Inorganica Chimica Acta, 140 (1987) 45–47

Characterization of Lanthanide Oxide-promoted Rhodium Alumina Catalysts[*]

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Metal oxide additives are often used as promoters in metal-based CO hydrogenation catalysts. Recent studies have shown that early transition metals are responsible for higher activity and selectivity towards oxygenates on CO hydrogenation over supported Rh catalysts. This promoting effect has been claimed to come from an activation of the CO molecule assisted by the metal ion.

Although there are some promising results [1], little effort has been devoted to the use of lanthanide oxides as promoters. The aim of this work is to contribute to the understanding of the promoting effect caused by lanthanide oxides on Rh/Al_2O_3 catalysts. To this end, a comparative study between the Al_2O_3 and La_2O_3/Al_2O_3 supports and the supported Rh phases has been carried out.

Experimental

A 10% La_2O_3/Al_2O_3 sample was obtained by impregnating γ-Al_2O_3 (Degussa) to incipient wetness with a solution prepared by dissolving La_2O_3 (Sigma, 99.9%) in HNO_3. The solution was evaporated to dryness and oven-dried at 373 K before calcination in air at 873 K for 4 h.

Rh catalysts were prepared using $Rh(NO_3)_3 \cdot xH_2O$ (Ventron, 37% rhodium content), as the precursor salt. The rhodium nitrate, from an aqueous solution, was deposited onto the supports (Al_2O_3 and La_2O_3/Al_2O_3) by an incipient wetness impregnation technique. In order to achieve the final rhodium loading (1%), six successive cycles of impregnation at 298 K, and drying in air at 383 K for 10 h, were necessary.

IR spectra were obtained on a Fourier Transform Nicolet 5DXE instrument (4600–225 cm^{-1}) with a resolution of 4 cm^{-1}. Self-supported pellets placed in a heatable and evacuable cell, with no metallic parts, were used. When recording the IR spectra, a satisfactory signal-to-noise ratio was obtained by coadding 100 interferograms.

Volumetric measurements were performed in a conventional diffusion pumped glass system. N_2 and CO_2 adsorbates were 99.998% pure (S.E.O.).

Results and Discussion

La_2O_3/Al_2O_3 Sample

After calcination, La_2O_3 species were not detected on the surface, either by X-ray diffraction or Raman spectroscopy, which suggests a uniform and high dispersion of the La^{3+} ions on the Al_2O_3 surface.

In Fig. 1 are shown the FT-IR spectra of the OH stretching region for both Al_2O_3 and La_2O_3/Al_2O_3 evacuated at 823 K. The main difference is in the appearance of a strong absorption at 3719 cm^{-1} in the sample containing lanthanide; according to Peri [2], this frequency could correspond to free OH groups on sites of moderate basicity, *i.e.* with local deficiency of O^{2-} and exposed cations in their close vicinity. The latter is in good agreement with the presence on the surface of deficiently coordinated La^{3+} ions, which have been inferred from XPS measurements by comparing the La $3d_{5/2}$ signals of both pure La_2O_3 (binding energy, BE, = 833.8 eV) and La_2O_3/Al_2O_3 (BE = 835.5 eV) samples.

CO_2 adsorption at room temperature has been carried out on activated La_2O_3/Al_2O_3 and Al_2O_3 samples, and followed volumetrically and by FT-IR. The so-called irreversible adsorption [3] and the pressure-dependent reversible adsorption at $P = 10$ torr are included in Table I. It is worth noting the amount of reversible CO_2 adsorption on La_2O_3/Al_2O_3 when compared with Al_2O_3. The difference could be related to the presence of the low coordinated La^{3+} ions acting as Lewis acid sites in the light of FT-IR data. Thus, the ν_3 mode of linear CO_2 has

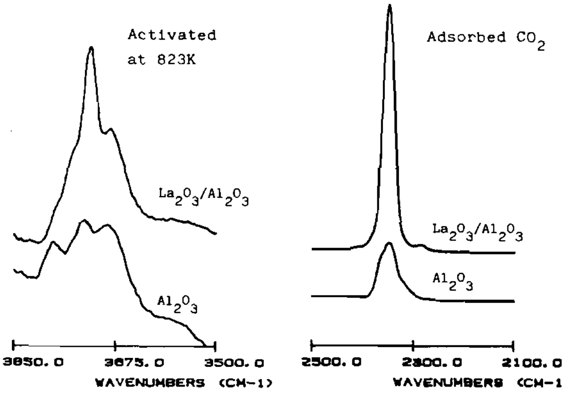

Fig. 1. FT-IR absorption spectra of the samples studied.

