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Advanced Sample Preparation Techniques for Surface Spectroscopy Analysis of Organic-Inorganic Hybrid Silica Particles

Harekrishna Panigrahi, Smrutirekha Mishra and Suraj Kumar Tripathy

Abstract

Silica due to its large inorganic amorphous wall and hydrophilic surface properties renders its suitability for designing different varieties of organic-inorganic silica-based materials. Characterization of such hybrid silica-based materials is one of the fascinating as well as challenging topics to be covered. Surface analysis of these hybrid materials can be done utilizing various techniques, out of which X-ray photoelectron spectroscopy (XPS), ^{29}Si Solid-state Nuclear magnetic resonance (NMR) spectroscopy, and Fourier-transform infrared spectroscopy (FTIR) is the most ideal ones. Thus, before analyzing these silica materials, it requires a massive study on its sample preparation for appropriate characterization of the organic molecules present in the inorganic network. Hence, this chapter will give a brief elucidation of the sample preparation techniques for analyzing the hybrid materials utilizing the above instrumentation techniques.

Keywords: Silica, Surface analysis, Sample preparation, XPS, ^{29}Si Solid-state NMR, FTIR

1. Introduction

Characterization of solid materials [1] is a vast and intense field that requires immense knowledge and practice to obtain the required properties. Other than characterization two important challenges that any solid sample require are understanding the results obtained and second is sample or specimen preparation techniques [2]. In the last few decades, exhaustive research has been carried out in understanding these solid sample's composition, chemistry [3], and its internal structure [4] to push these samples towards an efficient approach for specimen preparation and analysis.

Out of all the solid samples such as in powdered form [5] or film form [6], studying these hybrid silica materials has been a keen focus for many researchers. Silica materials [7] due to their rigid inorganic structure [8] make the material an overall highly amorphous [9] bulk powdered form. Thus, focusing on these organic-inorganic hybrid silica [10] particles requires more attention due to the presence of organic moieties [11] in the inorganic network. As the chances of exchanges of ions/molecules [12] and redistribution of molecules [13] are higher when it undergoes different techniques of specimen preparation for its analysis as compared to other materials. The Exchange of

ions/molecules is higher during the sample preparation technique due to the presence of impurities within the sample chamber. Sometimes it can lead to adsorption [14], vaporization [15], and corrosion on these powered surfaces. Due to its robust nature, the important parameter which needs to be king-pinned during its sample preparation is that the hybrid surface is majorly exposed to the probe of the characterization technique [16] rather than the contaminated one. Hence, in simple words maintaining the surface and cleaning it with very basic revision is the important challenge for its sample preparation technique. Thus, it is very important initially to understand the scope of the sample/specimen preparation technique prior to analyzing.

In this chapter we are focusing on the aspects of advanced sample preparation techniques that are required for analyzing these hybrid materials utilizing XPS [17], ^{29}Si Solid-state NMR [18], and FTIR [19] techniques. The very basic steps that are required for sample preparation utilizing all of these techniques are described in **Figure 1**.

One of the important features for these materials that are required for analysis utilizing surface characterization is the use of a very high vacuum system [20] (ultrahigh vacuum, 10^{-7} – 10^{-11}) since these materials involve the detection of charged particles [21]. Hence, the analyst should be aware that whether the surface of the sample is susceptible to alternation or degradation in the vacuum system. In some cases, differentially pumped sample holders can be used which can keep the surfaces stable even at high vacuum pressure. Owing to the sample preparation technique one must always remember that what vacuum should be used for processing the hybrid materials. Some of the very important information which should be focused on while analyzing these hybrid materials utilizing surface characterization techniques are shown described in **Figure 2**.

Hence, this chapter is organized in different sections which will give an overall idea of the traditional and advanced sample preparation techniques which are utilized for surface spectroscopy analysis (XPS, ^{29}Si Solid-state NMR, FTIR) for organic–inorganic hybrid silica samples.

