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Characterization of a cerium dioxide powder from its equilibrium with water vapour

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Abstract

The equilibrium between water and a cerium dioxide powder was studied by means of thermogravimetry between 373 and 573 K. The isotherms can be interpreted by the additive contribution of water adsorbed on two distinct sites which differ in their standard enthalpy of fixation and their relative population. The results agree with the model water is fixed on the ceria surface through direct bonds to cerium atoms and by hydrogen bonding to hydroxyl groups located in the micropores. The latter sites disappear following calcination at high temperature. This is confirmed by transmission electron microscopy photographs and nitrogen adsorption measurements.

INTRODUCTION

Cerium dioxide is known to be an efficient additive for automotive pollution control [1]. The importance of this application on an industrial scale explains the growing interest in the understanding of the chemical and physical properties of cerium dioxide. Recent investigations have focused on the redox properties of cerium-based catalysts owing to the oxygen-storage capacity of cerium [2,3]. Another interesting property is that of a stabilizing effect on the surface area of the catalyst [1,4]. It is now well known that water vapour may enhance the surface-area loss of metallic oxides. In recent studies we have pointed out the existence of such a catalytic effect of water on the initial sintering of titania [5] and alumina [6].

In the present work our objective was to characterize the interaction of water molecules with a cerium dioxide powder at moderate temperatures. A simple thermodynamic model has been successfully used in earlier studies to describe the fixation of water by solids such as hydrates [7] and a pyrochlo-

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ric tungsten trioxide [8]. The interaction between H_2O molecules and a solid containing the site "s" can be expressed by the equilibrium

$$[H_2O\text{–s}] = H_2O(g) + s \tag{1}$$

If n is the maximal number of sites and ϵ the amount of water fixed per mole of solid, we obtain the expression

$$\frac{1}{\epsilon} = \frac{K(T)}{n}\frac{1}{P} + \frac{1}{n} \tag{2}$$

in which P is the water vapour pressure and $K(T)$ the equilibrium constant. The value of n is independent of the equilibrium temperature.

It will therefore be possible to use the isotherms $\epsilon(P)$ for the fixation of water to determine n and $K(T)$. From measurements conducted at various temperatures the standard enthalpy of fixation $\Delta H^{\ominus}$ will thus be obtained. The determinations of n and $\Delta H^{\ominus}$ are reported in this paper in order to characterize the interaction of water with a powder of cerium dioxide.

METHOD

A sample of cerium dioxide was provided by Rhône–Poulenc, and calcined at 673 K for 6 h. Its surface area was then equal to 130 m^2 g^{-1} (sample A). When calcined at 943 K for 8 h, its surface area dropped to 35 m^2 g^{-1} (sample B). The two samples A and B were used for the determination of the amount of water fixed when the equilibrium conditions were reached.

The experiments were conducted using a Setaram MTB thermobalance equipped with a symmetrical furnace. A sample of about 400 mg of ceria was placed in a quartz crucible which was suspended in the balance. The sample was outgassed in a residual vacuum of 10^{-2} Pa for 14 h. Water vapour was then brought into contact with the sample. Its pressure was regulated to a constant value using a temperature-controlled water bath. The furnace temperature was monitored with a thermocouple placed near the sample.

The initial water vapour pressure was equal to 107 Pa and the system was maintained under constant H_2O pressure (107 Pa) until equilibrium between CeO_2 and H_2O was attained. The value of the mass variation (Δm) was then recorded. Consecutive introductions of water were repeated at constant temperature, until the H_2O pressure reached 4000 Pa. The same procedure was applied to decrease the water pressure in a stepwise manner. The superposition of the curves of Δm plotted as a function of increasing and decreasing P, ensured that equilibrium conditions were reached.

The values of Δm were converted to the number of moles of water fixed by 1 mol of CeO_2 (ϵ) and the experimental results were presented in the form of isotherms for the fixation of water as a function of the equilibrium pressure P.

