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Ferromagnetically modified zeolite catalysts for liquid-phase High–Throughput Experimentation

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ABSTRACT

A novel method for the separation of heterogeneous catalysts from liquid-phase reactions in High–Throughput Experimentation (HTE) libraries was developed based on a magnetic recuperation procedure. Ferromagnetic iron nanoparticles were introduced in a set of zeolite structures by means of aqueous impregnation of an iron precursor, followed by reduction in H_2. The obtained magnetic zeolites can be efficiently stirred in the catalytic reaction mixture using conventional magnetic stirring bars and they are automatically separated by depositing on the magnetic bar when the stirring is stopped. Characterization techniques demonstrated that the iron nanoparticles are distributed on the external surface of the zeolites, where the interference with the catalytic active sites is limited. Catalytic tests of a High-Throughput library of 10 wt. % Fe magnetic zeolites, performed using the liquid-phase benzylation of toluene with benzyl alcohol as test reaction, showed that the modified catalysts can be very easily and efficiently separated from the reaction mixture while they retain similar activity and selectivity to that of the unmodified samples.

1. Introduction

High–Throughput Experimentation (HTE) techniques find an increasing number of applications in areas such as catalyst preparation and testing [1–7]. Their use in homogeneous catalysis proved to be straightforward due to the similarities with drug discovery approaches. HTE in heterogeneous catalysis had a relatively slow start, partly due to specific problems related to the heterogeneity of the systems, *viz.* the requirement of solids removal from the reaction medium before sampling from liquid-phase batch reactors or liquids-solids separation before catalyst regeneration [8]. Moreover, many sequences of unit operations in catalyst preparation, such as ion exchange, impregnation, washing, drying, and calcination, require intermediate separation of liquid from solid phase, *viz.* centrifugation and/or filtration steps, which are difficult to automate and to apply with catalyst libraries. Therefore, HTE with heterogeneous catalysts has been focusing on applications related to gas phase reaction systems, reports of liquid-phase testing of heterogeneous catalysts still being scarce [1,9–14].

Sampling in time from a batch reactor allows extracting the kinetic parameters that form the necessary basis for ultimately determining the relation with catalyst properties and the reaction mechanism. In absence of efficient solid-liquid phase-separation procedures, only limited data can be obtained for each catalyst in the library. Reported attempts to circumvent this problem consist in sampling a very small volume from the reaction mixture containing invariably also small amounts of solid catalyst, followed by direct chromatographic analysis [15]. Such procedure may result in the undesired accumulation of catalyst in the chromatographic pre-column. Alternatively, it has been proposed to run a parallel set of identical reactions for different reaction times [16]. HTE equipment that allows fully automated catalyst preparation and on-line sampling in combination with fast chromatographic analysis would need fast and efficient liquid-solid separation to achieve optimum performance. In this context, an ideal solution would be represented by a catalyst that automatically separates from the reaction mixture as stirring is stopped. This can be achieved by magnetic separation, which therefore represents a technically attractive alternative to centrifugation or filtration. The preparation of magnetically separable ordered mesoporous carbons and mesostructured silica with surface grafted magnetic cobalt particles has been previously achieved [17,18]. Here, we describe the preparation of magnetic zeolite catalysts, enabling straightforward, fast and adequate separation of a solid catalyst from a batch catalytic reactor. At an HTE level, this methodology allows separation of catalysts in parallel vessels by their collection on the magnetic element upon stopping of the agitation. By restarting the stirring, the catalysts

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can be rapidly redispersed in the reaction mixture. This approach could also allow the establishment of a (small scale) stable fluidized catalytic bed. Obviously, this technique requires the use of heterogeneous catalysts exhibiting ferromagnetic properties or incorporation of ferromagnetic particles in a solid catalyst. Some authors reported on the magnetic modification of potential catalytic materials with magnetic particles, *viz.* composites consisting of NaY zeolite and Fe oxide, [19,20], carbon encapsulated Ni-Fe alloy particles [21] and chirally modified Pt supported on silica-coated Fe_3O_4 as catalyst for asymmetric hydrogenation [22].

In the present work, acid zeolites are ferromagnetically modified by means of incorporation of iron particles and tested in the Friedel-Crafts benzylation of toluene. Comparison of acid zeolite catalysts with different topologies in the original and magnetically modified form allowed to establish the validity of the proposed modification method for solids separation in batch reactors in an HTE set-up. The liquid-phase Friedel-Crafts benzylation of toluene was chosen as a test reaction due to the possibility of obtaining various *ortho-*, *meta-*, *para-* product distribution on each of the tested zeolite topologies [23]. HTE was used in order to identify the optimum zeolite for maximizing the yield for each individual mono-alkylated product. The products of the benzylation of toluene are industrially important compounds used as intermediates for pharmaceutical products and in fine chemistry [24]. Liquid-phase Friedel-Crafts alkylations either require up to stoichiometric amounts of Lewis acid catalysts such as $AlCl_3$ and BF_3, or alternatively catalytic amounts of acid zeolites, *viz.* for alkylaromatics production [25]. The shape selective properties characteristic of zeolites can allow driving the reaction selectivity towards a desired isomer [26]. Since zeolites can be synthesized in a large number of topologies, each with specific pore size, pore architecture, and widely varying composition and thus acid strength, the determination of the most suitable zeolite catalyst for a chosen reaction is significantly faster and more efficient with an HTE approach.

