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ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · JANUARY 1995

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# COMMENTS

## Comments on "Redox Processes on Pure Ceria and Rh/CeO<sub>2</sub> Catalyst Monitored by X-ray Absorption (Fast Acquisition Mode)"<sup>†</sup>

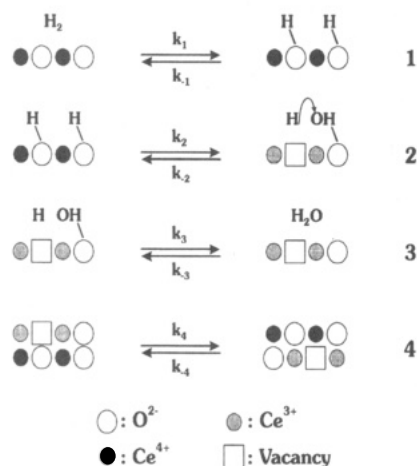
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Received: December 16, 1994

We comment on a recent paper in this journal by El Fallah et al.<sup>1</sup> It is generally acknowledged that ceria plays an important role in three way catalysts (TCW).<sup>2</sup> In particular, the investigation of the ceria oxidation state under different thermal and chemical conditions constitutes a major challenge in the characterization of the TCWs and related catalytic systems.<sup>3–6</sup> A number of techniques have been applied with this purpose: EPR,<sup>7,8</sup> XPS,<sup>9–11</sup> electronic conductivity measurements,<sup>12</sup> oxygen pulses/TPO,<sup>13,14</sup> magnetic balance,<sup>15–21</sup> UV-vis spectroscopy,<sup>20</sup> and even FTIR spectroscopy.<sup>22</sup> Very recently, X-ray absorption spectroscopy (XAS) has also been used.<sup>1</sup> As is shown in ref 1, XAS may constitute a very interesting alternative technique. Both quantitative and kinetic aspects of the problem can fruitfully be investigated.<sup>1</sup> In addition, the studies can be performed under various thermal and chemical environments, which is also critically important.<sup>16</sup>

If ref 1, the redox behavior of some bare ceria samples as well as of a Rh/CeO<sub>2</sub> catalyst, under both reducing and oxidizing conditions, has been investigated. To interpret their results, the authors<sup>1</sup> proposed the following reaction scheme.



In accordance with this scheme, the reduction process would be associated with the creation of oxygen vacancies, step 2, whereas the first one, that leading to the dissociative chemisorption of H<sub>2</sub> onto the cerium dioxide, would not imply its reduction. This latter assumption, however, does not seem to be supported by a number of recent studies in which a Faraday magnetic balance was used to investigate the evolution of the

TABLE 1: Faraday Magnetic Balance Study of the Redox Behavior of Two Ceria-Supported Rhodium Catalysts Prepared from Rh(NO<sub>3</sub>)<sub>3</sub>, Rh(N)/CeO<sub>2</sub>, and RhCl<sub>3</sub>, Rh(Cl)/CeO<sub>2</sub>, Metal Precursors<sup>a</sup>

run	treatment	% Ce <sup>3+</sup>	
		catalyst-N	catalyst-Cl
1	H <sub>2</sub> 623 K, cooled under H <sub>2</sub>	11.4	22.1
2	evacuation at 623 K	5.0	20.7
3	H <sub>2</sub> 298 K (20 h)	10.1	20.6
4	H <sub>2</sub> 523 K, cooled under H <sub>2</sub>	11.7	21.7
5	evacuation at 773 K	4.1	20.9
6	H <sub>2</sub> 773 K, cooled under H <sub>2</sub>	14.3	22.9
7	evacuation at 773 K	6.5	20.4
8	O <sub>2</sub> 295 K (20 h)	1.6	12.8
9	O <sub>2</sub> 623 K, cooled under O <sub>2</sub>	1.7	5.2
10	O <sub>2</sub> 773 K, cooled under O <sub>2</sub>	1.9	0.7
11	evacuation at 773 K	1.5	1.7

<sup>a</sup> Metal loading of the catalysts, 3% by weight; BET surface area of the catalyst, 49 m<sup>2</sup>·g<sup>-1</sup>; data taken from ref 18.

ceria redox state, when either Rh/CeO<sub>2</sub> catalysts<sup>15–19</sup> or CeO<sub>2</sub> samples<sup>20,21</sup> were heated under H<sub>2</sub>, vacuum, or O<sub>2</sub>. As is discussed in ref 13, hydrogen can induce the reduction of ceria in two ways (a) The process described by eq 1 in the scheme above and (b) the process leading to the creation of oxygen vacancies, eq 2 in the scheme above. These two processes can be distinguished from each other because in case a (reversible reduction), reoxidation would occur just by pumping off the sample. On the contrary, in case b (irreversible reduction), the ceria redox state would remain unmodified upon evacuation.

