Standard Nitrogen Adsorption Data for Manganese Oxide and Like (C_{BET} = 40–60) Surfaces

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ABSTRACT: Calcination to 1170 K of materials obtained by mild and intensive reduction of KMnO₄ and HMnO₄ solutions was found to produce manganese oxides assuming the crystalline bulk structure of α-Mn₃O₄. Nitrogen adsorption isotherms at 77 K revealed that they also assume non-porous surfaces of low specific area (4 ± 1 m²/g) with C_{BET} equal to 40–60; t- and αₙ-curves derived therefrom were found to coincide with those determined reportedly on non-porous surfaces of 11 < C_{BET} < ∞, irrespective of the surface chemical similarity. The experimental and reported standard adsorption data were used to analyze a type-IV nitrogen adsorption isotherm determined at 77 K on a porous manganese oxide (δ-MnO₂) which was obtained by sol–gel processing of a KMnO₄ solution, and found to similarly reveal a mesoporous surface of S_{BET} = 73 m²/g and C_{BET} = 125. The close agreement between the surface area values (S_i and S_a) derived for the test material (δ-MnO₂) from the t- and αₙ-plots thus obtained and its C_{BET} value (73 m²/g) was the basis on which reference materials with 11 < C_{BET} < ∞ were found to be appropriate. Since most of the appropriate reference materials were dissimilar chemically to the test material, the results of the present investigation may imply that the surface chemical similarity demanded by the αₙ-method is better manifested in terms of the surface activity (heat of adsorption monitored by the C_{BET} value) than the chemical composition.

INTRODUCTION

The ‘t’ (Lippens and de Boer 1965) and ‘αₙ’ (Sing 1968) methods are widely used in the analysis of nitrogen adsorption isotherms at 77 K in order to characterize the pore structure of solid surfaces (Lecloux 1981). The principle of both methods is to compare the volume of nitrogen adsorbed, Vₙ[ml(STP)/g], on a test surface at a given relative pressure of adsorptive (P/P⁰) with the adsorbate multilayer thickness \[t = (V_{n}/V_{m}) \times 3.54 \text{ Å}\], where Vₙ and 3.54 Å are respectively the adsorbed monolayer volume and thickness) or the αₙ-value (\[= V_{n}/V_{0.4}\], where V_{0.4} is the volume adsorbed at P/P⁰ = 0.4) determined on a non-porous reference surface at the same relative pressure and temperature of adsorption. The resulting relationships over the full range of relative pressures scanned (P/P⁰ = 0.1–1.0) are denoted, respectively, by the t- (Vₙ versus t) and αₙ- (Vₙ versus αₙ) plots, and are referred to the test surface. The respective reference adsorption data used (the t-curve, t versus P/P⁰, and the αₙ-curve, αₙ versus P/P⁰) are, in fact, reduced forms of the standard nitrogen adsorption isotherm determined on the non-porous reference surface at 77 K.

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According to Lecloux (1981), the t- and \( \alpha \)-methods are similar not only in the principle, but also in being strictly relevant to the BET theory (Brunauer et al. 1938) and thus associated with its limitations (Lecloux 1981).

However, the apparent difference between the t- and \( \alpha \)-method is the different degree of appropriateness put forward by the inventors for the reference material. Although both methods stipulate that the reference material must have a non-porous surface, the t-method further demands that the reference material must possess a similar \( C_{\text{BET}} \) constant to that of the test material (Lecloux 1981), i.e. a similar strength of adsorbent–adsorbate interaction (Brunauer et al. 1938), whereas the \( \alpha \)-method requires the reference material to have a surface chemical similarity to the test material (Sing 1968). Pierce (1968) and Lecloux (1981) have, accordingly, collated and classified a number of reported t-curves (derived from standard nitrogen adsorption isotherms measured on a variety of adsorbents) depending on the \( C_{\text{BET}} \) constant value. Similarly, \( \alpha \)-curves have been derived for nitrogen adsorption on hydroxylated silicas (Carruthers et al. 1968) and aluminas (Payne and Sing 1969) and like materials.

