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Nanoparticles of Fe_2O_3 inserted in SBA-15 silica at micropore mouth level: An experimental evidence of the confinement effect

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ABSTRACT

Nanometric Fe_2O_3 particles could be inserted inside the internal pore volume of SBA-15 mesoporous silica when Fe(III) chelates (EDTA, gluconate and citrate) were used as impregnating precursors. Fe(III) nitrate preferentially yields 8 nm uniformly sized Fe_2O_3 clusters that selectively plug the SBA-15 channels through a geometric confinement effect. An oxidative degradation of Fe-chelate precursors yielded Fe(III) oxidic particles of various sizes and dispersion, depending on the nature and geometry of chelate anion. Fe(EDTA) precursors specifically generated Fe_2O_3 nanoparticles that selectively migrate towards two types of positions where the silica surface exhibits a high curvature. In samples involving low Fe loadings, Fe_2O_3 particles first creep towards the silica micropore mouths (nests), in which they are readily confined and stabilized. For higher Fe loadings, when most of the micropore nests were filled, oxidic particles eventually settle as a superficial film on the mesopore walls and undergo stabilization onto the surface roughness that can also favors their confinement, as theoretically predicted by Derouane and co-workers. Upon further reduction, as selectively followed by combined cyclic voltammetry and TPR, Fe_2O_3 readily yield FeO nanoslabs that remain even more efficiently confined within their respective nest positions through a further acid–base type stabilization.

1. Introduction

In 1985, Anderson et al. [1] suggested that the strength of van der Waals type bonding of molecules (e.g. water, hydrocarbons...) on solids could be proportional to the curvature of the solid surface (e.g. internal surface in zeolites). Derouane [2] extended this concept by proposing the concept of "nest effect" image, wherein a (basically gaseous) molecule and its direct (basically solid) environment tend reciprocally to optimize their van der Waals interaction. The new concept emphasized that stereochemical, rather than diffusional effects, favor sorbate molecules to reach minimum energy points on the host (zeolite...) surface. The neat result is an increase of the sorption equilibrium constant and, hence, the local concentration of sorbate species, thereby further affecting the overall reaction kinetics. Nest effects not only concerned highly curved intracrystalline volumes in porous materials (zeolites) but also any active site (located on a flat surface) that sterically favors, through its own geometry, the confinement of a sorbate molecule. Alkylation of aromatics, as reported by Ducarme and Védrine [3], was among the first experimental observations to be readily explained by the "nest effect". Derouane et al. [4,5] could further quantify the role of surface curvature of the "nesting concept". For comparable sizes and shapes of the host surface and of the sorbate, these authors could describe the interaction energy between the host (curved) site and the guest molecule by proposing a simple van der Waals model. In short, the van der Waals interactions are amplified by the curvature of the pore walls with which the molecules optimally interact. The physisorption energy experimented by a guest molecule (idealized as a sphere), as it moves along a flat surface towards the pore opening (idealized as a hemispherical crater) indeed showed a very sharp drop as soon as the molecule sinks into the crater. Derouane and co-workers further demonstrated [4–6] that confinement of molecules in pores of near atomic size also affects various diffusional properties of molecules. They therefore proposed the concept of "floating molecule", where the mobility of small molecules increases when an optimal fit between the size and morphology of the sorbate and its close environment is achieved [4]. Among other examples derived from the so-defined confinement effect emerged the concepts of "molecular docking" [8], "molecular traffic control" [6,9,10] or "confinement catalysis" [6,7].

The "nest" and "confinement" effects developed by Derouane et al. for zeolites could be readily extended to mesoporous mate-

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rials by other groups. Such materials currently have mesopores that often present various pore wall “tortuosities” [11] but they can also involve some microporosity when prepared under specific synthetic conditions [12]. Various authors showed that conversions for some reactions, e.g. oligomerizeation of 1-butene [13] or acetalization of cyclohexanone with methanol [14] over mesoporous materials markedly increased when their pore diameters had restricted dimensions. In both examples, the highest activity was found for pore diameters close to 2 nm while it strongly decreased for narrower or for larger pore sizes, thereby discarding diffusion limitations. These findings were better explained by considering geometric and energetic effects based on the confinement model described by Derouane [4,7]. More recent determinations of the sorption energetics (measured through the corresponding heats of adsorption) in the case of isomerization of n-hexane over MCM-41 also suggested that geometric-dependent conditions (confinement effects) dominate over all other factors [15].

Several experimental evidences were reported showing that molecules can be embedded into narrow spaced voids of various matrixes on which they stay simply sorbed without further reaction. In most such cases, the term “confinement” then means the optimal fitting of a particle within a void space (usually channel) of similar dimensions (geometrical fitting), which does not necessarily imply any further energetic stabilization onto some rough surface, either in mesopores or on a more open system. As a typical example, xenon molecules were shown to first fill the very small mesopores of SBA-15 silica, where the strong sorption was explained by considering “sharp confinement effects” [11]. Similarly, dibenzodioxine was found strongly held only when the substrate pore size closely matches its molecular kinetic diameter, as in the case of mordenite or NaY zeolites that exhibit narrow pores, but not on mesoporous silicas in which they simply stay weakly H-bonded to the internal silanols [16]. Yang et al. [17] have prepared Pd nanoparticles that were found located both within the nanometer-sized SBA-15 silica walls and also within the micropores of the bimodal porous silica, where they could survive various oxidation–reduction treatments. Similarly, an effect of nanoscale pore space confinement on Zn particles was reported to occur when the latter were embedded in mesoporous alumina [18]. In that case, this nanoscale confinement was supposed to affect the particle sorption via the overlap of the electronic double layer within the mesopores, creating a surface complexation environment different from that of an unconfined surface.

