_x species (M = Mo, W or Re) have either poor activity or poor selectivity [17,19].

Therefore, one-step preparation methods represent desirable alternatives for the preparation of efficient metathesis catalysts with adapted texture, composition and dispersion. In this perspective, methods like flame spray pyrolysis [20] or non-hydrolytic sol–gel [21,22] constitute attractive options. Recently, an innovative hydrolytic sol–gel method was proposed for the one-step preparation of nanostructured silica–alumina materials [23] and MoO_3-SiO_2-Al_2O_3 catalyst [24]. The preparation takes advantage of the aerosol assisted sol–gel process [25]. In the latter, the evaporation induced self-assembly of a surfactant is used to generate a calibrated porosity. Moreover, the kinetics of the sol–gel process is quenched so as to obtain a homogeneous dispersion of all components of the mixed oxide. The obtained aerosol processed MoO_3-SiO_2-Al_2O_3 catalyst exhibited very high metathesis activity at low reaction temperature (40 °C). However, as classically observed with highly active Mo-based catalysts [26,27], it showed substantial deactivation with time on stream.

In this paper, we report on the controlled design and processing of a new WO_3-SiO_2-Al_2O_3 catalyst exhibiting optimized texture, tungsten dispersion, and acidity and being able to work at higher temperatures, close to those used in the industry. The catalyst is prepared in one step via an adapted version of the aerosol process already reported [24]. Its properties and performance are compared to those of reference catalysts prepared by impregnation on silica, alumina and silica–alumina supports. The metathesis activity of these W-catalysts is measured in the industrially relevant cross-metathesis reactions of ethene and 2-butene.

2. Experimental

2.1. Catalyst preparation

2.1.1. Reference catalysts

Three commercial supports were used as carrier to prepare WO_x-based catalysts by impregnation. Silica (SiO_2, Davisil grade 646), alumina (γ-Al_2O_3, Evonik) and silica–alumina (Aldrich, grade 135, about 13 wt.% Al_2O_3). These supports are denoted Si, Al and SiAl in the following. Prior to impregnation, the supports were calcined at 500 °C for 12 h under air flow. Ammonium metatungstate hydrate (STREM Chemicals, purity 99.9%) was used as a W precursor. The nominal WO_x loading was 10 wt.%. 13.8 g of each support was immersed in precursor solution consisting of 1.594 g ammonium metatungstate hydrate dissolved in 60 mL distilled water. The resulting suspension was stirred at 80 °C until evaporation of the water. The recovered wet cake was dried at 110 °C for 12 h and then calcined stepwise as follow: heating (1 K min^{-1}) up to 250 °C, hold 2 h, then heating (3 K min^{-1}) up to 550 °C, hold 8 h in air flow. At the end, the powder was pressed, crushed and sieved in the 250–600 μm fraction. These three reference catalysts are denoted WO_x-imp-Si, WO_x-imp-Al and WO_x-imp-SiAl.

2.1.2. Aerosol catalysts

The new catalyst was prepared by the aerosol process (Scheme 1). A surfactant solution is prepared by dissolving 11.5 g of Pluronic P123 in 77.8 g of water and 137 g of absolute ethanol. The solution is stirred at room temperature until complete dissolution of the surfactant. A tungsten precursor solution is prepared by dissolving 1.50 g of $H_3PW_{12}O_{40}$ Keggin heteropolyanion in 15 g of distilled water. An Al–Si precursors solution is obtained by basic hydrolysis of Si and Al alkoxides as follows: (i) 3.6 g of aluminum sec-butoxide is dissolved in 17.1 g of aqueous tetrapropylammonium hydroxide (TPAOH) solution (40% in water), (ii) after 15 min of homogenization 50 g of water and then 36.9 g of tetraethylortosilicate (TEOS) are added, (iii) the solution is stirred at room temperature for 16 h. All three solutions are then mixed together and atomized with a Büchi B-290 spray dryer. The input parameters are fixed as follows: 220 °C for the chamber temperature, 9 cm^3 min^{-1} for the solution flow and 35 m^3 h^{-1} for the suction flow of heated air. The recovered powder is then calcined under static air at 130 °C (2 K min^{-1}) for 2 h and then 550 °C (2 K min^{-1}) for 12 h. This catalyst is denoted WO_xSiAl-aer.

One silica–alumina powder was prepared by the same aerosol method, but in the absence of the W Keggin compound. This sample is denoted SiAl-aer. It was then impregnated with an aqueous solution of $H_3PW_{12}O_{40}$. The solution was added dropwise while the powder was mechanically stirred. The obtained material was then allowed to mature, at ambient temperature at a relative humidity of 100% during 24 h. A drying step was then applied for 24 h at 130 °C. This sample is denoted WO_x-impSiAl-aer. Denotations of studied catalysts together with some textural characteristics are listed in Table 1.

2.2. Catalyst characterization

2.2.1. Elemental analysis

The WO_3 weight loading of all catalysts was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on Iris Advantage from Jarrell Ash Co. The samples were dried at 105 °C prior to measurement.

2.2.2. Textural analysis

The specific surface area (S_{BET}) and porosity of the materials were calculated from nitrogen adsorption–desorption isotherm collected at −196 °C on BELSORB-mini II (BEL Japan, Inc.). Prior to measurements the samples were outgassed for 2 h at 250 °C. S_{BET} was calculated applying the Brunauer, Emmet and Teller (BET) equation for N_2 relative pressure in range of $0.05 < P/P_0 < 0.30$. Pore size distribution was determined by Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm. Mean pore size, listed in Table 1, was obtained using the formula $4{\cdot}V_p/S_{BET}$. The theoretical surface tungsten oxide density (C_W) was calculated using the equation [28]:

$$C_W = \left(\frac{L_{WO_3}/100}{231.8}\right) \times \left(\frac{N_0}{S \times 10^{18}}\right), \text{ where}$$

L_{WO_3} is the loaded amount of WO_3 (wt.%); 231.8 is the molecular weight of WO_3; N_0 is the Avogadro number (6.023×10^{23}) and S is the specific surface area (m^2 g^{-1}).