Adopting the same principle of the t- and \( \alpha \)-method, Lecloux and Pirard (1979) devised an equivalent method, denoted the \( n \)-method (employing the \( n \) versus \( P/P^0 \) curve, where \( n \) = number of adsorbed layers = \( V/V_n \)), which, in line with the t-method (Lippens and de Boer 1965), prefers the choice of appropriate standard adsorption data on a similar adsorptive strength surface (similar \( C_{\text{BET}} \) values) as its basis rather than a similar chemical nature. In line with this approach, Abdel-Khalik and Zaki (1985) have shown the \( \alpha \)-curves reported by Carruthers et al. (1968) and Payne and Sing (1969) to be applicable only to hydroxylated surfaces (\( C_{\text{BET}} \geq 100 \)) of silicas and aluminas, respectively. Silica and alumina surfaces subjected to considerable dehydroxylation (\( C_{\text{BET}} \leq 30 \)) have been shown by these authors (Abdel-Khalik and Zaki 1985) to require \( \alpha \)-curves determined essentially on low-heat (low \( C_{\text{BET}} \)) reference surfaces.

The present investigation was launched for two objectives. The first was to provide standard nitrogen adsorption data appropriate for manganese oxide and like surfaces. The second was to provide a deeper insight into the degree of appropriateness of standard adsorption data. Thus, manganese oxides with non-porous surfaces were prepared via different pathways and were subjected to surface and bulk characterizations using X-ray diffractometry, infrared spectroscopy, thermogravimetry and electron microscopy. Nitrogen adsorption isotherms were determined on these prepared reference (PR) materials at 77 K and converted into the reduced t- and \( \alpha \)-curves which were then compared with corresponding curves described in the literature for reported reference (RR) materials with varied surface and bulk properties. The PR and RR data were used to analyze a test nitrogen adsorption isotherm determined at 77 K on a synthetic, porous manganese oxide sample.

**EXPERIMENTAL**

**Materials**

*Prepared reference (PR) materials*

Three manganese oxide materials were synthesized; they are referred to below as the prepared reference (PR) materials so as to be distinguished from those selected from the literature [reported reference (RR) materials]. Amongst themselves, the three materials are distinguished as PR(1), PR(2) and PR(3), respectively. PR(1) and PR(2) were obtained by calcination (heating in air) to 1170 K of products obtained by the mild reduction of aqueous solutions of KMnO\(_4\) (BDH) and HMnO\(_4\), respectively, followed by subsequent treatment of the calcination products with an aque-
ous solution of HNO$_3$ (BDH) accompanied by filtration and drying at 360 K for 24 h. The mild reduction was effected by fumaric acid (BDH) at 300 K as described by Bach et al. (1990), while the permanganic acid (HMnO$_4$) was the product of the complete cation exchange of a KMnO$_4$ solution with protonated Dowex resin (Dow Chemicals) as detailed by Kappenstein et al. (1995).

In contrast, PR(3) was synthesized by calcination to 1170 K of the product of an intensive HCl reduction of KMnO$_4$ solution at 360 K, followed by filtration, thorough washing with distilled water and drying of the reduction product at 360 K for 24 h as described by Parida et al. (1981).

**Test material**

A manganese oxide test sample was prepared by the above described mild reduction of KMnO$_4$ solution (Bach et al. 1990), but calcination was carried to 970 K, instead of 1170 K, and maintained for 3 h. The calcination product was then treated with a solution of H$_2$SO$_4$, filtered, thoroughly washed with distilled water, dried at 360 K for 24 h and re-calcined at 620 K for 3 h, as described by Bach et al. (1990). Preliminary characterization of the material, using X-ray diffractometry and infrared spectroscopy, revealed that it consists of $\delta$-MnO$_2$ (birnessite-like MnO$_{1.86}$O$_{0.6}$H$_2$O), as previously found by Bach et al. (1990).

**Material characterization techniques**

**Nitrogen sorpometry**

Isothermal nitrogen adsorption measurements on the reference (PR) and test samples of manganese oxides were carried out at 77 K, using an automatic ASAP 2010 Micromeritics sorpometer (USA) equipped with an outgassing platform and an on-line data acquisition and handling system operating BET (Brunauer et al. 1938) and BJH (Barrett et al. 1951) analytical software for the adsorption data. The adsorptive gas was a 99.999% pure product obtained from KOAC (Kuwait). Small portions of adsorbents (500 ± 2 mg) were outgassed at 390 K for 3 h and then subjected to adsorption/desorption measurements conducted at 77 K. The reproducibility of the measurements was better than 98%. Data determined for the adsorption branch of the isotherm were BET-analyzed (Lectoux 1981) for the monolayer capacity, $V_m$ [ml(STP)/g], specific surface area, $S_{BET}$ (m$^2$/g), and the BET constant, $C_{BET}$. The data determined on the PR materials were further used to derive standard t- and $\alpha_i$-curves (Lecloux 1981). The curves thus obtained were used to analyze the adsorption data exhibited by the test manganese oxide for the pore structure, whereas the BJH method (Barrett et al. 1951) was applied to analyze the same set of adsorption data for the pore volume distribution calculations.

