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Versatile low-loaded mechanochemically synthesized supported iron oxide nanoparticles for continuous flow alkylations

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Experimental

Ball-milled assisted preparation of iron oxide nanoparticles (BM)

In a typical synthesis of ball-milled materials, 0.2 g Al-SBA-15 support was grinded with the adequate amount of iron precursor ($FeCl_2.4H_2O$) to reach a theoretical 0.5 wt.% iron loading in a Retsch PM-100 planetary ball mill using a 125 mL reaction chamber and eighteen 10 mm stainless steel balls. Optimised milling conditions were 10 minutes at 350 rpm. The resulting materials (Fe/Al-SBA-15) were then subjected to a conditioning methodology to ensure the removal of all unreacted precursor species. Briefly, the synthesized material was soaked with 2 mL water followed by a microwave treatment for 5+5 min in a domestic LG MS 19296/00 instrument (maximum power 800W). The final material (denoted hereafter as Fe/Al-SBA15-BM) was eventually thoroughly washed with 50 mL water and then calcined at 400ºC under air for 4 h. Fe content of the catalysts was estimated by EDX and ICP/MS, being 0.28 and 0.25 wt.% Fe, respectively.

Microwave synthesized material (MW)

These materials were prepared following a methodology previously reported.[S1] Briefly, the aluminosilicate support (0.2 g) and the desired quantity of iron precursor ($FeCl_2.4H_2O$) to achieve a 1 wt% loading dissolved in a acetone/ethanol mixture (1:1 v:v) were placed in a Pyrex vial and microwaved at maximum power settings (nominal magnetron output power 300 W) for 15 min in a CEM-DISCOVER microwave reactor in closed-vessel using a power controlled method (maximum temperature reached 100-120ºC). The resulting coloured materials was then filtered off, thoroughly washed with acetone, ethanol and water, dried overnight at 100ºC and calcined at 400 ºC prior to its utilisation in the investigated reaction. The material prepared was denoted as Fe/Al-MCM-MW, having an Fe content of 0.63 wt% (as measured by ICP).

Conventionally impregnated material (IMP)

The aluminosilicate support (0.2 g) was mixed with an ethanol/acetone solution (1:1 v:v) containing the desired quantity of iron precursor ($FeCl_2.4H_2O$) to achieve a 1 wt% loading and then the final mixture was stirred in a rotary evaporator at ca. 60ºC for 12 h to ensure the incorporation of the iron into the aluminosilicate. The material was then collected, dried overnight at 100ºC and then calcined at 400ºC under air for 4 h, in a similar way to that reported for BM and MW materials. The impregnated material was denoted as Fe/AlSBA15-IMP, having an Fe content of 0.78 wt% (as measured by ICP).

Materials characterisation

Pyridine (PY) and 2,6-dimethylpyridine (DMPY) titration experiments were conducted at 200ºC via gas phase adsorption of the basic probe molecules utilising a pulse chromatographic titration methodology.[S2, S3] Briefly, probe molecules (typically 1-2 μL) were injected in very small amounts (to approach conditions of gas-chromatography linearity) into a gas chromatograph through a microreactor in which the solid acid catalyst was previously placed. Basic compounds are adsorbed until complete saturation from where the peaks of the probe molecules in the gas phase are detected in the GC. The quantity of probe molecule adsorbed by the solid acid catalyts can subsequently be easily quantified. In order to distinguish between Lewis and Brönsted acidity, the assumption that all DMPY selectively titrates Brönsted sites (methyl groups hinder coordination of nitrogen atoms with Lewis acid sites) while PY titrates both Brönsted and Lewis acidity in the materials was made. Thus, the difference between the amounts of PY (total acidity) and DMPY (Brönsted acidity) adsorbed should correspond to Lewis acidity in the materials.

Iron content in the materials was quantified by TEM-EDX and AAS or ICP/MS as previously reported[S4] showing consistent results between materials and samples.

