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High alkylation activities of ball-milled synthesized low-load supported iron oxide nanoparticles on mesoporous aluminosilicates

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ABSTRACT

Low-load iron oxide nanoparticles on Al-SBA-15 prepared using a novel dry milling approach exhibited excelling activities in the microwave-assisted akylation of toluene with benzyl chloride (Lewis acids promoted reaction) and benzyl alcohol (Brönsted acids promoted reaction) as compared to the parent Al-SBA-15 and similar iron oxide nanoparticles supported on Al-MCM-41 materials. Materials prepared using the milling protocol possessed remarkably low iron loadings (<0.1 wt%) but featured highly accessible sites and small nanoparticle sizes that seemed to be related to the observed differences in activities in the systems.

1. Introduction

Supported nanoparticles on porous materials have attracted a great deal of attention in past years due to their interesting properties compared to bulk metals [1]. These include high surface areas and specificities which make them particularly suitable for various applications including sensors [2], biomedicine [3] and catalysis [1,4]. In terms of catalytic applications, transition metal and metal oxide nanoparticles have been reported to be highly active and selective in a number of processes including redox [5–7] and C–C and C-heteroatom couplings [8,9]. In particular, supported iron oxide nanoparticles have been the subject of most research endeavours from our group over the past years [8–12].

The most promising feature of such nanoentities is the bifunctional oxidative and acidic nature which in turn can be fine tuned to design highly active materials for both oxidation (e.g. alcohols, alkenes) [10] and acid-catalysed processes (e.g. alkylations) [11], as well as potentially in tandem acid/redox catalysed processes such as isomerisation–cyclisation/oxidation reactions. Apart from conventional impregnation/deposition protocols, several methodologies have been reported to prepare the aforementioned supported transition metal nanoparticles including co-precipitation [13], microwave irradiation [1,4,14], ultrasounds [15] and others [16].

We recently devised a novel dry milling approach to achieve the desired iron oxide nanoparticle decoration on the surface of mesoporous aluminosilicates [17]. This methodology involves simultaneous milling of the metal precursor (e.g. $FeCl_2$) and the mesoporous support (e.g. aluminosilicate), both in the solid phase, using a planetary ball mill. By means of this methodology, metal precursors undergo hydrolysis generating the corresponding hydroxides, which upon calcination subsequently form highly dispersed iron oxide nanoparticles on the surface of the support [17]. Despite their minimum Fe content (<0.2 wt% Fe), these materials were found to be highly active in the microwave-assisted selective oxidation of benzyl alcohol to benzaldehyde. Preliminary results were also obtained in the microwave-assisted alkylation of toluene with benzyl chloride [17]. Comparatively, the aluminosilicate support was poorly active in both processes.

Following these preliminary results, herein we report a detailed study of the activity of ball-milled prepared supported iron oxide nanoparticles on mesoporous aluminosilicates (Al-doped SBA-15 and MCM-41 with Si/Al ratio of 20 prepared as reported elsewhere [10]) in acid catalysed processes such as the alkylation of toluene with both benzyl chloride (Lewis acid-promoted) and benzyl alcohol (Bronsted acid-catalysed) under microwave irradiation and conventional heating conditions. These reactions generally require the utilisation of highly acidic materials as catalysts [18]. The catalytic properties of the ball-milled prepared materials in

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the aforementioned reactions were compared to those of similar materials prepared by microwave methods.

2. Experimental

2.1. Ball-milled assisted preparation of iron oxide nanoparticles

In a typical synthesis of ball-milled materials, 0.2 g Al-SBA-15 support was grinded with the adequate amount of iron precursor ($FeCl_2{\cdot}4H_2O$) 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 min at 350 rpm. The resulting materials (Fe/Al-SBA) were then subjected to two different conditioning methodologies to ensure the removal of all unreacted precursor species: (i) soaking with 2 mL water followed by a microwave treatment for 5 + 5 min in a domestic LG MS 19296/00 (maximum power 800 W). The final material (denoted hereafter as Fe/Al-SBA-W) was eventually thoroughly washed with 50 mL water and then calcined at 400 °C under air for 4 h. (ii) Soaking with 2 mL H_2O_2, microwaved (5 + 5 min at the same conditions as with H_2O_2), thoroughly washed with 50 mL water and calcined at 400 °C for 4 h (Fe/Al-SBA-HP). Fe content of the catalysts was estimated by EDX. We note that Al-MCM-41 was not selected as support in ball-milling experiments due to its reduced stability under the ball milling preparation conditions as compared to Al-SBA-15. Consequently, an alternative microwave-based route was used to prepare the Fe/Al-MCM-41 as described below.

