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Study of the CO–CeO_2 interaction in presence of highly dispersed rhodium

A. Laachir[a], V. Perrichon[a,*], S. Bernal[b], J.J. Calvino[b], G.A. Cifredo[b]

[a] *Institut de Recherches sur la Catalyse, 2 avenue A. Einstein, 69626 Villeurbanne Cedex, France*
[b] *Departamento de Quimica Inorganica, Facultad de Ciencias, Universidad de Cadiz, Puerto Real, 11510 Cadiz, Spain*

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Abstract

The interaction of CO at room temperature with a ceria supported rhodium catalyst was investigated using TPD-MS and a magnetic balance. The results have shown important differences in comparison with the H_2–Rh/CeO_2 system. In the presence of rhodium, the treatment with CO resulted in a much smaller degree of reduction of CeO_2 than with hydrogen. When, after CO adsorption at 294 K, the catalyst was heated at 773 K under vacuum, the reduction extent increased. In the case of hydrogen, the thermodesorption at 773 K almost completely reoxidized the ceria surface.

Key words: ceria; CO adsorption; magnetic susceptibility; rhodium

1. Introduction

In recent publications [1,2], we have shown that the presence of highly dispersed rhodium deeply modifies the chemistry of the hydrogen–ceria system. Both the extent and the degree of reversibility of the ceria reduction are increased, compared to those observed in the absence of rhodium [3]. In this paper, we present a similar study on the CO–(Rh–CeO_2) system. One of the objectives is to get a better knowledge of the interactions of the M/CeO_2 catalysts with the molecular probes generally used for their characterization. The techniques used are temperature-programmed desorption with mass spectrometry (TPD-MS) and a magnetic balance which was found to be very efficient estimating the Ce^{3+}

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*Corresponding author, present address: Laboratoire d'Application de la Chimie à l'Environnement (LACE), Unité mixte CNRS, Université Claude Bernard Lyon I, 43 bd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France, fax. (+33)78941995.

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concentration [1–3]. The results are analyzed in relation with previous data published on the systems H_2–CeO_2 and CO–CeO_2 [1–6].

2. Experimental

The catalyst 2.9% Rh/CeO_2 was prepared by impregnating a high-surface ceria with a $Rh(NO_3)_3$ solution using the incipient wetness method. The purity of CeO_2 (Rhône-Poulenc) was 99.9% and the surface area was 135 $m^2\ g^{-1}$. After air drying at 383 K during 10 h, the catalyst was stored in a dessicator. For each run, the initial sample was standardized by heating at 773 K for 1 h under helium flow or under vacuum (< 1 mPa). After this treatment, the specific area of the catalyst was 120 $m^2\ g^{-1}$. The HRTEM results have indicated that rhodium was very well dispersed with particles not larger than 1.5 nm [1].

Gravimetric and magnetic susceptibility measurements were carried out with a Faraday microbalance using an apparatus and procedures already described [3].

The thermodesorption experiments were performed under helium flow (1 $cm^3\ s^{-1}$) with a 10 K min^{-1} heating rate. The analytical device was a VG Spectralab SX200 quadrupole mass spectrometer [7].

3. Results

Table 1 summarizes the results of the gravimetric and magnetic measurements corresponding to the CO adsorption on the Rh/CeO_2 catalyst. The variations of the magnetic susceptibility can be directly related to the changes in the oxidation state of cerium since CeO_2 is diamagnetic whereas Ce_2O_3 is paramagnetic [3]. The calculated values of the degree of reduction of ceria after the various treatments are also given in Table 1.

After standardization, the catalyst was treated under oxygen at room temperature and then evacuated again 1 h at 773 K. The resulting solid contained 1.7% Ce^{3+}, which confirms that in presence of rhodium, the high-vacuum treatment induces a slight reduction of ceria [1].