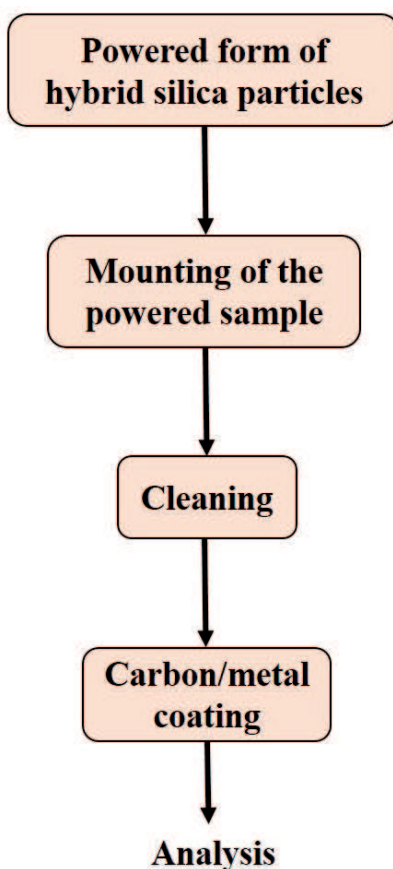


Figure 1. Basic steps required for specimen preparation-XPS, ^{29}Si solid-state NMR, and FTIR.

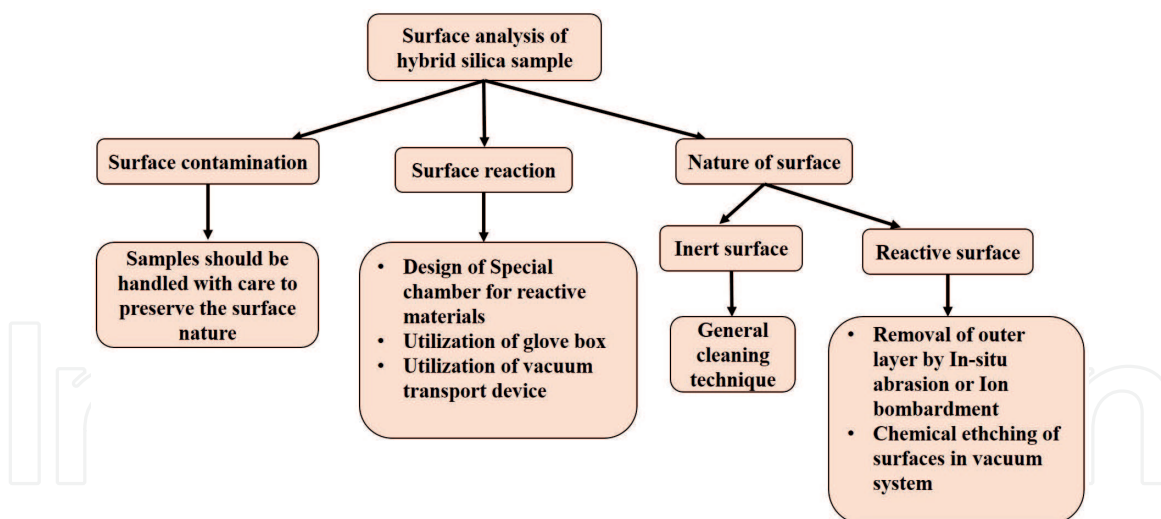


Figure 2.
 Basic handling steps required for surface analysis of hybrid silica samples.

2. Surface analysis techniques

Characterizing these organic–inorganic silica particles [22] is an interesting as well as challenging topic. Though these materials contain rigorous inorganic silica [23] network within them still the challenge remains to identify these organic molecules within this rigid inorganic network. Hence, characterizing and analyzing these sample surfaces requires different techniques. Some of the important techniques which are largely used are described in **Table 1**.

Techniques	Concerns
Auger electron spectroscopy (AES)	High-resolution analysis of surface and film from ~1 to 20 Å depth.
X-ray photoelectron spectroscopy (XPS)	Depth profiling of surfaces and films up to 1-3 μm. Determines individual chemical composition and chemical state of elements.
Ion scattering spectroscopy (ISS)	Provides general elemental information and determines usually the monolayer structure of surfaces and films.
Secondary-ion mass spectroscopy (SIMS)	An ultra-high sensitivity technique that provides a piece of qualitative information on the elemental composition of surfaces and films
Wavelength dispersive spectroscopy (WDS)	Provides both qualitative and quantitative information on the elemental composition of surfaces and films with a detection limit of ~0.2%.
Energy dispersive spectroscopy (EDS)	Provides qualitative and quantitative along with elemental mapping with a detection limit of ~0.1%.