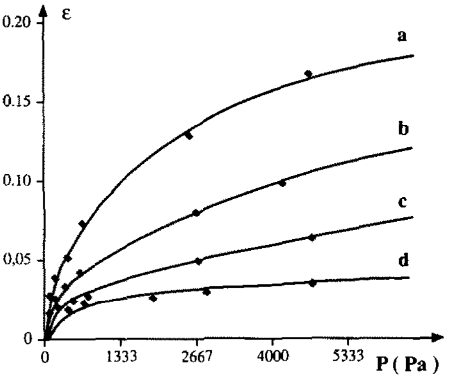


Fig. 1. Isotherms of fixation of water on ceria (sample A) at various temperatures: curve a, 373 K; curve b, 398 K; curve c, 423 K; and curve d, 473 K.

Transmission electron microscopy (TEM) micrographs were obtained with a Philips CM 30 microscope (300 kV). The samples were embedded in resin and cut with an ultramicrotome.

The nitrogen adsorption experiments were performed at 77 K using a Carlo Erba Sorptomatic 1800 apparatus.

RESULTS AND DISCUSSION

Water fixation isotherms at 373, 398, 423 and 473 K

The isotherms for water uptake on ceria at various temperatures are reported in Figs. 1 and 2 for samples A and B respectively. It was shown above that a linear relation may be obtained between $1/\epsilon$ and $1/P$ for the fixation of water on a given site of the solid. No assumption was expressed in the model regarding the location of this site, either at the surface or in the bulk. Figure 3 shows the experimental values of $1/\epsilon$ as a function of $1/P$ in the case of samples A (curve a) and B (curve b) respectively, for an equilibrium temperature of 373 K. We obtained a linear variation with sample B only. The experimental points do not fit with the model in the case

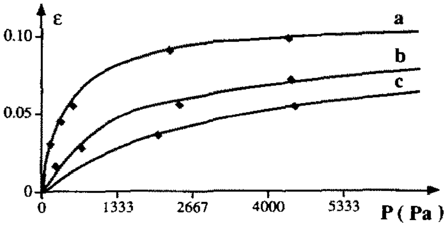


Fig. 2. Isotherms of fixation of water on ceria (sample B) at various temperatures: curve a, 373 K; curve b, 398 K; and curve c, 423 K.

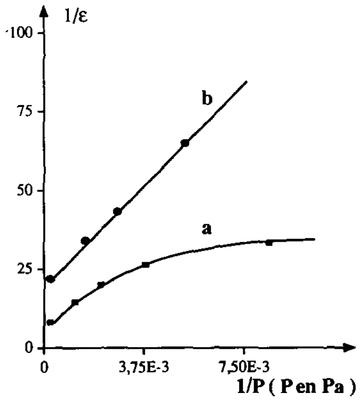


Fig. 3. Plot of $1/\epsilon$ as a function of $1/P$ for sample A (curve a) and sample B (curve b) at 373 K.

of sample A. Similar results were found at other equilibrium temperatures. In the case of sample B, the mean value of 0.05 mol per mole of CeO_2 was obtained for n at every temperature.

Model with two distinct sites of fixation of water

One of the assumptions which leads to the linear variation of $1/\epsilon$ with $1/P$ is that there is only one type of site, s, able to fix a molecule of water. If we now consider the existence of two distinct sites, s_1 and s_2, and the two equilibriums (3) and (4)

$$[H_2O\text{-}s_1] = H_2O(g) + s_1 \tag{3}$$

$$[H_2O\text{-}s_2] = H_2O(g) + s_2 \tag{4}$$

the application of the model to the uptake of water according to reactions (3) and (4) leads to the equation

$$\epsilon = \epsilon_1 + \epsilon_2 = \frac{n_1}{1 + (K_1/P)} + \frac{n_2}{1 + (K_2/P)} \tag{5}$$

in which ϵ_1, K_1, n_1 and ϵ_2, K_2, n_2 refer to the sites s_1 and s_2 respectively.

