New hydrotalcite-type anionic clays containing noble metals

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The synthesis and thermal evolution of new hydrotalcite-type (HT) anionic clays containing rhodium or ruthenium are investigated in order to obtain catalysts containing well dispersed and stable noble-metal particles, active, for example, in the partial oxidation of methane to synthesis gas.

Rh- and Ru-containing catalysts, widely employed in many reactions of scientific and industrial interest, are prepared by wet impregnation of different supports. This method is not fully reproducible and may give rise to some inhomogeneity in the distribution of the metal on the surface;[1] hence the interest in preparation methods able to produce homogeneous distributions of noble metals inside the structure of precursors, which, on further calcination and reduction, can give rise to well dispersed and stable metal particles.

Hydrotalcite-type (HT) anionic clays, having the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot H_2O$ (M^{II}, M^{III} = metal; A = anion, generally carbonate), fulfil these requirements, having all the cations homogeneously distributed inside brucite-type sheets of the clay structure.[2] HT compounds are already industrially employed as precursors of catalysts or catalyst supports, due to the wide range of preparation variables as well as the specific properties of the cubic mixed oxides obtained by their calcination.[2]

The aim of this work was to synthesize new Rh/Mg/Al or Ru/Mg/Al HT anionic clays (*i.e.* containing a noble metal inside an inert matrix) and to study their thermal evolution, in order to evaluate their possible application as catalyst precursors. This method gives a higher reproducibility and easier characterization in comparison to the analogous samples prepared by wet impregnation.

The Rh/Mg/Al or Ru/Mg/Al HT precursors (Table 1) were prepared by coprecipitation at pH 10.0, by adding a solution containing the nitrates of the elements to a solution containing a slight excess of Na_2CO_3, and maintaining the pH at the above value by dropwise addition of 1 mol dm^{-3} NaOH. The precipitates were washed with distilled water until a Na_2O content lower than 0.02 mass% was obtained, dried overnight at 363 K and then calcined at 923 or 1173 K for 14 h. The precursor compositions were determined after dissolution in concentrated HCl, using complexometric methods for aluminium and magnesium,[3] while rhodium or ruthenium were determined spectrophotometrically as chloride or thiourea complexes.[4].

Table 1 Composition and specific surface area of hydrotalcite-type anionic clays and samples obtained by their thermal decomposition

			Specific surface area/m^2 g^{-1}		
Sample	Composition	Atomic ratio	363 K, overnight	923 K, 14 h	1173 K, 14 h
1	Mg/Al	71.0/29.0	94	174	83
2	Rh/Mg/Al	0.04/71.0/29.0	84	162	96
3	Rh/Mg/Al	1.0/71.0/28.0	78	154	97
4	Rh/Mg/Al	5.0/71.0/24.0	95	166	91
5	Ru/Mg/Al	1.0/71.0/28.0	87	118	90
6	Ru/Mg/Al	5.0/71.0/24.0	84	94	86

XRD powder analysis was carried out using a Philips PW1050/81 diffractometer controlled by a PW1710 unit (λ = 0.154 18 nm, 40 kV, 40 mA), using a scanning speed of 70° h^{-1}. The lattice parameters were determined from diffractometric data of the most intense peaks using a least-squares refinement. On the Ru-containing calcined samples, XRD quantitative analyses[5] were carried out adding $RuO_2\cdot xH_2O$ (> 99%), previously calcined for 14 h at 1173 K. The specific surface areas were determined by N_2 adsorption using a Carlo Erba Sorpty 1700.