Table 1.
 Surface analysis techniques are largely used for the analysis of organic–inorganic silica samples.

3. Traditional sample Preparation techniques

Every sample preparation technique that is used for analyzing the surfaces of hybrid silica materials has its advantages [24] and disadvantages [25]. As the analysis techniques become more sophisticated, sample preparation becomes more and more precise [26]. However, focusing on surface analysis [27] of these hybrid samples they have special concerns. Since these hybrid materials have the presence of organic moieties on the outer surface which in return makes it more sensitive and fragile for sample preparation before analyzing through any technique.

Challenges which is concerned for these types of materials are (a) exchange of ions and atoms in the sample preparation environment and (b) redistribution and reconstruction of atoms/molecules within this bulk powdered sample. Other than these, one of the important parameters for analyzing hybrid surfaces is that they require an ultrahigh vacuum environment (10^{-7} – 10^{-11} torr) as they require detection of charged silica particles.

3.1 X-ray photoelectron spectroscopy (XPS)

XPS [28, 29] is one of the sensitive characterization techniques which requires extreme alertness while its sample preparation [30]. One of the vital points which need to be focused on first is its sample handling practice. The important highlights for handling the samples are as follows:

- Powder-free nitrile or polyethylene gloves should always be used. Tweezer or glassware if used should thoroughly be cleaned before use.
- Cleaning of the sample chamber preferably by Ar^+ etching should be done to remove oxide layers that will cause damage to the surface of the silica samples.
- Since these hybrid materials have a high surface area, they require a longer time for pumping before positioning for analysis.
- These materials are highly sensitive to moisture/oxygen thus these should be loaded and mounted onto the vacuum transfer vessel in the glove box.

Generally, for XPS analysis the sample thickness should not be more than 4 mm. Since these hybrid materials are powder in form thus the general methods that are followed for its sample preparation along with its drawbacks are as follows:

- **Pressing of the powdered silica form into clean indium foil (high purity, as shown in Figure 3).** One problem which arises with this method; since Indium is a high atomic number (Z) material thus chances of spectral contamination with many XPS peaks are possible.
- **Utilization of a mesh screen for pressing finely powdered silica samples (as shown in Figure 4).** The Only drawback with this method is the chances of the destruction of organic groups present on the outer surface due to high mechanical work. There is also the possibility of the irradiating beams hitting the mesh which can lead to the destruction of some of the groups. Sometimes if the powdered silica sample is not properly crushed entrapment of coarse particles in the mesh is possible which would ultimately not allow the passage of finer silica particles.
- **Preparation of pellets from powdered silica samples (as shown in Figure 5).** This is one of the advantageous methods for the preparation of samples. However, chances of potential structural changes due to the pressure applied are possible.
- **Placing of hybrid silica sample within the depression of the sample holder.** The major drawback of this technique is the potential loss of samples when high vacuum pressure is applied.

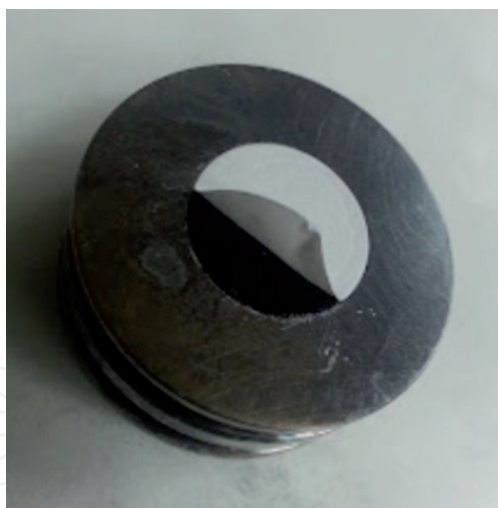


Figure 3.
Demonstration of the method used for pressing powdered silica samples onto indium foil [31].

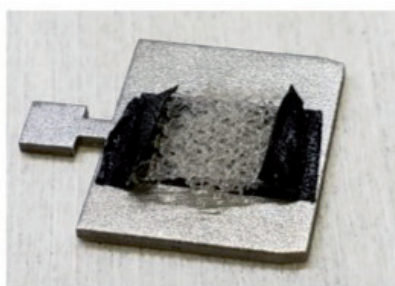


Figure 4.
Demonstration of the method used for pressing powdered silica samples onto mesh screens [32].



