**Different dispersions of group II catalysts over SBA 15 and MCM-41: Effects on transesterification reactivity.**

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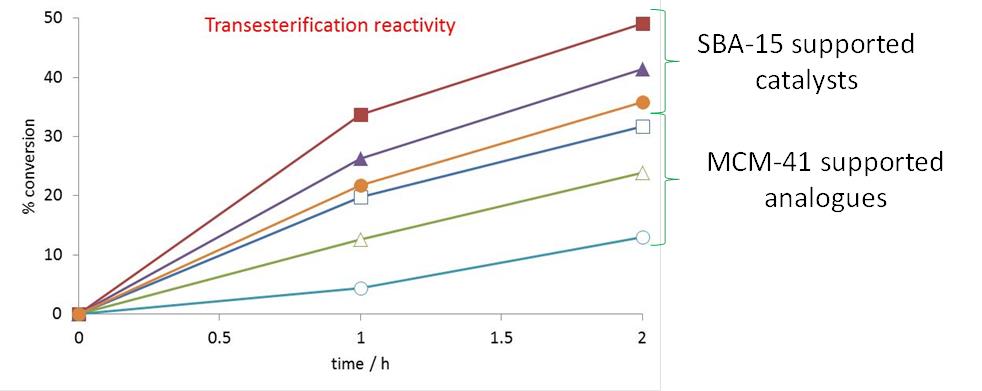
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**Abstract**. Activities of CaO catalysts on SBA-15 and MCM-41 have been compared in transesterification and SBA-15 supported samples invariably more active than those on MCM-41. Increased activity is not due to diffusional effects (as measured using substrates of differing size) but rather to increased dispersion of CaO on SBA-15 (as measured using NOx TPD). The effect, i.e. increased reactivity of SBA-15 supported catalysts being related to increased dispersion, is also noted in supported BaO catalysts while supported MgCO3 catalysts show little variation in dispersion (or in reactivity) as a function of the support used.

**Keywords:** mesoporous SiO2, catalyst characterisation, transesterification.

Graphical Abstract

Research highlights

* SBA-15 supported catalysts are more active than MCM-41 supported analogues
* The effect is independent of the nature of the active phase (Ca/Ba)
* It is also independent of the condition of the mesoporous SiO2 and substrate size
* Ba2+ and Ca2+ active phases are more dispersed on SBA-15 than on MCM-41

**1 Introduction**

MCM-41 and SBA-15 mesoporous SiO2 materials have found wide application as catalyst supports since they were first developed [1-4]. In several specific reactions it has been found that SBA-15 supported materials are more active and stable catalysts and this has been related to their larger pore sizes (which mitigates against diffusional constraints) and their thicker pore walls (which promotes the maintenance of structural stability). These features have also been used to explain the benefits of SBA-15 over MCM-41 as supports for alkaline earth catalysts in the important triglyceride transesterification reaction [5, 6].

Triglycerides consist of three long chain fatty acid esters on a glycerol backbone. They are the principal components of vegetable oils and animal fats and recently there has been significant interest in their conversion to fatty acid methyl esters (FAME) [7] and use as biodiesel fuel substitutes.

Under ideal conditions (notwithstanding social, economic and other serious environmental problems associated with their use [8, 9]) such molecules might provide a carbon-neutral fuel supply to augment or substitute hydrocarbon fuels that are currently derived from non-renewable petroleum resources [10].

Traditionally, the catalysts used to promote the transesterification reaction have been aqueous phase basic materials such as solutions of NaOH or KOH [11]. There are several problems associated with these catalytic solutions, including separation and recycling issues, the production of alkaline waste streams and the formation of soaps within the reaction mixture [12].

These problems have led to a significant amount of research into solid acid [13] and basic [14-17] catalysts to carry out the transesterification reaction. Of the basic materials that have been studied, supported and unsupported group II oxide materials are amongst the most prevalent.

Various types of mesoporous SiO2 (MPS), in particular MCM-41 and SBA-15 have been used as such supports. Of specific relevance to this work, Maireles-Torres *et al*. [5] have studied supported CaO on MCM and SBA-15 and report that the latter support formed more active catalysts. They ascribed this to the increased stability of SBA-15 over MCM-41. Li and Rudolf [6] have noted a similar effect on MgO supported catalysts (albeit at significantly higher temperatures (220 °C)) when they compared SBA-15, MCM-41 and KIT as supports.

