

Twente University of Technology, Department of Chemistry, P. O. Box 217,
Enschede, The Netherlands

Adsorption of the Halogens on Cerium Dioxide

By

W. Potman, J. G. van Ommen, and E. A. M. F. Dahmen

With 4 Figures

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Cerium dioxide has been used in elemental analysis for a long time. Ingram¹ developed a method for determination of carbon and hydrogen, in which he used CeO_2 as a tube-filling which functioned as a catalyst for the combustion as well as an adsorbent for halogens. Monar², Kakabadse et al.³, Padowetz⁴ and Kozłowski et al.⁵ have also drawn attention to CeO_2 , especially its take-up of halogens.

Although it appears that cerium dioxide does possess halogen-adsorption properties, quantitative information about the individual halogens is lacking. Also the optimal conditions under which it can be used for this purpose are not known.

The purpose of our investigation was to obtain a more quantitative insight into the halogen-adsorption behaviour of CeO_2 , especially with respect to its application in determination of carbon and hydrogen.

Because La_2O_3 also shows halogen-adsorption properties² some experiments were done on it too.

Experimental

Reagents

HF	gas,	Baker,	99.9%	purity
HCl	gas,	Baker,	99.0%	purity
HBr	gas,	Baker,	99.8%	purity

HI gas, Baker, 99.0% purity
 Cl₂ gas, Baker, 99.5% purity
 CO₂ gas, Baker, 99.8% purity
 CeO₂, Koch-Light, 99.9% purity (batches I and II*)
 CeO₂, Merck („Zur Elementaranalyse“)
 CeO₂, Auer Remy
 CeO₂, Merck („Handelsübliche Qualität“)
 Ce(NO₃)₃·6H₂O, Merck, „reinst“ grade
 Ce₂(C₂O₄)₃, Fluka, „puriss.“ grade
 Ce(OH)₄, BDH
 Ce(NH₄)₂(NO₃)₆, Baker, A. R. grade
 CeCl₃, Koch-Light, 99.9% purity
 La₂O₃, Koch-Light 99.9% purity (batches I and II*)
 Körbl catalyst, Merck

CeO₂ was prepared in the laboratory by thermal decomposition of Ce(C₂O₄)₃, Ce(OH)₄, Ce(NO₃)₃, CeCl₃ and Ce(NH₄)₂(NO₃)₆ in a crucible, round-bottomed flask or quartz tube in a furnace; an air-current was used to drive out the gases.

The oxide powder was compressed into tablets (pressure: 10 tons/cm²) and granulated into sizes varying from 20 to 30 mesh. The purity of all the oxides was checked by X-ray fluorescence analysis with a relative error within 1%.

All other chemicals were of analytical grade.

Apparatus

Figure I shows the apparatus. Oxygen gas, previously purified with "Ascarite" and "Anhydrone" flows into a Pyrex tube (225 × 11 mm, inner tube 57 × 5 mm). After passing through a quartz reaction tube (237 × 5 mm, wide-section length 50 mm, bore 9 mm) the oxygen flows via a heated (80⁰) Pyrex connection capillary (bore 2 mm) into the absorption vessel⁶. The tubes are connected with NS 7/16 sleeves. The reaction tube is charged with a 1-cm layer of CeO₂ or La₂O₃ (about 1.3 g). The measuring system used for the determination of halides consists of an ion-selective electrode (Orion 94-16, Orion 94-09), double-junction Ag/AgCl reference electrode (Ingold 373-90 M5NS), pH meter (Knick, type 23, range 140 mV) and a recorder (Kipp, BD8). HCl, Cl₂, HBr, HI and CO₂ are introduced via a septum (Dohrmann 523 728) with a Hamilton 1001 (1000-μl) gas-tight syringe.

HF is introduced with a Hamilton 1725 (250-μl) Teflon syringe. The needles are made of stainless steel. For the determination of CO₂ a colori-

* Because of differences in surface area it was necessary to distinguish between batches I and II.

meter (Metrohm, Herisau E 1009) is used, together with a potentiograph (Metrohm, Herisau E 336).

