

Improving the accuracy of catalyst pore size distributions from mercury porosimetry using mercury thermoporometry



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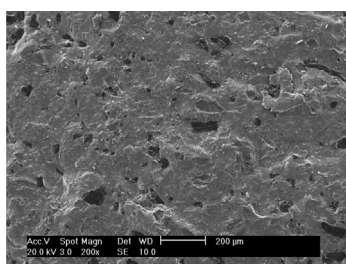
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HIGHLIGHTS

- Resolution of controversy over impact of heavy metals.
- Demonstration of utility of complementary thermoporometry.
- Further use of integrated gas sorption in mercury porosimetry.
- Test of classification scheme for mercury porosimetry curves.

GRAPHICAL ABSTRACT



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ABSTRACT

Mercury porosimetry is still frequently used to obtain the pore size distributions (PSDs) for porous heterogeneous catalyst pellets. However, unless the contact angle in the Washburn equation is correctly calibrated, porosimetry strictly remains only a relative technique. There is a particular potential issue for catalyst samples containing heavy metals, which may present (relatively) wetting surfaces to mercury, when the standard analysis is based upon the presumption of consistent non-wetting behaviour. Data in the literature on the impact of heavy metals on mercury intrusion is conflicting with some studies suggesting they do impact intrusion and some suggesting they do not. This study uses complementary gas sorption and mercury thermoporometry experiments that were fully serially-integrated with porosimetry to provide additional information to improve the interpretation of the basic mercury porosimetry data and validate the pore sizes obtained from it. These complementary data have been used to show that the wetting effect from heavy metals on intrusion may be confined to the smallest nanopores in the sample where the pore wall potentials begin to overlap. It has also been shown that confined mercury shows a significant advanced melting effect during thermoporometry. The thermoporometry studies revealed that the common interpretation of sharp intrusion curves and high entrapment levels in porosimetry data as implying ink-bottle pore geometries is flawed.

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1. Introduction

Mercury porosimetry remains a frequently used structural characterisation method for use with heterogeneous catalysts because it is still one of only a few techniques that can provide data over the complete length-scale range from ~ 3 nm to ~ 100 μ m in a single

experiment. A substantial body of past work on porosimetry has both greatly expanded its capabilities and revealed particular problems. For instance, there is much previous work in the literature on improving the interpretation of mercury porosimetry data and addressing key issues such as the pore-shielding effect (Androutsopoulos and Mann, 1979; Matthews et al., 1995). Mercury porosimetry relies upon the basic underlying principle that mercury is a non-wetting fluid for most surfaces and, thence, to intrude it into ever smaller pores a greater pressure is required, which according to the Washburn (1921)

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equation is given by:

$$p_f^l = \frac{-2\gamma \cos \theta}{r} \quad (1)$$

where p_f^l is the hydrostatic pressure in the liquid phase to enter a pore of radius r , γ is the surface tension, and θ is the contact angle. The macroscopic contact angle can readily be measured using techniques such as the sessile drop experiment. However, there is often doubt as to whether the macroscopic measurement applies to mercury menisci with a small radius of curvature, as would be found in nanopores. Previous workers have attempted to calibrate the physical properties term in the Washburn equation using model materials with independently known pore sizes, such as controlled pore glass (CPG) (Liabastre and Orr, 1978; Kloubek, 1981).

In the usual mercury porosimetry experiment, the hydrostatic pressure is increased in small steps, and the intruding mercury volume allowed to reach equilibrium at each step. The pore size is derived using Eq. (1), and the corresponding pore volume from the intruded liquid volume at each step. The accuracy of the pore size distribution relies upon Eq. (1), or its calibrated equivalents, being valid throughout the intrusion process, and, hence, that mercury always stays non-wetting to the surface. However, many of the catalysts used in the chemical industry use supported metal crystallites or mixed oxides of relatively heavy elements like copper, platinum and molybdenum. The dispersion force interaction of platinum is such that its Leonard–Jones potential parameters are the same as for mercury (Zhu, 1995). Hence, it is conceivable that the surface of catalysts containing heavy elements may wet mercury, contrary to the assumptions of the conventional analysis of mercury porosimetry data.

