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Heterogeneous hydrogenation of nitroaromatic compounds on gold catalysts: Influence of titanium substitution in MCM-41 mesoporous supports

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ABSTRACT

A series of Ti-modified MCM-41 supports and their respective Au catalysts were prepared and characterized to study the effect of titanium into the support and on the characteristics of the Au surface species for heterogeneous hydrogenation of aromatic nitrocompounds. The systems were characterized by X-ray diffraction, Infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), diffuse reflectance UV–vis (DRUV–vis), N_2 adsorption–desorption isotherms, ICP-MS and X-ray photoelectron spectroscopy (XPS). Additionally, these catalysts were tested for the hydrogenation of nitrobenzene in a batch-type reactor using ethanol as the solvent at 25 °C. Based on a combined FT-IR and DRUV–vis was possible to conclude that the Ti(IV) is incorporated into the framework of MCM-41 and Ti-containing MCM-41 catalysts were more active than an MCM-41 unmodified catalyst. The Ti(X)-MCM-41 supports prepared with Ti 2.0 wt% incorporation showed the best catalytic performance, which was attributed to an optimal number of isolated Ti sites that increased the Au stability on the support surface. For this system, the effect of the H_2 pressure, solvent nature and recyclability of the catalyst was also studied. Finally, a quantitative structure property relationship (QSPR) model was obtained for the catalytic activities of *para*-substituted nitrobenzenes. The multilinear model considered two parametric descriptors: the sigma constant (σ) and the hydrophobic π-constant, which account for the electronic and hydrophobic effect of the substituents.

1. Introduction

Inorganic materials with controlled pore size distribution are very interesting because of the wide number of applications in which they are used [1]. In 1992, Mobil Corporation [2] reported a novel concept in the synthesis of molecular sieves that used the advantageous properties of surfactant molecules to self-assemble and form liquid crystal-type structures, creating a new family of mesoporous molecular sieves called M41S [3,4]. These types of solids have pore diameters ranging from 2 to 10 nm, a mesoporous volume ranging from 0.7 to 1.2 $cm^3\ g^{-1}$ [5] and large and accessible internal areas (higher than 1000 $m^2\ g^{-1}$). The most important and used mesoporous molecular sieve is MCM-41 because of its hexagonal arrangement of uniformly sized mono-dimensional pores and its reliable synthesis [6–9]. Thus, pure silica MCM-41, heteroatom-doped MCM-41, and functionalized MCM-41 materials have been widely investigated because they have important applications in catalysis, separation, and nano-engineering fields [10–16].

On the other hand, gold nanoparticles (Au NPs) supported on mesoporous oxides are widely employed as heterogeneous catalysts for fine chemical production [17,18]. It is well established that the catalytic activity of supported gold nanoparticles depends on the particle size and the nature of the support [19–21]. Among the reactions studied, the hydrogenation of nitroaromatic derivatives is important because the aromatic amines are intermediates in the production of a range of pharmaceuticals, agrochemicals, cosmetics, herbicides, dyes and polymers [22,23]. Moreover, hydrogenation using molecular hydrogen is non-polluting and is