Catalytic activity

Microwave-assisted reactions

In a typical reaction, 2 mL toluene, 0.2 mL benzyl alcohol or benzyl chloride and 0.025 g catalyst were added to a Pyrex vial and microwaved in sealed vessel mode in a CEM-Discover microwave reactor for 3 min irradiation time at 300 W nominal magnetron output power (110-120ºC, maximum temperature reached) under continuous stirring. Samples were then withdrawn from the reaction mixture and analysed by GC and GC/MS Agilent 6890N fitted with a capillary column HP-5 (30 m × 0.32 mm × 0.25 μm) and a flame ionisation detector (FID). The identity of the products was confirmed by GC-MS and ^{1}H and ^{13}C NMR. Response factors of the reaction products were determined with respect to the substrates from GC analysis using standard compounds in calibration mixtures of specified compositions.

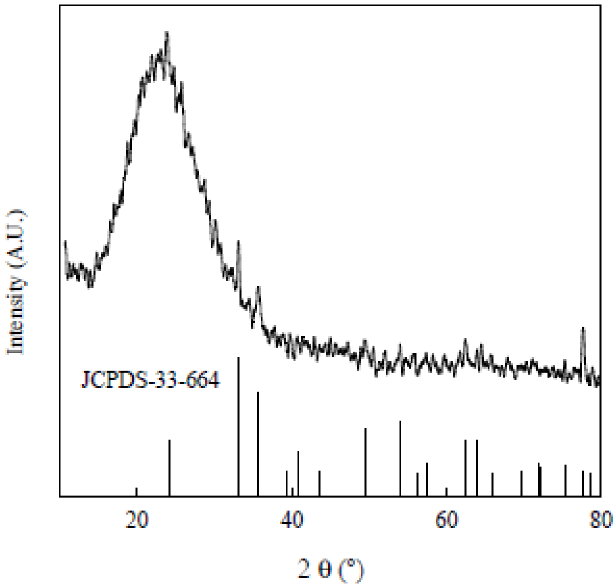

Figure S1. XRD patterns of synthesized Fe/Al-SBA15-BM catalyst containing 0.25 wt.% Fe.