Table 1 summarizes the results obtained from a Faraday magnetic balance study of the reduction/reoxidation of two Rh/CeO<sub>2</sub> catalysts.<sup>18</sup> They were prepared by the incipient wetness impregnation technique from an aqueous solution of either Rh(NO<sub>3</sub>)<sub>3</sub>, Rh(N)/CeO<sub>2</sub> or RhCl<sub>3</sub>, Rh(Cl)/CeO<sub>2</sub>, respectively. In both cases the metal loading was 3% by weight. The support surface area, which did not significantly change throughout the whole series of treatments applied, was 49 m<sup>2</sup>·g<sup>-1</sup>.

First, we shall comment on the results obtained for Rh(N)/CeO<sub>2</sub>. In accordance with Table 1, the contribution of the so-called reversible process (reaction 1 in the scheme) is very important. This is true for the two reduction temperatures applied: 623 and 773 K. In effect, the data in Table 1 show that, for the catalyst reduced at 623 K and further cooled under H<sub>2</sub> to 295 K, the percentage of paramagnetic Ce<sup>3+</sup> ions present in the sample is 11.4%, run 1. If the sample is further pumped off at 623 K, run 2, ceria becomes strongly reoxidized, and the percentage of Ce<sup>3+</sup> ions is 5.0%. The reoxidation is even larger, 4.1% Ce<sup>3+</sup>, upon evacuation at 773 K, run 5. Also worth noting, the process can be reverted just by treating the sample with H<sub>2</sub> at fairly low temperatures, even at 295 K, run 3. The same is true for the catalyst reduced at 773 K, runs 6–7. In this second case, however, the irreversible contribution, 6.5%, is a bit larger than that determined for the catalyst reduced at 623 K and further evacuated at 773 K. These observations are in good agreement with those reported earlier for some other Rh(N)/CeO<sub>2</sub> catalysts.<sup>15–17</sup> It is implicitly assumed that the evacuation treatment at 773 K eliminates most of the hydrogen chemisorbed on ceria. The magnetic balance and TPD-H<sub>2</sub> data reported in ref 17 would support such an assumption.

<sup>†</sup> Published with the consent of El Fallah et al. (ref 1).

An important conclusion can be drawn from the results above: the identification of  $\text{Ce}^{3+}$  species by using a magnetic balance or XAS technique does not necessarily imply the existence of oxygen vacancies. This means that for a given reduction treatment, depending on the specific conditions under which the amount of  $\text{Ce}^{3+}$  ions is determined, the actual concentration of oxygen vacancies can be strongly overestimated. In accordance with Table 1, to obtain reliable data about the stoichiometry of the reduced ceria,  $\text{CeO}_{2-x}$ , measurements under  $\text{H}_2$  should in general be avoided. In effect, as is shown in ref 16 for a  $\text{Rh(N)}/\text{CeO}_2$  catalyst other than that considered here, the ceria reduction percentage determined from magnetic data is very sensitive to the conditions under which the measurement is carried out. When determined at a reduction temperature of 623 K, under  $\text{H}_2$ , the reported value is 26.1%, much larger than that determined after evacuation at 623 K, 9.5%.<sup>16</sup>

Though less conclusive experimental evidence is available for bare ceria, the contribution of the two processes above should not be disregarded. In this respect, it should be mentioned that in refs 20 and 21, for medium reduction temperatures (623 K), the ceria reduction degree determined from magnetic data is larger than that estimated from weight loss measurements, which is from water evolution. This observation is also consistent with results of a TPD-MS study of the hydrogen evolution from bare ceria,<sup>13</sup> in accordance with which samples reduced at 623 and 773 K can retain quite important amounts of hydrogen. The TPD-MS diagrams reported in ref 13 also suggest that this strongly chemisorbed hydrogen cannot be thoroughly eliminated upon evacuation at 673 K. It would be noted, however, that the results reported in ref 16 show that, compared to  $\text{Rh(N)}/\text{CeO}_2$  catalysts, the relative contribution of the so-called irreversible reduction process is larger for bare ceria.