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[*] Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

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0020-1693/87/$3.50

TABLE I. CO_2 Adsorption at 298 K on the Samples Studied

Sample	S_{BET} (m^2/g)	$\theta(CO_2)$ (mol/nm^2)	Reversible CO_2 $\theta(CO_2)$ (P = 10 torr)
La_2O_3/Al_2O_3	94	0.97	0.41
Al_2O_3	114	0.10	0.10
La_2O_3	11	1.01	0.05

0.76 absorbance units in La_2O_3/Al_2O_3 and 0.07 in Al_2O_3 (Fig. 1). The observed ν_3 frequencies, 2353 cm^{-1} in La_2O_3/Al_2O_3 and 2347 cm^{-1} in Al_2O_3, slightly shifted from gaseous CO_2 (ν_3 = 2349 cm^{-1}), confirm the weak nature of the interaction. The very strong capacity of La_2O_3/Al_2O_3 for weakly adsorbed CO_2 could be of interest in catalytic reactions involving such a substrate.

Concerning the irreversible adsorption, a remarkable enhancement was also observed for the supported lanthana sample (Table I). It has been studied on both samples by FT-IR as well. Al_2O_3 presents a spectrum with two well-defined HCO_3^- species (ν_a (C–O) 1650 cm^{-1}, ν_{sym} (C–O) 1478, 1448 cm^{-1} and δ_{C-O-H} 1232 cm^{-1}); the one with ν_{sym} at 1478 cm^{-1} is more unstable and is eliminated by evacuation at 350 K. As shown in Fig. 2, the Al_2O_3 surface is practically free of CO_2 at 450 K.

On the other hand, the spectrum of La_2O_3/Al_2O_3 after CO_2 adsorption is rather more complex. At least two types of HCO_3^- species appear, coming from the interaction with two kinds of OH surface groups of different basicity (ν = 3768 and 3721 cm^{-1}) whose intensities strongly diminish upon CO_2 adsorption, whereas a band at 3613 cm^{-1} corresponding to bicarbonate OH stretching emerges. In the 1700–1150 cm^{-1} region, broad bands and shoulders are observed at 1605, 1430, 1363 and 1229 cm^{-1}. On evacuation at 400 K the HCO_3^- species disappears, as shown by the loss of the bands at 3613 and 1229 cm^{-1}. Two broad bands at 1504 and 1378 cm^{-1} remain, which according to Parkyns [4] could be assigned to uni- and bidentate carbonate species, whose formation is likely to occur on highly exposed oxide ions. Such sites should be present on the La_2O_3/Al_2O_3 surface to compensate the poorly coordinated La^{3+} ions.

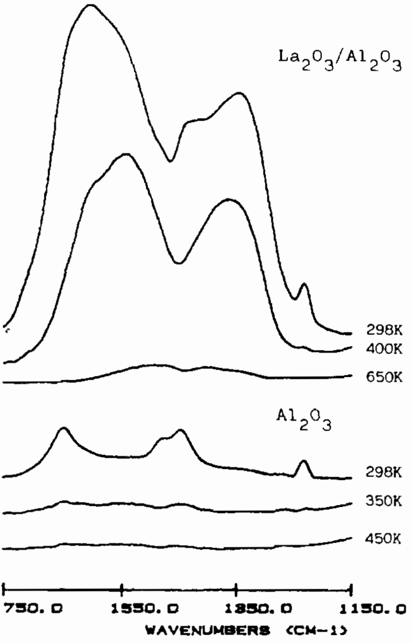

Fig. 2. FT-IR absorption spectra of CO_2 adsorbed at 298 K and then evacuated at temperatures indicated.

In addition to the great capacity for adsorbing CO_2, an interesting feature of the supported oxide is its low decarbonation temperature when compared with the pure La_2O_3 oxide, which reacts with CO_2 at room temperature, giving rise to bulk carbonate phases decomposing at temperatures over 873 K.

Rh/Al_2O_3 and $Rh,La_2O_3/Al_2O_3$ Samples

In order to ascertain the effect of La_2O_3, samples of Rh(1% weight)/Al_2O_3 and Rh(%),La_2O_3(10%)/Al_2O_3 were studied and compared. We have found strong differences between them, which point out the promoter effect of La_2O_3.

As shown in Fig. 3, La_2O_3 strongly improves the thermal reducibility of the Rh(III) precursor. By monitoring the $3d_{5/2}$ XPS signal of rhodium, a mixture of Rh^{III}, Rh^{I} and Rh^{0} is observed when activating the lanthanum-promoted sample at 623 K; at 773 K rhodium is almost completely reduced to Rh^0. On the contrary, in the non-promoted sample, Rh^{III} is not affected by the same thermal treatment. In hydrogen flow at 623 K both catalysts are completely reduced, but their properties strongly differ. Thus, La_2O_3 promotes higher Rh dispersion, as shown by H_2 and CO adsorption data in Table II, expressed as species adsorbed by 100 rhodium atoms on the catalyst. This higher dispersion in $Rh,La_2O_3/Al_2O_3$ could be related to the thermal decomposition of complex hydroxycarbonate phases formed during the impregnation process and further storage. TPD profiles of aged prereduced samples account for such a process.

