Oxidative Coupling of Methane over La₂O₃–CaO Catalysts

Effect of Bulk and Surface Properties on Catalytic Performance

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The oxidative coupling reaction of methane to higher hydrocarbons over lanthanum–calcium-oxide catalysts was studied in a microcatalytic fixed-bed reactor in the temperature range from 973 to 1013 K applying inlet partial pressures of methane and oxygen of 93 and 7 kPa, respectively. Lanthanum to calcium atom ratios of the catalyst were varied as follows: 0/100, 1/99, 5/95, 10/90, 14/86, 20/80, 27/73, 30/70, 50/50, 70/30, and 100/0. Maximum C_{2+} selectivities of 76% and C_{2+} yields of 9% were achieved (1013 K). The bulk-phase and surface compositions of the catalysts were determined by XRD and XPS, respectively. A relative measure of surface basicity and acidity was derived from the product distribution of the isopropyl alcohol conversion used as a probe reaction. The catalytic performance of the differently composed materials is affected by their surface composition and not by their bulk composition. Maximum selectivity is achieved with a surface content of lanthanum between 60 and 90%. It is tentatively suggested that a catalyst which is primarily basic in nature requires acidic sites also for achieving high C_{2+} selectivity. © 1991 Academic Press, Inc.

INTRODUCTION

Previous studies on the oxidative coupling reaction of methane to C_{2+} hydrocarbons (*1, 2*) have shown that alkaline earth and alkali-alkaline earth oxides (*3–6*) as well as rare earth oxides (*7–16*) are suitable catalysts for converting methane to higher hydrocarbons. An advantage of the rare earth oxide catalysts is their constant selectivity and activity (*9*) during long-term operation, a feature which is frequently not achieved by the previously tested alkali-alkaline earth catalysts (*4, 5*). The reason for the addition of alkali compounds to various catalytic materials was to enhance the basicity of the systems (*3*), which is assumed to be necessary for obtaining high selectivities to C_{2+} hydrocarbons (*17*). Additionally, La₂O₃ has been shown to be an active material in producing methyl radicals, which are proposed intermediates in the coupling reaction (*13*). Similarly, deuterium exchange experiments (*18*) showed that CaO and La₂O₃ have the ability to activate methane. Against this background it was anticipated that La₂O₃/CaO mixtures are suited as catalysts for the oxidative coupling reaction. This suggestion is supported by results with La₂O₃/CaO catalysts containing up to 17 mol% La which were recently published (*19*): a maximum C₂ selectivity of 66% at a methane conversion of 25% ($P_{CH_4}^0$ = 80 kPa, $P_{O_2}^0$ = 20 kPa, T = 1073 K) was achieved using a 5 mol% lanthanum containing catalyst, and the catalysts were also very active and stable. When La₂O₃ was doped with 1 wt% alkali or alkaline earth oxides including CaO (*15*), selectivity increased compared to pure lanthanum oxide (selectivity for pure La₂O₃ was 59%, for Sr/La₂O₃ 69%; methane conversion was in both cases about 20% at $P_{CH_4}^0$ = 30 kPa, $P_{O_2}^0$ = 5 kPa, and a bed inlet temperature of 1023 K) (*15*). The high melting points and the nonreducibility of the basic oxides La₂O₃ and CaO are probably advantageous with respect to time-on-stream behavior. One would expect that the La₂O₃–CaO system should cover a range of

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basicity depending on its composition; hence, the possibility of studying the dependence of the catalytic properties on basicity was anticipated. Since the ionic radii of the two metal ions are approximately equal, it may be expected that one of the ions might be incorporated into the lattice of the other oxide. Although mixed oxides or solid solutions of the La_2O_3/CaO system are not known, new structures were detected in the La_2O_3/BaO (20) and in the Y_2O_3/CaO (21) system. The substitution of La ions into the CaO matrix may cause either lattice defects in oxygen or different surface charges.