Grind the entire sample



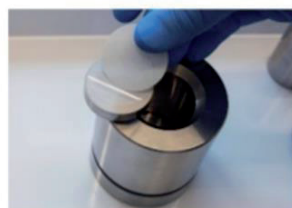
Weigh the sample



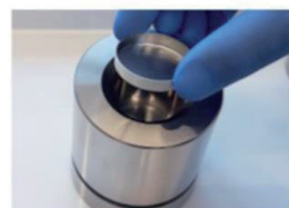
Add binder (if required)



Mix for 2 minutes



Add a pellet film



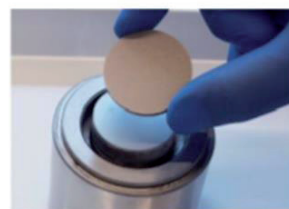
Introduce a aluminum cup



Fill in the mixture



Press the mixture



Perfect pellet obtained

Figure 5.
Demonstration of the method used for the preparation of pellets from powdered silica samples [33].

- **Placing of hybrid silica sample in the container and then tilting of the container towards the sample analyzer.** High chances of spilling silica samples within the vacuum chamber are possible when the alignment of the sample holder is performed.

3.2 ^{29}Si solid-state NMR

^{29}Si Solid-state NMR [34, 35] is a special NMR spectroscopy technique specifically used for the study of silica/silicon samples [36]. This technique can provide a depth of knowledge and understanding about the organic–inorganic hybrid silica samples [37]. However, sample preparation for this technique is purely different than standard solution NMR. Some of the important features of ^{29}Si Solid-state NMR are as follows:

Probes: Different types of probes [38, 39] are used for ^{29}Si Solid-state NMR which are efficiently capable of handling high power running systems (as shown in **Figure 6**).

Experiment: Parameters for ^{29}Si Solid-state NMR are quite different than the solution NMR. Such as chemical shift anisotropy (CSA) and dipolar coupling are usually averaged out in solution NMR due to the random motion. However, in the case of ^{29}Si Solid-state NMR CSA and dipolar coupling are quite dominating providing an entirely different experimental setup. Thus, one should have a piece of deep theoretical knowledge on the user's part.

Generally, sample preparation in the case of ^{29}Si Solid-state NMR is performed using specially designed “rotors” of different diameters usually made of zirconia. These rotors and their setup are highly expensive. These rotors packed with silica samples are spun at high frequency and a particular angle. This spinning of rotors at a magic angle (ca. 54.74° , where $\cos 2\theta_m = 1/3$) concerning the magnetic field applied is referred to as magic angle spinning (MAS). These rotors are tube-like structures [40] used for MAS are quite small often white. There are different types of rotors of different capacity used for ^{29}Si Solid-state NMR such as (**Figure 7**):



Figure 6.
A general model of ^{29}Si solid-state NMR probe [39].

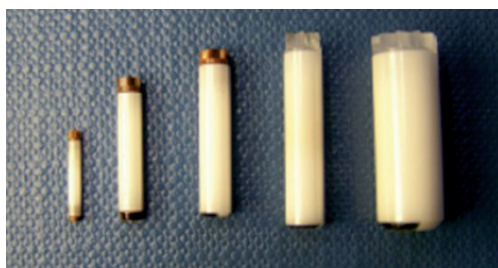


Figure 7.
Rotors of different capacities are used for sample packing in ²⁹Si solid-state NMR [40].



Figure 8.
Type of caps used for rotors (typical materials used ZrO₂, Macor, KeI and Vespel) [40].

These rotors are closed with caps after the hybrid silica samples are packed in them with caps. These caps are also of different sizes according to the rotor system and are made of different materials. Commonly used materials are Vespel, Ke1-F, Zirconia, and Boron nitride (**Figure 8**).

These hybrid silica samples are usually agglomerated powdered in form. Thus, it is always recommended to grind these samples to a fine powder using mortar and pestle before inserting them into the rotor system. Then keep the rotors in a standing position and pack the silica samples in stages using a clean spatula. Filling of sample is required up to the cap's place.