Determination of n_1, K_1, n_2 and K_2

The problem is now to determine the values of n_1, K_1, n_2 and K_2 from the isotherms. As a direct determination is not easy, we proceed with consecutive approximations deduced by considering the shape of the isotherms (Fig. 1). First, if we consider the isotherm at 473 K (curve d), it appears that ϵ varies linearly with P at elevated pressure according to the expression

$$\epsilon = \frac{n_1}{K_1} P + n_2 \tag{6}$$

TABLE 1

Determination of n_1, n_2, K_1 and K_2 for sample A

Temperature (K)	n_1		n_2		K_1		K_1/P		K_2		K_2/P	
							$P=133$ Pa	$P=4000$ Pa			$P=133$ Pa	$P=4000$ Pa
	(a) [a]	(b) [b]	(a) [a]	(b) [b]	(a) [a]	(b) [b]	(c) [c]	(d) [c]	(a) [a]	(b) [b]	(c) [c]	(d) [c]
373	0.21	0.20	0.03	0.03	0.310^{-1}	0.210^{-1}	15.2	0.5	0.210^{-3}	0.810^{-3}	0.608	0.02
							>1	≈ 1			≈ 1	$\ll 1$
398	0.20	0.20	0.04	0.03	1.010^{-1}	0.810^{-1}	60.8	2.027	1.310^{-3}	1.310^{-3}	0.988	0.03
							$\gg 1$	≈ 1			≈ 1	$\ll 1$
423	0.20	0.20	0.03	0.03	2.710^{-1}	2.210^{-1}	167.2	5.6	2.610^{-3}	2.510^{-3}	1.9	0.06
							$\gg 1$	≈ 1			≈ 1	$\ll 1$
473	$n_1/K_1 =$ 2.610^{-1}	0.20	0.020	0.03	–	12.910^{-1}	980	32.7	2.610^{-3}	3.510^{-3}	2.66	0.089
							$\gg 1$	$\gg 1$			≈ 1	$\gg 1$
	n_1?		0.021									

[a] Values obtained with approximations as described in the text.

[b] Values obtained from numerical fitting with eqn. (5) in the text.

[c] Verification of the approximations.

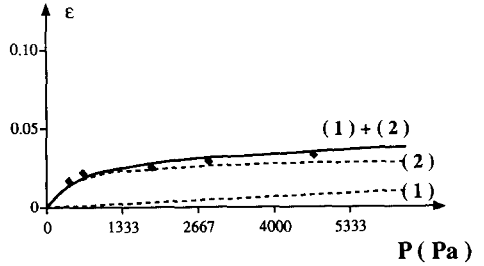


Fig. 4. Calculated isotherms on sites s_1 (curve 1) and s_2 (curve 2) of sample A and the experimental isotherm at 473 K.

which is deduced from eqn. (5) when $K_1/P \gg 1$ and $K_2/P \ll 1$. Thus n_2 and n_1/K_1 can be determined. On the same isotherm, in the low pressure area, the amount of water fixed can therefore be approximated using the equation

$$\epsilon = \frac{n_1}{K_1}P + \frac{n_2}{1 + (K_2/P)} \tag{7}$$

from which n_2 and K_2 can be obtained, since a linear variation must be found for $[\epsilon - (n_1/K_1)P]^{-1}$ as a function of $1/P$. A comparison of the values of n_2 determined from eqns. (6) and (7) shows a good agreement (see Table 1, last row the of the fourth column). Figure 4 shows the experimental and calculated isotherms; curves 1 and 2 correspond to sites s_1 and s_2 respectively, and curve "(1) + (2)" corresponds to the total contribution of these two sites.