**Thermogravimetry (TG)**

TG analysis was conducted by heating (at 10 K/min) small portions (20 ± 1 mg) of the materials under study up to 1470 K in a dynamic atmosphere of air (flow rate, 50 cm$^3$/min). A model TGA-50 Shimadzu automatic analyzer (Japan), equipped with a TA-50 work station for data acquisition and handling, was employed for these studies.

**X-Ray powder diffractometry (XRD)**

The crystalline bulk structure of the study materials was elucidated by matching observed XRD
patterns with JCPDS standards. XRD studies were carried out at 300 K in the 2θ range between 5° and 80° using a Siemens D5000 diffractometer equipped with Ni-filtered Cu Kα radiation (λ = 1.5406 Å). The diffractometer was operated with 1° diverging and receiving slits at 50 kV and 40 mA, and a continuous scan was carried out with a step size of 0.02° and a step time of 5.0 s. The pattern matching was automatically realized by means of an on-line library search system (PDF database).

Infrared spectroscopy (IR)

IR absorption spectra were measured for KBr-supported study materials (< 1 wt%) over the frequency range 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹ using a Perkin-Elmer model 2000 FT-IR spectrometer (UK).

Electron microscopy

The PR materials were examined by means of a JEOL model JSM-6300 scanning electron microscope (SEM) at 20 kV. In addition, energy dispersive spectroscopic (EDS) data were measured to ascertain the elemental composition.

RESULTS AND DISCUSSION

Prepared reference materials

Bulk structure

Despite the different methods of preparation used for the three PR materials [PR(1)–PR(3)], they all exhibited virtually the same XRD pattern [Figure 1(A)] and IR spectrum [Figure 1(B)]. The XR diffractogram [Figure 1(A)] exhibits peaks whose relative intensities and d-spacings (Å) match those filed for bixbyite α-Mn₃O₄ (JCPDS Card No. 41-1442) very well. Consistently, the IR spectrum [Figure 1(B)] exhibits four absorptions at 670, 608, 529 and 415 cm⁻¹, respectively, which are quite close to those (at 666, 601, 523 and 411 cm⁻¹) reported for the Mn–O bond vibrations of α-Mn₃O₄ by White and Keramidas (1972). Moreover, the IR spectrum exhibits weak absorptions at ca. 3395 cm⁻¹ and 1656 cm⁻¹ due, respectively, to the ν(OH) and δ(OH) vibrations of associated surface hydroxy groups and retained water molecules.

α-Mn₂O₃ is known to exhibit pronounced thermal stability on heating in air up to 1220 K (Nohman et al. 1992), at which temperature it decomposes into Mn₃O₄ (3Mn₂O₃ → 2Mn₃O₄ + ½O₂; ~3.4% weight loss). The TG curves obtained for PR(1), PR(2) and PR(3) [Figure 1(C)] all exhibit a 3.3–3.6% weight loss at 1220–1230 K. The curves of the former two materials [PR(1) and PR(2)] moreover show a ca. 1% weight loss at 370–870 K, whereas that of the latter material [PR(3)] shows a ca. 0.5% weight loss near 370 K. The low-temperature weight loss may be attributed to elimination of entrapped water molecules in PR(3), whereas the high-temperature weight loss may involve the decomposition of a minor fraction of PR(1) and PR(2) which is likely composed of amorphous MnO₃ species of tetravalent manganese (Nohman et al. 1992). Thus, while α-Mn₂O₃ is shown to be the sole constituent of the bulk structure of PR(3), the TG results may imply the existence of a minor proportion of a less stable, amorphous MnO₃ species together with α-Mn₂O₃ in PR(1) and PR(2).
Figure 1. (A) X-Ray powder diffractogram, (B) IR spectrum and (C) TG curves for the reference materials prepared.
Figure 2. Scanning electron micrographs for the prepared reference materials.
Particle morphology and elemental composition

The scanning electron micrographs displayed in Figure 2 show that both PR(1) and PR(2) consist of large particles with ill-defined edges and shape, but having apparently smooth surfaces. However, the particles of PR(2) appear to have a relatively wider range of sizes (600–1000 nm) in comparison with the particles of PR(1) (500–600 nm). The particles of both materials appear as if they have been produced from a molten parent. It is worthy of note that these materials were rather unstable during examination with an electron beam at >20 kV due probably to their amorphous content.

