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Catalytic behaviour and surface properties of supported lanthana

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Abstract

This paper deals with the role of dispersed lanthana as an active phase in several catalytic reactions: CO hydrogenation, CO oxidation, and oxidative dimerization of methane.

Characterization of the prepared catalysts indicates that lanthana can be effectively dispersed on silica and on ceria. While in the case of silica-supported catalysts lanthana appears at the surface, leading to an almost full coverage for loadings higher than 40%, in the case of ceria-based systems, lanthana forms a solid solution with the support.

In all the reactions studied, the presence of lanthana can be related to significant changes in the catalytic properties of the bare supports. Thus, the selectivity towards the total oxidation products observed on pure ceria is decreased, and the low activity shown by silica is enhanced. For the $CO+H_2$ reaction, the addition of lanthana also generates upgraded products.

1. Introduction

Lanthana-containing catalysts have attracted considerable attention during recent years. The role of lanthana in these systems can be very diverse, including (1) the promotion of supported metal catalysts [1–4], (2) textural stabilization of high-surface-area supports [5, 6], and (3) as the active phase for several oxidation and hydrogenation reactions [7–12].

This paper focuses on the use of supported lanthana as an active phase, which has scarcely been studied up to date.

Silica and ceria high-surface-area supports were used to disperse lanthana. Pure silica, ceria and lanthana were also studied as reference compounds.

The reactions considered in this work include CO hydrogenation, CO oxidation, and oxidative coupling of methane. Catalytic behaviour is discussed with respect to the results of characterization of the catalyst.

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2. Experimental details

SiO_2 M5 Cabosil kindly donated by Cabot, and CeO_2 from Union Molicorp, were used as high-surface-area support materials. These samples were impregnated with aqueous solutions prepared from $La(NO_3)_3 \cdot 6H_2O$ supplied by Fluka. The concentration of the solutions was adjusted to obtain the desired loadings. Such loadings, defined as the weight percentage of La_2O_3 referred to 100% of support, ranged from 7.5% to 75% for La_2O_3–SiO_2 samples, and from 5% to 18.3% for La_2O_3–CeO_2. Following impregnation, the samples were dried in an oven at 363 K to give the catalytic precursors, which were further calcined in air.

Thermogravimetric analysis (TGA) of the precursors was carried out with a Mettler HE 20 thermobalance and mass spectrometry (MS) with a VG Spectralab SX200 mass spectrometer. A Siemens D500 diffractometer, operating with Cu Kα radiation, was used for the X-ray diffraction (XRD) measurements. Surface acid and basic properties of the catalysts were measured by titration with pyridine and benzoic acid respectively, according to procedures described elsewhere [13, 14]. High resolution electron microscopy (HREM) images were obtained in a JEM 2000 EX microscope, equipped with a top entry specimen holder and an ion pump, with a structural resolution of 2.1 nm. An FTIR Nicolet 510 was used to obtain IR spectra of the aged catalyst samples, in order to determine the occurrence of carbonation of lanthana during the catalytic reactions.

The CO hydrogenation reaction was carried out in a copper-lined stainless steel reactor operating at 40 MPa and 748 K. A 1:1 $CO+H_2$ gas mixture at a flow rate of 2 l h^{-1} g^{-1} was allowed to come into contact with the samples to test the catalytic activities. The CO oxidation studies were performed with a 3% CO, 3% O_2 and 94% helium gas mixture, at atmospheric pressure and 673 K, in a quartz reactor, at a flow rate of 16 l h^{-1} g^{-1}. The CH_4 dimerization was also run at atmospheric pressure, in a quartz reactor, with a gas mixture containing 6.7% O_2, 13.3% CH_4 and 80% helium. The flow rate selected for these experiments was 15 l h^{-1} g^{-1}. The reaction products were analysed by gas chromatography as described elsewhere [9, 10].

3. Results and discussion

3.1. Characterization of the catalyst samples

The thermal evolution of the lanthanum nitrate precursor dispersed on SiO_2 and on CeO_2, studied by TG and by MS, indicate that the decomposition of the nitrates is complete after heating up to 823 K. Thus, pretreatment of the samples consisted of calcination in air for 4 h at 873 K for La_2O_3–SiO_2, and at 823 K for La_2O_3–CeO_2 samples.