2.2. Microwave synthesized materials

These materials were prepared following a methodology previously reported [10,19]. Briefly, the aluminosilicate support (Al-MCM-41, 0.2 g) and the desired quantity of iron precursor ($FeCl_2{\cdot}4H_2O$) to achieve a 1 wt% loading dissolved in a acetone/ethanol mixture (1:1, v:v) were placed on a pyrex vial and microwaved at two different power settings (150 and 300 W) for 15 min in a CEM-DISCOVER microwave reactor in closed-vessel (pressure controlled) and power controlled method (maximum temperature reached 100–120 °C). The resulting coloured materials was then filtered off, thoroughly washed with acetone, ethanol and water, dried overnight at 100 °C and calcined at 400 °C prior to its utilisation in the investigated reaction. The two materials prepared were denoted as Fe/Al-MCM-MW-150 (150 W power) and Fe/Al-MCM-MW-300 (300 W power).

2.3. Material characterisation

Pyridine (PY) and 2,6-dimethylpyridine (DMPY) titration experiments were conducted at 200 °C via gas phase adsorption of the basic probe molecules utilising a pulse chromatographic titration methodology [20,21]. 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 catalyst 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.

Diffuse Reflectance Fourier-Transform Infrared (DRIFT) spectra of adsorbed PY were carried out in an ABB IR-ATR instrument equipped with an environmental chamber. PY was adsorbed at room temperature for a certain period of time (typically 1 h) to ensure a complete saturation of the acid sites in the catalyst and then spectra were recorded at different temperatures according to the previously reported methodology [20]. With this purpose, the different types of acid sites in the materials (Brönsted and Lewis) could be measured and quantified.

Iron content in the materials was quantified by TEM-EDX and AAS or ICP/MS as previously reported [10,17], showing consistent results between materials and samples.

2.4. Catalytic activity

2.4.1. Conventional heating

In a typical experiment, 10 mL of toluene and 1 mL of benzyl alcohol or benzyl chloride were pre-heated at 110 °C in a round bottomed flask for a few minutes and then 0.1 g of catalyst was added to the reaction mixture, which was further stirred at 110 °C for 10–12 h until reaction completion. The filtrate was 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. The blank reaction showed the thermal effects in the reaction were negligible (less than 5% conversion was obtained after 24 h). 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.

2.5. 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 a pressure-controlled CEM-Discover microwave reactor for 3 min at 300 W (110–120 °C, maximum temperature reached) under continuous stirring. Samples were then withdrawn from the reaction mixture and analysed in a similar way to that reported above. The microwave method was generally temperature controlled (by an infra-red probe) where the samples were irradiated with the required power output (settings at maximum power, 300 W) to achieve the desired temperature.

3. Results and discussion

As indicated in Section 2, the acid properties of the materials were measured using a pulse adsorption chromatographic mode using pyridine (PY) and 2,6-dimethyl pyridine (DMPY) as probe molecules [20]. A recent report by Anderson et al. discloses that DMPY has the ability to titrate some Lewis acid sites (mainly those on edges and imperfections originated by a low temperature calcination—200 °C) in silica–alumina systems [22]. However, the nature and synthetic protocol of the current systems is likely to minimise the presence of such claimed defects thus maximising DMPY adsorption on Brönsted sites and validating our protocol.

Results included in Table 1 show, in general, the remarkable differences in acidity of the synthesized materials (as compared to the parent aluminosilicate support) upon iron incorporation, mostly in terms of Lewis acidity (2–4 times the Lewis acidity of the support). Interestingly, Brönsted acidity also increased in some cases as compared to the parent support, especially for microwave materials in which a larger Fe content was present (ca. 0.5 wt%). Nevertheless, the observed increase in both Brönsted and Lewis acidity for extremely low loaded materials (e.g. Fe/Al-SBA-W containing only a 0.04 wt% Fe) is a remarkable feature of the proposed synthetic methodology which points to a synergetic effect Fe/Al in

Table 1
Surface acid properties measured via adsorption of PY and DMPY (200 °C) of supported iron oxide nanoparticles on various aluminosilicates.