Mercury porosimetry is frequently used to obtain PSDs for catalyst pellets including those containing heavy metals, such as hydrotreating catalysts. However, since interpretation of mercury porosimetry is based upon the presumption that it is a non-wetting fluid, the presence of elements/surfaces for which it has a high affinity casts doubt over the accuracy of the PSDs obtained. Indeed, it has been found that increasing the content of MoO₃ or WO₃ in alumina-supported catalysts resulted in a gradual decrease in the apparent surface area from mercury intrusion porosimetry compared to that measured by the nitrogen adsorption BET method (Milbum et al., 1994). It was further found that altering the mercury contact angle towards a more wetting value improved agreement between the two methods. This suggested that the presence of heavy elements in the surface may alter the wetting properties of mercury and decrease the accuracy of the PSD. However, other workers Lowell and Shields (1982) found that the presence of other heavy elements, namely copper, nickel or cobalt, only increased the width of the hysteresis, and the amount of entrapment, but did not significantly alter the intrusion pressure. It could be argued that, since the pressure for mercury intrusion is controlled by the radius of curvature of the mercury meniscus at the pore mouth, then the presence of heavy elements down inside the pore will not impact intrusion pressure, but only retraction pressure due to the pore potential effect. Hence, uncertainty remains over the impact of heavy elements in the internal surface of a porous solid on the accuracy of the PSD obtained. The aforementioned contrasting findings could potentially be explained by the difference in atomic numbers of the elements studied, since molybdenum and tungsten are heavier elements, with larger dispersion forces, than copper, nickel or cobalt. However, even though both sets of workers studied alumina supports these differed in the pore size or surface roughness, and, thus, other characteristics of the system may explain the results. Lowell and Shields (1982) did not obtain independent validated measures of pore properties such as modal pore size to compare with mercury

intrusion. Hence, the particular influence of heavy metals on mercury intrusion remains an open question.

Recently, complementary methods have been developed that enable the more direct validation of mercury porosimetry. Following mercury intrusion the pressure is released in small steps to obtain a corresponding retraction curve as mercury extrudes from the sample. However, in many samples, not all of the mercury leaves the sample, and some may remain entrapped in the sample even when the pressure returns to ambient. The entrapped mercury remaining behind can itself be used as the probe fluid for thermoporometry. The mercury thermoporometry method (Bafarawa et al., 2014) enables the probing of the entrapped mercury directly to obtain information such as the size of the remaining mercury ganglia. Hence, mercury thermoporometry can be used to independently determine the size of pores that mercury has entered but then has become entrapped in the retraction step, and, thus, validate the mercury pore size obtained.

However, when using thermoporometry to probe complex pore geometries, the impact of that geometry on the melting mechanism and temperature has been shown to be important (Bafarawa et al., 2014). In particular, when the probe liquid ganglia extend between, and connect, several different pores, then so-called pore–pore interaction effects, such as advanced melting, become important (Hitchcock et al. 2011). In advanced melting, the melting of the fluid within a small pore connected directly to a larger pore can facilitate the melting of the probe fluid in the larger pore at a temperature lower than expected (for an isolated larger pore). Hence, in order to interpret (mercury) thermoporometry data correctly, the influence of pore and fluid ganglion connectivity, and network effects, needs to be taken into account, and will be considered in this study.

In order to use thermoporometry to validate porosimetry using entrapped mercury it is also necessary to fully understand the entrapment mechanism so that the correct interpretation of the thermoporometry data can be made. Typically, in thermoporometry, the porous solid is completely filled with probe fluid. While glass micro-model experiments (Wardlaw and McKellar, 1981) have shown that some particular pore geometries result in the pores being completely filled with mercury following entrapment, many other pore configurations only result in pores that are partially-filled with entrapped mercury. However, it has been shown previously (Rigby et al., 2006) that complementary integrated gas sorption experiments run on the same sample before and after mercury entrapment will reveal when the entrapment process leads to partial, rather, than full pore saturation with mercury. Hence, complementary integrated gas sorption will be used to resolve between different potential interpretations of the thermoporometry data.

Based on findings from mercury porosimetry experiments conducted on glass micro-models with simple created pore geometries (Wardlaw and McKellar, 1981) and other data, some authors (Day et al., 1994) have attempted to draw up a general classification scheme for the shapes of mercury porosimetry curves similar to the classification scheme developed by the IUPAC for nitrogen sorption isotherms and hysteresis loops (Rouquerol et al., 1999). However, there is doubt concerning the general applicability of these schemes to the wide variety of potential sample materials.

This work will show how the complementary measure of pore size provided by mercury thermoporometry can eliminate uncertainty over the accuracy of PSDs for catalysts containing heavy elements. In addition, this work will test the general applicability of the classification scheme for mercury porosimetry data, particularly the classical theory on the detection of ink-bottle pore geometry. The work comprises a detailed case study that makes use of the particular characteristics of the specific material chosen that make this type of study possible. Besides containing a

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