The surface areas of the catalysts following calcination, as determined by means of the Brunauer, Emmett and Teller (BET) method, are shown in Table 1. These results, when compared with the surfaces of the pure supports,

TABLE 1

Surface acidity and basicity of the samples

Sample	BET surface[a]	Acidity[b]		Basicity[c]	
		per gram	per m^2	per gram	per m^2
SiO_2	187	291	1.6	89	0.5
7.5%La_2O_3–SiO_2	169	289	1.7	442	2.6
18.7%La_2O_3–SiO_2	149	228	1.5	540	3.6
37.5%La_2O_3–SiO_2	113	161	1.4	690	6.1
75%La_2O_3–SiO_2	90	–	–	789	8.8
La_2O_3	20	22	1.1	178	9.1
CeO_2	130	117	0.9	611	4.8
8.7%La_2O_3–CeO_2	52	37	0.7	112	2.1
18.3%La_2O_3–CeO_2	26	48	1.8	241	9.1

[a] Square metre per gram.
[b] μmol pyridine.
[c] μmol benzoic acid.

show a strong sintering of the ceria-based systems, while for silica-dispersed lanthana, the sintering level is low if the specific surface is referred to grams of SiO_2.

Concerning the La_2O_3–SiO_2 samples, several experimental findings indicate the feasibility of a model in which lanthana is strongly interacting with the support, thus leading to a well dispersed lanthanum-containing phase. First of all, the decomposition temperature of lanthanum nitrate on silica is decreased by about 100 K, when compared with pure $La(NO_3)_3 \cdot 6H_2O$. XRD lines characteristic of lanthanum-containing compounds could not be observed for these samples, even for La_2O_3 loadings as high as 75%. The surface basicity of the La_2O_3–SiO_2 samples, shown in Table 1, increases with the La_2O_3 loadings. For the higher loading, 75%, the surface concentration of basic sites gives a similar value to that corresponding to lanthanum oxide (Table 1). As the lanthana loading equivalent to monolayer coverage would be around 39%, these results also suggest a tendency to adopt an adequate dispersion of lanthana on silica. The HREM results are also in line with the occurrence of a well dispersed lanthanum-containing phase. Thus, for loadings higher than 37.5%, an amorphous layer about 1.0 nm thick covering the silica particles can be observed. In contrast, for lower loadings, pillbox shape amorphous dispersed particles are formed, and a significant fraction of the silica surface remains uncovered.

For La_2O_3–CeO_2 samples, XRD and HREM results confirm the formation of solid solutions, in agreement with former results on these systems reported in the literature [15]. The lattice spacings determined by XRD for the La_2O_3–CeO_2 samples are shifted to higher values, when compared with pure CeO_2. Thus, the 0.541 nm spacing characteristic of pure CeO_2 (cerianite) appears at 0.546 nm for the 18.3%La_2O_3–CeO_2 sample. When these samples were studied by HREM, particles characteristic of a dispersed phase were not observed on the support material, but instead a series of well defined crystallites with CeO_2-like structure was seen. On the grounds of these results, the formation of mixed compounds such as $La_2Ce_2O_7$ with pyroclore structure [16] can be ruled out. The strong sintering which takes place during the calcination of these samples is also in agreement with the formation of solid solutions, which implies the occurrence of high ionic mobility during the calcination stage.

3.2. CO hydrogenation

The results shown in Table 2 indicate that the addition of lanthana improves the catalytic properties of the bare silica and ceria supports. For La_2O_3–SiO_2 samples, the conversion towards hydrocarbons increased with the La_2O_3 loading. In parallel, a decrease in the selectivity towards CH_4 and an increase in the formation of branched C4 compounds (referred to as iso-C4 in Table 2) were observed.

For La_2O_3–CeO_2, it is worth noting the decrease in the methanation activity, which is associated with the addition of lanthana. The selectivity towards branched C4 compounds is also increased. This means that La_2O_3 modifies the behaviour of the CeO_2 support, thus leading to upgraded reaction products.

The CO hydrogenation, by means of a chain growth mechanism leading to the formation of branched-C4 hydrocarbons, is known as the isosynthesis reaction [17]. According to the literature, the most accepted chain growth mechanisms take place through an aldol condensation process [10, 11], or by CO insertion in an enolate specie [18], both processes being promoted by catalytic basic sites. The hydrogenating properties (on reduced sites) and the dehydrating abilities (on acid sites) allow the formation of hydrocarbon from oxygenated intermediates.