In addition, Figure 2 also shows that PR(3) consists of large particles with smooth surfaces, but of a markedly different morphology. These particles have a platelet shape and an apparent hexagonal projection. The particle edges are much more clearly defined than those of PR(1) and PR(2). This may be related to the fact that PR(3) was more stable under an electron beam at >20 kV, such behaviour being attributed to the absence in the material bulk of amorphous MnO₄⁻ species.

In addition to the expected manganese and oxygen atoms, the use of EDS showed the presence of minute amounts of potassium atoms (2–4 atom%) in PR(1) and PR(3). The detection of potassium in these materials is presumably associated with their methods of preparation which involve KMnO₄ as the manganese parent material (see Experimental section). The absence of potassium contaminants in PR(2) can, therefore, be related to the use of HMnO₄ instead of KMnO₄. The EDS results may also reflect the surface chemical composition of the materials examined.

Nitrogen adsorption characteristics

Nitrogen adsorption/desorption isotherms determined on PR(1), PR(2) and PR(3) at 77 K were of type II (Gregg and Sing 1967), thus confirming the non-porous nature of their surfaces. A typical isotherm is that given for PR(1) depicted in Figure 3. According to Gregg and Sing (1967), the formation of type II isotherms can exclude the presence of mesopores but cannot rule out the presence of narrower pores (e.g. nitrogen-inaccessible pores) and wider pores (e.g. macropores and interparticle voids). The BET characteristics (specific surface area and C constant) derived from the isotherms are listed in Table 1 together with those documented in the literature for a set of reported reference (RR) materials with non-porous surfaces. The table also shows the chemical composition of the materials listed.

Table 1. Nitrogen-probed BET Characteristics for the Prepared (PR) and Reported (RR) Non-porous Reference Materials

| Material | Composition* | C constant, C_BET | S_BET (m²/g) | Source |
|----------|--------------|-------------------|--------------|--------|
| PR(1) α-MnO₄ (j) + am. MnO₄ (m) | 42 | 3 | Present work |
| PR(2) α-MnO₄ (j) + am. MnO₄ (m) | 65 | 4 | Present work |
| PR(3) α-MnO₄ (s) | 54 | 5 | Present work |
| RR(1) Mn₂O₇ (s) | 11 | 28 | Nohman and Zaki (1994)* |
| RR(2) dehydr. SiO₂ | 11 | 2 | Abdel-Khalik and Zaki (1985) |
| RR(3) Al₂O₃ | 60 | 65 | Lippens et al. (1964) |
| RR(4) hyd. SiO₂ | 100 | 39 | Carruthers et al. (1968) |
| RR(5) carbon | 350 | 4 | Rodriguez-Reinoso et al. (1987) |
| RR(6) treat. TiO₂ | ∞ | 10 | Cranston and Inkley (1957) |

* s = sole; j = major; m = minor; dehydr. = dehydroxylated; hyd. = hydroxylated; treat. = treated.
The t- and σₜ-curves derived from the isotherms for the PR samples are compared in Figures 4(A) and 4(B), respectively. The coincidence between each set of curves over the relative pressure range up to P/P₀ = 0.8 is quite obvious. Equally, the disagreement exhibited at higher P/P₀ values is insignificant. This behaviour justifies the very close BET characteristics (Sₐₛ = 4 ± 1 m²/g and Cₐₛ = 50 ± 10) determined for the PR materials (Table 1). It implies, moreover, that despite some structural, compositional and morphological differences monitored for their particles, their surfaces assume an almost identical adsorptive reactivity towards nitrogen molecules. Accordingly, the standard adsorption data (t- and σₜ-curve) determined on PR(3) (Table 2) have been selected for analytical treatment of the adsorption data determined on the test material (vide infra), particularly in that this involves the most homogeneous bulk structure (α-Mn₂O₃, Table 1) and well-defined particle morphology (Figure 2).