While disassembling and removing the powdered silica samples from the rotor one must be extremely careful in the opening of the system without breaking them apart as these are highly expensive. For example, in the case of the Ke1-F cap cooling of the rotor is first required to reduce the risk of breaking the cap. In the case of hybrid silica, samples remove samples from the rotor using a spatula. Then all of the parts should be washed properly preferably by a solvent (acetone) and dried in an oven.

3.3 Fourier-transform infrared spectroscopy (FTIR)

FTIR [41, 42] is a simple process that operates through transmission technique [43] and it does not require a separate accessory for analysis. It allows the users to simply place the powdered hybrid silica samples onto the infrared (IR) [44] beam setup. Since the IR beam passes through the silica samples, the transmitted energy is recorded and a final spectrum is obtained. However, there are different techniques for preparing samples specifically for silica materials. One very old method of preparing silica samples for analysis is *via* pressed pellet/KBr pellets and disks. To prepare pellets using silica sample and KBr, one must follow some rules such as:

- **Sample/KBr ratio:** A proper concentration of silica samples is required to be mixed with KBr powder to get a clear spectrum. Usually, between 0.2–1% of silica samples should be used to obtain a clear pellet.



Figure 9.

Pistil setup along with stainless steel disks for sample preparation of hybrid silica materials for analysis utilizing FTIR technique [45].

- **Sample preparation:** A homogenous mixture between the silica sample and KBr powder is expected to obtain the best results. The hybrid silica sample and KBr powder absorb humidity very fast (due to hygroscopic nature) from the environment which would eventually lead to increased background noises in the spectrum. Thus, drying of silica samples as well as KBr (preferably at 100°C) is highly required. After drying the materials take nearly 1 to 2% of the sample along with KBr powder and mix it properly using mortar and pestle [45] as shown in **Figure 9**. As these hybrid silica samples are a little bit hard thus first silica samples should be added and ground followed by the addition of KBr.

Clutch two stainless steel disks and transfer the silica samples carefully onto one disk with a spatula that is inside the pistil. Then put another disk on top of the sample. Finally, transfer the pistil setup to the hydraulic press. Put a maximum pressure of 20,000 prf. Wait for few seconds so that the powdered silica samples bind properly with the KBr and form a uniform pellet. Release the pressure and carefully remove the pistil out of the hydraulic press system. Slowly open the pistil and take out the pellet formed. The pellet should look homogenous and clear (mostly transparent) in nature.

Sometimes, very uneven cloudy pellets are formed due to some of the reasons such as improper mixing of KBr powder, moisture in silica sample, sample to KBr ratio is quite high and pellet too thick.

4. Modern sample Preparation techniques

Due to increased demand for purity of samples leading to acceptable results are currently the hot topics; thus an advanced form of sample preparation technique is highly required. Sample preparation has always been a crucial factor for surface analysis techniques leading to most labor-intensive parts. This in turn makes an analysis slower and increases its cost leading to multi-step procedures. Usually, an ideal sample preparation technique should be simple, efficient, and inexpensive. The most important factors that have increased the curiosity in researchers for modern sample

preparation techniques are increasing the sample loading capacity, decrease in labor cost, and good data collection. Hence, this section will provide an overview of the advanced sample preparation techniques are currently used for surface analysis using XPS, ^{29}Si Solid-state NMR, and FTIR specifically for organic–inorganic hybrid silica samples.

4.1 X-ray photoelectron spectroscopy (XPS)

As discussed above some of the traditional methods have been used for ages for preparing samples. These traditional methods lacked proper utilization of samples sometimes leading to loss of samples and time consumption. Highlighting these points researchers tried to design an advanced XPS system where sample preparation along with analysis would be much more efficient. Some of the advanced sample preparation techniques for XPS is as follows:

- Recently, a multi-function XPS having load-locked advanced sample preparation stages was developed which has additional ultraviolet photoelectron spectroscopy along with sample pre-treatments units. This XPS system has an in-situ sample preparation stage. This system has additional chambers attached along with the analysis vessel allowing loading of more than one sample at a single time. As this technique is quite advanced thus predictions of organic groups in the inorganic silica samples would be possible to measure quantitatively. Also, one must not follow the long procedures of the traditional method of sample preparation technique saving time as well as cost.
- One more advanced technique which has attracted quite an attention recently is a custom-made multi-chamber ultra-high vacuum [46] (UHV) system as shown in **Figure 10** for easy sample transport along with additional characterization ability. Its auxiliary system allows these silica samples to transport to the analysis vessel at very low pressure (10^{-10} mbar). It also has a central radial distribution channel where more than one sample can be kept in the second sample preparation chamber or sample storage chamber when one is being analyzed. The sample can be heated and cooled during its measurements and these chambers are equipped with gas dosing for in-situ sample preparation. It has a total of six sample holders in the storage chamber.

