MIL-100(Fe) as catalyst precursor and host of gold nanoparticles for low temperature CO oxidation

Lide Oar-Arteta[a], Demetrio Garzas[a], Bart van der Linden[a], Robert Franz[a], Jorge Gascon[a,b], Freek Kapteijn[a]*

[a]*Catalysis Engineering, Chemical Engineering Department, Delft University of Technology, Delft, 2629 HZ, The Netherlands*

[b] *King Abdullah University of Science and Technology, KAUST Catalysis Center, Advanced Catalytic Materials, Thuwal, 23955, Saudi Arabia*

**Corresponding author: +31 15 278 3516, F.Kapteijn@tudelft.nl*

Abstract: MOF mediated synthesis arises as a new tool for designing materials of unprecedented characteristics for heterogeneous catalysis. In this work, the technique is applied to obtain highly active and selective catalysts for the low temperature CO oxidation reaction. After calcination and pyrolysis and calcination of the parent MOF MIL-100(Fe) the resulting *C*-Fe_2O_3 and *PC*-Fe_2O_3 were tested and found to be more active than the commercial oxide. Moreover, after addition of 2 wt% Au to the calcined *C*-Fe_2O_3 the activity increased drastically and the catalyst kept its activity the same over 2 heating-cooling steps.

Keywords: MOF mediated synthesis, CO oxidation, MIL-100 derived oxides, gold.

1. Introduction

Engineering materials from metal organic frameworks (MOFs) has recently emerged as a powerful synthetic tool in the field of heterogeneous catalysis[1]. This technique known as the MOF mediated synthesis (MOFMS) entails heating a MOF under a certain atmosphere until its framework collapses, giving way to metal oxides (MOs) or metal nanoparticles (NPs) in a carbon matrix (NP@C). MIL-100(Fe) is a fair example of the success of this technique for obtaining highly active, selective and stable NP@C catalysts for CO hydrogenation[2]. MIL-100(Fe) is a porous iron trimesate based MOF, easy to synthesize and stable upon annealing at 280 °C[3]. Gold deposited on transition metal oxides such as Fe_2O_3 is very active in the low temperature oxidation of carbon monoxide. Accordingly, hereby we study the possibilities of MIL-100(Fe) as both MO catalyst precursor and as host of gold nanoparticles for the low temperature oxidation of CO.

2. Experimental

MIL-100(Fe) was prepared according to the fluoride free route reported by Bezverkhyy *et al*[4]. Calcination of MIL-100(Fe) in air at 370 °C for 1 h and 5 °C/min gave place to a material indicated by *C*-Fe_2O_3. A pre-pyrolysis step at 500 °C in N_2 for 1 h prior to calcination resulted in sample *PC*-Fe_2O_3. In order to prepare *C*-Au/ Fe_2O_3 and Au/*C*-Fe_2O_3 samples, a $HAuCl_4 \cdot 4H_2O$ solution in C_2H_3N was added dropwise to MIL-100(Fe) and *C*-Fe_2O_3, respectively. After sonication for 30 min and overnight storage, the mixtures were washed with acetonitrile and water. Finally, *C*-Au/ Fe_2O_3 was calcined at 370 °C for 1 h and Au/*C*-Fe_2O_3 was dried in air at 50 °C for 10 h[5]. The samples were characterized by N_2 physisorption and Powder X-ray diffraction (PXRD) and subsequently tested in CO oxidation under the following conditions: 1% CO, 0.5% O_2 and 98.5% He, GHSV= $4.5 \cdot 10^{-6}$ $mol_{CO}s^{-1}g_{cat}^{-1}$, atmospheric pressure and increasing temperature from RT to 400 °C and down for 2 heating-cooling steps, testing both the activity and the stability.

3. Results and discussion

Table 1 shows the porous structure of MIL-100(Fe) (915 m^2/g) collapses after the heat treatment for the MOF derived *C*-Fe_2O_3 (25 m^2/g) and *PC*-Fe_2O_3(40 m^2/g), the latter having a higher S_{BET} as consequence of the pre-pyrolysis step. However, the S_{BET} for both these MOF derived oxides is higher than that of the commercial Fe_2O_3 (5 m^2/g). Regarding the Fe_2O_3 crystallite size (d_{Fe2O3}), that of the commercial Fe_2O_3 (40 nm) is almost double the size of the MOF derived *C*-Fe_2O_3 (27 nm) and *PC*-Fe_2O_3 (25 nm) materials.