Catalyst	Fe loading (wt%)	PY (μmol g^{-1})	DMPY (μmol g^{-1})	Lewis acidity[a] (μmol g^{-1})
Al-MCM-41	–	135	88	47
Fe/Al-MCM-MW-150	0.60	352	169	183
Fe/Al-MCM-MW-300	0.63	269	165	104
Al-SBA-15	–	80	36	44
Fe/Al-SBA-W	0.04	162	37	125
Fe/Al-SBA-HP	0.08	101	52	49

[a] Lewis acidity obtained as the difference between DMPY and PY data.

the materials, similar to that observed in previously reported oxidation reactions [10]. Ball milling and/or microwave irradiation of the aluminosilicate support did not originate any structural or acidity changes in the materials so that the Fe/Al synergetic effect in the materials (due to the deposition of the iron oxide nanoparticles) is believed to be the main reason for the enhanced acidity.

DRIFTs spectra of selected materials (microwave vs ball milled samples) are depicted in Fig. 1. An increase in Brönsted (B) and particularly Lewis (L) acidity in the characteristic peaks at 1543 and 1454 cm^{-1}, respectively, can be clearly spotted in the DRIFTs spectra even at remarkably low Fe loadings (0.04 wt%, Fe/Al-SBA-W). These results were in general in good agreement with those obtained in the PY titration experiments (Table 1). Remarkably, materials possessed noticeable acidities (both Brönsted and Lewis) even at temperatures as high as 200–300 °C (Fig. 1, bottom, spectra d) for which the presence of these sites is still marginally distinguishable from the background noise. This enhanced acidity is highly valuable for acid catalysed processes such as the alkylation of toluene.

Importantly, acidity measurements from both methodologies (PY DRIFTs and most importantly PY and DMPY pulse chromatography titration data) were generally in good agreement between them, supporting the validity of our assumption on DMPY adsorbing selectively on Brönsted acid sites.

Aromatic alkylation processes are among the most versatile and widely investigated processes which can grant access to a wide range of compounds as important intermediates, fragrances, agrochemicals and pharmaceuticals [23,24]. In particular, the alkylation of toluene with benzyl chloride or benzyl alcohol has been reported to be promoted by Lewis and Brönsted acid sites, respectively [18]. In this way, this test reaction is a promising approach to distinguish between Brönsted and Lewis sites in the materials.

Initially, the activity of the synthesized supported iron oxide nanoparticles in the alkylation of toluene with benzyl alcohol was screened under conventional heating. In general, all materials possessed comparatively improved activities compared to the parent support, with complete conversions obtained after 2–3 h of reaction (data not shown) regardless of the method of preparation (ball milling or microwaves). The comparison of activity with time of reaction for the particular case of microwave prepared materials has been included in Fig. 2.

However, the striking differences in terms of activity were observed for microwave-assisted experiments. Microwaves have been reported as a highly useful tool to speed up rates of reactions in heterogeneously catalysed processes as well as often improving selectivities to the target products [25]. Reactions run under microwave irradiation are summarised in Table 2.

In general, both ball-milling and microwave prepared materials provided remarkably superior activities to those of their respective supports in both the alkylation of toluene with benzyl chloride (Lewis promoted) and benzyl alcohol (Brönsted promoted). Nevertheless, ball-milled materials exhibited an unusual activity under microwave irradiation conditions despite their extremely low Fe

