

## CHAPTER 6: SUMMARY AND CONCLUSIONS

### 6.1 Summary

Although zeolites and their potential industrial applicability were realized centuries ago, the methods to extend their pore sizes beyond the micropore range has remained elusive until very recently (*Mobil discovery in 1992*).

The work in this thesis was inspired by the confluence of two major scientific breakthroughs in recent years: (i) the discovery by Mobil of the M41S family of micelle-templated mesoporous silicates and aluminosilicates (1992), and (ii) the discovery by Haruta and coworkers of the exceptional catalytic activity of appropriately-prepared Au catalysts for low-temperature CO oxidation (1987/9).

Breakthrough (i) offers a special advantage of having highly ordered support materials, with exceedingly high BET surface areas ( $\geq 1000 \text{ m}^2/\text{g}$ ) that would help counter the need for high levels of loading of relatively expensive transition metal components of heterogeneous catalysts in order to achieve high catalytic activity. The mesoporous structures in this family include MCM-41, MCM-48 and MCM-50, produced by an LCT mechanism using surfactants as templates. MCM-41 has a honeycomb type structure with highly ordered, one-dimensional hexagonal channels. It has, in addition, high thermal stability and high hydrocarbon sorption capacity.

Breakthrough (ii) offers an alternative and promising means of abating pollution problems associated with present day energy sources like combustion of transportation fuels (gasoline and diesel). Incomplete combustion of these carbon-based energy sources produces toxic levels of carbon monoxide (CO), which is lethal even at ppm concentrations. This calls for the development of catalytic materials for the conversion of CO to CO<sub>2</sub> that would be effective at reasonably low temperatures

for use in the cold-start phase of the TWC. About 80 % of atmospheric pollutants are produced in this startup phase.

Based on these two breakthroughs, it is hypothesized that the use of the high  $S_{\text{BET}}$  materials (MCM-41 and derivatives) as supports for Au nanoparticles could produce highly dispersed catalyst systems with improved catalytic activity for the near-ambient CO oxidation. Fundamental to this work was the synthesis of Si-MCM-41. The synthesis parameters were optimized to yield (in a reproducible manner), good-quality Si-MCM-41 with high  $S_{\text{BET}}$ , increased long-range order, and improved thermal and/or hydrothermal stability. Chapter 2 contains the synthesis details.

Unfortunately, physicochemical properties of Si-MCM-41 such as the lack of framework charge, low PZC, weak metal-support interactions, etc., make it unsuitable as a support for Au nanoparticles in order to produce highly active and durable catalysts. These features of Si-MCM-41 would render the resulting Au/MCM-41 systems unstable with respect to processes like active metal leaching and catalyst sintering at high temperatures. To partially address these problems, we have influenced the chemistry of Si-MCM-41 by premodification with Fe(III) and Co(II) either during the synthesis stage or after generating Si-MCM-41. The chemistry of the resultant Fe-MCM-41 and Co-MCM-41 materials has been studied using techniques like XRD, BET surface area measurements, High Resolution Transmission Electron Microscopy (HRTEM), Temperature Programmed Reduction (TPR), Electron Spin Resonance (ESR) spectroscopy, Raman spectroscopy (RS) and Infrared (IR) spectroscopy. The details are given in chapter 3.

The process of pre-modification of Si-MCM-41 with Fe(III) and Co(II) has allowed the use of solution chemistry techniques (DP, CP, etc.) for the preparation of supported Au catalysts on mesoporous supports. Chapter 4 describes the synthesis and characterization of Au catalysts on Me-MCM-41 (Me = Si, Fe, Co) supports.

The resulting materials, designated Au/Me-MCM-41 (where Me = Si, Fe, or Co), have been evaluated for catalytic activity in the oxidation of CO to CO<sub>2</sub> using O<sub>2</sub> as an oxidant. The CO oxidation reactor design used as well as the analysis conditions used are also described in chapter 5.

