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ScienceDirect

Catalysis Today 129 (2007) 102–109

CATALYSIS TODAY

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Screening of different zeolite-based catalysts for gas-phase selective photooxidation of propan-2-ol

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Abstract

In the present piece of research photocatalytic activity of TiO_2 and V_2O_5 (as measured for gas-phase selective photoxidation of propan-2-ol) is substantially improved through their sol–gel synthesis on USY zeolites. The decrease in the crystallite size of TiO_2 (anatase) and V_2O_5 thus exhibiting the so-called quantum size effect (as determined by XRD and UV–vis spectroscopies, respectively) is to account for that. In the case of vanadium, the use of zeolites means a decrease in selectivity to acetone whereas no noticeable change is observed for titanium. Subsequent photodeposition of platinum on the Ti- and V-containing zeolites results in a sharp increase in molar conversion, low or negligible deactivation with a time-on-stream of 5 h and significant increase in selectivity to acetone which was in the range 90–96%.

Keywords: Propan-2-ol; Photocatalysis; Selective photooxidation; Titania; Vanadia; Zeolite-based photocatalysis; USY; Platinum-doped systems; Silver-doped systems; Quantum-size effect

1. Introduction

The main application of heterogeneous photocatalysis (at least as far as the number of the publications on the topic is concerned) is degradation of pollutants present in waters through complete mineralization [1–3]. One could think of the possibility of selectively oxidizing the pollutant to a non-toxic high-valued chemical which would be even more interesting though, unfortunately, it is not possible in aqueous media. There are some examples in the literature of selective adsorption of a chemical making use of the shape-selectivity (zeolites) [4] or the so-called adsorb-and-shuttle concept [5,6]. These approaches allow selective adsorption though once adsorbed, the chemical will tend to be mineralized. Nevertheless, selective oxidations can be performed in non-aqueous media. Therefore, gas-phase selective oxidation of propan-2-ol to acetone is often used as a model reaction for characterization of photocatalytic activity [7–9].

As regards the photocatalyst itself, titania is by far the most-widely used system, but it has some drawbacks such as the absorption in the UV-region or the low surface area. In this sense, as pointed out by Corma and García [10], some of the advantages of using zeolites in photocatalysis are as follows:

(i) High surface area, thus enabling high adsorption of chemicals to be photo-oxidised/reduced.
(ii) Transparency to UV–vis radiation above 240 nm thus allowing a certain penetration of the exciting light into the powder which can be useful in order to allow exciting light to reach a photoactive guest.
(iii) Possibility to vary the chemical composition of framework and out-of-framework position in a large extent, thus rendering these molecular sieves photoactive (e.g. introducing Ti or V atoms).
(iv) Possibility to modulate both the micropolarity of the zeolite interior and the size of the channels.

Two of the most common methods of preparation of titania into zeolites are ion exchange from titanyl solutions [11,12] or hydrolysis of titanium alkoxide [13,14].

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doi:10.1016/j.cattod.2007.09.005

The relatively high electron–hole recombination rate of TiO_2 constitutes an additional drawback since it is detrimental to its activity. In this sense, doping with metals could make a double effect: (i) firstly, it could reduce the band gap energy, thus shifting the absorption band to the visible region and (ii) secondly, metals could provoke a decrease in electron–hole recombination rate, acting as electron traps.

The present piece of research is aimed at exploring the possibility of improving the photocatalytic activity of titania, vanadia and zinc oxide through their sol–gel synthesis on USY zeolites and the subsequent doping with Pt or Ag.

2. Experimental

2.1. Synthesis of Ti, V and Zn-containing zeolites

Zeolite-based photocatalysts were synthesized through the sol–gel method starting from titanium isopropoxide [$Ti(OCH(CH_3)_2)_4$,] vanadyl acetylacetonate [$VO(acac)_2$] and zinc acetylacetonate [$Zn(acac)_2$] which were incorporated, in a nominal content of 2 mmol/g of catalyst, on USY (Si/Al = 62 and 4.7) zeolites.

In order to obtain titanium-containing systems, 10 g of zeolite previously treated at 400 °C in air flow for 4 h were introduced in a 250 mL round-bottom flask together with 60 mL of propan-2-ol and 6.14 mL titanium isopropoxide. The mixture was heated at ca. 90 °C (propan-2-ol reflux) for 14 h. Then, a solution of 322.5 mg dipicolinic acid in a mixture of 20 mL propan-2-ol and 2.5 mL water was added in order to favor formation of the gel and the mixture was kept under reflux for two more hours. The solid was then vacuum-filtered and washed with 10 mL of propan-2-ol three times. Finally, the system was calcined at 550 °C for 4 h in static air.