A detailed discussion of our results is by no means simple, because of the parallel formation of CO_2, CH_4 and higher hydrocarbons. An additional problem in the case of rare earth oxides, is the occurrence of strong carbonation phenomena of the catalysts due to the presence of CO_2 in the reaction

TABLE 2

Catalytic behaviour in the $CO+H_2$ reaction at 40 MPa and 748 K

Sample	Conversion (%)		Selectivity	
	HC	CO_2	CH_4	iso-C4
SiO_2	2.3	2.1	60	3
7.5%La_2O_3–SiO_2	2.9	3.2	54	4
18.7%La_2O_3–SiO_2	3.6	6.3	37	6
La_2O_3	6.1	12.6	32	24
CeO_2	45.0	20.0	80	1
5%La_2O_3–CeO_2	7.1	12.7	44	8
18.3%La_2O_3–CeO_2	8.7	15.4	41	10

atmosphere [19]. Nevertheless, the improvement in selectivity towards iso-C4 associated with the addition of lanthana could be interpreted on the grounds of the increasing concentration of basic sites. The formation of large amounts of CH_4 on CeO_2 could be related to the enhanced hydrogenating properties of this catalyst. In the first stage of the reaction the formation of CH_4 is in competition with that of formaldehyde, the precursor specie for the formation of isobutane [10, 11]. The reducibility of high-surface-area ceria [20] could be considered as a factor which favours the hydrogenation towards CH_4, thus explaining the low selectivity observed on pure CeO_2 for iso-C4.

3.3. CO oxidation

Figure 1 shows the percentage of CO conversion at 673 K for La_2O_3–SiO_2 and La_2O_3–CeO_2 catalysts. These data can be compared with the 10.3% conversion observed on pure La_2O_3.

The results indicate that La_2O_3 leads to an increase in the oxidative properties of SiO_2, and to a decrease in the oxidative properties of CeO_2. This suggests that a proper selection of the support, loading, and reaction conditions, could make lanthana a good catalyst to run controlled oxidation reactions. Breysse *et al.* [21, 22] have proposed that the very strong oxidizing properties of CeO_2 can be attributed to the presence of labile surface oxygen species, which favours the formation of vacancies involved in the oxidation mechanism. The formation of a solid solution between ceria and lanthana would moderate the oxidizing character of ceria. In contrast, SiO_2 is a very poor catalyst for the oxidation reaction which can be activated by dispersing lanthana on its surface.

Nevertheless, one problem to be considered in the particular reaction conditions used here, is the progressive decay in the catalytic activities. These deactivation phenomena are clearly related to the gradual formation of carbonate species, made evident by Fourier transform IR (FTIR) spectroscopy.

3.4. Oxidative coupling of CH_4

Table 3 shows the catalytic results for the CH_4+O_2 reaction. The pure supports, silica and ceria, show low levels of catalytic activity for the

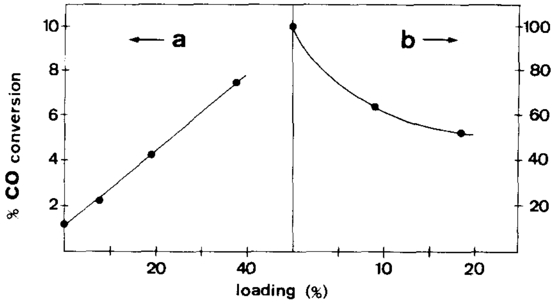

Fig. 1. Catalytic results for the CO oxidation reaction, at 673 K, over lanthana supported on (a) silica and (b) ceria.

TABLE 3

Catalytic results for the oxidative coupling of CH_4 at 1023 K

Sample	Conversion of CH_4 (%)	Yield		
		CO	CO_2	$C_2H_4+C_2H_6$
SiO_2	2.9	1.7	0.4	0.8
7.5%La_2O_3–SiO_2	3.3	1.8	0.7	0.8
18.7%La_2O_3–SiO_2	12.7	2.3	6.9	3.4
La_2O_3	33.7	3.0	21.4	9.3
CeO_2	25.0	1.6	22.9	0.5
8.7%La_2O_3–CeO_2	24.8	1.8	22.2	0.8
18.3%La_2O_3–CeO_2	29.2	2.7	22.1	4.4

dimerization process. In the case of SiO_2 the total conversion of CH_4 is very low, whereas the conversion on CeO_2 is high, although the reaction is mainly oriented towards the formation of CO_2.