## 6.2 Conclusions

### • *Si-MCM-41*

The versatility of the synthesis of Si-MCM-41 has been demonstrated, producing highly ordered materials both at room temperature and under hydrothermal treatments, and under both stirred and static conditions. Hydrothermal synthesis produced Si-MCM-41 with superior structural properties (XRD) than that produced by the room temperature synthesis. The metal showed at least four well-resolved diffraction peaks in the range  $1^\circ < 2\theta < 7^\circ$ , indexable on a hexagonal unit cell to (100), (110), (200) and (210). The reproducibility of the synthesis approach used in this study was also demonstrated, yielding materials with similar XRD patterns and  $a_0$  values each time the synthesis was carried out. Also, larger batches of Si-MCM-41 were prepared without sacrificing the XRD properties of these materials.

Room temperature synthesis is not economically viable as longer crystallization times are needed to obtain highly ordered Si-MCM-41. Prolonged synthesis of Si-MCM-41 under hydrothermal conditions (e.g., 5 days at 100 °C) is accompanied by a decrease in  $a_0$  and an increase in  $S_{\text{BET}}$ , as the product became increasingly amorphous due to longer contact with the alkaline mother liquor. The presence of the amorphous phase in this material was also confirmed by corresponding TEM micrographs.

High synthesis gel pHs (> 10) are detrimental to the mesoporosity and long-range order of Si-MCM-41 (and its metal-containing variants) prepared by the hydrothermal route. Our data have shown, based on  $a_0$  values, that the optimum synthesis

conditions for best quality Si-MCM-41 are a crystallization time 2 days, a synthesis temperature of 100 °C, and a gel pH of 10.

The lattice parameters of Si-MCM-41 materials prepared at room temperature over 5 days decreased from 47.2 to 42.1 Å when the synthesis gel SiO<sub>2</sub>/CTAB ratio was increased in the range 1.25 - 8.00, suggesting less structural order when relatively smaller amounts of the structure-directing agents were used.

The nature of the SiO<sub>2</sub> source used in the hydrothermal synthesis of Si-MCM-41 influences the quality of the final product. The results in this study provided a ranking of the SiO<sub>2</sub> sources according to their ability to produce good-quality Si-MCM-41 (based on XRD data): TEOS << Fumed SiO<sub>2</sub> < (Fumed SiO<sub>2</sub> + water-glass) < Si-MCM-41.

The good quality of *sec*-Si-MCM-41 made by using Si-MCM-41 as a SiO<sub>2</sub> precursor is demonstrated by (i) the appearance of the d<sub>300</sub> peak in the XRD pattern, (ii) the extreme thermal stability (retains significant XRD mesoporosity after calcination at 850 °C (see Figure 2.22)), and (iii) the decrease in both the a<sub>0</sub> and S<sub>BET</sub> values relative to the parent primary Si-MCM-41. Previous studies have attributed the decrease in a<sub>0</sub> of *sec*-Si-MCM-41 to restructured, thickened pore-walls, which are amorphous in primary Si-MCM-41. The recrystallized pore wall structure of *sec*-Si-MCM-41 was further illustrated by Raman spectroscopy (see Figure 3.55), which showed bands of higher intensities and resolution in the region below 1000 cm<sup>-1</sup> when compared to primary Si-MCM-41. Also, the most intense Raman peak at 850 cm<sup>-1</sup> in *sec*-Si-MCM-41 appeared at 825 cm<sup>-1</sup> in the Raman spectrum of primary Si-MCM-41 (Figure 3.55), suggesting a reinforced and more crystalline pore-wall in the former sample.

Milder synthesis conditions (80 °C for 6 h under magnetic stirring) using a mixture of water-glass and TEOS for a SiO<sub>2</sub> source produced Si-MCM-41 with characteristic

XRD properties, exceptionally high BET surface areas, and a highly regular array of hexagonal channels (HRTEM).

HRTEM micrographs of the Si-MCM-41 materials prepared at 100 °C also revealed an ordered array of hexagonal pores and channels permeating the bulk of these materials.

