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TEMPERATURE PROGRAMMED DESORPTION STUDY OF HYDROGEN ADSORPTION ON $LaMO_3$ OXIDES

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ABSTRACT

Temperature programmed desorption spectra of H_2 adsorbed on $LaMO_3$ (M = Cr, Fe, Co and Ni) perovskite oxides were obtained as a function of the adsorption temperature and the reduction temperature of the oxide. In the systems H_2–$LaCrO_3$ and H_2–$LaNiO_3$, activated adsorption is observed when the adsorption is effected above room temperature. After adsorption of H_2 at room temperature on reduced $LaMO_3$, the spectra present a desorption peak between 340 and 380 K. $LaNiO_3$ presents, in addition, a second desorption peak at 610–615 K. These peaks increase in intensity with the reduction temperature of the oxide. The TPD peaks observed for H_2–$LaCoO_3$ (red) and H_2–$LaNiO_3$ (red) are assigned to hydrogen adsorbed on metallic cobalt and nickel. On $LaCrO_3$ (red) and $LaFeO_3$ (red) more oxidized metal centers (M^{n+}; $n < 3$) should be involved in hydrogen adsorption. After reduction of the $LaMO_3$ oxides in several zones of temperature and adsorption of hydrogen at room temperature, $LaFeO_3$ (red) exhibited the lowest desorption of H_2. This result is similar to the minima for O_2 adsorption and catalytic activity for total oxidation observed for this oxide.

INTRODUCTION

In our laboratory, $LaMO_3$ oxides (M = first-row transition metal) are being tested as catalysts for the synthesis of oxygenated products, from $CO + H_2$. At the same time, the surface interactions of the reactants, CO and H_2, with these oxides are being studied. Frequently, a given molecule adsorbs on the surface of a solid catalyst yielding more than one chemical species. For example, Baranski and Cvetanović [1] detected five forms of adsorbed hydrogen on the surface of ZnO. Temperature programmed desorption (TPD) is a useful technique for the detection of different surface species and for obtaining information on their reactivities. In this paper, data of hydrogen adsorption on $LaMO_3$ oxides obtained by TPD are reported. TPD spectra were obtained as a function of the adsorption temperature and the reduction degree of the oxide.

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EXPERIMENTAL

A 0.5-g $LaMO_3$ (M = Cr, Fe, Co and Ni) sample was placed in a quartz microreactor which could be heated at 1 K s^{-1}. The analysis of the effluent gases, from the flow system used in the temperature programmed desorption, was effected by means of a UTI model 100 C mass spectrometer. A data acquisition system based on a microprocessor was used to record the signal intensity for H_2 and H_2O, and the temperature of the catalytic bed.

The preparation and characterization of $LaMO_3$ samples have been described previously [2]. Their BET specific surface area as determined by N_2 adsorption ($S_{N_2} = 0.162$ nm^2) at 77 K are given in Table 1. The gases used, H_2 and He were purified by standard methods. TPD experiments were performed after gas-adsorption on oxidized and reduced samples (Tables 1, 2 and 3). For oxidation, a mixture of 21% O_2 + 79% He was passed for 1 h through the sample at 823–923 K (Table 1; these temperatures are 50–100 K below the final heating temperature used in the preparation of each oxide). The reduced samples were prepared from oxidized $LaMO_3$ by passing a H_2 flow for 1 h at the desired temperature. The samples so treated will be referred to as $LaMO_3$ (ox OT) and $LaMO_3$ (red RT) where OT or RT stand for oxidation or reduction temperature in degrees K. After the appropriate oxidation and/or reduction treatments, the sample was outgassed by passing a He flow for 1 h at the same temperature used for

TABLE 1

$LaMO_3$ oxides used in TPD runs

Oxide	BET specific surface area (m^2 g^{-1})	Oxidation temperature (K)
$LaCrO_3$	4.3	923
$LaFeO_3$	10.0	823
$LaCoO_3$	9.1	873
$LaNiO_3$	5.8	923