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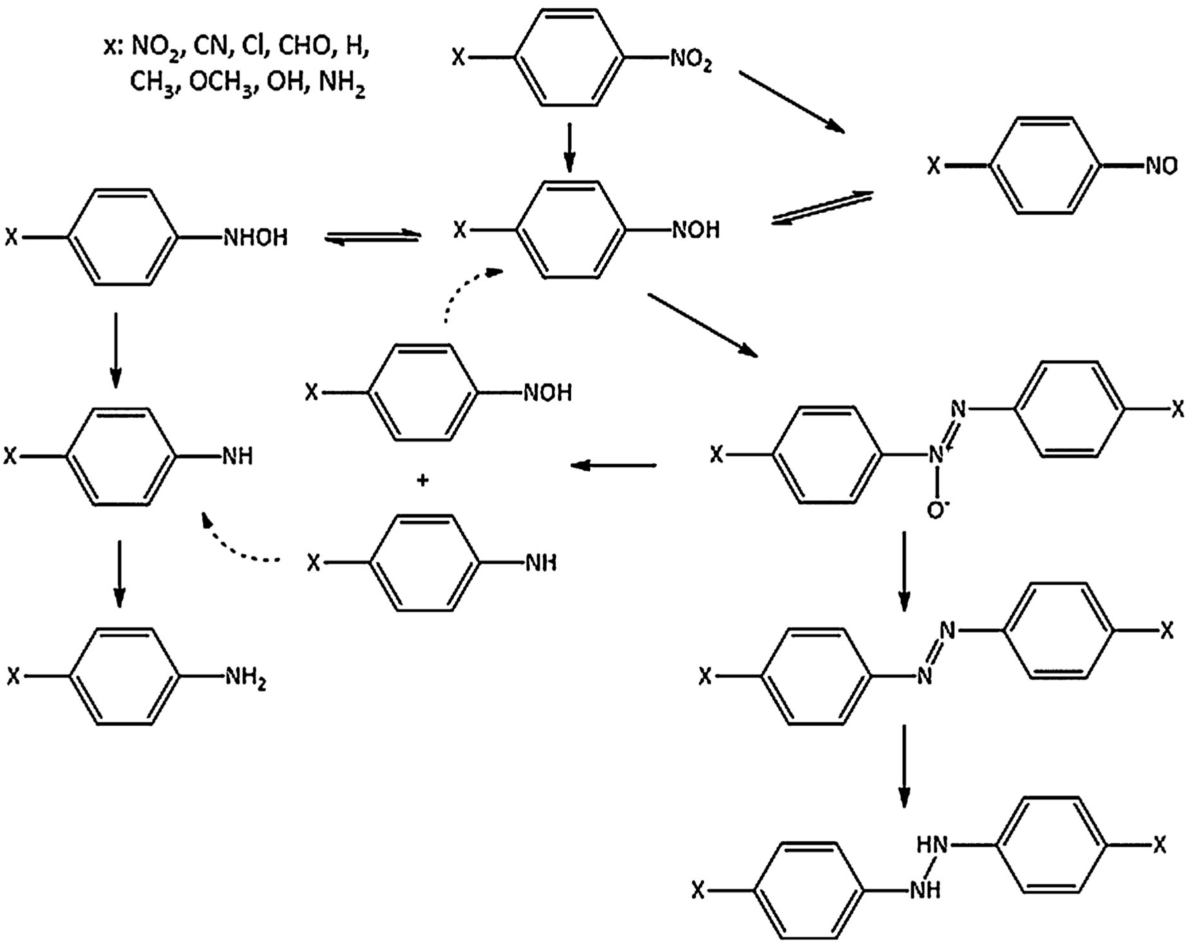

Scheme 1. Reaction pathways for *para*-substituted nitrobenzene hydrogenation (hydrogen and water are not depicted) adapted from Ref. [59].

considered an ecofriendly alternative to the commonly used reduction reactions to obtain the desired aromatic amines.

The use of Au as an active phase requires the development of newer and novel catalysts in order to achieve higher catalytic activity and selectivity under mild or ambient reaction conditions. Many studies have been attempted on supported Au in order to achieve a high catalytic performance using supports in the form of nanocomposites in which gold nanoparticles are loaded onto support materials such as molecular sieves, metal oxides, polymers and activated carbon [18,20,24,25].

In this paper, a series of titanium-containing mesoporous molecular sieves with a Ti wt% from 0 to 10.7 were prepared by hydrothermal synthesis. These materials were used as a support for Au NPs to obtain metallic catalysts at 1 wt% on the Ti(X)MCM-41. The application of an MCM-41 molecular sieve as a support for Au NPs is limited to some extent because of a lack of active sites in the neutral purely siliceous framework during the Au deposition [17,26]. The incorporation of heteroatoms as extra-framework nanoscale oxide clusters or in an appropriate valence state as a tetrahedral framework species might generate preferential sites for the deposition of the metal clusters. Ti is one of the most attractive heteroatoms introduced into mesoporous molecular sieves due to suitable acid/redox properties and good enough stabilization of Au NPs, as was previously reported for Au/TiO_2 catalysts [21].

The hydrogenation of nitrobenzene (NB) was chosen as the test reaction in semi-batch conditions for the Ti(X)MCM-41 systems to evaluate the activity and selectivity of the catalysts at different nominal Ti substitutions on the surface of the supports. For the best Au/Ti(X)-MCM-41 systems, reaction parameters such as the H_2 pressure, solvent nature, and recyclability were investigated in

Table 1
Chemical composition and surface properties of Ti(X)-MCM-41 supports.

Support Ti(X)-MCM-41	Ti (%wt)	ZPC[a] pH	S_{BET}[b] (m^2g^{-1})	Pore[c] (nm)	V_T[d] (cc/g)	d_{100}[e] (nm)	a_0[f] (Å)
0	–	1.5	1035	3.7	0.98	3.882	44.9
1.0	0.9	2.0	1000	2.6	0.57	3.623	41.8
2.0	2.0	2.4	979	2.9	0.43	3.610	41.7
5.4	5.3	2.8	864	4.7	0.31	3.594	41.2
10.7	9.3	3.2	786	3.6	0.40	3.516	40.5

[a] Determined from ZPC vs pH measurement.
[b] Specific area calculated from BET method.
[c] Determined from BJH method.
[d] Pore volume determined at $P/P^{\circ} = 0.99$.
[e] determined by XRD.
[f] $a_o = 2d_{100}/\sqrt{3}$.