In the present paper catalysts consisting of pure CaO as well as pure La_2O_3 and of their mixtures were applied to identify the optimum composition for maximum C_{2+} selectivity. Catalysts were prepared from different precursors to investigate whether their performance is thereby affected. The catalytic materials were characterized by their bulk phase composition (XRD), surface composition (XPS), and surface basicity (using the isopropyl alcohol (IPA) conversion to acetone and/or propene as a probe reaction (22–24)). The relationship between catalytic results and these characteristic bulk and surface properties is discussed.

EXPERIMENTAL

Catalyst Preparation and Characterization

Preparation. Catalysts were prepared by mechanical mixing of (a) La_2O_3 (Fluka, purity 99.98%) and CaO (Aldrich 99.95% or Alfa Products 99.95%) in the presence of water and (b) $La(NO_3)_3 \cdot 6 H_2O$ (Janssen 99.9% or Aldrich 99.999%) and CaO (see above) to which a small amount of water was subsequently added during further mixing to improve the distribution of the components by dissolving the nitrate. From method (a) catalysts with a lanthanum content (La/(La + Ca)) of 0, 1, 5, 10, 30, 50, 70, and 100% (chemicals from Fluka and Aldrich) and 27 and 50% (chemicals from

Fluka and Alfa Products) were prepared; the lanthanum content of the method (b) catalysts amounted to 14, 27, and 50% (chemicals from Janssen and Aldrich), 10, 27, and 100% (from Janssen and Alfa Products), and 27, 30, 50, and 70% (from Aldrich and Alfa Products). The compositions were calculated from the proportions of the various materials used for preparation. All catalysts were dried for 16 hr at 393 K and at a reduced pressure of about 50 kPa. Thereafter, the catalysts were calcined for 24 hr at 1173 K in ambient air to decompose the nitrate and to remove any water. Due to this pretreatment of the catalysts no further sintering was expected during the catalytic reaction.

Bulk phase composition. X-ray diffraction patterns of the catalysts and their precursors were obtained from a Philips powder diffractometer PW 1050/25 with $CuK\alpha$ radiation.

Surface composition. The surface composition was determined by XPS (Leybold Heraeus LHS-10 spectrometer, $AlK\alpha$ X-ray source). For determining the surface compositions, the La $3d_{5/2}$, O $1s$, Ca $2p$, and C $1s$ peaks with Wagner's sensitivity factors were used (25).

Acid/base properties. Measures of surface basicity and acidity of the catalysts were derived from the IPA conversion. The basicity is related to the acetone-to-propene ratio; the larger the ratio the higher the surface basicity. The propene-formation rate is a measure for the surface acidity (22–24). IPA conversion was carried out at 573 K in the same tubular fixed-bed reactor as described for the coupling reaction (see below). The feed consisted of 2.5% IPA and 97.5% nitrogen. The catalyst weight varied from 0.2 to 0.6 g and the flow rate was 23 ml_{STP} min^{-1} in all experiments.

Apparatus

A tubular fixed-bed reactor made of quartz was used; its inner diameter was reduced from 8 to 2 mm directly after the catalytic bed to minimize gas phase reactions

in the postcatalytic zone. The reactor was surrounded by an electrically heated furnace. The product gas of the oxidative coupling reaction from which water was removed by condensation as well as from IPA conversion was analysed by g.c. (Carbosieve S II (TCD) for H_2, O_2, N_2, CO, CH_4 and CO_4 and Porapak Q (FID) for C_1 to C_4 hydrocarbons, IPA and acetone). The Carbosieve S II column was run at an initial temperature of 313 K for 5.6 min; then it was heated up to 498 K (20 K/min). For the methane coupling experiments (Porapak Q column) the analysis was started at 323 K; after 8 min the temperature was raised to 393 K (30 K/min). For the product analysis of the IPA conversion the Porapak Q column was run isothermally at 403 K.

Conditions of Catalytic Testing

The feed gas consisted of methane (93 kPa) and oxygen (7 kPa); no gas for dilution was added. The applied reaction temperature was varied between 973 and 1013 K. The mass of catalyst amounted to 33 to 350 mg (particle sizes approximately 250 to 355 μm). The contact time ranged from 0.02 to 0.11 g s ml^{-1} at reactor conditions.