Under both room temperature- and hydrothermal-synthesis, the water content of the Si-MCM-41 synthesis gel, designated as  $H_2O/SiO_2$  ratio, had no significant effect on  $a_0$  values when  $40 \leq H_2O/SiO_2 \leq 140$ . In addition, regardless of the synthesis temperature, the  $S_{BET}$  values of product materials remained very high (~800 – 1100  $m^2/g$ ).

• *Me-MCM-41 (Me = Fe or Co): IWI Method*

Secondary Si-MCM-41 is resistant to structural collapse when 5 wt% Fe was introduced by IWI method, as demonstrated by both XRD (Figure 3.4) and HRTEM (Figure 3.26). The lattice parameter of both the siliceous support and its 5 wt% Fe-containing variant remained constant at 46.7 Å. HRTEM showed a restructured morphology of the support (elongated rod-like structures with thickened walls observed instead of a honeycomb-type structure), with some Fe species dispersed all over the surface. In general, the materials prepared by IWI maintain the microstructure and lattice parameter similar to that of pristine Si-MCM-41, regardless of the Fe or Co loading. The small changes in  $a_0$  values may arise because very little of the metal species gets into the framework, as ESR spectroscopy has demonstrated for 16 wt% Fe-containing MCM-41 prepared by IWI (Figure 3.51). The Co-containing counterpart also showed little framework involvement of the  $Co^{2+}$  ion. For metal loadings around 16 wt%, the Fe and Co phases were positively identified as  $Fe_2O_3$  and  $Co_3O_4$  respectively (see for example, Figures 3.5 and 3.6).

Reduction of Fe- and Co-containing MCM-41 prepared by the IWI method showed reduction features analogous to their bulk oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ , respectively), i.e. a two-peak reduction profile is observed. The shift of the reduction peaks to higher temperatures in the TPR profiles of metal-containing MCM-41 relative to the bulk metal oxides suggest stabilization of the metal ions by the silica matrix, and the formation of a metal silicate was signaled by a reduction peak above 700 °C. Calcination of 16 wt% Fe-MCM-41 (IWI) at 560 °C led to higher reduction temperatures than for samples calcinated at 450 °C, probably due to the formation of the Fe silicate in the former case.

Surprisingly, 5 wt% Fe/sec-Si-MCM-41 prepared by IWI method showed a three-peak reduction profile, suggesting reduction to metallic Fe through wustite (FeO). Therefore, the texture of the support seems to play a role in the dispersion of the metal species. Restructured Si-MCM-41 (sec-Si-MCM-41) seems to attain a high dispersion.

The presence of Co or Fe in 16 wt% Me-MCM-41 prepared by the IWI method enhanced the intensity of the framework peak at  $\sim 693\text{ cm}^{-1}$  observed in the Raman spectrum of primary Si-MCM-41. This suggests that the presence of metal ions in the framework strengthen MCM-41.

• *Me-MCM-41 (Me = Fe or Co): Aqueous incorporation of  $\text{Me}^{n+}$*

The structural properties of pure silica MCM-41 are influenced by the incorporation of Fe or Co during a one-pot synthesis. High Fe or Co contents ( $\sim 9\text{ wt}\%$ ) introduced from water solutions of the precursors decrease both the lattice dimension  $a_0$  and the BET surface area of the resulting materials. Reduction in both  $a_0$  and the intensity of the  $d_{100}$  with metal content, as well as the corresponding reduction in  $S_{\text{BET}}$  are good and convincing evidence for the partial collapse in mesostructure upon transition metal incorporation.