In the literature [7, 8, 21, 22] it has been suggested that CeO_2 can easily undergo changes in the oxidation states of cerium, which would favour the formation of total oxidation products; such a type of catalyst is not effective for the formation of $\cdot CH_3$ radicals [7, 8], the proposed active species in the dimerization reaction.

The addition of lanthana to both silica and ceria supports, results in an increase in the activities towards CH_4 dimerization products (Table 3). This effect can be explained if it is assumed that lanthana is a poor radical scavenger, which allows the escape of $\cdot CH_3$ species to the gas phase where they may couple to form C_2H_6. Nevertheless, for ceria-supported catalysts the yields towards CO_2 remain high. This can be explained because cerium remains present at the surface owing to the formation of a solid solution between lanthana and ceria.

For these reactions, the carbonation of the surface, determined by FTIR, is not as strong as it was for the CO oxidation, and the deactivation of the catalytic phases cannot be considered as a significant problem. According to our experience [19], the higher reaction temperatures at which the dimerization reaction operates must prevent the formation of carbonate species on the active centres.

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References

1 R. Kieffer, A. Kiennemann, M. Rodríguez, S. Bernal and J. M. Rodríguez-Izquierdo, *Appl. Catal.*, *42* (1988) 77.
2 R. P. Underwood and A. T. Bell, *J. Catal.*, *109* (1988) 325.
3 J. S. L. Ledford, M. Houalla, A. Proctor, D. M. Hercules and L. Petrakis, *J. Phys. Chem.*, *93* (1989) 6770.
4 L. Q. Dou, Y. S. Tan and D. S. Lu, *Appl. Catal.*, *66* (1990) 235.
5 M. Bettman, R. E. Chase, K. Otto and W. H. Weber, *J. Catal.*, *117* (1989) 447.
6 H. Schaper, D. J. Amesz, E. B. M. Doresburg and L. L. Van Reijen, *Appl. Catal.*, *9* (1984) 129.
7 Y. Tong, M. P. Rosyneck and J. H. Lunsford, *J. Phys. Chem.*, *93* (1989) 2896.
8 C. H. Lin, K. D. Campbell, J. X. Wang and J. H. Lunsford, *J. Phys. Chem.*, *90* (1986) 534.
9 A. Kaddouri, R. Kieffer, A. Kiennemann, P. Poix and J. L. Rehspringer, *Appl. Catal.*, *51* (1989) L1.
10 R. Kieffer, G. Cherry and R. El Bacha, *C1 Chem.*, *2* (1987) 11.
11 R. Kieffer, G. Cherry, J. Varela and R. Touroude, *J. Chim. Phys.*, *24* (1987) 901.
12 S. Bernal, G. A. Martin, P. Moral and V. Perrichon, *Catal. Lett.*, *6* (1990) 231.
13 J. M. Campelo, A. García, D. Luna and J. M. Marinas, *Afinidad*, *39* (1982) 61.
14 J. M. Campelo, A. García, D. Luna and J. M. Marinas, *Afinidad*, *39* (1982) 325.
15 E. Zintl and U. Croatto, *Z. Anorg. Allg. Chem.*, *242* (1939) 79.
16 F. Brisse and O. Knop, *Can. J. Chem.*, *45* (1967) 609.
17 F. Fischer, H. Pichler and K. H. Ziesecke, *Brennstoff Chem.*, *30* (1949) 13.
18 N. B. Jackson and J. Ekerdt, *J. Catal.*, *126* (1990) 31.
19 S. Bernal, F. J. Botana, R. García and J. M. Rodríguez-Izquierdo, *React. Solids*, *4* (1987) 23.
20 A. Laachir, V. Perrichon, A. Badri, J. Lamotte, E. Catherine, J. C. Lavalley, J. El Falla, L. Hilaire, F. Le Normand, E. Quemere, G. N. Sauvion and D. Touret, *J. Chem. Soc. Faraday Trans.*, *87* (1991) 1601.
21 M. Breysse, M. Guenin, B. Claudel, H. Latreille and J. Veron, *J. Catal.*, *27* (1972) 275.
22 M. Breysse, M. Guenin, B. Claudel, H. Latreille and J. Veron, *J. Catal.*, *28* (1973) 54.