Development of nanoparticle catalysts and total internal reflection (TIR) Raman spectroscopy for improved understanding of heterogeneous catalysis

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Appendix: Chapter 6

KIT-6 X-ray diffraction (XRD)

The XRD powder diffraction pattern was recorded. Literature spectra and those recorded are shown in Figure 6A.1 and Figure 6A.2. The literature XRD spectra is given for KIT-6 mesoporous silica synthesised with differing amounts of hydrochloric acid (0.25 to 0.75 M) and SBA-15 mesoporous silica (0.75 to 1.6 M). From the literature spectra the cubic Ia3d phase of the KIT-6 was characterised.[1] Correspondence of the recorded with the literature spectra (with 0.25 M hydrochloric acid) confirmed the synthesis of a material with the structure expected for KIT-6.

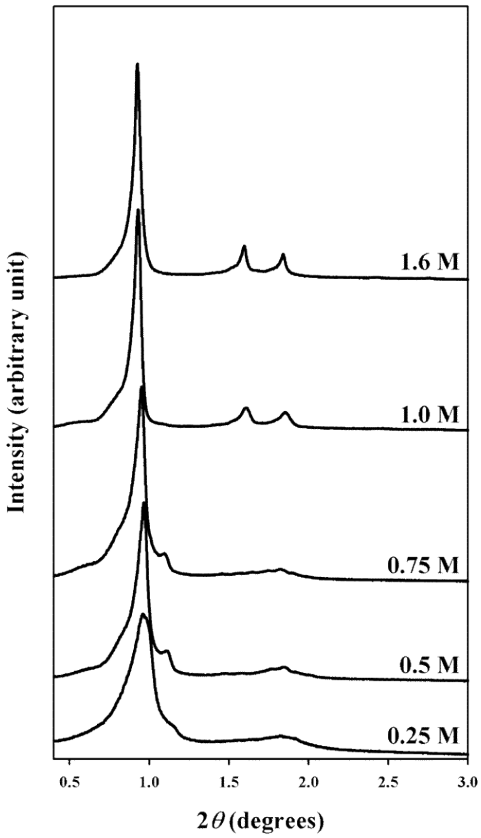

Figure 6A.1. Literature XRD spectra for KIT-6 mesoporous silica support material with differing amounts of hydrochloric acid. Reprinted with permission from (Kim, T.-W.; Kleitz, F.; Paul, B.; Ryoo, R. MCM-48-like Large Mesoporous Silicas with Tailored Pore Structure: Facile Synthesis Domain in a Ternary Triblock Copolymer–Butanol–Water System. J. Am. Chem. Soc. ***2005****, 127 (20), 7601–7610). Copyright (2005) American Chemical Society.*

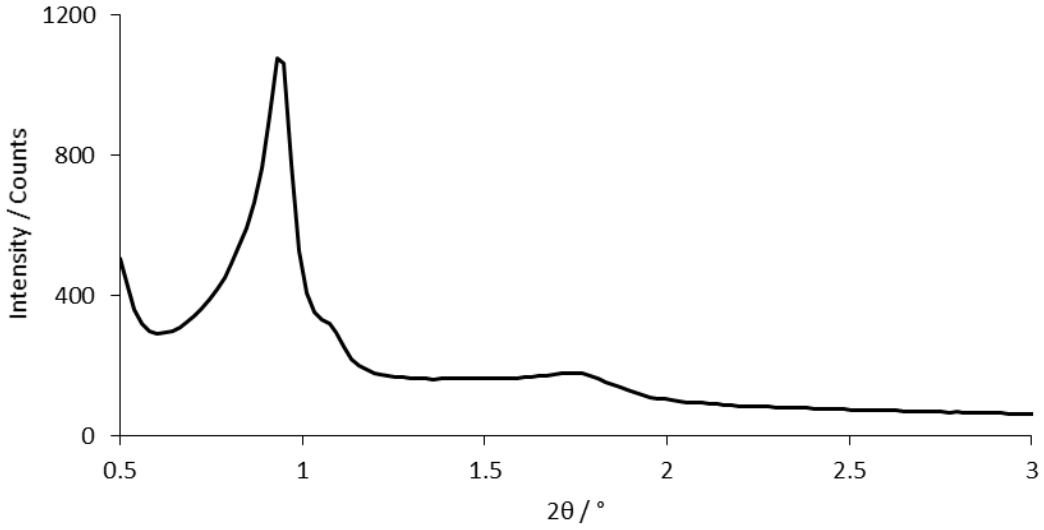

Figure 6A.2. XRD spectra for KIT-6 mesoporous silica support material.

Worked calculation-response factor and yield calculations

Effective carbon number (ECN) for products and internal standard

ECN values were calculated for the products (N-benzoylpiperidine, and benzylidene benzylamine) and internal standard (methylnaphthalene) as described in Scanlon and Willis.[2]

Methylnaphthalene – aromatic (10x1), alipthatic-1, **ECN=11**

N-benzoylpiperidine – aromatic (6x1), carbonyl (1x0), amine (1x0), aliphatic (7x1), **ECN=13**

Benzylidene benzylamine – aromatic (12x1), carbonyl (1x0), amine (1x0), aliphatic (1x1), **ECN=13**

Response factors for products

Using the ECNs calculated above the response factor F(R-wt) can be calculated for each of the products using Equation 6A.1 as described in Scanlon and Willis.[2]

$$F(R-wt) = \frac{M_w\ of\ compound \times ECN\ of\ internal\ standard}{M_w\ of\ reference \times ECN\ of\ compound} \qquad \textit{Equation 6A.1}$$

N-benzoylpiperidine –

$$F(R-wt) = \frac{189.3\ \text{g mol}^{-1} \times 11}{142.2\ \text{g mol}^{-1} \times 13} = 1.13$$

Benzylidene benzylamine –

$$F(R-wt) = \frac{195.3\ \text{g mol}^{-1} \times 11}{142.2\ \text{g mol}^{-1} \times 13} = 1.16$$

Amount of product measured by gas chromatography (GC)

The amount of the product measured by the GC could then be calculated using Equation 6A.2.

$$Mass\ compound = \frac{Mass\ of\ internal\ standard \times Area\ of\ compound \times F(R-wt)}{Area\ of\ internal\ standard}$$ *Equation 6A.2*

One example of the calculations undertaken can be given for the 10 min reduced catalyst shown in the second row of Table 6.1:

$$Mass\ compound = \frac{0.07103\ g\ \times\ 0.004585244\% \times 1.13}{2.400248129\%} = 1.8\ x10^{-4} g$$

This gives a value of 9.54 x 10^{-7} mol. The product yield can then be calculated using Equation 6A.3.

$$Product\ yield = \frac{product\ measured\ by\ GC}{reactant\ into\ reaction} \times 100$$ *Equation 6A.3*

$$Product\ yield\ (10\ \mathrm{min}\ reduced\ catalyst) = \frac{9.54\ \mathrm{x}\ 10^{-7}\ \mathrm{mol}}{0.5\ \mathrm{x}\ 10^{-3}\ \mathrm{mol}} \times 100 = 0.2\%$$

Bibliography

(1) Kim, T. W.; Kleitz, F.; Paul, B.; Ryoo, R. MCM-48-like Large Mesoporous Silicas with Tailored Pore Structure: Facile Synthesis Domain in a Ternary Triblock Copolymer−Butanol−Water System. *J. Am. Chem. Soc.* **2005**, *127* (20), 7601–7610.

(2) Scanlon, J. T.; Willis, D. E. Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept. *J. Chromatogr. Sci.* **1985**, *23* (8), 333–340.