TABLE 2

Reduction in H_2 of bulk $LaMO_3$ oxides

Oxide	Reduction temperature (K)	Reduction degree [a] (e^- per molecule)
$LaCrO_3$	1270	1.3×10^{-2}
$LaMnO_3$	1173	0.9
$LaFeO_3$	1273	3.0
$LaNiO_3$	773	3.0

[a] $3e^-$ per molecule would amount to full reduction of M^{3+} to M°.

oxidation. The adsorption step was carried out by passing through the sample a flow of H_2 for 0.5 h at room temperature (r.t.) (unless indicated otherwise) and then a He flow for 15 min at r.t. After the oxidation–reduction, outgassing and adsorption steps, heating of the catalyst at 0.5 K s^{-1} was started and the data acquisition system activated. The flow rates of the O_2–He mixture (for oxidation), H_2 (for reduction and adsorption) and He (for outgassing and as carrier during TPD) were, in all cases, 50 cm^3 min^{-1}. The mass spectrometer was calibrated daily against a 409 ppm H_2–He mixture.

RESULTS AND DISCUSSION

Desorbed hydrogen as a function of the adsorption temperature

The effect of the adsorption temperature (T_a) on the TPD spectra has been determined by performing experiments on both extremes of the series of perovskites, namely $LaCrO_3$ and $LaNiO_3$ (Figs. 1 and 2). No H_2 desorption has been detected from the oxidized samples when the adsorption was carried out at r.t. However, after adsorption at 623 K, desorption of H_2 from $LaCrO_3$ (ox 923) was observed above 800 K (Fig. 1a). The amount of desorbed H_2 (q_{H_2}) is significantly larger for $T_a = 773$ K, as can be seen in Fig. 1b where two well-defined peaks at 380 and 835 K are observed (H_2O accompanies H_2 desorption from these oxidized samples). H_2 desorption from the reduced sample $LaCrO_3$ (red 973) was found to be much higher

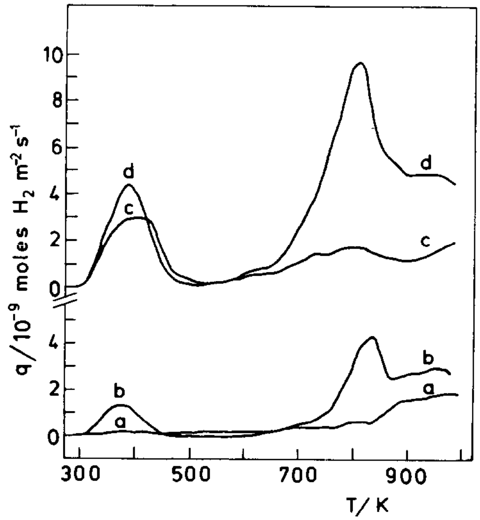

Fig. 1. TPD spectra of H_2 adsorbed on $LaCrO_3$ (ox 923) (a, b) and on $LaCrO_3$ (red 973) (c, d). Adsorption temperature: 623 (a, c) and 773 K (b, d).

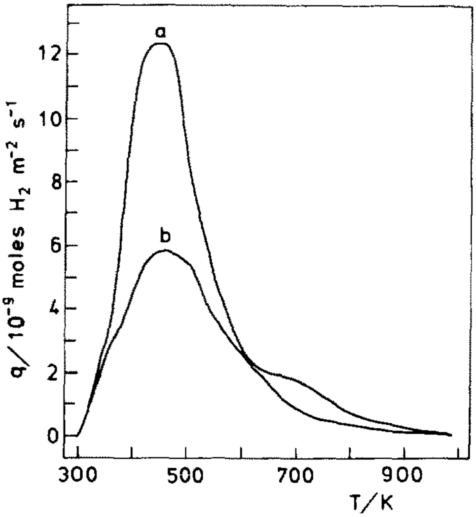

Fig. 2. TPD spectra of H_2 adsorbed on $LaNiO_3$ (red 773). Adsorption temperature: 473 (a) and 623 K (b).

than that recorded from $LaCrO_3$ (ox 923). Also, the increase in hydrogen uptake (and therefore desorption) with increasing T_a observed for the reduced sample (Fig. 1c, d) was more pronounced than for the oxidized sample (Fig. 1a, b). The value of q_{H_2} desorbed from $LaCrO_3$ (red 973) after H_2 adsorption at 623 K (Fig. 1c) is larger (by a factor of 4) than q_{H_2} desorbed from $LaCrO_3$ (red 923) after H_2 adsorption at r.t. (Table 3). This increase in desorbed H_2 should come from the higher adsorption temperature used in the former case since the increase of q_{H_2} with the reduction temperature of the oxide (T_r) is comparatively small (Fig. 3).