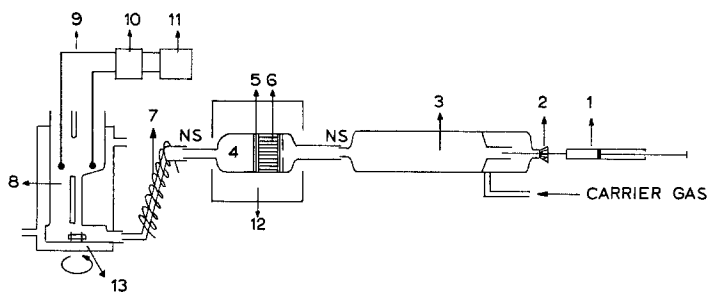


Fig. 1. Scheme of the apparatus used for the determination of the halogen adsorption

- | | |
|---|----------------------|
| 1. syringe | 8. absorption vessel |
| 2. septum | 9. electrodes |
| 3. Pyrex tube | 10. pH meter |
| 4. quartz reaction tube | 11. recorder |
| 5. quartz wool | 12. furnace |
| 6. filling of CeO_2 or La_2O_3 | 13. stirrer |
| 7. heating coil | |

Procedure

For the determination of the halogen-adsorption capacity a quantity of hydrogen halide or free halogen gas was injected and led through a bed of CeO_2 with oxygen as carrier-gas. The breakthrough of halide was detected with ion-selective electrodes. The methods of final determination for Cl^6 , Br^6 , I^7 and F^8 have already been published. This procedure does not completely reproduce the actual situation during carbon and hydrogen determination, but was only meant to be used for comparative purposes. The test-gas was injected slowly every 1—3 min. The first deflection of the electrode signal from its initial value (the smallest detectable deflection was about 1 mV, corresponding to about $0.1 \mu\text{eq}$ of halide) was taken as indicating breakthrough and the volume of test-gas injected up to that point gave the breakthrough capacity. The quantity of test-gas introduced by one injection was $350 \mu\text{l}$ of HCl, HBr or HI, or $175 \mu\text{l}$ of Cl_2 . The reproducibility of injection was found by titration of halide, and for $350 \mu\text{l}$ of HCl the relative standard deviation was 0.6% (10 determinations).

The amount of one injection of HF was determined⁸ experimentally and found to correspond to $0.57 \pm 0.07 \text{ mg}$ of fluorine. For the determination of the specific surface area (m^2/g) of the adsorbent the BET-method^{9,10} was used with argon at -196° .

Results

Halogen Adsorption as a Function of Temperature

It was found that all the adsorption curves showed a distinct maximum at a certain temperature*, depending upon the adsorbent

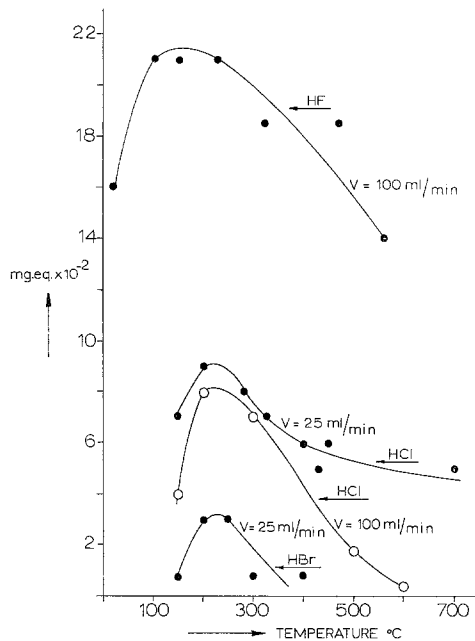


Fig. 2. Adsorption of hydrogen halide on a 1-cm layer of CeO_2 (Koch-Light batch I) as a function of temperature
Oxygen flow $V=25$ or 100 ml/min

and the adsorbate (Table I). The typical adsorption curves presented in Fig. 2 clearly show such maxima. The Koch-Light CeO_2 batch I did not adsorb a measurable amount of iodide. It was ob-

Table I. Temperature at which Adsorption is Maximal, $^{\circ}\text{C}$

Adsorbent	Adsorbate				
	HF	HCl	Cl_2	HBr	HI
CeO_2	150	210	210	230	250
La_2O_3	270	300		300	300

* Measured with a thermocouple (NiCr-Ni), placed against the outside wall of the tube containing the layer of oxide; the error was $<10^0$.

served that the adsorption capacity of some samples of CeO_2 was in fact too low at the temperature for which maximum adsorption was to be measured.