However, changing the SiO<sub>2</sub> source from water-glass to Si-MCM-41 allowed the synthesis of highly ordered and mesostructured 16 wt% Fe-MCM-41 by aqueous incorporation of Fe(III) during direct hydrothermal synthesis. This material maintained a constant lattice parameter of  $a_0 = 45 \text{ \AA}$ , regardless of the extent of calcination at 560 °C (Tables 3.3 and 3.4). In TPR studies, this material showed three well-resolved reduction peaks in the temperature range up to  $\leq 660 \text{ °C}$ , suggesting the presence of the  $\text{FeO} \rightarrow \text{Fe}^0$  reduction step. For this material, little Fe(III) was incorporated into the framework sites (very small signal at  $g = 4.3$  in the ESR spectrum). By comparison with *sec*-Si-MCM-41, the intense Raman peak at  $850 \text{ cm}^{-1}$  has shifted to  $886 \text{ cm}^{-1}$ , and that at  $615 \text{ cm}^{-1}$  has shifted to  $\sim 700 \text{ cm}^{-1}$  in the Raman spectrum of the 16 wt% Fe-MCM-41 material. These shifts in the Raman bands to higher frequencies suggests that in addition to pore-wall strengthening from secondary synthesis, the framework involvement of the Fe(III) also contributes to the pore-wall strength. It is to be *rememberd that the effect of secondary synthesis is to strengthen the pore wall of Si-MCM-41 by thickening.*

One-pot hydrothermal synthesis of 3 wt% Fe-MCM-41 under milder conditions (80 °C for 6 h with magnetic stirring) using water-glass as a SiO<sub>2</sub> source also produced a highly ordered hexagonally mesostructured material, with no observable agglomeration of iron oxides in the TEM micrograph (Figure 3.29). The mesoporosity of this product was further supported by its high BET surface area ( $1226 \text{ m}^2/\text{g}$ ).

• *Me-MCM-41 (Me = Fe or Co): Acid Incorporation of  $\text{Me}^{n+}$*

The use of acid solutions as solvents instead of aqueous solutions of metal precursors improved the structural order of the products, as acid solutions minimized local precipitation of metal ions in highly alkaline sodium silicate gels. An 8.8 wt% metal loading was chosen to model the synthesis.

A comparative study on the efficiency of acids in the preparation of 8.8 wt% Fe-MCM-41 was undertaken. Organic acids produced 8.8 wt% Fe-MCM-41 materials with lower  $a_0$  and  $S_{\text{BET}}$  values than  $\text{HNO}_3$ . Since  $\text{HNO}_3$  gave the highest mesoporous properties in the final materials, it was chosen for further syntheses of Fe-MCM-41 materials.

The 5 wt% Fe-MCM-41 prepared hydrothermally using  $\text{HNO}_3$  solutions of Fe(III) showed thermal stability in the calcination temperature range 560 – 750 °C, with the corresponding  $a_0$  range of 44.4 – 44.2 Å. These results also suggest that a plot of  $a_0$  versus calcination temperature for the as-synthesized material can provide a means of estimating the optimum calcination temperature, as is normally done with TGA. ESR spectroscopic studies of this material in its as-synthesized form revealed that  $\text{Fe}^{3+}$  is present in both framework ( $g \approx 4.3$ ) and extraframework ( $g \approx 2.0$ ) positions, and that the amount of framework Fe decreases with increasing calcination temperature until all Fe was present as extraframework species ( $T_{\text{calc}} \geq 400$  °C). The presence of two different coordination environments of  $\text{Fe}^{3+}$  were also observed in the ESR spectrum of 8.8 wt% Fe-MCM-41 prepared at room temperature for 5 days by a similar approach. Very little framework Fe has been detected in the ESR spectrum of calcined 8.8 wt% Fe-MCM-41 prepared at room temperature from an oxalic acid solution of ferric nitrate (Figure 3.50).