TPD spectra after adsorption of H_2 at 473 (a) and 623 K (b) on $LaNiO_3$ (red 773) are given in Fig. 2. In both cases, the amount of desorbed H_2 is

TABLE 3

Adsorbed hydrogen q_{H_2} (moles H_2 m^{-2}) on $LaMO_3$ oxides at 298 K as a function of the reduction temperature T_r (K)

	$LaCrO_3$	$LaMnO_3$	$LaFeO_3$	$LaCoO_3$	$LaNiO_3$
q_{H_2}	1.81×10^{-6}	4.49×10^{-7}	1.11×10^{-7}	9.29×10^{-7}	5.40×10^{-6}
T_r	923	873	823	773	773
q_{H_2}	1.22×10^{-6}	3.80×10^{-7}	8.60×10^{-8}	3.11×10^{-7}	5.73×10^{-6}
T_r	823	723	723	673	673
q_{H_2}	1.29×10^{-6}	6.27×10^{-8}	4.32×10^{-8}	8.88×10^{-8}	7.00×10^{-6}
T_r	723	573	623	573	573
q_{H_2}	0.97×10^{-6}	6.55×10^{-8}	3.96×10^{-8}	2.05×10^{-8}	1.03×10^{-7}
T_r	523	473	523	473	473

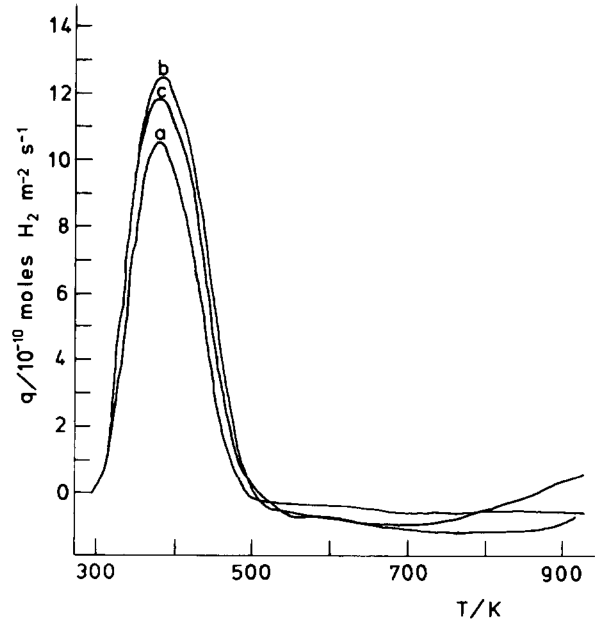

Fig. 3. TPD spectra of H_2 adsorbed on reduced $LaCrO_3$. Reduction temperature: 523 (a), 723 (b) and 823 K (c).

substantially higher than that recorded after H_2 adsorption at r.t. on this reduced oxide (Table 3). Thus, H_2 adsorption passes through a maximum for $T_a = 473$ K and then decreases at higher T_a.

The data in Figs. 1 and 2 indicate that the adsorption isobars (adsorbed H_2 vs. adsorption temperature) in the systems H_2–$LaCrO_3$ (red 973) and H_2–$LaNiO_3$ (red 773) present an ascending branch in the zones 298–773 K and 298–473 K, respectively. Similar behaviour in frequently observed in gas–solid systems [3], for example, H_2–Cr_2O_3 [4], H_2–Sc_2O_3 [5] and H_2–Ni