The CO adsorption (40 kPa) was performed during 24 h at 294 K. The adsorbed quantity was 596 μmole CO g^{-1} catalyst assuming that no CO_2 desorbed. It corresponds to an apparent CO/Rh ratio of 2.2. This high value is in good agreement with that obtained by volumetric measurement. The corresponding variation in the magnetic susceptibility indicates an increase in the reduction of ceria, from 1.7 to 5.5%. This value was enhanced to 7.4% when the sample was evacuated afterwards at 773 K. The total quantity of CO associated with the support reduction could be estimated to 165 μmole g^{-1} according to the reaction:

$$2Ce^{4+} + CO + O^{2-} \rightarrow 2Ce^{3+} + CO_{2(ads.)}$$

Introduction of O_2 at 294 K resulted in the adsorption of 247 μmole of oxygen per gramme of catalyst and in a complete reoxidation of Ce^{3+} ions. A further evacuation at 773 K fully restored the state of the standardized catalyst, as deduced from the magnetic susceptibility.

Table 1
Mass and susceptibility changes during the various treatments

Treatment	wt. changes ($mg\ g^{-1}$ cat)	$\times 10^{-6}$ (emu CGS)[a]	Percentage Ce^{3+}
starting catalyst		−0.18	0
evacuation, 773 K O_2 (19 kPa) 294 K evacuation, 773 K; $t=1$ h		0.00	1.7
CO (40 kPa); 294 K; $t=24$ h	+16.7	+0.40	5.5
evacuation 294 K; $t=24$ h	−4.4	0.42	5.7
evacuation 773 K; $t=1$ h	−17.0	0.60	7.4
O_2 (15 kPa); 294 K	+7.9	−0.13	0.5
evacuation			
294 K; $t=3$ h	−0.2	0.00	1.7
773 K; $t=1$ h	−3.1	0.00	1.7

[a] To be multiplied by 12.56 to obtain SI units in $m^3\ g^{-1}$.

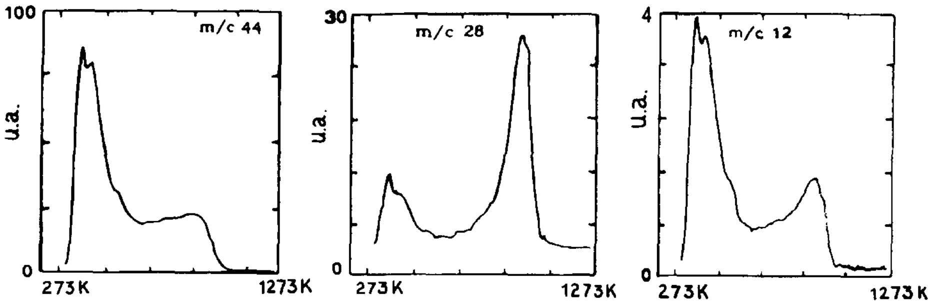

Fig. 1. TPD-MS diagrams (*m/e*: 44, 28 and 12) from a 773 K helium pretreated Rh/CeO_2 catalyst, then treated 1 h with flowing CO at 295 K.

Fig. 1 presents the TPD-MS diagrams obtained up to 1273 K after the catalyst was treated with flowing CO (101 kPa) at room temperature for 1 h. The signals are relating to CO^+ (*m/e*: 28; CO and CO_2), CO_2^+ (*m/e*: 44; CO_2) and C^+ (*m/e*: 12; CO and CO_2). As seen on Fig. 1, for temperatures lower than 773 K, carbon dioxide was practically the only desorbed gas with two maxima centered at 370 and 410 K and a small shoulder at 520 K. Consequently, the weight losses given in Table 1 after the evacuation treatments at 294 and 773 K can be attributed essentially to CO_2. However it cannot be excluded that a part of the

4.4 mg desorbed at 294 K was due to desorbed CO. Thus we can calculate that the quantity of desorbed CO_2 is between 386 μmoles (17.0 mg g^{-1}) and 486 μmoles g^{-1} (17.0 + 4.4 mg$\cdot g^{-1}$) and that of CO is at the maximum of 157 μmoles g^{-1} (4.4 mg g^{-1}). It must be noted that the oxygen treatment at room temperature leads to an incorporation of 494 μmoles of atomic oxygen per gramme, a quantity very close to the calculated value of 486 μmoles of CO_2.