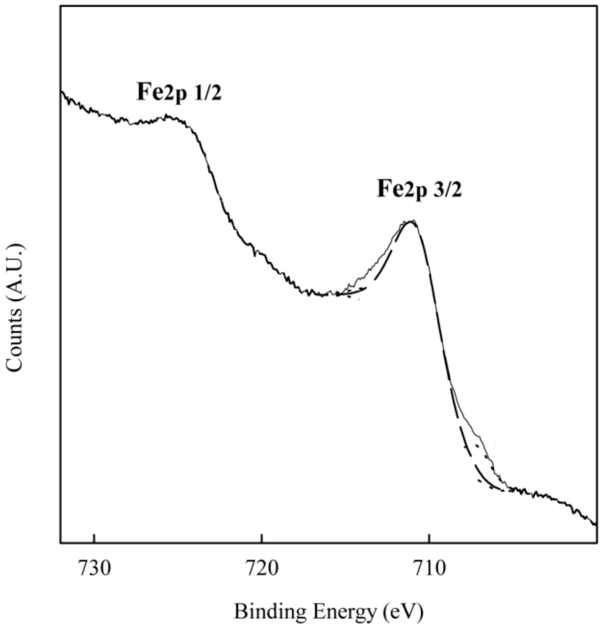

Figure S2. XPS of synthesized Fe/Al-SBA15-BM catalyst containing 0.25 wt.%

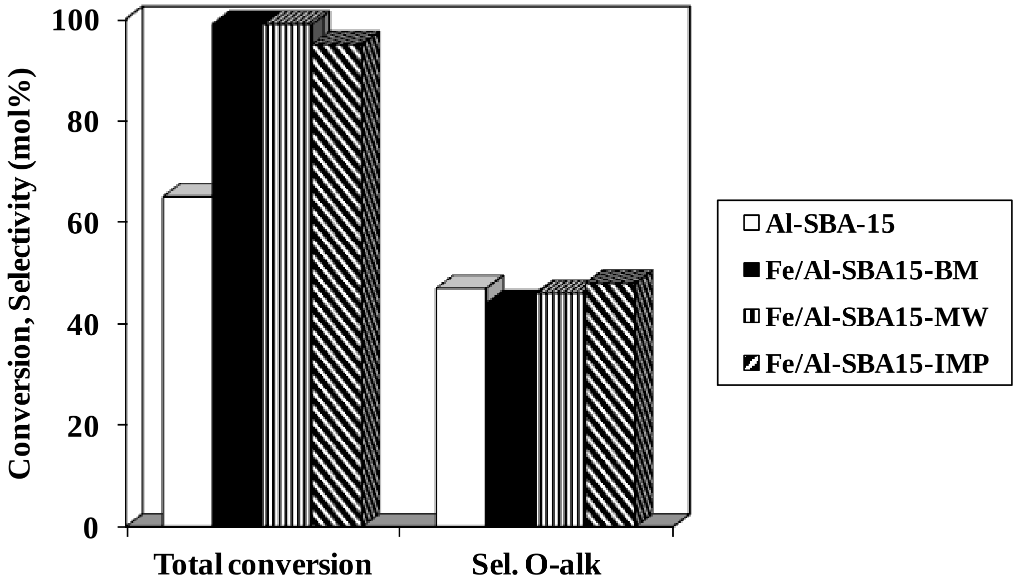

Figure S3. Conversion and selectivity to C-C ortho-alkylation (Sel. O-alk) of different catalysts investigated in the microwave-assisted alkylation of toluene with benzyl chloride. Reaction conditions: 2 mL toluene, 0.2 mL benzyl chloride, 0.025 g catalyst, 300 W, 3 min, 110-120ºC (maximum temperature reached). Catalysts: Fe/Al-SBA15-BM (0.25 wt% Fe), Fe/Al-SBA-15-MW (0.63 wt% Fe), Fe/Al-SBA-15-IMP (0.78 wt% Fe).

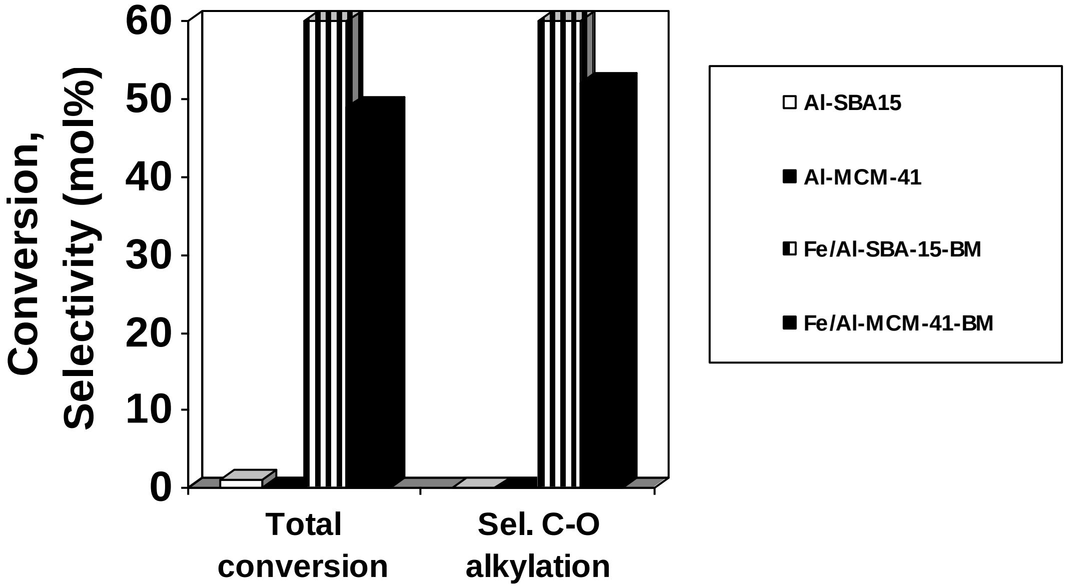

Figure 4S. Comparison of activity and selectivity to C-O alkylation (to dibenzylether) of different Fe- containing catalysts and their corresponding parent supports investigated in the microwave-assisted alkylation of toluene with benzyl alcohol. Reaction conditions: 2 mL toluene, 0.2 mL benzyl alcohol, 0.025 g catalyst, 300 W, 3 min, 110-120ºC (maximum temperature reached). Catalysts: Fe/Al-SBA15-BM (0.25 wt% Fe), Fe/Al-MCM-41-BM (0.3 wt% Fe).

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