The preparation chambers provide in-situ sample preparation facilities such as sputtering and annealing which allows in-situ characterization of samples. These chambers are equipped with the precision manipulator, electron beam evaporator, pumping system, pressure gauges, and ions sources for surface cleaning. Since these have numerous UHV systems which allow the analysis of powdered silica samples having different surfaces.

4.2 ^{29}Si solid-state NMR

Hybrid silica samples require special analytical methods that can allow these samples to be analyzed both on macroscopic as well as atomic levels to co-relate the structure and property practically. Thus, ^{29}Si Solid-state NMR is a highly efficient technique for providing a wealth of information about these materials. As described above sample preparation techniques that are used traditionally have their own advantages and disadvantages. However, an upgraded version for the sample preparation technique is always required to efficiently use these silica samples. As

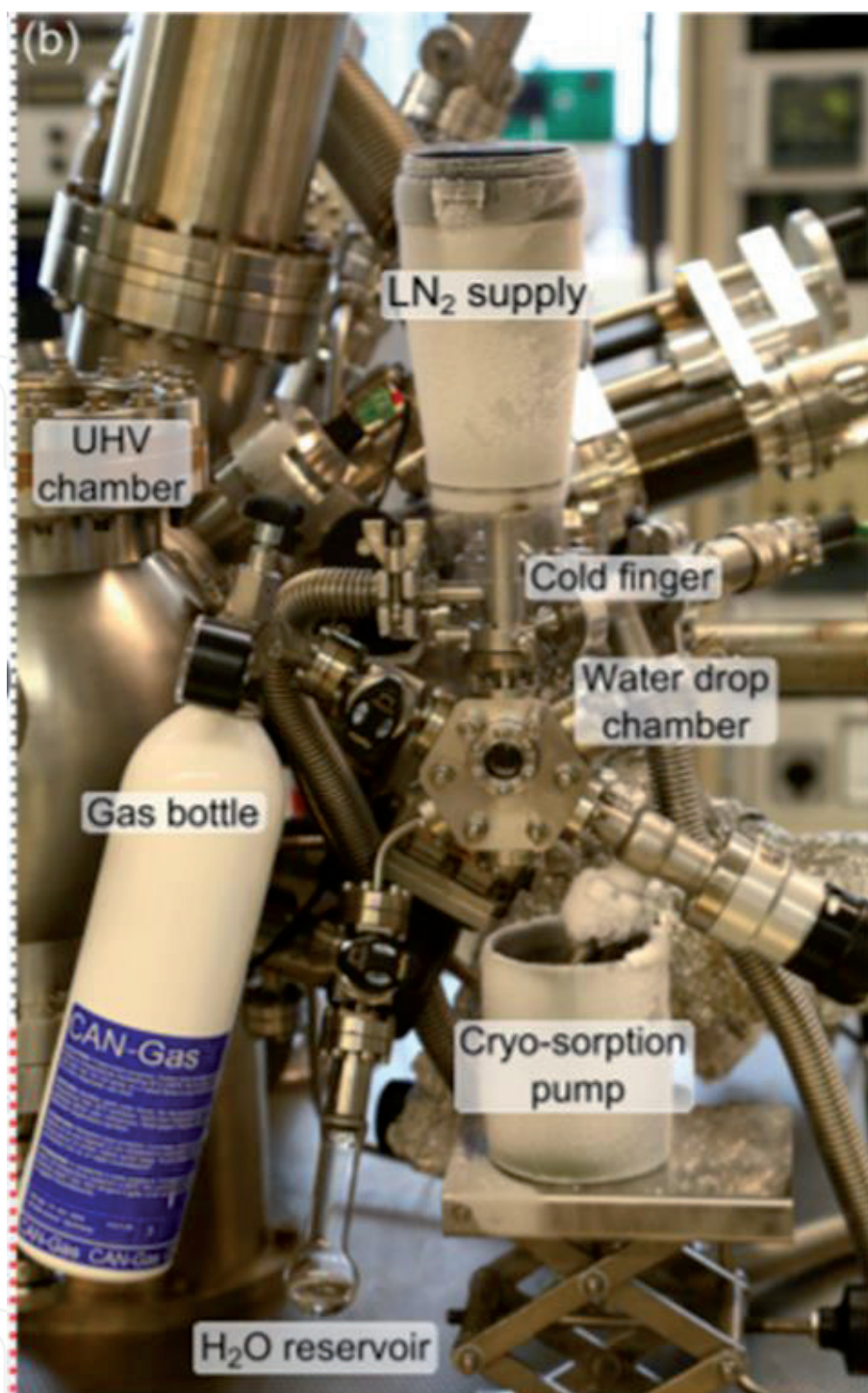


Figure 10.

A typical in-situ sample preparation chamber is attached to the UHV system XPS [46].

described above rotors play an important role in sample preparation and packing in ^{29}Si Solid-state NMR. Thus the efficiency of these rotors while spinning depends on the type of materials it is made up of. Hence, new types of rotors are now being introduced into the market with improved efficiency. KeI-F rotors are now upgraded to Torlon based rotors. Torlon is a green thermoplastic poly-imide-based material that has very strong chemical resistance (**Figure 11**).

As these hybrid silica samples are quite moisture/air sensitive materials thus it requires set-up which would allow the least moisture contact. O-ring caps are the best option for such types of materials. Macor rotors are also more preferred for silica-based samples. Usually, these O-ring caps are best suited for macor rotors.



Figure 11.
A general torlon based rotor was used for ^{29}Si solid-state NMR technique [38].



Figure 12.
Typical setup of FTIR for sample preparation for both traditional and modern methods [47].

4.3 Fourier-transform infrared spectroscopy (FTIR)

The most common method for sample preparation in FTIR for hybrid silica samples involves grinding of sample into fine powdered form and then dispersing it into a matrix. KBr is the most widely used matrix material. As discussed above, initially drying of silica samples as well as KBr (preferably at 100°C) is highly required. After drying the materials addition 1 to 2% of the sample along with KBr powder and mix it properly using mortar and pestle. As these hybrid