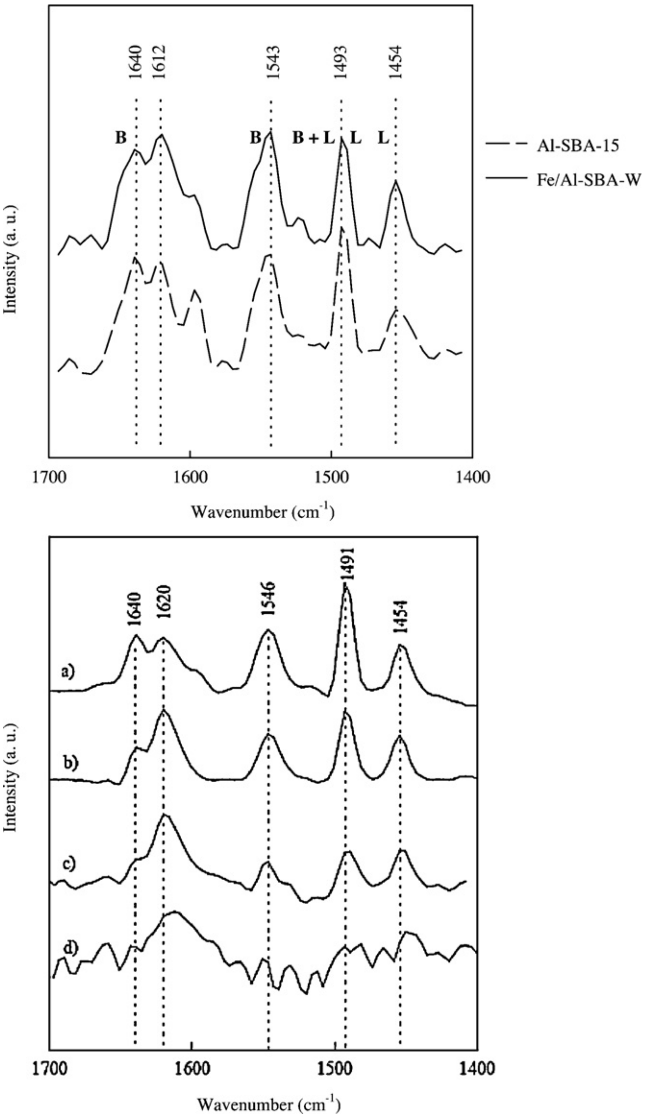

Fig. 1. DRIFTs of (top figure) PY adsorption on Al-SBA-15 (dashed line, bottom spectrum) and Fe/Al-SBA-W (solid line, top spectrum) and (bottom figure) Fe/Al-MCM-MW-300 material at different temperatures: (a) 100 °C; (b) 150 °C; (c) 200 °C; (d) 300 °C.

Table 2
Activity of Fe/Al-SBA-15 materials in terms of total conversion of starting material (X_T, mol%) and selectivity to 1-benzyl-2-methylbenzene (S_{F2}, mol%) in the alkylation of toluene with benzyl chloride and benzyl alcohol under microwave irradiation.

Catalyst	Benzyl chloride		Benzyl alcohol	
	X_T	S_{F2} [a]	X_T	S_{F2} [a]
Blank	–[b]	–	–	–
Al-MCM-41	–	–	27	49
Fe/Al-MCM-MW-150	81	53	62	46
Fe/Al-MCM-MW-300	60	52	65	50
Al-SBA-15	<10	50	<20	52
Fe/Al-SBA-W	>99	52	47	50
Fe/Al-SBA-HP	85	45	52	47

Reaction conditions: 2 mL toluene, 0.2 mL alkylating agent, 0.025 g catalyst, microwave irradiation, 300 W, 110–120 °C, 3 min reaction.

[a] The remaining selectivity to 100 corresponds to the formation of 1-benzyl-4-methylbenzene.

[b] No reaction.

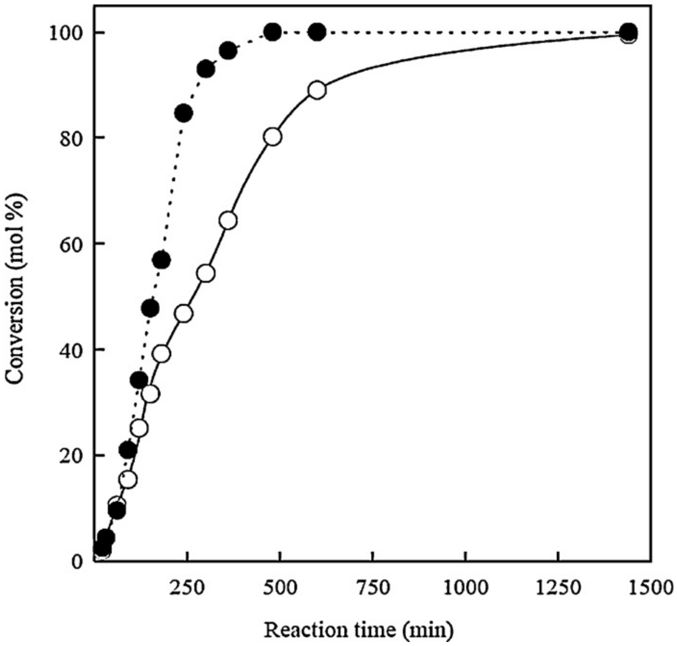

Fig. 2. Activity comparison of Al-MCM-41 (white symbols) and Fe/Al-MCM-41 (black symbols) (conversion vs time of reaction) in the alkylation of toluene with benzyl alcohol under conventional heating. Reaction conditions: 10 mL toluene, 1 mL benzyl alcohol, 0.1 g catalyst, 110 °C.