We consider now the isotherms obtained at 373, 398 and 423 K. The shapes for the curves at elevated equilibrium pressures show that a simplification similar to the previous case is not possible. Thus the following relation between ϵ and P must be considered if P is sufficiently high:

$$\epsilon = \frac{n_1}{(K_1/P) + 1} + n_2 \tag{8}$$

The values of K_1 and n_1 can be calculated by considering the linear relation between $(\epsilon - n_2)^{-1}$ and $1/P$, since the value of n_2 has been obtained previously. For lower pressures, we have the general expression of ϵ as a function of n_1, K_1, n_2 and K_2 as given by eqn. (5). The values of K_2 and n_2 can be calculated using the linear variation of $[\epsilon - n_1/(1 + K_1/P)]^{-1}$ as a function of $1/P$ given that n_1 and K_1 are known. The results of these determinations are listed in the (a) columns of Table 1. A comparison between the values of n_2 obtained from the isotherm at 473 K and eqn. (6), and from the isotherms at 373, 398 and 423 K shows good agreement. The calculated and experimental isotherms at 373, 398 and 423 K are represented in Figs. 5, 6 and 7 respectively.

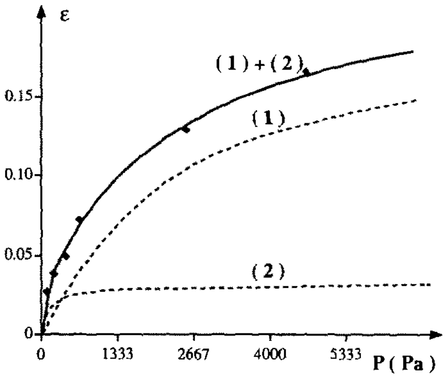


Fig. 5. Same as in Fig. 4 for isotherms at 373 K.

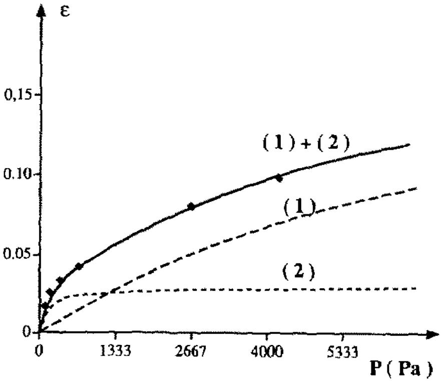


Fig. 6. Same as in Fig. 5 for isotherms at 398 K.

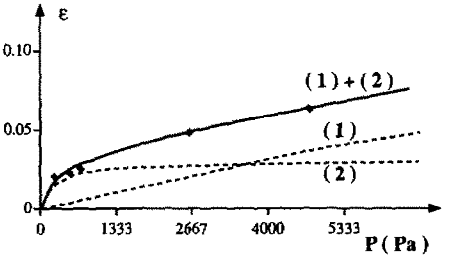


Fig. 7. Same as in Fig. 5 for isotherms at 423 K.

Finally, it is possible to enter these values of n_1, n_2, K_1 and K_2 in a numerical fitting procedure between the experimental points of the isotherms and the general expression of ϵ given in eqn. (5), and for all the range of pressures of water vapour. The best results are given in the (b) columns of Table 1. In columns (c) and (d) of Table 1, one can verify that the approximations which were used to obtain the values of n_1, n_2, K_1 and

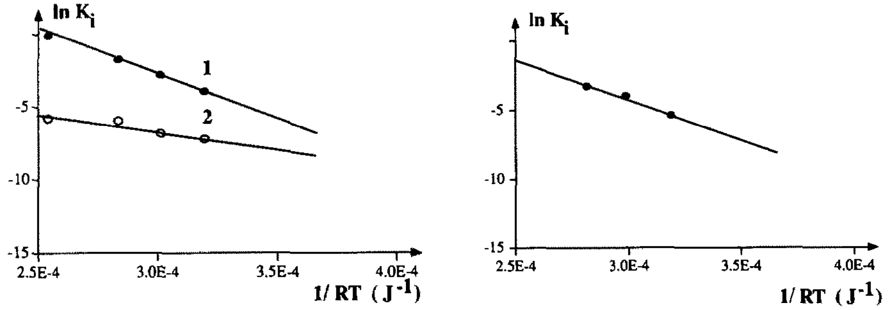


Fig. 8. Variation of ln K as a function of $1/RT$ for sites s_1 (curve 1) and s_2 (curve 2) of sample A (left side) and sites s of sample B (right side).