Evidence of the effect of the promoter ions has been gained by FT-IR spectroscopy of adsorbed CO. In fact, bands in the 2100–1850 cm^{-1} region are found in both Rh/Al_2O_3 and $Rh,La_2O_3/Al_2O_3$ catalysts, and can be ascribed to linear and bridged carbonyl groups, as well as to *gem*-dicarbonyl groups. In addition, a broad intense band centered at *ca.* 1650 cm^{-1} is found in the promoted sample. This fact suggests an interaction between the oxygen of the CO with oxophilic Lewis acid sites on the surface, *i.e.* La^{3+} cations [5]. Thermal evolution of the adsorbed CO leads to the formation of CO_2, as detected by

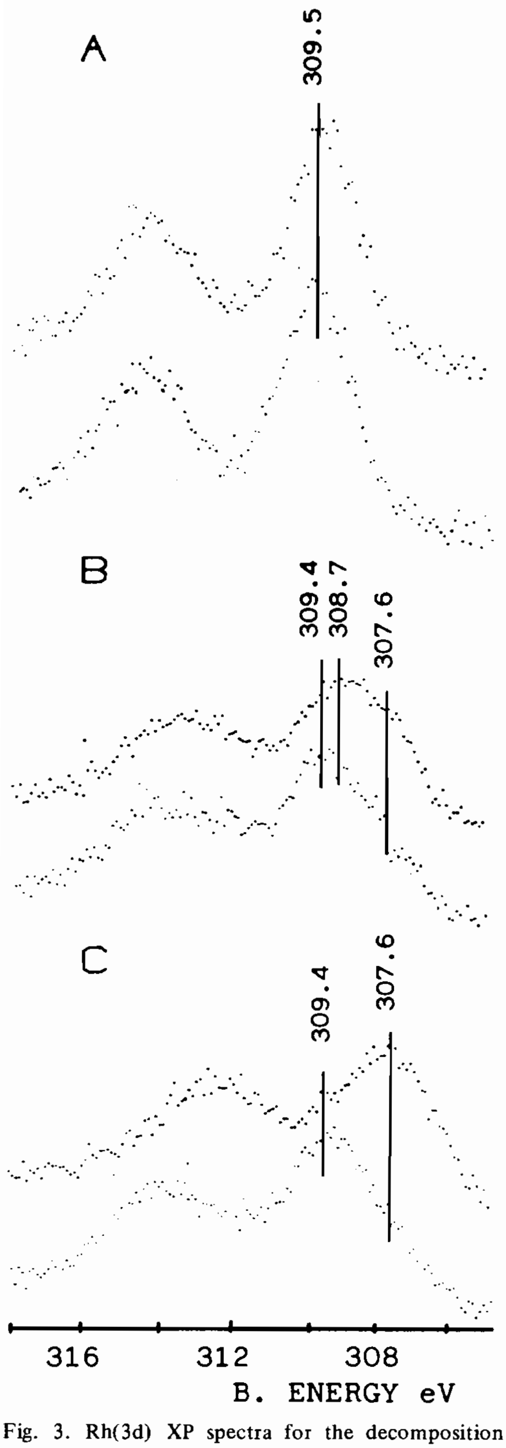

Fig. 3. Rh(3d) XP spectra for the decomposition of the rhodium precursor salt of a 1%Rh/Al_2O_3 (lower traces) and 1%$Rh,La_2O_3/Al_2O_3$ (upper traces) heated *in situ* at: (A) 298 K, (B) 623 K, (C) 773 K. Rh^0: 307.0 eV; Rh^I: 308.7 eV; Rh^{III}: 309.5 eV.

TABLE II. Rh Dispersion on the Samples Studied H_2-Reduced at 623 K

Sample	H/100 Rh	CO/100 Rh
Rh/Al_2O_3	19	54
$Rh,La_2O_3/Al_2O_3$	57	61

both IR and thermal desorption measurements. These results could be an indication of a synergic action of Rh and La^{3+} to predissociate the CO molecule. This fact must be relevant to the activity and selectivity of the catalyst toward methanation and higher oxygenates on Fischer–Tropsch synthesis.

Additionally, we have observed an interesting promoter effect of La_2O_3 on the Rh/Al_2O_3 catalyst: the CO_2 dissociation at room temperature in the absence of hydrogen, which is not observed in our Rh/Al_2O_3 catalyst under the same conditions [6]. The evidence of the CO_2 dissociation came from the appearance of a linear CO stretching band at 2020 cm^{-1} upon CO_2 adsorption at room temperature. At the same time, the XPS $3d_{5/2}$ signal for rhodium showed the presence of oxidized species, probably Rh^I. Again, the cooperative action of Rh and La^{3+} could give an explanation for these findings.

The observed activation of the CO_2 molecule for the $Rh,La_2O_3/Al_2O_3$ catalyst can be of interest in the use of such a substrate as a source of carbon for the synthesis of bulk and fine chemicals.

Acknowledgement

We thank CAICYT (Project no. 1112/84) for financial support.

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