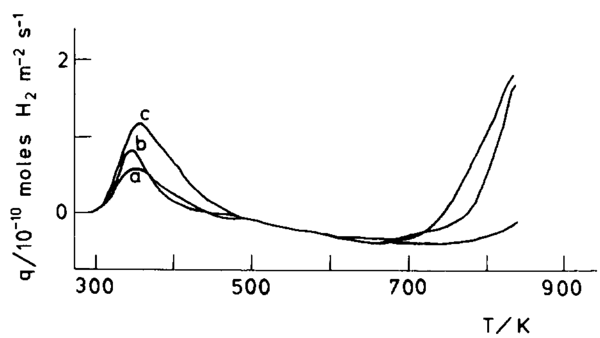

Fig. 4. TPD spectra of H_2 adsorbed on reduced $LaFeO_3$. Reduction temperature: 523 (a), 623 (b) and 723 K (c).

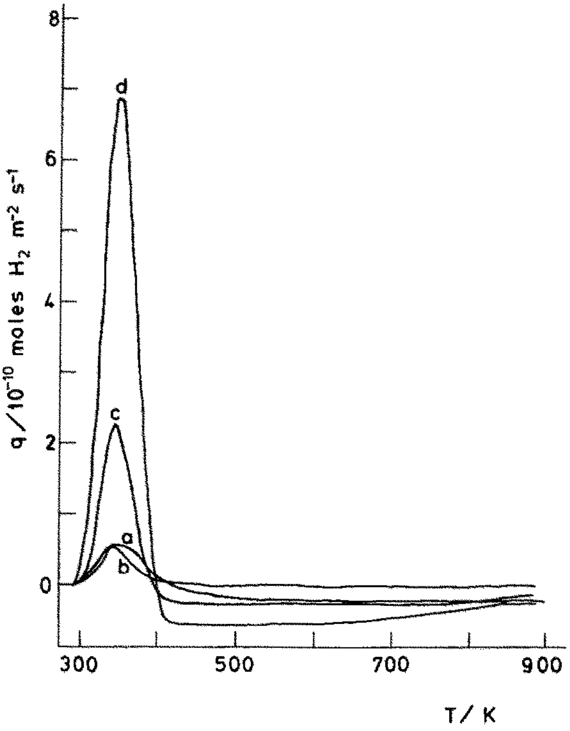

Fig. 5. TPD spectra of H_2 adsorbed on reduced $LaCoO_3$. Reduction temperature: 373 (a), 473 (b), 573 (c) and 673 K (d).

[6]. The presence of an ascending branch of endothermic adsorption indicates a transition zone between non-activated and activated adsorption. The temperature zone where this transition is observed and, also, the dependence of q_{H_2} with T_a is a function of the transition metal cation M. Therefore, to study the effect of the reduction temperature T_r, T_a was kept constant (at 298 K) in the series of experiments described in Figs. 3–6. It would be

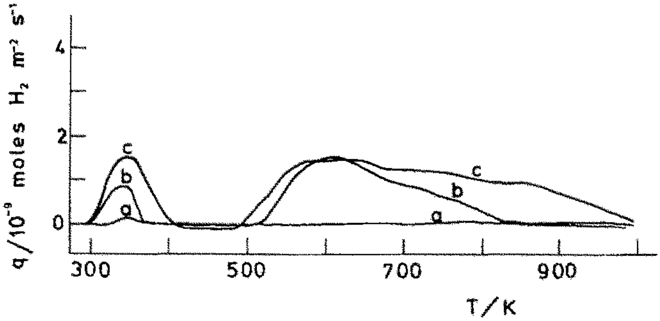

Fig. 6. TPD spectra of H_2 adsorbed on reduced $LaNiO_3$. Reduction temperature: 473 (a), 573 (b) and 673 K (c).

possible to compare TPD spectra after H_2 adsorption on the oxidized samples by effecting H_2 adsorption above r.t. ($T_a \geqslant 623$ K for $LaCrO_3$), but we note that, also, in this case an activated adsorption occurs (Figs. 1a, b). On the other hand, H_2 adsorption at increasing temperatures would alter the oxidation state of the surface in the oxidized samples (and probably, although to a lesser degree, in the reduced ones).