silica samples are a little bit hard thus first silica samples should be added and ground followed by the addition of KBr. Then clutch two stainless steel disks and transfer the silica samples carefully onto one disk with a spatula that is inside the pistil. Then put another disk on top of the sample. Finally, transfer the pistil setup to the hydraulic press. Put a maximum pressure of 20,000 prf. Wait for few seconds so that the powdered silica samples bind properly with the KBr and form a uniform pellet. Release the pressure and carefully remove the pistil out of the hydraulic press system. Slowly open the pistil and take out the pellet formed. The pellet should look homogenous and clear (mostly transparent) in nature.

This is a universal method used always for sample preparation techniques in FTIR as this method is quite advantageous. Hence, an advanced sample preparation technique is not required for this technique (**Figure 12**).

5. Conclusions

Observing all the procedures for sample preparation utilizing different techniques, a detailed explanation is provided about the hybrid silica samples and their handling procedure before its sample preparation. As these materials have large inorganic amorphous walls and hydrophilic surface properties thus characterization of such hybrid silica-based materials is one of the fascinating as well as challenging

topics to be covered. Surface analysis of these hybrid materials can be done utilizing various techniques, out of which X-ray photoelectron spectroscopy (XPS), ^{29}Si Solid-state Nuclear magnetic resonance (NMR) spectroscopy and Fourier-transform infrared spectroscopy (FTIR) are the most ideal ones. Thus, before analyzing these silica materials, it requires a massive study on its sample preparation for appropriate characterization of the organic molecules present in the inorganic network. Hence, this chapter provided a brief elucidation on the sample preparation techniques for analyzing the hybrid materials utilizing the above instrumentation techniques utilizing both traditional and advanced methods. Nevertheless, many approaches for sample preparation have been developed recently that would allow easy investigations of the target surfaces. In order to highlight the surface analysis of organic–inorganic hybrid materials implementation of new methods such as chip-based systems, optical tweezers, and micro-fluid-based systems would provide high potentiality to this technique. The extensive study still needs to be performed specifically for surfaces analysis that would push the traditional sample preparation methods towards high outturn measurements.

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