RESULTS

The catalytic results, i.e., activity, C_{2+} hydrocarbon selectivity and yield are described first, and then the physical and physicochemical properties, i.e., bulk phase and surface composition and surface basicity of the various catalysts, are presented.

Catalytic properties

Effect of La/Ca ratio on activity and selectivity. The contact time $m_{cat}/\dot{V}$ ($\dot{V}$ is related to T and P in the reactor) required to achieve an oxygen conversion of about 95% was in the range of about 0.02 (e.g., for all catalysts with 27% and 50% La/(La + Ca)) to 0.11 g s ml^{-1} (pure CaO); this is to say that the catalysts are rather active and their activity is increased by adding La_2O_3 to
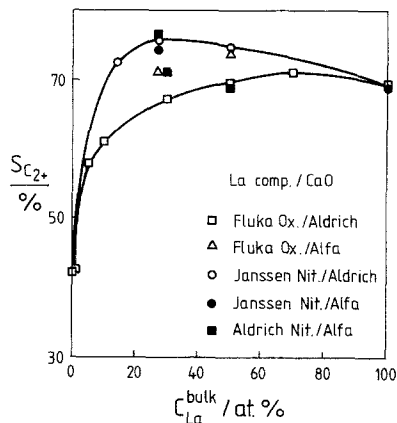

FIG. 1. Dependence of C_{2+} selectivity on overall bulk composition of La_2O_3/CaO catalysts prepared by different methods and using different precursor compounds supplied by different distributors (see text). $P^0_{CH_4} = 93$, $P^0_{O_2} = 7$ kPa, $X_{O_2} > 90\%$, $T_R = 1013$ K.

CaO. The relationship between C_{2+} hydrocarbon selectivity and composition of the catalysts prepared by different methods and partly using different starting materials is shown in Fig. 1 for a reaction temperature of 1013 K and inlet partial pressures of methane and oxygen of 93 and 7 kPa, respectively. A maximum in selectivity (ca 71 (75)%) is obtained for the catalysts prepared from the two types of oxides with a La content of 70 (50)%. For the catalytic materials produced from lanthanum nitrate the highest selectivity of about 78% for the three different starting materials was found with the 27% La/(La + Ca) samples. The C_{2+} yield of these catalysts was 9%. The experimental error was about 2%, i.e. the different results obtained for the catalysts of one type of preparation using different starting materials (see Fig. 1) have to be considered to be real. These differences may be due to possibly indetectable traces of impurities and/or to an incompletely reproducible method of preparation. C_{2+} selectivities of catalysts based on nitrate as lanthanum oxide precursor were generally superior to those prepared directly from the oxides.

TABLE 1

Crystalline Phases in Different
La–Ca-oxide Catalysts

Composition La/(La + Ca)	Crystalline phases					
	CaO	Ca(OH)$_2$	CaCO$_3$	La$_2$O$_3$	La(OH)$_3$	La$_2$O$_2$CO$_3$
Dried samples						
1%[a]	−	+	−	−	+	−
30%[a]	−	+	−	−	+	−
30%[b]	−	−	−	−	−	−
70%[a]	−	+	−	−	+	−
Calcined samples						
1%[a]	+	−	−	+	−	−
27%[b]	+	−	−	+	(+)[c]	−
30%[a]	+	−	−	+	−	−
30%[b]	+	−	−	+	−	−
50%[a]	+	−	−	+	(+)[c]	−
50%[b]	+	−	−	+	(+)[c]	−
70%[a]	+	−	−	+	−	−
After 24 h oxidative coupling						
30%[a]	+	−	+	+	−	+
30%[b]	+	−	−	+	−	−

[a] Prepared from La$_2$O$_3$.
[b] Prepared from La(NO$_3$)$_3$ · 6 H$_2$O.
[c] Probably due to handling conditions.