Here we have looked at the reactivity of model CaO / MPS catalysts (where MPS is MCM-41 or SBA-15) under conditions where structural stability is not compromised (50 °C, atmospheric pressure, in the absence of any extreme pH) and noted similar results.

We have explored whether the increased reactivity is related to diffusional effects (through the use of differently sized triglyceride reactants) and dispersion of the active phase (through the use of NOx TPD measurements) and concluded that the group II active phase is more dispersed on the SBA-15 support than the MCM-41 analogue. We propose that this effect is responsible for the increased catalytic reactivity of the SBA-15 supported materials. We show the effect (increased activity and increased active phase dispersion) is also present in related Ba-containing catalysts while Mg-containing analogues show similar activities to one another (and interestingly also have similar active phase dispersions).

**2 Experimental**

**2.1 Preparation of Mesoporous SiO2 Materials**

The materials used in the preparation of MCM-41 were tetraethylorthosilicate (TEOS) as the silica source, cetyltrimethylammonium bromide (CTAB) as the surfactant, NH4OH (for pH control) and distilled H2O. Many synthesis procedures have been detailed in the preparation of MCM-41 and we have adapted that of Cai *et al.* first reported in 2001 [18].

Changes to the above used in the preparation of the SBA-15 catalysts involved the use of pluronic 123 as the surfactant and HCl (for pH control). Once again, numerous methods have been reported in the synthesis of SBA-15 and we have adopted that first published and since widely cited, by Zhao *et al.* in 1998 [19].

**2.2 Preparation of metal oxide/carbonate modified mesoporous materials.**

Appropriate masses of calcium acetate (or Ba / Mg acetate) were dissolved in H2O (to the pore volume of the support) and samples of 0.9 g of MCM-41 or SBA-15 were impregnated with the solutions giving eventual theoretical mass loadings of 13.8% MgO, 10.6% CaO and 10.0% BaO in any final oxide material (note: the MgO phase never forms, as MgCO3 is the product of magnesium acetate calcination under these conditions [20]).

The samples were then dried at 80 °C overnight and then calcined at 800 °C for 5h in order to ensure the conversion into its oxide state [20]. This treatment results in some degradation of the MPS structures (as measured by SAXS). Mg and Ba containing catalysts were calcined at 600 °C to produce samples of supported BaO and MgCO3 [20] respectively.

**2.3 Characterisation techniques**

Nitrogen adsorption/desorption isotherms were recorded using a Quantachrome NOVA 2000E Series instrument. The BET method was used to determine surface area while the BJH treatment was applied to the data to determine pore sizes.

Powder XRD measurements were performed on a Siemens D500 Kristalloflex using CuKα radiation over a 2θ range of 20 – 60 °, while SAXS measurements were performed on an Anton Paar SAXSees mc2 over a q range of 0.05 – 5 nm-1.

Temperature Programmed Desorption (TPD) experiments involved saturating the surface of a catalyst in a flow of NO/O2 (an acidic gas mixture to probe surface basic sites) at low temperature (50 °C) to prevent bulk nitrate formation. After saturating the catalyst surface and removing physisorbed NOx, the catalyst was subjected to a temperature ramp to remove the adsorbed species. A mass spectrometer continually monitored the exit gas.

**2.4 Activity studies**

The activities of the catalysts in the transesterification of short and long chain model triglycerides and a commercial rapeseed oil were analysed. The reactions used a triglyceride: methanol molar ratio of 1:9, a catalyst loading of 1 wt.% (relative to the oil mass) and a reaction temperature of 50 °C with constant stirring.

1H NMR was used as a quantitative method to monitor reaction progress. We used a similar technique to that described by Morgenstern *et al.* [21] Aliquots of reaction mixture were removed from a batch reaction at t = 1, 2, 3, 4, 5, 6 and 24 h and prepared for analysis by 1H NMR in deuterated chloroform using acetone as a standard. The integrated value of the acetone CH3 peak (~ 2.17 ppm) was compared to that of the methyl group of the methyl ester CH3 peak (~ 3.67 ppm) for quantification.

**3 Results and Discussion**

**3.1 Characterisation studies**

The measured surface area of MCM-41 was 955 m2 g-1 while its pore size was 3.1 nm. In the case of the SBA-15 material the surface area and pore size were 653 m2 g-1 and 9.6 nm respectively.

