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The synthesis and study of some metal catalysts supported on modified MCM-41

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Scope and Content of the Thesis

Pure silica has a neutral framework in which the Si^{4+} is tetrahedrally bonded to four bridging O atoms, and consequently cannot show cation exchange properties. Metal components can be introduced into the silica to induce cation exchange capacity, redox properties and nucleation sites for the growth or development of metal nanoparticles. This thesis examines Si-MCM-41 and metal-containing variants, i.e., Fe- and Co-MCM-41 as supports for Au catalysts. Au catalysts have recently gained popularity because of their ability to catalyze a wide range of reactions at low temperature.

Chapter 1 covers the literature on inorganic porous materials, with particular reference to addressing the issue of shape selectivity in microporous materials and improving the surface area of the resulting materials. The survey includes a discussion of the first templated synthesis of a mesoporous family of zeolitic materials, designated M41S, to which belong a range of interesting materials such as MCM-41, MCM-48 and MCM-50. The survey includes the synthesis, characterization, catalytic and technical applications of the Si-MCM-41 materials.

Chapter 2 presents the results of the work carried out on pure silica MCM-41 materials that were prepared in this thesis. Covered in this study are the role of various synthetic variables (i.e. optimization of the synthesis conditions) that lead to a highly ordered Si-MCM-41 with improved structural integrity, as well as enhanced thermal and hydrothermal stability. These variables include the crystallization time and reaction temperature, the synthesis gel composition (SiO_2/CTAB molar ratio and the water content), inclusion of additives as co-templates in the synthesis gel, the pH of the synthesis gel, and the nature of the silica source. These materials were characterized using X-ray diffraction (XRD) to assess structural integrity, High Resolution Transmission Electron Microscopy (HRTEM) to evaluate the microstructure of the pores, and Brunauer-Emmett-Teller (BET) surface area analysis. Conclusions at the end of the chapter are based on the findings of these characterization techniques. The optimized Si-MCM-41

materials so obtained were used as benchmarks in the synthesis of base metal-containing mesoporous MCM-41 materials described in **chapter 3**.

Chapter 3 focuses on Fe- and Co-MCM-41 materials, with particular emphasis on their synthesis and characterization. The metal precursors were introduced at various stages of the synthesis, and in various forms (i.e., as solutions or as freshly-prepared gelatinous precipitates). The synthesis was carried out under both ambient and hydrothermal temperature conditions, and the amount of the heterometal that was incorporated into the mesostructure with structural retention has been optimized. Incipient wetness impregnation was also used for the synthesis of Fe- and Co-MCM-41 derivatives. Physicochemical characterization of the resulting materials included XRD, HRTEM, BET, temperature programmed reduction (TPR), ESR spectroscopy and Raman spectroscopy. Conclusions are also included at the end of this chapter, based on the observations from these characterization techniques. These heteroatom-containing mesoporous materials, with their associated redox and cation exchange properties, were used as supports in the preparation of supported Au catalysts discussed in **chapter 4**.

Chapter 4 focuses on an investigation of different methods used to prepare supported gold nanoparticles. These methods range from deposition-precipitation, co-deposition-precipitation (both Fe(III) or Co(II) and Au(III) deposited simultaneously on Si-MCM-41), co-precipitation of Au(III) with either Fe(III) or Co(II) in the presence of a preformed Si-MCM-41, or direct one-pot hydrothermal synthesis where the metal components form part of the initial synthesis gel. Characterization of the final materials involved XRD, HRTEM, BET and EDS techniques. These materials and other related materials were evaluated for catalytic activity as described in **chapter 5**.

Chapter 5 describes the catalytic properties of the Au/Me-MCM-41 materials, with Me = Si, Fe and Co, in the reaction:

$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g), \qquad \Delta G_{298\ K} = -257.1\ kJ/mol$

The results are interpreted in terms of the light-off temperature, i.e., the temperature at which the catalyst starts converting carbon monoxide into carbon dioxide. Conclusions based on the observed catalytic behaviour are found at the end of the chapter.

Chapter 6 presents the summary of the work done, and the main conclusions of the study entailed in this thesis.