At higher temperature, the diagram of Fig. 1 shows the formation of CO in significant quantity with a maximum at 920 K. It can be attributed to the decomposition of inner carbonate species present in the initial catalyst [3].

4. Discussion

Three main points must be underlined in relation with previous results obtained with pure ceria and with hydrogen as adsorbate.

(1) On the 596 μmole g^{-1} of CO initially adsorbed on the catalyst, 165 μmole can be attributed to the reduction of ceria. The remaining (431 μmole g^{-1}) must be related to the reduction of rhodium ions and to the CO chemisorption according to the equations:

$$Rh^{3+} + O^{2-} + CO \rightarrow Rh^{+} + CO_2$$

$$Rh^{+} + 2CO \rightarrow Rh^{+}(CO)_2$$

$$2Rh^{+} + O^{2-} + 3CO \rightarrow 2Rh^{0}\text{–}CO + CO_2$$

This is supported by FT-IR results obtained in a parallel experiment under CO which show the presence of a mixture of rhodium–gem dicarbonyl $Rh^{+}(CO)_2$ and Rh^{0}–CO species [8]. The rhodium content being 280 μmole g^{-1}, each of these reactions would consumme 280, 560 and 420 μmoles of CO per gramme respectively if the conversion was total. Considering the value of 431 μmoles of CO fixed on the solid, it can be deduced that rhodium is not totally reduced by CO and that, initially, the pretreatment at 773 K has already started to reduce the rhodium as reported by Munuera et al. for a Rh/TiO_2 catalyst [9].

Moreover, the fixation by the catalyst of 247 μmoles O_2, 83 of which are related to the support reoxidation, indicates that the rhodium atoms are easily reoxidized. As previously underlined, the almost same quantity for the desorbed carbon dioxide and the oxygen readsorbed after evacuation suggests that the intermediate oxidation state of the rhodium in the standardized catalyst can be recovered after an oxygen treatment at room temperature.

(2) After 24 h under CO, in the presence of rhodium, the ceria reduction percentage is limited to 5.5%. It is slightly higher than that determined in the absence of rhodium, on pure ceria (2.5%) [4]. This slight increase in the reduction percentage (3% equivalent to 175 μmole Ce^{3+}) can be tentatively attributed to the reduction of specially reactive cerium sites located at the interface with rhodium. However despite this, the influence of the rhodium on the reducibility of the ceria surface is very limited.

(3) The 5.5% reduction percentage is much lower than the 21% reduction obtained when the same Rh/CeO_2 catalyst was treated with hydrogen under the same conditions [1]. When rhodium was absent, the reduction by hydrogen was observed only above 473 K [3] Thus,

we can conclude that highly dispersed rhodium plays a more important role in the chemistry of the H_2–CeO_2 system than in the corresponding CO–CeO_2.

In the same comparison, the effect of an evacuation treatment at 773 K is very different in each case. According to Table 1, the degree of reduction increases after such a treatment. That suggests that some forms of CO linearly adsorbed on Rh(0) or Rh(I) gemdicarbonyls or even some formate type species created by adsorption of CO on CeO_2 [3,5–6] are transformed in other more oxidized forms by reacting with ceria and finally are decomposed to produce CO_2. In contrast, in the case of H_2, the evacuation at 773 K results in a reoxidation of CeO_2, which practically restores the initial catalyst. In this case, the extent of reversibility in the ceria reduction was very high. In refs. [1,2], we have shown that rhodium plays a key role in the mechanism of the adsorption–desorption processes of hydrogen on ceria. The distinct mobility of the superficial species created by the interaction of H_2 and CO with the cerium dioxide could be at the origin of these differences.

5. Conclusion

The interaction of ceria with CO at room temperarure is slightly modified by the presence of highly dispersed rhodium. However, the degree of reduction remains much smaller than that observed with hydrogen. By evacuation at 773 K, the reduction extent increased, in contrast with the case of the system H_2–Rh–CeO_2 for which the reduction of ceria and the hydrogen spillover were found almost reversible by heating under vacuum. With CO, a treatment under oxygen is required to fully reoxidize the ceria.

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