Incorporation of zinc and vanadium into zeolites was carried out in a similar way as described for titanium-systems but using 2.5 mL of 6.7 M ammonia solution as the precipitation agent instead of the dipicolinic acid mixture. Moreover, vanadyl acetylacetonate had to be previously dissolved in 2 mL 30% HNO_3.

For comparative purposes, pure TiO_2, ZnO and V_2O_5 were also obtained by the same sol–gel process as described above.

All chemicals were obtained from Aldrich. Zeolites were purchased from Zeolyst Int. (CBV300 and CBV780). Prior to its use, CBV300 was calcined at 550 °C for 4 h in static air in order to convert it to its acidic form.

The nomenclature of the systems include the zeolite type (USY), together with a prefix indicating the atom (Ti, V or Zn) incorporated into the zeolite and a suffix corresponding to the Si/Al ratio as determined by ICP-MS. Therefore, for instance, Ti-USY62 refers to the USY zeolite with Si/Al = 62 into which titanium has been incorporated.

2.2. Further incorporation of platinum and silver

The most active systems containing V and Ti were then selected to incorporate Ag and Pt using silver or platinum (II) acetylacetonates (Aldrich) as the corresponding precursors. Incorporation was performed either by impregnation or photodeposition.

2.2.1. Impregnation method

1.5 g of zeolite-based photocatalyst are introduced in a round-bottom flask together with the appropriate amount of the Ag or Pt precursor as to have a nominal (Pt or Ag)/(Ti or V) atomic ratio of 0.1 dissolved in 400 mL propan-2-ol. The vanadium and titanium content in zeolites had been previously determined by inductively coupled plasma-mass spectrometry (ICP-MS). The mixture is submitted to vigorous stirring while propan-2-ol is distilled. The solid is then vacuum-filtered and washed three times with volumes of 15 mL of propan-2-ol. Finally, the system is calcined in static air at 550 °C for 4 h, thus yielding the solids belonging to the "I" series (standing for Impregnation).

2.2.2. Photodeposition method

Photodeposition of Pt and Ag was carried out in a Pyrex cylindrical double-walled immersion well reactor (23 cm long, 5 cm internal diameter, with a total volume of ca. 450 cm^3) open to air starting from 1.5 g of zeolite and the Pt and Ag precursor dissolved in 400 mL propan-2-ol. Irradiation of the reaction solutions was carried out by using a medium pressure 125 W Hg lamp ($\lambda_{max} = 365$ nm) supplied by Photochemical Reactors Ltd. (Model 3010). Lamp output was calculated to be ca. 1.5×10^{-3} einstein/s (potassium ferrioxalate actinometry). Water used for cooling was thermostated at 20 °C. Constant agitation of the suspension was insured by a magnetic stirrer placed at the reactor base. Further details on the experimental device are given elsewhere [15]. Irradiation time was 2 h. The systems were vacuum-filtered, washed with propan-2-ol and calcined at 550 °C for 4 h, thus yielding the solids belonging to the "P" series (standing for Photodeposition).

The nomenclature of the systems includes a prefix referring to the incorporation method (impregnation or photodeposition) and the metal incorporated (Ag or Pt). Therefore, for instance, PPt-Ti-USY62 refers to a USY zeolite with a Si/Al ratio equal to 62, to which titanium had been incorporated by the sol–gel method and platinum was then added by photodeposition.

2.3. Characterization

Elemental analyses were carried out by the staff at the Central Service for the support of research (SCAI) at the University of Córdoba. Measurement was made on a ICP-MS ELAN-DRC-e (Perkin Elmer), after dissolution of the samples in a H_2SO_4:HF:H_2O (1:1:1) mixture. Atomic spectroscopy standards from Inorganic Ventures Inc. (ISO-CAL-28, ISO-CAL-29, ISO-CAL-30 and CGAU1-1) were used for calibration.

As far as EDX analyses are concerned, they were performed on a JEOL JSM-6300 SEM apparatus operating at an accelerating voltage of 20 keV with a resolution of 65 eV. EDX values corresponded to the average value of four measurements carried out at different areas of the solid with an amplification of 5000×.