The XRD powder patterns of the Rh-containing dried precipitates show the presence of only a well crystallized HT phase, with a decrease in crystallinity as a function of the amount of rhodium present. The crystallographic parameters of the different HT phase, calculated for a hexagonal cell on the basis of a rhombohedral *R*3*m* symmetry, show an increase as a function of the Rh-content of both *a* and *c* values in comparison to those determined for the Mg/Al sample (Table 2). The increase of the *a* parameter is in accord with the larger size of Rh^{3+} compared to Al^{3+} (0.67 *cf.* 0.53 Å),[6] while that of parameter *c* can be attributed to weaker interactions between the cationic sheets and the anions present in the interlayer region, due to the smaller effective charge of the Rh^{3+} ions.[7] The XRD patterns of the Ru-containing precipitates show the presence of only a well crystallized HT phase, although for the sample with the higher Ru content (sample 6) the baseline was not perfectly level. Further, for these samples the trend of the lattice parameters is not so evident as for the Rh-containing samples, showing only small changes as a function of the Ru content (Table 1), even though octahedrally coordinated Ru^{3+} ions have a slightly larger ionic radius than Rh^{3+} (0.70 *cf.* 0.67 Å).[5] Therefore, Ru^{3+} ions do not appear to enter into the HT structure in as high concentrations as Rh^{3+} ions, probably also being incorporated in an amorphous side phase in the higher Ru-content materials.

After calcination at 923 K, the XRD powder patterns of the Rh-containing samples show the presence only of a cubic mixed oxide, with a smaller crystal size than that of the corresponding Mg/Al sample (Fig. 1). The increase of the lattice parameter *a*

Table 2 Lattice parameters of samples after different thermal treatments (composition as in Table 1)

	363 K, overnight		923 K, 14 h	1173 K, 14 h	
Sample	*a*/Å[a]	*c*/Å[a]	*a*/Å[b]	*a*/Å[c]	*a*/Å[d]
1	3.063(4)	23.16(5)	4.178	4.214(1)	8.077(2)
2	3.067(7)	23.10(9)	4.184(2)	4.216(6)	8.094(4)
3	3.072(7)	23.13(3)	4.193(3)	4.222(5)	8.102(3)
4	3.075(8)	23.34(9)	4.197(2)	4.220(6)	8.144(4)
5	3.064(4)	23.07(5)	4.194(1)	4.220(2)	8.101(4)
6	3.067(5)	23.21(6)	4.201(1)	4.216(2)	8.087(9)

[a] Hydrotalcite-type phase. [b] Cubic mixed oxide phase. [c] Oxide phase. [d] Spinel phase.

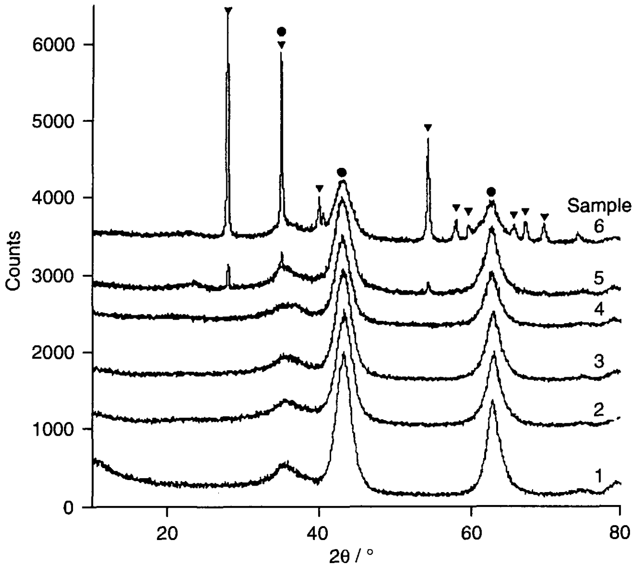

Fig. 1 XRD powder patterns of the samples calcined for 14 h at 923 K (compositions as in Table 1); (●) cubic mixed oxide phase, (▼) RuO_2 phase

of the cubic mixed oxide as a function of the Rh content (Table 2) confirms the presence of the Rh^{3+} ions inside the lattice. In contrast, the XRD powder patterns of Ru-containing samples show the presence of some highly crystalline RuO_2, together with the cubic mixed oxide phase previously mentioned. Also for these samples the lattice parameter *a* of the cubic mixed oxides increases with respect to the Mg/Al sample, in agreement with only partial segregation of RuO_2 as evidenced by XRD quantitative analysis (sample 5 = 0.6 ± 0.1 instead of 3.0 mass%; sample 6 = 7.5 ± 0.3 instead of 14.0 mass%). The significant increase of surface area for the Mg/Al and Rh/Mg/Al samples calcined at 923 K with respect to the precursors (Table 1) suggests that decomposition occurs without any extensive change in crystal morphology.[8] The lower values obtained for the Ru-containing samples can be explained by hypothesizing that the segregation of crystalline RuO_2 phase may occlude the small pores and/or give rise to a structural rearrangement.