Impregnation of calcium acetate and calcination at 800 °C for 5 h resulted in falls in the surface areas to 368 m2g-1 (for the MCM-41 supported sample) and to 207 m2g-1 (for the SBA-15 supported materials). The pore sizes also fell (to 2.7 nm and 7.6 nm respectively) and these data are in line with results previously published [22, 23].

X-Ray characterisation (see supporting information) confirmed that these supports are essentially amorphous [23] (figure S1). A broad peak centrered at 2 θ ~ 23 ° in the profiles of both materials relates to the presence of amorphous silica [24]. XRD evidence for CaCO3 and CaO (following different calcination treatments) can also be seen on each sample. SAXS (Figure S2) gives information about the coherence of the support materials following the various preparations [25, 26].

This technique (figure S2) confirms significant changes to the Ca-containing materials following high temperature calcination, *i.e.* decreased pore ordering and a contraction of the unit cell, but has confirmed retention of the mesoscopic order and the hexagonal features of the support. MgCO3 and BaO catalysts show no change to the profiles collected from the support confirming little change to the pore structure or ordering following incorporation of precursors to these species and calcination to 600 °C (results not shown in S2).

**3.2 Temperature programmed desorption of NOx**

Neither SBA-15 nor MCM-41 adsorb or desorb appreciable amounts of NOx during the NOx TPD experiments, so all NOx measured during TPD arose from interaction with, and desorption from, the group II species. The principal results are detailed in Table 1. These include the total amount of NO desorbed (giving information about the concentration of surface sites), the temperatures of maximum desorption (giving information about the enthalpy of desorption – which is related to the basic strength of the material) and the ratio of NO desorbed to the total group II metal ion content in the material (giving information about the group II phase dispersion).

**Table 1**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MCM-41 | | | SBA-15 | | |
|  | mol NO desorbed g-1 | mol NO / mol M(II) | Tmax / °C | mol NO desorbed g-1 | mol NO / mol M(II) | Tmax / °C |
| CaO | 548 | 0.29 | 545 | 770 | 0.41 | 540 |
| BaO | 359 | 0.55 | 595 | 573 | 0.88 | 595 |
| MgCO3 | 571 | 0.17 | 475 | 563 | 0.16 | 470 |

Table 1. Showing the number of moles of NO desorbed in TPD experiments g-1 of catalyst and mole-1 of group II cation from MCM-41 and SBA-15 supported catalysts. The Tmax of each desorption profile is also shown.

In all cases a single NOx desorption peak was seen – confirming that only one type of adsorbed surface nitrate species formed following the treatment in NO + O2 at 50 °C. Surface basicity (as measured by the temperatures of maximum desorption) tallies with the basicity of the different materials (which increase down group II).

Regarding the substantive issue in this work (where we are seeking information about the dispersion of the active phase) we can draw several conclusions from the data.

In the case of the supported CaO catalysts the dispersion varied depending on the particular mesoporous support used with the oxides supported on SBA-15 having a greater dispersion than those supported on MCM-41.

This is relatively surprising given the larger BET surface area of the latter compared to SBA-15 (both before and after calcination). So, even though MCM-41 supports have a far higher BET surface area, the species deposited on the SBA-15 support following incipient wetness impregnation, are more dispersed (leading to eventually more dispersed oxide phases following calcination).

The same is true for the BaO catalysts but this effect is not seen over MgCO3 catalysts where equivalent amounts of NOx were desorbed from both the SBA-15 and the MCM-41 supported materials (recall treatment at 600 °C leads to the formation BaO and MgCO3 from calcination of the analogous acetates).

**3.3 Activity studies**

Before discussing the activity of the various catalysts in these reactions it should be noted that there was no reactivity in the absence of catalysts and that the mesoporous SiO2 materials also showed no reactivity. Therefore, catalytic activity is related to the presence of the group II oxide (CaO or BaO) or carbonate (MgCO3) on the materials.

Elemental analysis of the catalysts before and after reaction confirmed there was no substantial leaching of group II materials from the catalyst to the solution during reaction. This is unsurprising given the relatively low temperatures (50 °C) at which the reactions were carried out. Finally, catalyst recycling experiments showed that, while catalytic activity decreased upon recycling, this was not due to leaching of active material from the catalyst but rather related to the deposition of organic material onto the active sites (reactivity could be restored by a calcination treatment).