Halogen Adsorption as a Function of Surface Area and Starting Material

CeO_2 was prepared at different temperatures by heating $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ in a round-bottomed flask. [By DTA it was found that $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ starts to dissociate at a temperature of about 300° .]

Table II. CeO_2 Prepared from $\text{Ce}_2(\text{C}_2\text{O}_4)_3$

Preparation Temp. $^\circ\text{C}$	Time hr	Specific surface area m^2/g	Adsorption of HCl (m/cq) on a 1-cm bed of CeO_2 (about 1.3 g) $V = 100 \text{ ml O}_2/\text{min } T = 210^\circ$
480	17	54	0.59
600	2	45	0.39
820	2	21	0.11

The experimental parameters and the results of adsorption in relation to preparation temperature and specific surface area are presented in Table II.

As shown in Table III, the time and temperature of preparation has (within an acceptable variation of about 10%) no influence on

Table III. CeO_2 Prepared from $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ at $400\text{--}500^\circ\text{C}$

Preparation time hr	Specific surface area m^2/g
71	58
24	45
18	50
17	54
6	51

the specific surface area. In Table IV some results for halogen adsorption on several samples of CeO_2 and La_2O_3 are presented in order of decreasing surface area, together with the experimental conditions of gas flow-rate and temperature. The minimum test-volume used was one injection. No marked influence on the adsorption of HCl was observed on changing the carrier-gas from O_2 to N_2 or CO_2 . Some results obtained with Körbl catalyst are also given.

Table IV. Adsorption of Halogens on Various Preparations

Sample	Specific surface area, m ² /g	Carrier gas	Flow rate ml/min	T °C	mg (absorbed on 1-cm bed of sample)				
					F ⁻	Cl ⁻	Br ⁻	I ⁻	Cl ₂
CeO ₂ prepared from Ce ₂ (C ₂ O ₄) ₃ , 480 °C	54	O ₂	25	210				20	
CeO ₂ prepared from Ce ₂ (C ₂ O ₄) ₃ , 480 °C	54	O ₂	100	210	21		12		
CeO ₂ Koch-Light II	47	O ₂	100	210	25		9		10
CeO ₂ Koch-Light II	47	N ₂	100	210	27				9
CeO ₂ Koch-Light II	47	CO ₂	100	210	23				4
CeO ₂ Koch-Light I	20	O ₂	100	150	4	2	<0.8	<1	
CeO ₂ prepared from Ce(OH) ₃ , 680 °C	7	O ₂	25	210	6.5				
CeO ₂ Auer Remy	5	O ₂	25	210	<0.6	<0.5	<0.8	<1	
CeO ₂ Merck (Handelsübliche Qualität)	4	O ₂	100	150	<0.5	<0.5	<0.8	<1	
CeO ₂ Merck („Zur Elementaranalyse“)	3	O ₂	25	210	<0.6	<0.5	<0.8	<1	
CeO ₂ Merck („Zur Elementaranalyse“)	3	O ₂	100	150	<0.5	<0.5	<0.8	<1	
La ₂ O ₃ Koch-Light II	17	O ₂	100	210	30	40			
La ₂ O ₃ Koch-Light II	17	O ₂	100	300	228	488		7	
La ₂ O ₃ Koch-Light II	17	O ₂	100	600	3	7			
La ₂ O ₃ Koch-Light I	7	O ₂	100	210	9	13	16	<1	<0.5
Körl catalyst Merck	5	O ₂	100	500	125	101			

Tests were made of the performance of CeO_2 made from various cerium salts under the same conditions of preparation, i. e. the salt was heated at 530° for 24 hr in a stream of dried air in a quartz

Table V. CeO_2 Prepared from Various Salts

Salt	Specific surface area, m^2/g	Cl^- adsorption mg
$\text{Ce}_2(\text{C}_2\text{O}_4)_3$	34	7.5
$\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$	11	1.5
$\text{Ce}(\text{OH})_4$	12	6
$\text{Ce}(\text{NO}_3)_3$	57	16
CeCl_3	5	1.5

tube. The results are shown in Table V. The CeO_2 obtained from the nitrate or oxalate seems the best.