2. Experimental

2.1. Materials

Commercially available zeolites: HY PY-44/1C (Si/Al = 2.5) from Zeocat; NaY CBV100 (Si/Al = 2.6), USY CBV600 (Si/Al = 2.8), USY CBV712 (Si/Al = 5.8), USY CBV720 (Si/Al = 13), USY CBV760 (Si/Al = 30) and USY CBV780 (Si/Al = 37) from PQ; HMOR ZM980 (Si/Al = 100) from Zeocat; HBeta CP81BL-251 (Si/Al = 25) from PQ; HZSM-5 (Si/Al = 50) from Degussa. These zeolites were impregnated with an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ with different concentrations and constant volume of 1 ml per gram of zeolite. The samples were dried at 60 °C in air, and subsequently heated at 400 °C in oxygen for 1 h (heating ramp: 5 °C/min), then in nitrogen for 30 min (to prevent the explosive reaction between O_2 and H_2), and finally in hydrogen for 1 h. Under these conditions, the Fe_2O_3 oxide stemming from calcined $Fe(NO_3)_3$, is reduced by H_2 to metallic iron, which is dispersed in the zeolite crystals, yielding zeolite/iron composites.

As an alternative to the impregnation route, magnetically modified zeolites were synthesized by precipitation of iron oxides with a 1 M NaOH solution following a method reported by Oliveira et al. [19]. Another approach consisted in dispersing both zeolite crystals and ferromagnetic particles in a silica matrix that acts as a binder: first, Fe nanoparticles covered in a protective Ni shell were prepared according to a procedure published by Yang et al. [27]; then, a composite material containing 10 wt. % of these Fe/Ni nanoparticles and 25 wt. % of ZSM-5 crystals, was prepared using a previously reported method [28].

2.2. Magnetic recuperation procedure

Samples of the zeolite/iron composites were introduced in an acetone containing glass vial and stirred for 10 min on a magnetic stirring plate at room temperature. As soon as the stirring was stopped, an external magnet was used to attract the composite to the wall of the vial (Fig. 1). After removal of the solvent with a syringe, the glass vial with catalyst was dried in an oven at 90 °C for 12 h. The total weight of the vial with catalyst allowed the determination of the magnetic separation efficiency. Repetition of this cycle for three more times, unequivocally proved the efficiency of the separation of magnetic zeolites from solvent or reaction medium.

2.3. High-Throughput testing

A catalytic test with magnetic recuperation was performed using a Genesis RSP-100 liquid-handling robot equipped with a stirring and heating reaction block with 60 parallel wells [8]. A library of dry zeolite samples was impregnated with Fe^{3+} solution. Impregnation of 0.1 ml of the ferric nitrate stock solution to 100 mg of dry zeolite was done in 10 ml glass vials, followed by drying. Calcination and reduction under H_2 were done in a separate oven. The final catalysts had a 10 wt. % Fe. In the benzylation experiments, magnetic stirrers (12 × 4.5 mm bar-shaped magnets encapsulated in PTFE with a permanent magnetic field of 15–25 mT) were rotated at 500 rpm, causing good dispersion of the magnetic zeolite (110 mg) in the reaction medium in each HTE vial. When the stirring was stopped, the zeolite powder was rapidly and quantitatively collected at the surface of the permanent magnets. In a typical catalytic test, each 10 ml reactor containing a zeolite sample and a magnetic stirring bar was sealed with a rubber cap. After addition of 5 ml of toluene via the robot, the library of samples was heated to the reaction temperature (80 °C), followed by addition of the second reactant (benzyl alcohol; 1 mmol). Separation of the catalyst from the reaction medium when stopping the magnetic stirring, followed by sampling via septum piercing and transfer to a 98 position GC-rack, took around 17 s for each reactor. The sampling volume was set at 50 μl (1% of total volume) in order to allow multiple sampling steps without causing a significant decrease of the volume of the reaction medium. Sampling was performed at 1, 3, 6, 10 and 15 h reaction time. Sample analysis was performed on a Thermo Finnigan Ultra Fast GC, equipped with a very low volume capillary column (FT: 0.1 μm; L: 5 m; i.d.: 0.1 mm), the analysis time for each sample being 3 min (starting temperature 125 °C; 25 °C/min up to 175 °C; 150 °C/min up to 250 °C; dwell for 0.5 min).

2.4. Characterization

The type of crystalline phase of the zeolites was confirmed by powder X-ray diffractometry (XRD) analysis on a STOE StudiP diffrectometer. TEM investigations were performed with a Phillips

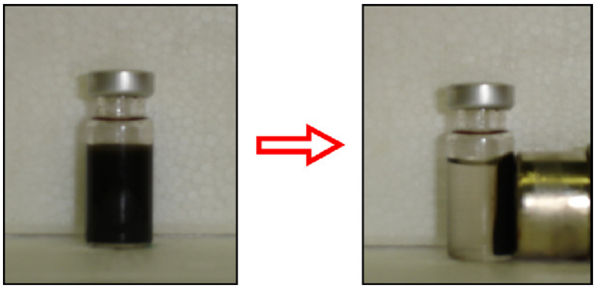

Fig. 1. Magnetic separation procedure.