The  $\text{HNO}_3$ -assisted hydrothermal synthesis of Fe-MCM-41 samples with the Fe content in the range  $0 \leq \text{wt\% Fe} \leq 10$ , produced mesoporous composites with surface areas in the range  $940 \geq S_{\text{BET}} \geq 800$  m<sup>2</sup>/g and lattice parameters in the range  $47 \geq a_0 \geq 44$  Å. A slight decreases in  $a_0$  and  $S_{\text{BET}}$  with increasing Fe content was noted. The Co-based counterpart also shows mesoporosity in terms of  $a_0$ , with a pronounced decrease in  $S_{\text{BET}}$ . Although the Raman spectra of Si-MCM-41 confirms a high concentration of surface silanol groups, the 3476 cm<sup>-1</sup> OH band area (in Voigt units) of these materials decreased with increasing Fe content of Fe-MCM-41, qualitatively implying a decrease in the density of silanol groups as Fe is increased.

Regardless of the high total metal content (19.3 wt%) of the hydrothermally-prepared bimetallic (7.8 wt%, 11.5 wt%) Co-MCM-41 formed from the HNO<sub>3</sub> solution of the metal precursors, its lattice parameter ( $a_0 = 44 \text{ \AA}$ ) remained similar to that of its monometallic counterpart, i.e., 8.8 wt% Fe-MCM-41 prepared analogously with the same amount of Fe in the gel (see Figure 3.17). The main reduction features in the TPR profile of this bimetallic material (Figure 3.45) are at 420, 574 and 650 °C, suggestive of the reduction sequence  $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ , as was found for 16 wt% Fe-MCM-41 prepared with Si-MCM-41 as a SiO<sub>2</sub> source (reduction peaks at 433, 548 and 660 °C). Since no peak readily assignable to the reduction of the Co species was observed, it is proposed that Co serves mainly as a promoter for the reduction of Fe species. The monometallic counterpart, 8.8 wt% Fe-MCM-41, was difficult to reduce and showed a major reduction peak at 431 °C (Figure 3.35), suggesting that only reduction to Fe<sub>3</sub>O<sub>4</sub> takes place.

• *Me-MCM-41 (Me = Fe, Co and Ru): The Base Precipitate Route*

Both TEM and XRD showed that the mesostructure of 5 wt% Fe-MCM-41 prepared by the base precipitate route under hydrothermal conditions is highly ordered. Some ill-defined FeO<sub>x</sub> peaks appeared in the XRD pattern, and TEM showed them to arise from some Fe species existing as a separate phase on the silica surface (Figure 3.30). This material is difficult to reduce as shown by the presence of only one reduction peak at ~460 °C in its TPR profile, and no further reduction to elemental Fe. *Room temperature synthesis of 5 wt% Fe-MCM-41 by this route for 4 days produced a material with XRD mesoporosity and a characteristic two-peak reduction profile (with shoulders), suggesting reduction to metallic Fe (Figure 3.40).*

The metal phases (Fe or Co) in composite materials prepared by the base precipitate route are generally resistant to total reduction to metallic states. The identity of the precipitant in the hydrothermal synthesis of 16 wt% Fe-MCM-41 did not have a significant effect on the XRD and BET properties of the product Fe-MCM-41, as did

long synthesis times. However, in TPR studies, the 16 wt% Fe-MCM-41 materials prepared from either NaOH or Na<sub>2</sub>CO<sub>3</sub> precipitates showed only one major reduction peak (signifying resistance to reduction to Fe<sup>0</sup>), whereas that obtained from a TEA precipitate showed reduction features similar to Fe<sub>2</sub>O<sub>3</sub> reduction. The reason for this anomaly is not known at this stage, but the XRD pattern of the latter sample confirms the presence of dispersed Fe oxide clusters.

Room temperature-synthesized Fe- and Co-MCM-41 materials generally have higher BET surface areas than their counterparts prepared under hydrothermal conditions. Also, for the same metal loading, Co-MCM-41 has a higher surface area than Fe-MCM-41.

The incorporation of high loadings (16 wt%) of Fe(III) and Co(II) by the base-precipitate route during synthesis, both hydrothermally and at room temperature, conserved the mesoporous characteristics (XRD patterns,  $a_0$  and BET) in the final metal-MCM-41 materials. Hydrothermally-incorporated metal ions in MCM-41 can be arranged in the order Co < Fe < Ru according to their increasing degree of mesostructure destruction (Note: this is also the order of increasing ionic radius). Table 6.1 confirms this deduction in terms of  $a_0$  and BET data.