Behaviour of the Surface of CeO_2 and its Degree of Coverage in Relation to Several Parameters

At first, water was supposed to be condensed in the capillaries of the oxide: therefore a bed of CeO_2 (Koch-Light, batch I) was dried at temperatures of 200, 300 and 400° for $1\frac{1}{2}$ hr by means of

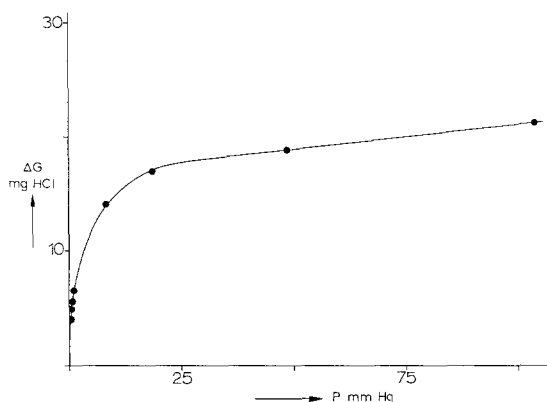


Fig. 3. Adsorption of HCl on CeO_2 as a function of HCl pressure. $T=200^\circ\text{C}$
Sample: CeO_2 prepared from $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ at a temp. of 480°C , spec. surface area $44 \text{ m}^2/\text{g}$, weight of sample 1.021 g

an air-current (previously dried with "Anhydrone") but no change in the adsorption behaviour for HCl was observed.

It was found by X-ray diffraction that the crystallinity of CeO_2 increased with increase in temperature (see also the literature¹¹)

[CeO₂ (Koch-Light, batch II) was heated at 600, 800 and 1000° for 6 hr].

Furthermore it was found that heating the Koch-Light CeO₂ (batch II) or the CeO₂ prepared from Ce(NH₄)₂(NO₃)₆ at higher temperatures caused a rapid decrease of the specific surface area during the first 10—20 hr, but then no further change even after 200 hr at 500 and 650°. The specific surface area of CeO₂ heated at 1000° fell to 1.2 m²/g. A few experiments were done to see whether the chloride remains adsorbed on the surface of the CeO₂ or diffuses into the bulk of the oxide. In this connection Fig. 3 presents an isotherm ($T = 200^\circ$) for the adsorption of HCl on CeO₂ as a function of pressure of HCl (max. 100 mm Hg), determined by a quartz-spring balance¹². Here equilibrium at a certain pressure was reached within 5 min; the weight of the oxide remaining constant for at least one hour. From this the fraction of coverage θ could be estimated.

$$\theta = \frac{\frac{\Delta G}{M} \cdot N \cdot \text{surface area of one molecule of HCl}}{G \cdot \text{spec. surface area of CeO}_2}$$

where ΔG = increase in weight (g) of the CeO₂ as a result of chloride adsorption, G = weight of CeO₂ (g), N = Avogadro's number, M = molecular weight of HCl. It was assumed that the surface area of CeO₂ occupied by one molecule of HCl is of the order of $(d_{\text{Cl}^-})^{2*}$ [based on the (111) planes of the face-centred cubic structure¹³ for HCl], viz.¹⁴ $\sim 13 \text{ \AA}^2$.

A value of θ greater than unity was not found. However, after >70 hr equilibration θ did exceed unity.

Samples of CeO₂ prepared from Ce₂(C₂O₄)₃ at temperatures of 480, 790 and 850° showed a decrease of surface area (44, 35 and 7 m²/g respectively) with increase in the temperature of preparation and at the same time a decrease in θ (0.8, 0.4 and 0.2) at maximum adsorption ($T = 200^\circ$).