After calcination at 1173 K, the XRD patterns show the presence of oxide and spinel phases in the Rh-containing samples, again with decreasing crystal size with increasing rhodium content. While the lattice parameter of the oxide phase remains practically constant (Table 2), the value of the *a* parameter of the spinel phase increases linearly with the %Rh, showing that Rh^{3+} ions are preferentially located in the spinel phase, randomly distributed with Al^{3+}. The Ru-containing samples confirm the presence, together with the spinel and oxide phases, of a highly crystalline RuO_2 phase. For samples 5 and 6 the lattice parameters of the spinel phase are larger than those of the Mg/Al sample, but do not change upon increasing the Ru content. Quantitative XRD analysis shows, for both samples, an incomplete segregation of RuO_2 (sample 5 = 1.0 ± 0.1 instead of 3.0 mass%; sample 6 = 13.0 ± 0.5 instead of 14.0 mass%), confirming that Ru^{3+} ions are also located inside the spinel lattice. The similar amounts of non-segregated ruthenium (1–2 mass%) explain the unchanged value of lattice parameter on increasing the Ru content. The specific surface areas decrease upon increasing the calcination temperature from 923 to 1173 K (Table 1), with similar values for all samples due to the structural rearrangement related to phase segregation; however, the values observed indicate the high thermal stability of these samples.

These samples are stable under severe reaction conditions and may be used in many reactions of industrial interest,[9] for example, Table 3 illustrates the results of catalytic tests concerning partial oxidation of methane. It is worth noting that this reaction would give synthesis gas with a significant reduction of the production costs; however, an industrial process based on catalytic substoichiometric combustion has not yet been developed and commercialized.

Table 3 Catalytic performances in the methane partial oxidation of the Rh- and Ru-containing catalysts [reaction mixture CH_4–O_2–He = 2 : 1 : 4 (*v*/*v*); reaction temperature = 1023 K; contact time = 7.2 ms]

Sample	O_2 conversion (%)	CH_4 conversion (%)	CO selectivity (%)	H_2 selectivity (%)
2	100	73	90	93
3	100	87	87	98
4	100	91	93	99
5	100	77	89	95
6	100	82	89	96
Supported catalyst[a]	100	85	89	95

[a] Rh/Al_2O_3 catalyst (Rh = 0.5 mass%) prepared by wet impregnation of α-Al_2O_3.

The Rh/Mg/Al samples were contacted with a CH_4–O_2–He (2 : 1 : 4 *v*/*v*) reaction mixture, maintaining the oven temperature at 1023 K, and showed very good activity and selectivity for synthesis gas production. The catalyst with the lowest Rh content shows the lowest activity, with activity increasing as a function of the noble metal content; however, at high Rh contents differences in activity are reduced. The conversion of methane and the CO selectivity increase to values of *ca.* 90% while that towards H_2 is over 90%: these results are comparable with the best values reported in the literature.[10] While the lowest Rh-content sample (0.04% atomic ratio) is not sufficient to obtain a high activity, a maximum noble-metal content exists, over which improvements in conversion or selectivities cannot be achieved, and is probably related to the full coverage of the catalyst surface. The lower activity of the Ru-containing samples may be explained by considering the segregation of most of the ruthenium as highly crystalline RuO_2.

For comparison, the results of a rhodium/alumina catalyst prepared by wet impregnation are also reported in Table 3: this sample shows a high activity, similar to that of sample 3; although for a lower Rh-content (0.5 *cf.* 2.3 mass%, corresponding to a 1% atomic ratio). The same activity for a lower Rh content can be justified considering that in the impregnated catalyst all the rhodium is present on the surface, whereas in the HT samples it is partially located inside the bulk. However, it must be noted that in the catalysts obtained by calcination of HT precursors, the rhodium particles are stabilized in an inert matrix and no sintering and/or segregation phenomena have been observed after the catalytic tests, notwithstanding the severe reaction conditions.

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