Desorbed hydrogen as a function of the reduction temperature

Representative TPD spectra obtained after H_2 adsorption at 298 K on $LaMO_3$ oxides reduced in H_2 at 523–823 K ($LaCrO_3$), 523–723 K ($LaFeO_3$), 373–673 K ($LaCoO_3$) and 473–673 K ($LaNiO_3$) are given in Figs. 3–6. The spectra for $LaMnO_3$ were given elsewhere [7]. All the series of spectra present a desorption peak at low temperatures: 375–380 K for $LaCrO_3$, 355–365 K for $LaMnO_3$ [7], 345–355 K for $LaFeO_3$, 345–350 K for $LaCoO_3$ and 340–355 K for $LaNiO_3$. In addition a second desorption peak at 610–615 K was observed for H_2–$LaNiO_3$. The desorption temperature either is constant or undergoes a slight shift towards higher temperatures with increasing reduction temperature. On the other hand, H_2 desorption increases with the reduction degree of the oxides.

In Table 2 data of reduction in H_2 of $LaMO_3$ oxides are given. These were taken from temperature programmed reduction diagrams [8] (heating rate 4 K min^{-1}). $LaCrO_3$ and $LaMnO_3$ are difficult to reduce while $LaNiO_3$ is easily reducible, yielding an intermediate reduction state (Ni^{2+}). The presence of metallic nickel, in addition to Ni^{2+}, was observed after reduction of $LaNiO_3$ at 513 K and sintering in He at 1073 K. $LaFeO_3$ presents an intermediate reducibility within the $LaMO_3$ series.

The absence of desorbed H_2 from oxidized samples rules out the M^{3+} ions as adsorption centers. The observed increase of desorbed H_2, in all cases, with the reduction temperature indicates that the adsorption takes place on reduced metallic centers M^{n+} ($n < 3$). Nickel in $LaNiO_3$ (red 673) should be nearly reduced to metallic Ni (Table 2). On the other hand, the TPD spectrum of H_2 adsorbed on $Ni \cdot SiO_2$ [9] is very similar to that in Fig. 6. Therefore, we assign the TPD peaks observed for H_2–$LaCoO_3$ and H_2–$LaNiO_3$ to hydrogen adsorbed on metallic cobalt and nickel. While the TPD peak at lower temperatures appears after H_2 adsorption on $LaNiO_3$ reduced at 473 K and above, the second peak was observed for reduction temperatures of 573 K or higher. This suggests that the hydrogen adsorption on this oxide corresponding to the TPD peak at lower desorption temperature takes place on metallic centers (Ni°) interacting with neighbouring oxide ions. These two peaks might be associated with molecular and dissociatively adsorbed hydrogen. Cadenhead and Wagner [6] observed dissociatively chemisorbed hydrogen on nickel at adsorption temperatures of 273 K and below. $LaCrO_3$, $LaMnO_3$ and $LaFeO_3$ are more stable in a H_2

atmosphere (Table 2). For example, $LaCrO_3$ at 870 K in H_2 undergoes a surface reduction of only 0.51 e^- per molecule [8]. For these oxides more oxidized metallic centers should be involved in H_2 adsorption.

In Table 3 some data of desorbed H_2 after hydrogen adsorption at r.t. on $LaMO_3$ oxides reduced at different temperatures are given. For comparative purposes, T_r has been chosen to decrease from $LaCrO_3$ to $LaNiO_3$ since the oxide reducibility increases in this direction. The increase of desorbed H_2 with increasing T_r is a maximum for the more reducible oxide ($LaNiO_3$). It is noticed that $LaFeO_3$ after reduction in several zones of T_r presents the lowest H_2 desorption. Minima for O_2 adsorption and catalytic activity for total oxidation of CO, propene and isobutene [10] were also found for this oxide within the $LaMO_3$ series. These results seem to indicate that the stable $Ar3d^5$ electronic configuration of the Fe^{3+} ion (with its five half filled $3d$ orbitals) in the initial perovskite confers to this oxide properties which are significantly different from those of the rest of the $LaMO_3$ series. It would be of interest to know whether a parallelism between H_2 adsorption and catalytic activity for CO hydrogenation similar to that found for O_2 adsorption and activity in oxidation processes [10] also holds for $LaMO_3$ oxides.

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