K_2 are justified. We can therefore take $n_1 = 0.20$ mol and $n_2 = 0.03$ mol of sites per mole of CeO_2. Similar calculations performed using the sample model with one type of site for the calcined ceria (sample B) have given $n = 0.05$ mol of sites per mole of CeO_2.

Enthalpies of fixation of water

Figure 8 shows the variation of ln K as a function of $1/RT$, corresponding to the sites s_1 and s_2 of sample A and sites s of sample B. The determination of the slope of each straight line leads to the values of standard enthalpies of fixation of water given in Table 2. Since the values obtained for sites s_1 of sample A and sites of sample B are very similar, these sites are probably of the same nature on the two samples. Furthermore their population in both samples calculated for 1 m^2 of surface is of the same order, about 10^{-5} mol m^{-2}.

Nature of sites s_1, s_2 and s

The models used previously to describe the fixation of water do not require any assumption on the localization of the sites in the solid. The results are of the same kind for water uptake either in the bulk or at the surface of ceria. This is because in earlier studies such models were used to

TABLE 2

Values of the standard enthalpy of fixation of water on samples A and B

	Site	ΔH (kJ mol^{-1})
Sample A	s_1	-59 (ΔH_1)
	s_2	-23 (ΔH_2)
Sample B	s	-55

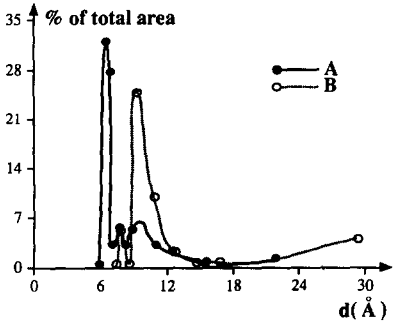


Fig. 9. Surfacic distribution of porosity as a function of pore size for samples A (———) and B (---) from nitrogen adsorption measurements at 77 K.

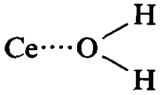
characterize the water contained in compounds like hydrates or zeolites, localized at crystallographic sites in the solid lattice. In the present case, ceria exhibits a fluorite-like structure in which there are no holes (interstitial sites) large enough for water molecules. Thus, the water is necessarily bound to superficial sites.

In order to characterize the texture of the samples A and B, nitrogen adsorption measurements and TEM observations were performed [9]. The interpretation of the nitrogen adsorption isotherms according to the t method [10] leads to the pore size distribution shown in Fig. 9. The solid curve, which corresponds to sample A, shows the presence of two groups of pores, with a mean size of 0.6 and 1.0 nm. On sample B (broken curve), one can see that only the group with the larger pore size is present.

The TEM micrographs corresponding to samples A and B are shown in Figs. 10(a) and 10(b) respectively. The microporosity can be observed in Fig. 10(a) as very short, narrow channels. In Fig. 10(b), this disordered aspect has disappeared and only small holes can be observed which correspond to the pores.

From these and the previous results, the following interpretations can be made concerning the nature of the sites of fixation of water:

(1) The s_1 sites of sample A and s of sample B are located at the surface of ceria particles, which also includes the surface of the two groups of pores. The value of the enthalpy of fixation (-55 and -59 kJ mol^{-1}) is of the same order as that of water molecules bound directly to cerium atoms, as recently reviewed by Thiel and Madey [11], and represented as



(2) The s_2 sites on sample A must be attributed to the surface developed by the most narrow pores or micropores. The energy of interaction between water molecules and these sites is of the same order as that of hydrogen