Adsorption of CO₂

In order to apply CeO₂ in the determination of carbon and hydrogen it is of importance to know to what extent CO₂ is adsorbed. The apparatus to measure the CO₂ breakthrough was similar to that in Fig. 1 except for the absorption vessel, which was of a design that allowed the CO₂ breakthrough to be estimated by photometric titration¹⁵.

* d_{Cl^-} = diameter of the chloride ion.

The CO_2 was absorbed in dimethylformamide containing 7% monoethanolamine and the carbamic acid formed was titrated with 0.05 M tetrabutylammonium hydroxide with thymolphthalein as indicator, a wavelength of 650 nm and set-point transmission of 50% being used for end-point detection. The relative standard

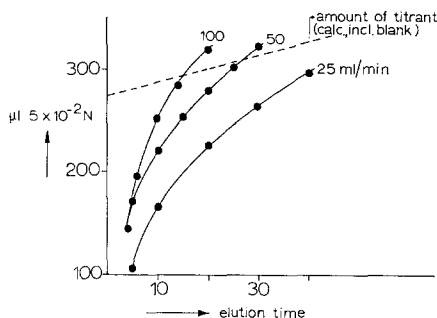


Fig. 4. CO_2 retention on a 1-cm layer of CeO_2 (Koch-Light batch II). Oxygen flow $V=25, 50$ and 100 ml/min, $T=210^\circ\text{C}$

deviation (11 determinations) for $350 \mu\text{l}$ of CO_2 , the quantity of one injection, was 1%. Fig. 4 shows the retention of CO_2 on Koch-Light CeO_2 (batch II) as a function of time and for different oxygen flow-rates. It should be mentioned that after some time no more CO_2 is given off. The dashed curve shows the calculated amount of

Table VI. Retention of CO_2 (1-cm bed; Oxygen Flow 100 ml/min)

Sample	Specific surface area m^2/g	Retention of CO_2		
		200 $^\circ\text{C}$	600 $^\circ\text{C}$	800 $^\circ\text{C}$
CeO_2 , Merck („Zur Elementaranalyse“)	4	—	—	—
CeO_2 , Koch-Light I	20	—	—	—
CeO_2 , Koch-Light II	47	++	+	—
CeO_3 , (prepared from $\text{Ce}_2(\text{C}_2\text{O}_4)_3$, 400 $^\circ\text{C}$)	45	++	—	—
CeO_3 , (prepared from $\text{Ce}_2(\text{C}_2\text{O}_4)_3$, 600 $^\circ\text{C}$)	12	++	—	—
CeO_2 , (prepared from $\text{Ce}(\text{OH})_4$, 680 $^\circ\text{C}$..)	7	++	+	—
La_2O_3 , Koch-Light I	7	++	+	—

— quantitative elution within 4 min.

+ quantitative elution within 15 min.

++ quantitative elution > 15 min.

titrant including the blank. As the result of a CO_2 blank present in the CeO_2 , in two cases more than the calculated amount of CO_2 was found. However, it was found, that increasing the temperature

to 800° causes the oxide to release this extra CO₂. A product treated in this way was, however, capable of adsorbing 1—3 injections of CO₂ completely ($T = 210^{\circ}$, $V = 100$ ml of O₂/min).

A qualitative survey of CO₂ retention on several samples of CeO₂ and La₂O₃ is given in Table VI together with the corresponding surface area and measurement conditions.