Table 6.1 Lattice parameters and BET data for 16 wt% Me-MCM-41 (Me = Fe, Co, Ru)

Metal	$a_0/\text{\AA}$	$S_{\text{BET}}(\text{m}^2/\text{g})$
Co	46.9	751
Fe	44.4	617
Ru	39.4	223

The destructive effect of Ru on MCM-41 is due to the penetration of the framework by the relatively large Ru ion, as demonstrated by a peak at  $g \approx 4.2$  in the ESR

spectrum. The OH region of the Raman spectra of Me-MCM-41 (Me = Si, Fe, Co) shows the presence of a high population of hydroxyl groups, probably in the form of silanol groups. The area of the Raman OH bands seemed to decrease in accordance with the type of metal introduced by the hydroxide precipitate route for the 16 wt% Me-MCM-41.

It was also demonstrated that increasing the metal content of the synthesis gel in this approach causes partial structural collapse. In the case of Fe, the lattice parameters of the Fe-MCM-41 samples were essentially constant in the Fe content range  $0 \leq \text{wt\% Fe} \leq 20$ , but the  $S_{\text{BET}}$  of the pure support decreased from 930 to 536  $\text{m}^2/\text{g}$  as a result of this one-pot incorporation of Fe. Thus, mesoporosity of the silica is retained even at high metal contents. A similar behaviour was observed with Co-MCM-41.

• *Au/Me-MCM-41 (Me = Fe or Co): Physical and catalytic characterization*

The use of sodium silicate as both a co-precipitant and a  $\text{SiO}_2$  source prior to synthesis at 100 °C for 5 days produced 1.92 wt% Au/6.5 wt% Fe-MCM-41 with good mesoporosity properties (existence of  $d_{100}$  and  $d_{110}$  peaks in the XRD pattern). In addition, metallic Au peaks were observed at higher angles, and the seemingly absent  $\text{FeO}_x$  peaks suggest that Fe is either well-dispersed or buried in the silica matrix. The TPR profile of this material also showed/confirmed the absence of ionic Au, and demonstrated that the Fe species was only reducible to  $\text{Fe}_3\text{O}_4$  (single reduction peak).

Regardless of the synthesis temperature, synthesis method and synthesis gel composition, the one-pot synthesized Au-containing materials showed high  $S_{\text{BET}}$ , close to the pristine Si-MCM-41 (Table 4.2). Although the mesostructure is similar to Si-MCM-41, the need for high temperature calcination to remove the surfactant produced extremely large Au nanoparticles, which were inactive for the low-temperature CO oxidation.

Au catalysts prepared by post-synthesis methods were calcined at low temperatures ( $\leq 400$  °C), and produced relatively small Au particles compared to those obtained by one-pot surfactant-templated synthesis. Materials prepared post-synthetically (by the ethylenediamine route, for example) using Si-MCM-41 and its base-metal-containing variants also showed high  $S_{\text{BET}}$ .

A sample prepared by electrostatic interaction between  $\text{AuCl}_4^-$  and the occluded  $\text{CTA}^+$  cation in as-synthesized Si-MCM-41, produced large particles (12.1 nm) as a result of the need to calcine at 500 °C for 12 h to remove the template. This method is unsuitable to prepare active supported Au catalysts.

Regardless of the preparation method, composition and conditions, all Si-MCM-41 based catalysts do not show catalytic activity until after a reaction temperature of 200 °C. The large Au particle sizes obtained through high temperature calcination (500 °C) of directly-synthesized materials were observed by both their TEM micrographs and catalytic performance.

The high surface areas of the resulting catalyst systems play no role in improving the catalytic activity.