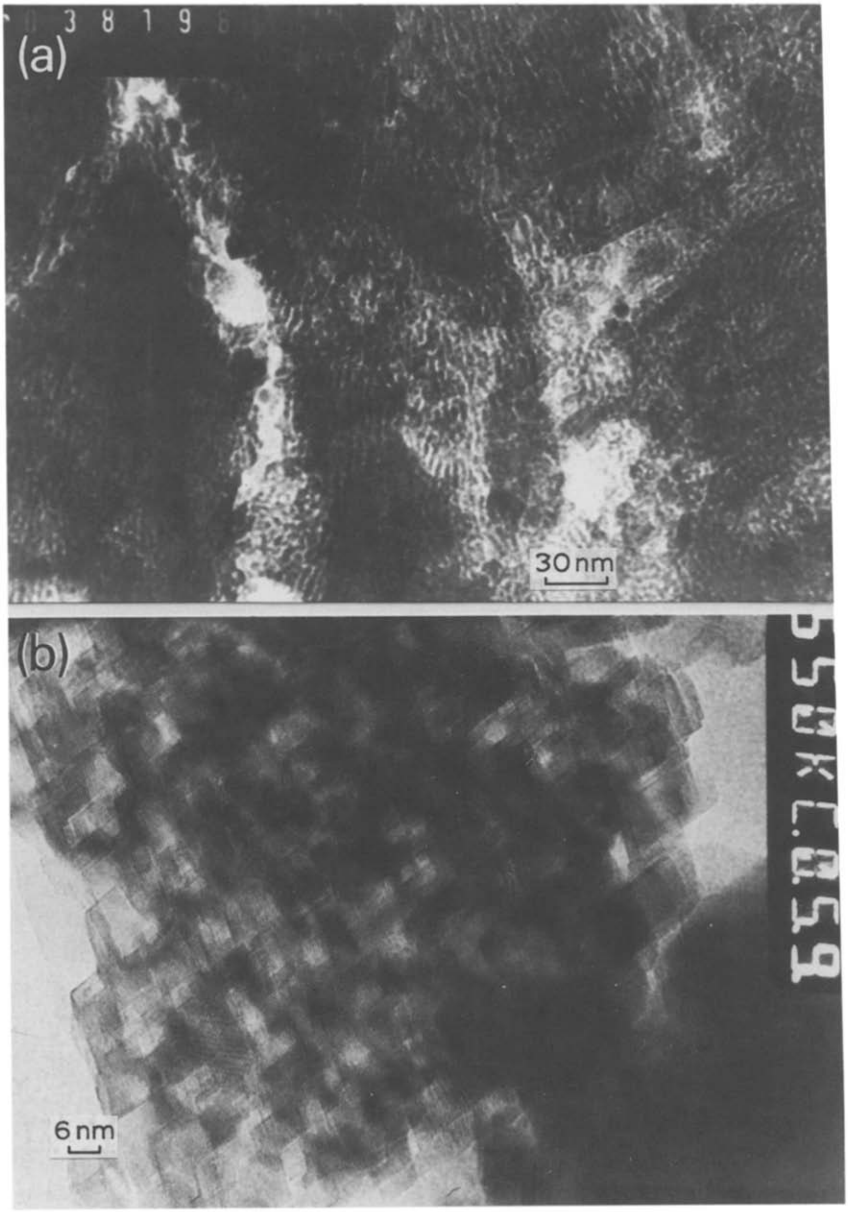
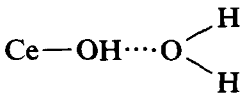


Fig. 10. TEM micrographs of samples A (a) and B (b).

bonding [11]. Thus the s_2 sites can be attributed to hydroxyl groups already present at the surface of the micropores, i.e.



$$Ce{-}OH\cdots O\begin{smallmatrix}\diagup H\\ \diagdown H\end{smallmatrix}$$

Though their number is rather small compared to s_1 sites, they must not be neglected, otherwise the isotherms of water fixation cannot be interpreted.

The good agreement between the experimental results and the model, which involves two localized sites for water adsorption, indicates that water condensation does not occur in the micropores. Moreover, the models generally used to describe adsorption in this kind of very narrow pore assume slit-like pores [10], in which no condensation can occur whatever their size.

CONCLUSION

The equilibrium isotherms between water vapour and a ceria powder have led to the characterization of two distinct sites of fixation. These sites have different standard enthalpies of fixation and different populations. The most frequently occurring sites appear to involve water bound to superficial cerium atoms, whereas the others correspond to water bound to hydroxyl groups present at the surface of the micropores. These last sites disappear after calcination at high temperature.

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