As is shown in Table 1, the nature of the salt used as metal precursor has a notable influence on the redox behavior of ceria. In particular, the presence of chlorine in the catalyst can strongly modify this behavior.<sup>3,18</sup> In this respect, it would be recalled that the  $\text{Rh}/\text{CeO}_2$  catalyst investigated in ref 1 was prepared from  $\text{RhCl}_3$ .

The analytical results reported in ref 1 show that the chlorine content of the calcined metal/ceria precursor is fairly high, 1.16% by weight of the catalyst, i.e., 1.8 Cl atoms/nm<sup>2</sup>. This value represents 75% of the chlorine deposited onto the ceria during the impregnation step. In accordance with our TPR-MS study of the  $\text{Rh(Cl)}/\text{CeO}_2$  sample included in Table 1, no chlorine evolution occurs throughout the reduction treatment in a flow of  $\text{H}_2$ .<sup>18,23</sup> This suggests that the chlorine retained by the calcined metal precursor/support system would also be present in the final reduced catalyst.<sup>1</sup>

Upon analyzing the results reported in Table 1 for  $\text{Rh(Cl)}/\text{CeO}_2$ , we may conclude that the  $\text{H}_2$  treatment for 1 h, at 623 K, leads to an almost completely irreversible reduction of ceria, runs 1–5. In effect, if the catalyst reduced at 623 K is further evacuated, even at 773 K, a very slight modification of the ceria reduction degree could be observed. This strongly contrasts with the behavior noted for the  $\text{Rh(N)}/\text{CeO}_2$  sample. Under these circumstances, a good estimate of the irreversible reduction degree can be obtained from measurements carried out under  $\text{H}_2$ , as is done in ref 1.

To summarize, the results commented on above allow us to draw a number of conclusions worthy of being outlined:

1. Both reversible and irreversible contributions to the total ceria reduction degree should always be considered. Otherwise the real concentration of oxygen vacancies can be strongly overestimated. Reliable information about this point can be

crucial to thoroughly understanding the nature of the metal/support interaction phenomena in ceria-containing metal catalysts.

2. The relative importance of these two contributions can be very different depending on variables like (a) The reduction temperature,<sup>15–17</sup> (b) the presence of a dispersed metal,<sup>16</sup> (c) the nature of the metal precursor salt,<sup>18</sup> and (d) the BET surface area of the ceria sample. It should be recalled in this respect that the hydrogen chemisorption on ceria seems to be a purely surface reaction,<sup>13</sup> and, therefore, that the reversible contribution would be necessarily small in low surface area ceria samples. This latter point can be particularly important for high reduction temperatures.

3. To make a quantitative estimate of these two contributions, the magnetic or XAS measurements should be performed under  $\text{H}_2$ , but also on the evacuated sample.

A second aspect to be commented on in relation to the results reported in ref 1 is that concerning the reoxidation studies. In accordance with Table 1,  $\text{Rh(N)}/\text{CeO}_2$  and  $\text{Rh(Cl)}/\text{CeO}_2$  catalysts behave quite differently when treated with  $\text{O}_2$  ( $P_{\text{O}_2}$ , 300 Torr), at 295 K, run 8. Sample N becomes oxidized to a large extent. This observation is in good agreement with the reoxidation experiments carried out on  $\text{Rh(N)}/\text{CeO}_2$  catalysts by using XPS<sup>10</sup> and  $\text{O}_2$  pulses/TPO<sup>14</sup> techniques. By contrast, for  $\text{Rh(Cl)}/\text{CeO}_2$ , Table 1 shows that more than 50% of the paramagnetic species generated during the reduction treatment are still present. It is necessary to heat the catalyst under  $\text{O}_2$ , at 773 K, run 10, to arrive at its complete reoxidation. In conclusion, the use of a chlorine-containing rhodium precursor can strongly disturb the ceria redox behavior in  $\text{Rh}/\text{CeO}_2$  catalysts. On the one hand, a much deeper irreversible reduction occurs. On the other hand, its reoxidation becomes much slower.

**Acknowledgment.** This work has been supported by the Junta de Andalucía and the DGICYT (Project with Ref. PB92-0483). We also acknowledge Johnson Matthey for a loan of precious metals.

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JP943381+