Figures 5(A) and 5(B) compare the respective t- and σₜ-curves (Table 2) exhibited by PR(3) with the corresponding curves previously determined on the RR materials compiled in Table 1. It is obvious that over the region of monolayer formation (up to P/P₀ = 0.2) the curves for PR(3) coincide with those determined on the RR materials assuming Cₐₛ ≥ 60 (Table 1) and lie above those exhibited by materials having Cₐₛ < 60. Over the post-monolayer region, particularly at P/P₀ ≥ 0.6, the curves for PR(3) reflect the relatively largest restriction to multilayer formation on this material as compared to the other RR materials. This behaviour may imply that PR(3) contains some micropores [pore radius (rₚ) < 20 Å (Gregg and Sing 1967)] and is thus not entirely non-porous.
Figure 4. (A) $t$- and (B) $\alpha$-Curves determined on the PR materials indicated.
Figure 5. (A) $t$- and (B) $\alpha_s$-Curves determined on PR(3) relative to those reported by the authors indicated for the RR materials listed in Table 1.
TABLE 2. Standard Adsorption Data for Nitrogen at 77 K on Non-porous Manganese Oxide \([= \text{PR}(3)]\), \(C_{\text{BET}} = 65\) and \(V_m = 0.94\) ml (STP)/g

| Relative pressure, \(P/P^0\) | Adsorption (\(V_a\)) per unit weight [ml (STP)/g] | Multilayer thickness, \(t\) (Å)\(a\) | Reduced adsorption, \(\alpha_a^\star\) |
|-----------------------------|---------------------------------|----------------|----------------|
| 0.01                        | 0.55                            | 1.67           | 0.37           |
| 0.03                        | 0.68                            | 2.22           | 0.46           |
| 0.07                        | 0.84                            | 2.83           | 0.57           |
| 0.08                        | 0.86                            | 3.03           | 0.58           |
| 0.10                        | 0.94                            | 3.31           | 0.64           |
| 0.12                        | 0.98                            | 3.59           | 0.66           |
| 0.14                        | 0.99                            | 3.71           | 0.67           |
| 0.16                        | 1.00                            | 3.72           | 0.68           |
| 0.20                        | 1.11                            | 3.89           | 0.75           |
| 0.25                        | 1.21                            | 4.37           | 0.82           |
| 0.30                        | 1.32                            | 4.80           | 0.89           |
| 0.35                        | 1.41                            | 5.13           | 0.95           |
| 0.40                        | 1.45                            | 5.45           | 0.98           |
| 0.45                        | 1.55                            | 5.82           | 1.05           |
| 0.50                        | 1.60                            | 6.01           | 1.08           |
| 0.60                        | 1.75                            | 6.57           | 1.18           |
| 0.65                        | 1.85                            | 6.95           | 1.25           |
| 0.70                        | 1.90                            | 7.14           | 1.28           |
| 0.75                        | 1.93                            | 7.25           | 1.30           |
| 0.80                        | 2.00                            | 7.51           | 1.35           |
| 0.85                        | 2.20                            | 8.37           | 1.49           |
| 0.90                        | 2.45                            | 9.49           | 1.66           |
| 0.95                        | 3.01                            | 11.83          | 2.03           |

\(\tau = 3.54 \times (V_a/V_m); \alpha_a = (V_a/V_{ad}) = \tau/4.15.\)

**Test material**

**Nitrogen adsorption characteristics**

The nitrogen adsorption/desorption isotherm determined on the test material (δ-MnO₂) [Figure 6(A)] is of type IV, which indicates that the material possesses a largely mesoporous surface (Gregg and Sing 1967). BET analysis (Brunauer et al. 1938) of the adsorption branch resulted in values of \(S_{\text{BET}} = 73\) m²/g and \(C_{\text{BET}} = 125\). Thus, the material possesses a high surface area and exhibits extensive adsorptive interactions with nitrogen molecules. BJH analysis (Barrett et al. 1951) of the adsorption branch in the isotherm produced the pore volume distribution (PVD) curve shown in Figure 6(B) which reveals consistently that the pore structure is dominated by mesopores with an average pore diameter of 70 Å.

**t- and \(\alpha_s^\star\)-Analyses of the adsorption isotherm**

t- and \(\alpha_s^\star\)-Analyses (Lecloux 1981) of the adsorption branch of the isotherm determined on the test materials [Figure 6(A)] were carried out using the t- and \(\alpha_s^\star\)-curves exhibited by the PR(3)
Figure 6. (A) Nitrogen adsorption/desorption isotherm determined at 77 K on the test material (δ-MnO$_2$) and (B) the pore volume distribution curve derived therefrom.
and RR materials (Figure 5). The resulting t- and $\alpha$-plots are displayed in Figures 7(A) and 7(B), respectively. The obvious upward deviation from initial linearity exhibited by all the plots constructed (Figure 7) is consistent with the mesoporous character of the test material [Figure 6(B)] (Lecloux 1981). Thus all of the standard curves employed succeed in revealing the true pore structure of the test material.