Determination of Carbon and Hydrogen

CeO₂ (Koch-Light, batch I) and CeO₂ prepared from Ce₂(C₂O₄)₃ at 480° (specific surface areas 20 and 54 m²/g respectively) were tested in an analysis of benzoic acid and hexachlorobenzene for carbon and hydrogen by essentially the method published by Martin et al.¹⁶ with a titrimetric finish¹⁵ according to Jones et al. A two-cm-layer of CeO₂ (about 5 g) was placed in the combustion tube behind a filling of Körbl catalyst (the temperature of the catalyst zone was 550°). Complete oxidation of carbon to CO₂ was ensured before the combustion products reached the CeO₂ (the temperature of which was 210°). Good results were obtained with the Koch-Light CeO₂ (benzoic acid, mean C 68.9%, H 5.0%, 6 determinations; hexachlorobenzene, mean C 25.4%, 3 determinations) but the halogen adsorption capacity of this oxide was very small (Table IV). The CeO₂ prepared from Ce(C₂O₄)₃ adsorbed more halogen (Table IV) but caused CO₂-retention in the determination of carbon and hydrogen, so no good results could be obtained. Placing the oxide before the Körbl catalyst under the same conditions gave no improvement. These experiments show that in an actual determination of carbon and hydrogen retention of CO₂ was obtained with a sample of CeO₂ which was also active in taking up halogens. The most interesting temperature from the point of view of halogen adsorption was used for these determinations. As shown, a less active CeO₂ gave at this temperature good carbon (and hydrogen) values for both substances because the adsorption of the combustion products (CO₂, H₂O, Cl₂) was noticeably small. Furthermore the chlorine not adsorbed on the CeO₂ is taken up by the Körbl catalyst.

Remarks and Conclusions

From the results obtained with the quartz-spring balance it can be concluded that the adsorption of halogens takes place mainly on the surface of the CeO₂. The relatively small adsorption capacity is in agreement with this.

In the adsorption process not only the area but also the structure of the surface plays an important role. Infrared analysis for OH

groups and electron microscopy gave no useful information about the surface of the CeO_2 . However it was ascertained that the maximum degree of coverage decreases with decreasing area. This means that the number of active sites for adsorption per unit of surface area decreases with decreasing surface area. The starting material for the CeO_2 preparation also has an influence on the surface area and adsorption behaviour. The CO_2 and halogen adsorption experiments show that an increase in halogen adsorption is accompanied by an increase in CO_2 retention. Raising the temperature decreases CO_2 retention but simultaneously decreases halogen adsorption.

Of the commercial products, only the Koch-Light batch II adsorbed the halogens relatively well, but this product could not be used in the determination of carbon and hydrogen because it had a high CO_2 retention. La_2O_3 is more active in taking up halogens than CeO_2 but also retains CO_2 at relatively low temperature. To prevent this CO_2 -retention a temperature higher than 600° is necessary in general for using CeO_2 and La_2O_3 as a halogen adsorbent in the carbon and hydrogen determination. A high temperature is also necessary to catalyse the oxidation¹⁷ of hydrogen from hydrogen halides to water. Formation of hydrogen halides is, however, dependent on the presence of hydrogen in the organic compound. The halogen-adsorption capacity at such a high temperature is relatively low.

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Summary

Adsorption of the Halogens on Cerium Dioxide

CeO_2 , alone or mixed with La_2O_3 , is used as halogen adsorbent in the determination of carbon and hydrogen. Quantitative data are given on the adsorption of the single halogens on various samples of pure CeO_2 and La_2O_3 . Retention of CO_2 and the influence of several parameters of special interest in the carbon and hydrogen determination, have been examined. It has been found that the conditions for optimum adsorption of the halogens are a large surface and relatively low adsorption temperature. Unfortunately these conditions cannot be applied in the determination of carbon and hydrogen.

Zusammenfassung

CeO₂ allein oder im Gemisch mit La₂O₃ wurde als Adsorbens für Halogen bei der CH-Bestimmung verwendet. Quantitative Angaben über die Adsorption der einzelnen Halogene an verschiedenen Mustern von reinem CeO₂ und La₂O₃ wurden gebracht. Die Retention von CO₂ und der Einfluß einzelner Parameter, die für die CH-Bestimmung von besonderem Interesse sind, wurden geprüft. Die besten Bedingungen für die Adsorption der Halogene sind große Oberfläche und relativ niedere Temperatur. Beide Bedingungen können leider bei der CH-Bestimmung nicht eingehalten werden.

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Correspondence and reprints: W. Potman, Twente University of Technology, Department of Chemistry, P. O. Box 217, Enschede, The Netherlands.