Physical and Physicochemical Properties of the Catalysts

Bulk phase composition. The crystalline phases (determined by XRD) of the bulk of dried and calcined catalyst samples as well as for those exposed for 24 h to the coupling reaction are shown in Table 1. Various phases

CaO, Ca(OH)$_2$, CaCO$_3$, La$_2$O$_3$,

La(OH)$_3$, La$_2$O$_2$CO$_3$

were observed. No quantitative results were derived from the XRD data due to undetectable noncrystalline phases and their unknown effect on the detectable reflections. The diffractograms of the dried samples prepared from the oxides consisted only of the lines of the hydroxides; this is an indication that at least part of the oxides were hydrolyzed during wet mixing. Whether any lanthanum oxide was dispersed on the hydroxides cannot be derived from the XRD patterns. High dispersion is, however, likely for the samples prepared from lanthanum nitrate and calcium oxide where no crystalline phases were observed

at all; i.e., the material is either amorphous or it consists of very small crystallites which could not be identified by XRD. All calcined samples showed La$_2$O$_3$ and CaO as crystalline phases independent of their previous preparation; minor amounts of La(OH)$_3$ in three of the samples may have been caused by exposure to water vapor during handling in ambient air. Although the XRD patterns look exactly the same for the two differently prepared samples of 30% La/(La + Ca) after calcination, they differ, however, after synthesis: carbonate-containing phases were formed during the catalytic reaction in the catalyst prepared from the oxides whereas no crystalline CaCO$_3$ or La$_2$O$_2$CO$_3$ was observed in the sample based on La(NO)$_3$ and CaO.

Surface composition. The XPS spectra consist of the peaks of the metal ions (La $3d_{5/2}$ 834.5 (sat. 838) eV, Ca $2p_{3/2}$ 346.45 eV) and two lines for carbon (284.8 and 289 eV) and for oxygen species (529 and 531 eV), respectively. The carbon line at 284.8 eV is due to hydrocarbon contamination; the other C $1s$ line at about 289 eV is characteristic for carbonate carbon of La as well as Ca. The O $1s$ line at 529 eV is ascribed soley to the lattice oxygen of La$_2$O$_3$, whereas the other line at 531 eV belongs to the lattice oxygen of CaO, as well as to oxygen in the carbonates and hydroxides of La and Ca. Therefore, the amount of lanthanum as well as of calcium carbonate in the surface cannot be determined whereas the La$_2$O$_3$ content can be derived. For these reasons we confine the comparison of the La content of the surface with the bulk concentration (see Table 2).

The catalysts prepared from CaO and La$_2$O$_3$ show different XPS results after drying and calcination as compared to the catalysts from CaO and La(NO$_3$)$_3$ · 6 H$_2$O. The lanthanum content of the catalyst surface of the former (in particular the samples with lower bulk contents (up to 30%)) is higher than the corresponding bulk composition whereas the surface composition of the latter corresponds to the bulk after drying.

TABLE 2

La Surface Content (XPS Results) of
La/Ca Oxide Catalysts

Catalyst composition La/(La + Ca)	La/(La + Ca) (surface) %		
	Dried	Calcined	After reaction
From CaO and La$_2$O$_3$			
1%	7.7	5.5, 6.3[a]	
5%		29.0, 29.4[b]	
30%	44.9	45.4	48.0
50%		71.9, 87.2[a]	
70%	79.9	72.0	
From CaO and La(NO$_3$)$_3$ · 6 H$_2$O			
10%		40.2	
14%		59.6	
20%	10.3	74.3	
27%		82.1	
30%	31.5	82.4	77.4
50%	68.8	57.9, 73.9[a]	
70%		85.1	

[a] Value derived for a sample of a new prepared catalyst.

[b] Value derived for a different sample of the same catalyst.

Calcination leads to a strong increase of the lanthanum concentration on the surface in the case of catalysts prepared from nitrate. For the catalysts prepared from La$_2$O$_3$ and CaO, the surface composition does not change significantly during calcination. After the catalytic reaction the surface content of lanthanum remains nearly constant. Additional data on surface composition (see Table 2) for some calcined samples show that the determination of the surface content as well as the catalyst preparation are reproducible within experimental error except for the lanthanum-rich samples.