Many metal oxide nanoparticles could be similarly encapsulated into the straight channels of various mesoporous silica substrates and stabilized through the same geometrical effect. The internal volume is then called “a confined reactor” into which particles should be considered rather as “encapsulated” (within the walls) than “anchored” (onto the rough surface). Typical recent examples deal with various transition metal oxides readily stabilized into SBA-15 channels through a perfect size fitting, after a controlled calcination of the corresponding precursors [19], or of nanosized La_2O_3 inserted within MCM-41 mesopore walls through some “stereoscopic confinement effect of the host channel on the guest” [20]. To our knowledge, no experimental evidence was reported demonstrating that solid (sub)nanoparticles could be stabilized on external surfaces of bulk substrates or on internal pore walls of mesoporous materials through an energetically favored stabilization on the surface roughness.

We have recently developed the preparation and characterization of a series of SBA-15 mesoporous silica-supported iron oxide composite catalysts, by using the so-called chelate route [21]. It was earlier proposed that when chelate-type transition metal-bearing precursors impregnate MCM-41 silica mesopores, a gel-like phase readily forms and favors, upon further drying, an optimal dispersion of the chelate over the substrate surface as a film, thereby preventing further sintering of the resulting metal oxidic particles after thermal degradation of the metal chelate precursor [22]. Our preliminary findings [21,23] on the Fe/silica system has lead to more elaborated conclusions. It was found that iron chelate precursors were first stabilized through hydrogen-type interactions with the superficial silanols of the silica substrate during the drying step of the impregnated composites. This stabilization caused a decrease of the interaction of the chelate anions with their Fe(III) counterions that were readily released and converted into (sub)nanometric Fe_2O_3 particles during the subsequent chelate thermal degradation. Only strong chelates such as Fe(III)-EDTA had yielded sub-nanometric stable and extremely well dispersed Fe_2O_3 particles. Conversely, the pores of the Fe/SBA-15 composite prepared using Fe(III) nitrate were filled with Fe_2O_3 isolated but more bulky particles, their size being limited by the mesopore diameter of the substrate. In a further in depth comparative study of both systems (Fe-chelate versus Fe nitrate) by combined thermal analysis [24], we have proposed a decomposition model in each case and explained why strong Fe(EDTA) chelates readily yield subnanometric oxidic particles while about 8 nm agglomerates were systematically generated when non chelating Fe precursors (Fe(III) nitrate) were used. While these latter were probably stabilized through an eventual encapsulation in the mesopores of equivalent diameter by a classical pore size/particle size fitting (geometric confinement), the remarkable thermal stability of the sub-nanometric Fe_2O_3 particles on the internal mesoporous surface is yet to be explained.

The aim of the present contribution is to further compare the role of different Fe precursors (Fe(III) nitrate and three different iron chelates, namely (Fe(III),Na)-EDTA, (Fe(III),NH_4)-citrate and Fe(II)-gluconate) in yielding Fe_2O_3 particles of variable sizes. In particular, we want to bring convincing experimental evidences arguing for a steady stabilization of Fe_2O_3 (sub)nanoparticles readily generated in the case Fe(EDTA)/SBA-15 composites prepared using increasing Fe(EDTA) loadings. More specifically, we wish to question whether their possible confinement within potential nests or traps intentionally generated onto the mesopore internal walls of SBA-15 prepared by selected synthesis recipes, could be the reason for their high dispersion and strong retention. Several complementary techniques, including TEM/EDX, nitrogen sorption isotherms, TPR and cyclic voltammetry were used to evaluate the final textural and redox properties of the calcined Fe/SBA-15 composites.

2. Experimental

2.1. Sample preparation

Pure siliceous mesoporous SBA-15 was prepared using classical literature procedures [25], but by varying the hydrothermal conditions so as to tailor the pore geometry and “tortuosity” of the substrate [12]. The surfactant, Pluronic P123, was dissolved in a mixture of water and HCl at 40 °C. Tetraethylorthosilicate (TEOS) was added to the surfactant solution and the mixture stirred for 24 h. It was then transferred to Teflon bottles and heated at 100 °C for 3 days. The white solid was filtered, washed with distilled water, air-dried and calcined at 550 °C for 8 h under flowing air. Two different batches with very similar properties were prepared (referred to as SBA-15/1 and SBA-15/2) (Table 1).

Dispersed Fe_2O_3 nanoparticles were generated through a TG/DTA-controlled calcination of the SBA-15/1 silica support containing different Fe(II) and Fe(III) chelate precursors, namely (Fe(III),Na)-EDTA, (Fe(III),NH_4)-citrate and Fe(II)-gluconate, as well as Fe(III) nitrate, used for comparison. Before being used as support, the calcined mesoporous silica was preliminary dehydrated into a Schlenck reactor under vacuum at 120 °C during 4 h. The iron