loadings (<0.1 wt% Fe). Thus, an almost quantitative conversion of starting material was obtained for Fe/Al-SBA-W in the alkylation of toluene with benzyl chloride after 3 min reaction, as compared to a moderate 45% observed using benzyl alcohol as the alkylating agent (Table 2). These results are in good agreement with those previously reported in our group with similar ball-milled Fe/Al-SBA materials in the microwave-assisted alkylation of toluene with benzyl alcohol (50% conversion to alkylation product) [17]. Remarkably, as shown in Table 2, activities obtained for ball-milling materials for both alkylation reactions were at least comparable to those obtained for materials prepared under microwave irradiation, despite their significantly lower Fe content (0.5 wt% vs 0.04 wt%). Also, when compared with materials prepared by conventional impregnation techniques with ten times higher iron content, ball-milled Fe/Al-SBA materials showed higher activities in the alkylation of benzene with benzyl alcohol [17]. Ball-milled materials also showed superior activities compared with other SBA-15 based materials such as AlGa-SBA-15. The Ga-doped mesoporous materials showed low activities after 3 h (conversion <10%) in the conventional heating alkylation of benzene with benzyl chloride [27]. Reused Zr-SBA15 materials showed, however, higher activities than their Ga-counterparts (complete conversion after 1 h) at similar conditions [28]. Nevertheless, longer reaction times are generally required under conventional heating conditions (6–12 h) as compared to the 3–5 min required to achieve almost quantitative conversion of the starting material under microwave irradiation over Fe/Al-SBA (Table 2). This represents a great advantage in terms of time and energy consumption that, together with the simplicity of preparation of ball milled materials as compared with other protocols, give this approach a valuable green character.

The activity of microwave-prepared Fe materials generally correlated well with the acid properties of the materials (Table 1), in good agreement with the Lewis and Brönsted acid sites of the materials promoting the alkylation with benzyl chloride and alcohol, respectively. Comparatively, the high activity obtained (especially in the reactions run under microwave irradiation) for ball-milling synthesized materials does not particularly correlate well with their measured relatively low acidity, so there seem to be other important factors influencing the catalytic activity in these materials.

Acidity may in fact influence the activity in the materials but there are two key properties on ball milled materials that make them unique as compared to those obtained under microwave irradiation: the accessibility of the active sites (which has been maximised due to the presence of the iron oxide nanoparticles in the external surface of the supports [10,17]) and the small nanoparticle sizes (typically 2–3 nm) of the iron oxide supported nanoparticles. These two properties have been already proved to be crucial in other related chemistries for the transformation of bulky molecules [17,26]. The presence of uniform and small nanoparticles supported in the aluminosilicates and the previously reported synergy observed between Fe and Al [10] may prevent the loss of metals as well as their sintering, therefore leading to an increase in activity. The small nanoparticle size distribution previously reported in ball-milling materials (2–3 nm) [17] as compared to that obtained for microwave prepared materials (4–6 nm) [10–12] might as well contribute to an uniform performance of the catalyst.

Furthermore, the presence of such small and homogeneously distributed nanoparticles on the external surface of the supports (being the ball-milling approach mainly a surface phenomenon) also improves the accessibility of the reactants to the active sites and may contribute to the observed increase in activity. In any case, the combination of these features turned ball-milling materials into highly active and better performing catalysts as compared to "classical" catalysts prepared by other conventional methods.

4. Conclusion

The alkylation of toluene with benzyl chloride and alcohol as alkylating agents has been investigated using different iron oxide nanoparticles supported on aluminosilicate materials (Al-MCM-41 and Al-SBA-15) prepared using two novel methodologies, namely microwave-assisted and dry milling deposition. Unexpected activities in the investigated reactions were obtained for low Fe content (<0.1 wt%) ball-milled materials, particularly under microwave irradiation. In spite of their low acidity as compared to other microwave-prepared materials, the presence of small and homogeneously distributed nanoparticles on the external surface of the supports is believed to contribute to the observed unexpected activities which were in all cases at least comparable to those of higher Fe content (>0.5 wt%).

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