Surface basicity. IPA reacts to propene on an acidic site of the catalyst surface, whereas it needs one acidic and one basic site to react to acetone (23). Acetone itself was not converted under the applied reaction conditions. Therefore the ratio of acetone to propene may serve as a relative measure of the surface basicity. The relationship between catalyst bulk composition and this relative measure of basicity is illustrated in Fig. 2. There appears to be a sharp maximum in basicity at a La content of 1%. The ratio of acetone to propene reaches 130 for this catalyst whereas it amounts to 33 and 1 for CaO and La$_2$O$_3$, respectively.

DISCUSSION

The catalytic performances of the catalysts prepared from the different starting materials (nitrates or oxides) differ in two ways: for the catalysts produced from nitrate (i) the maximum selectivity is reached at a lower overall lanthanum content and (ii) the maximum selectivity is higher than in the case when La$_2$O$_3$ is used in the preparation (see Fig. 1). The first observation is easily explained by assuming that catalytic performance depends on surface but not on bulk composition as illustrated in Fig. 3, wherein the selectivities of the catalysts prepared from La$_2$O$_3$ and CaO as well as from La(NO$_3$)$_3$ · 6 H$_2$O and CaO follow more or less the same pattern with respect to the lanthanum surface concentration. The highest selectivities, which were significantly superior to those of the La$_2$O$_3$ itself, were obtained with a La(surface) content of 60 to 90%. This surface composition is attained with a bulk content of more than 14% La/(La + Ca) for the nitrate samples and with more than 50% for the oxide samples (see
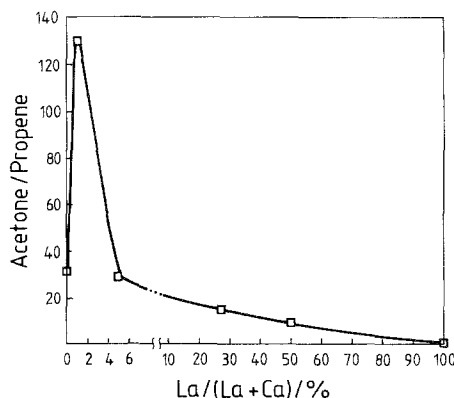

FIG. 2. Dependence of the relative measure of basicity (acetone-to-propene ratio) on the bulk composition of various La–Ca oxide catalysts.
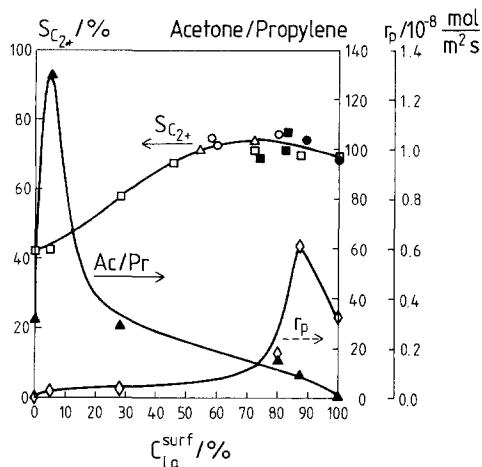
FIG. 3. Effect of the surface content of lanthanum on C_{2+} selectivity, acidity (r_P, rate of IPA conversion to propene), and relative basicity of La–Ca oxide catalysts; symbols as in Fig. 1. $P_{CH_4}^0 = 93$, $P_{O_2}^0 = 7$ kPa, $X_{O_2} > 90\%$, $T_R = 1013$ K.

Table 2); this explains the difference in the catalytic behavior of the differently prepared catalysts described above. Hence, the hydrocarbon selectivity depends on the La surface content. This reasoning explains why Choudhary et al. (*19*) found the highest selectivity at a comparatively low La bulk concentration of about 5%, at which probably the optimum surface content was reached due to their method of catalyst preparation (impregnation of CaO with a solution of lanthanum nitrate).