Table 1. S_{BET} and d_{Fe2O3} for the catalysts

Catalyst	S_{BET} **m^2/g**	d_{Fe2O3} **nm**
MIL-100(Fe)	915	-
***C*-Fe$_2$O$_3$**	26	27
***PC*-Fe$_2$O$_3$**	40	25
Fe$_2$O$_3$	5	40
Au/ *C*-Fe$_2$O$_3$	24	27

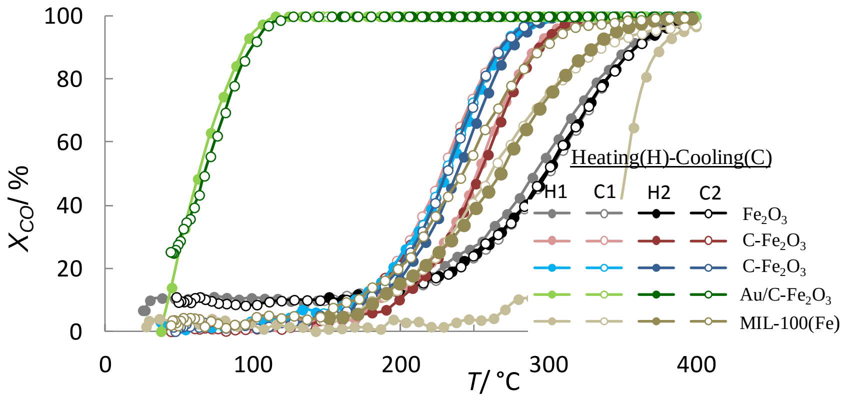

Figure 1. CO oxidation light-off curves over MIL-100(Fe) and Fe$_2$O$_3$ catalysts.

Figure 1 shows that during CO oxidation, MIL-100(Fe) undergoes decomposition at 300 °C in the first heating step thus starting its transformation into Fe$_2$O$_3$ and becoming more active after each heating-cooling step. Accordingly, the calcined *C*-Fe$_2$O$_3$ and pyrolyzed and calcined *PC*-Fe$_2$O$_3$ were tested in the reaction and compared to MIL-100(Fe) and a commercial Fe$_2$O$_3$. Both MOF derived *C*-Fe$_2$O$_3$ (T_{50}= 250 °C) and *PC*-Fe$_2$O$_3$ (T_{50}= 230 °C) show higher activity than the commercial Fe$_2$O$_3$ (T_{50}= 293 °C) and similar to that for the MIL-100(Fe) after the 2nd cooling step (T_{50}= 244 °C). Considering the stability, *PC*-Fe$_2$O$_3$ is stable during the four reaction cycles. However, the light-off curve for *C*-Fe$_2$O$_3$ shows a hysteresis loop, its activity being higher during the cooling than during the heating branch. This is most likely due to the creation of defects during the heating which makes the catalyst more active during the cooling branch via what is thought to be a Mars-Van Krevelen reaction mechanism[6]. After addition of 2 wt% gold prior to calcination for the *C*-Au/ Fe$_2$O$_3$ sample the activity is hardly improved (T_{50}= 220 °C ,not shown). Nonetheless, when the gold is added to the already calcined *C*-Fe$_2$O$_3$, the CO conversion drastically increases over the Au/*C*-Fe$_2$O$_3$ catalyst (T_{50}= 64 °C) and the activity remains stable during the 4 cycles.

4. Conclusions

In this work we have synthesized MIL-100(Fe) derived Fe$_2$O$_3$ catalysts via calcination and pyrolysis and calcination of the MOF precursor. These MOF derived MOs have higher S_{BET} and lower average d_{Fe2O3} than a commercial oxide. When tested for the CO oxidation reaction, *C*-Fe$_2$O$_3$ and *PC*-Fe$_2$O$_3$ show higher activity and are stable over the 2 heating-cooling cycles. After gold addition to the calcined *C*-Fe$_2$O$_3$ giving Au/*C*-Fe$_2$O$_3$, the activity drastically increases and the stability is not compromised. Accordingly, in this preliminary study, it is concluded that Fe-based MOFs are promising precursors and hosts of gold nanoparticles to develop highly active and stable catalysts for the low temperature CO oxidation reaction.

References

1. L. Oar-Arteta, T. Wezendonk, X. Sun, F. Kapteijn and J. Gascon, Materials Chemistry Frontiers 1 (2017) 1709.
2. V. P. Santos, T. A. Wezendonk, J. J. D. Jaén, A. I. Dugulan, M. A. Nasalevich, H.-U. Islam, A. Chojecki, S. Sartipi, X. Sun, A. A. Hakeem, A. C. J. Koeken, M. Ruitenbeek, T. Davidian, G. R. Meima, G. Sankar, F. Kapteijn, M. Makkee and J. Gascon, Nat Commun 6 (2015) 6451.
3. A. Dhakshinamoorthy, M. Alvaro, P. Horcajada, E. Gibson, M. Vishnuvarthan, A. Vimont, J.-M. Grenèche, C. Serre, M. Daturi and H. Garcia, ACS Catalysis 2 (2012) 2060.
4. I. Bezverkhyy, G. Weber and J.-P. Bellat, Microporous and Mesoporous Materials 219 (2016) 117.
5. L. Liu, X. Tai, N. Zhang, Q. Meng and C. Xin, Reaction Kinetics, Mechanisms and Catalysis 119 (2016) 335.
6. K. Zhao, H. Tang, B. Qiao, L. Li and J. Wang, ACS Catalysis 5 (2015) 3528.