The initial linearity of the slopes of the t- and $\alpha$-plots yielded, respectively, the values of the specific surface areas $S_t$ and $S_\alpha$ listed in Table 3. It is well known that agreement between these area values and the $S_{\text{BET}}$ value indicates a proper selection of the standard adsorption data, i.e. the non-porous reference material (Lecloux 1981). Accordingly, the close agreement between the $S_t$, $S_\alpha$ (Table 3) and $S_{\text{BET}}$ ($= 73 \text{ m}^2/\text{g}$) values implies that the most appropriate standard adsorption data for the analysis of the adsorption isotherm of the test material are those determined on RR(4). On the same basis, the standard data determined on PR(3), RR(3) and RR(5) can also be considered adequate.

The sole similarity between the test material ($\delta$-MnO$_2$) and the most appropriate reference material [PR(4) = SiO$_2$] is that both assume high and close $C_{\text{BET}}$ values (125 and 100, respectively). The same can be considered applicable to PR(3), RR(3) and RR(5), since these materials also have comparably high $C_{\text{BET}}$ values (Table 1). Thus, any disagreement between the $S_{\text{BET}}$ ($= 73 \text{ m}^2/\text{g}$) and the $S_t$ and $S_\alpha$ values determined for the test material using standard adsorption data exhibited by RR(1), RR(2) and RR(6) can be attributed to the too low $C_{\text{BET}}$ values ($= 11$) for the former two reference materials and the too high value ($= \infty$) for the latter one.

It is worth noting, in this respect, that the reference materials having the closest surface composition to that of the test material ($\delta$-MnO$_2$) are PR(3) ($= \alpha$-Mn$_2$O$_3 + \text{am. MnO}_2$) and RR(1) ($= \text{Mn}_3\text{O}_4$). The former material failed to provide an acceptable $S_\alpha$ value (Table 3) while the latter proved inappropriate because of its too low $C_{\text{BET}}$ value (Table 1). By virtue of the very nature of the $C_{\text{BET}}$ constant (Lecloux 1981), the similarity of its value amongst different materials means that they expose surfaces with similar adsorptive interaction intensities towards a given adsorptive. Thus, in practice, the chemical similarity demanded by the $\alpha$-method (Sing 1968) is better demonstrated by similar surface reactivities (heat of adsorption $\equiv C_{\text{BET}}$) than chemical compositions. In a previous investigation, Abdel-Khalik and Zaki (1985) have found that standard nitrogen adsorption data determined on an intensively dehydroxylated SiO$_2$ material (low $C_{\text{BET}}$) were

| Reference material | $S_t$ (m$^2$/g) | $S_\alpha$ (m$^2$/g) |
|-------------------|----------------|------------------|
| PR(3)             | 79             | 101              |
| RR(1)             | 105            | 105              |
| RR(2)             | 105            | 105              |
| RR(3)             | 76             | 77               |
| RR(4)             | 74             | 73               |
| RR(5)             | 74             | 79               |
| RR(6)             | 64             | 83               |

$S_t = 15.47 \times (V/t)$ and $S_\alpha = f \times (V/\alpha_t)$ with the normalizing factor ($f = 3.724-2.729$) being calculated by considering the $S_{\text{BET}}$ area (Table 1) of the reference material, according to Sing (1970).
Figure 7. (A) t- and (B) $\alpha_s$-Plots constructed for the test material using the t- and $\alpha_s$-curves determined on PR(3) and those reported by the authors indicated for the RR materials listed in Table 1.
more appropriate for the analysis of the nitrogen adsorption isotherms exhibited by similarly low $C_{\text{BET}}$ surfaces of intensively dehydroxylated silicas than standard adsorption data determined on the high $C_{\text{BET}}$ surfaces of a hydroxylated SiO$_2$ (Carruthers et al. 1968). This was despite the fact that both the dehydroxylated and hydroxylated surfaces of SiO$_2$ are of almost identical chemical composition relative to each other and to the test material. Hence, we believe that the two different degrees of appropriateness for the reference (non-porous) material required by the $t$- and $\alpha_1$-methods, i.e. surface $C_{\text{BET}}$ similarity and surface chemical similarity, respectively, become quite relevant when the surface chemistry is looked at not in terms of just the composition but of its reactivity.

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