The fact that the maximum C_{2+} selectivity depends on catalyst composition and is larger than for the pure compounds leads to the assumption that selectivity is governed by a synergetic effect between CaO and La_2O_3. This synergetic effect is probably caused by the dispersion of the lanthanum ions on or within the CaO. High dispersion is obtained when lanthanum nitrate is dissolved in water during catalyst preparation, as indicated by the XRD pattern of the dried samples, which did not show any crystalline phases (cf. Table 1). This is supposed to be the reason for the higher selectivities of the catalysts prepared from the

nitrate. Furthermore, it may tentatively be assumed that formation of carbonate-containing phases is suppressed by the dispersion of lanthanum over CaO, since carbonate phases were only detected in samples prepared from La_2O_3 and CaO, which showed lower selectivities. The synergetic effect may be further related to the existence of mobile charge carriers as observed by Freund et al. (*26*) by Charge Distribution Analysis (CDA). Their preliminary results indicated that mobile charge carriers and a positive surface charge appear on CaO-based catalysts above 550°C, temperatures which correspond to those at which the coupling activity of these catalysts starts. They identified the positive surface charge carriers to be O^- (instead of O^{2-}) species (the existence of H^+ as carrier of the positive surface charge could be excluded by magnetic susceptibility measurements). The amount of positive charge carriers of the La/CaO sample was greater than with pure CaO; therefore it seems to be reasonable to propose that they influence activity and selectivity although no final conclusions can be drawn at present.

Surface basicities as a function of the La (surface) content are shown in Fig. 3; the basicity defined as the acetone-to-propene ratio passes through a sharp maximum at low La (surface) content. Thus C_{2+} selectivity strongly depends on the lanthanum surface content and does not depend on basicity. This, however, is not to be understood as an indication that basicity is not a requirement; the materials are essentially basic. The relationship between basicity and C_{2+} selectivity presented in Fig. 4 is surprising when it is assumed as outlined earlier that selectivity increases with surface basicity. An optimum basicity with respect to C_{2+} selectivity exists when the acetone-to-propene ratio is about 20. A minor increase in basicity above this value leads to a strong decrease in selectivity. This is supposed to be an indication of a change in reaction mechanism. At comparatively low basicity the formation of methyl radicals
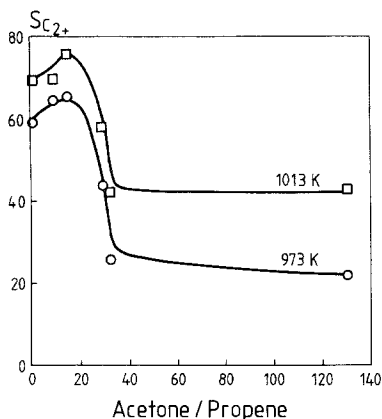
FIG. 4. Effect of relative basicity, i.e., ratio of acetone to propene formed from IPA, on C_{2+} selectivity. $P^0_{CH_4} = 93$, $P^0_{O_2} = 7$ kPa, $X_{O_2} > 90\%$.

may occur as the initial step for the reaction to higher hydrocarbons (27). More basic materials are supposed to act as acid/base catalysts; cleavage of the C–H bond of the weakly acidic CH_4 may occur heterolytically at strong basic sites. Due to the lower selectivity of the most basic catalyst (1% La/(La + Ca)) this mechanism involving the formation of negatively charged CH_3 species seems to be disadvantageous for the selective coupling reaction; this may be ascribed to the preferred formation of methoxy intermediates under these conditions, which further react to CO_x.

More information about the influence of the acid–base properties of the catalyst's surface in the methane coupling reaction may be derived from the rate of propene formation which is a measure for the number and/or strength of acidic surface sites (see Fig. 3). The acidity passes through a maximum at about 80% La/(La + Ca) on the surface. From this it appears that maximum selectivity is achieved when a certain proportion of acidic sites exists. This observation leads us to the tentative conclusion that acidic sites of still unknown nature and strength are required within the basic surface to improve C_{2+} selectivity.

It has to be emphasized that some of the assumptions proposed and conclusions drawn are still speculative and have to be considered as tentative, but it is hoped that they will stimulate further work in this area even though they may be regarded as controversial at present.

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