The series of catalysts with compositions 1.36 wt% Au/, 2.6 wt% Au/ and 5 wt% Au/3 wt% Fe-MCM-41 prepared by a one-pot synthesis (80 °C for 6 h) showed mixed trends in CO oxidation activity. Although the 5 wt% Au/3 wt% Fe-MCM-41 is the only sample showing some activity ( $\sim 2.25$  % CO conversion) at room temperature, the 2.6 wt% Au/3 wt% Fe-MCM-41 shows better activity at higher temperatures. The very low RT activity of 5 wt% Au/3 wt% Fe-MCM-41 decreased to a steady state after 50 minutes.

Supported Au catalyst systems prepared by the ethylenediamine DP route showed the following reactivity patterns:

(i) The 5 wt% Au/5 wt% Co-MCM-41 system showed much more activity (lower  $T_{50}$ ) than the 1 wt% Au/5 wt% Co-MCM-41. Increasing the calcination temperature of the 1.48 wt% Au/5 wt% Co-MCM-41 material from 325 to 400 °C reduced the activity even further.

(ii) For the 3 wt% Fe-MCM-41 support, increasing the Au content from 1 to 5 wt% was accompanied by an improvement in the catalytic activity (lowered  $T_{50}$ ) of the catalyst systems after calcination at 400 °C for 4 h, i.e., 1 wt% Au/ < 2.57 wt% Au < 5 wt% Au. No direct correlation between activity and particle size could be deduced, as the most active catalyst in the series had the largest average Au particle size. There was also no systematic trend in Au particle size with this increasing Au content. However, the Au particle size remained smaller than that found in hydrothermally-derived samples and those on siliceous supports.

(iii) At a fixed Au content, e.g., 5 wt% Au, increasing the amount of Fe in the preformed support was accompanied by improved catalytic activity: 5 wt% Fe-MCM-41 > 3 wt% Fe-MCM-41 > Si-MCM-41 (i.e. 0 wt% Fe-MCM-41). Thus the amount of dispersed Fe in the support plays a role (a promoter role) in the activity of the supported Au catalysts. Also, the presence of Fe in the support improved the surface area by about 5 % relative to the siliceous support, whereas increasing the Fe content of the support from 3 to 5 wt% Fe did not produce a significant change in the surface area of the resulting materials.

(iv) At a fixed Au content, the identity of the heteroatom in the support plays a role in the activity of supported Au catalyst. The activity order observed on a set of three catalysts was 5 wt% Au/5 wt% Co- > 5 wt% Au/5 wt% Fe- > 5 wt% Au/Si-MCM-41, i.e., the presence of heteroatoms in the supports improved the  $T_{50}$ 's of the resulting systems relative to Si-MCM-41. Since these systems have similar apparent activation energies ( $E_a$  obtained from Arrhenius plots), the observed difference in catalytic activity can be proposed to arise from the different numbers of active sites contained

in each catalyst system. The decreasing average Au particle size as one moves from the least active to the most active catalyst seems to better explain the activity difference noted, i.e., Si-MCM-41 (10.0 nm), 5 wt% Fe-MCM-41 (9.0 nm) and 5 wt% Co-MCM-41 (7.0 nm).

(v) Treatment of the 5 wt% Au/5 wt% Fe-MCM-41 with a reducing alkaline solution,  $\text{NaBH}_4/\text{NaOH}/\text{H}_2\text{O}$ , drastically reduced both the CO oxidation activity and the  $S_{\text{BET}}$  value ( $221 \text{ m}^2/\text{g}$ ). This reductive treatment is proposed to convert ionic gold to metallic Au.

(vi) Increasing the Au content to 10 wt% Au did not produce high activity, neither did increasing the support Fe content to 14 wt% Fe.

Of the other preparation methods explored in this thesis, only coprecipitation of Au(III) and either Fe(III) or Co(II) in the presence of preformed Si-MCM-41 produced more active catalysts, but without attaining 100 % CO conversion. The Co-based systems were more active than the Fe-based systems, a parallel trend to that seen in the other (e.g. en) route.

The preparation methods employed in this thesis still need some refinement before an active catalyst can be produced. This will be a focus of future work in our group.