While these features are interesting in themselves, the purpose of this contribution was to compare the effects of the different supports on reactivity and we will not comment on them further here.

Figure 1 shows the activity profiles for the six catalysts in the conversion of triacetin (a model triglyceride containing acetate esters on a glycerol backbone). It is clear that CaO supported catalysts are the most effective, followed by BaO supported materials with supported MgCO3 catalysts being the least effective in catalysing the transesterification.

What is of more specific interest in relation to this work is the fact that in the cases of the Ba and Ca catalysts the SBA-15 supported materials are more active than their MCM-41 supported analogues. Recall that in both of these catalytic systems the dispersed oxide phase was more dispersed on the SBA-15 support than on the MCM-41 analogue (see table 1) so reactivity correlates with dispersion.

**Figure 1**

Figure 1. Activity versus time profiles from the conversion of triacetin over mesoporous SiO2 supported CaO (▲,△), BaO(⚫,🔾) and MgCO3 (◼,🞐). Filled symbols represent SBA-15 supported catalysts and empty symbols represent MCM-41 supported materials.

Neither of the two MgCO3 catalysts is particularly active and under these (low temperature) conditions. Regarding this work the interesting aspect is that both catalysts are essentially equivalent regarding reactivity (albeit with the SBA-15 supported materials converting slightly more substrate in the earlier parts of the reaction). It should be recalled that the NOx TPD measurements of basic site distribution on these catalysts suggests their dispersions were equivalent (see table 1).

Therefore, while the nature of the active phase is important in determining the overall reactivity (CaO > BaO > MgCO3), there is a noticeable effect associated with the support in the case of the BaO and CaO catalysts.

Another feature that may be important is the pore sizes of the materials. SBA-15 materials have significantly larger pores than those of the MCM-41 materials and it should be considered whether this has an influence on the diffusion of reactants and products to and from the active sites of the material. It has previously been shown that diffusional constraints do not affect this reaction [27].

In order to extend this comparison, the activity of CaO-containing catalysts were further analysed in reactions where the substrate was changed. We looked at larger model triglycerides, i.e. triglyceryl octanoate (C8) and a commercially available rapeseed oil (~C19). The results of these reactions are presented in figure 2 where the conversion to FAME is shown as a function of reaction time.

**Figure 2**

Figure 2. Activity versus time profiles from the conversion of triacetin (◼,🞐), triglyceryl octanoate (▲,△) and a commercial rapeseed oil (⚫,🔾) over mesoporous SiO2 supported CaO. Filled symbols represent SBA-15 supported catalysts and empty symbols represent MCM-41 supported materials.

The most obvious result from these experiments is that the reaction is more rapid when the substrate is a shorter chain triglyceride with larger triglycerides being more difficult to convert. Apart from this, it is clear that the Ca-containing catalysts supported on MCM-41 are less active than those supported on SBA-15 for all the different reactions. The fact that the effect is equivalent, irrespective of the size of the substrate molecule suggests that diffusion is not an important feature here.

**4 Conclusions**

The main result we present in this work is that, even in the absence of diffusional limitations in the reactions themselves [26], for Ca and Ba supported catalysts; the larger pored SBA-15 supported materials are invariably more active than smaller pored MCM-41 analogues.

The effect is independent of the composition of the active phase and also independent of the pre-treatment of the catalyst. It is also independent on the size of the triglyceride substrate used (suggesting this effect is not related to diffusion).

It appears to be related to the different dispersion of the active phase over each (as measured using NOx TPD). SBA-15, notwithstanding its smaller surface area, generates more dispersed group II oxide catalysts than MCM-41.

While both sets of catalysts were prepared using incipient wetness impregnation of aqueous solutions of acetate salts, it seems that the manner in which these deposited onto the MPS surfaces following H2O evaporation has led to more dispersed active phases in the SBA-15 catalysts than in the MCM-41 analogues.

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Supplementary information

**Figure S1**

Figure 1. Displaced XRD profiles of (from bottom) MCM-41, SBA-15, CaCO3 / MCM-41, CaO/MCM-41, CaCO3/SBA-15 and CaO/SBA15 (top).

**Figure S2**

Figure S2. Displaced SAXS profiles of MCM-41 (◆), CaO/MCM-41 (◼), SBA-15 (⚫) and CaO/SBA-15 (⏶) supported catalysts.