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Bond Energy Effects in Methane Oxidative Coupling on Pyrochlore Structures

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Compounds of general formula $A_2B_2O_7$ have been characterized by X-ray diffraction and tested for catalytic activity in oxidative coupling of methane. Calculations of the rare earth–oxygen (A–O) and cocation–oxygen (B–O) bond energies provide a new way to estimate the influence of bulk parameters on the formation of C_2 hydrocarbons. The observed values of C_2 yields on $A_2B_2O_7$ catalysts (A = Sm, Gd or Eu) (B = Ti, Zr, or Sn) indicate that they increase with decreasing cocation–oxygen bond energy. The best of these systems ($Sm_2Sn_2O_7$) gives a C_2 yield amounting to 20% at 973 K.

INTRODUCTION

Since the early studies of Keller and Bhasin (*1*) and of Ito *et al.* (*2*), a large-scale catalytic screening has been carried out by numerous workers (*3*) in oxidative coupling of methane. Most single metal oxides have been tested as catalysts and among them, rare earth metal oxides have been shown to have high catalytic activities and selectivities in C_2 hydrocarbon formation (*4*).

The obtained C_2 yields rarely exceed 25% for the most selective oxides, and the work of Labinger (*5*) predicts an upper limit of about 30% yield of higher hydrocarbons at atmospheric pressure. The mechanism of this catalyzed reaction is only partially understood. The widely assumed initial and rate-determining step for ethane formation is the appearance of a methyl radical caused by the removal of one hydrogen atom from methane by the oxide catalyst. A fundamental part of the mechanism is the role of oxygen. This is a factor which controls the C_2 selectivity by its influence both on the methane to C_2H_6 conversion rate and on the secondary reaction impeding the primary C_2 selectivity. Oxygen vacancy sites are involved in the oxygen adsorption (*6*) and in the formation of O^- ions on rare earths (*7*) and O^{2-} ions on Li/MgO (*2, 8*).

The influence of the crystal structure on the catalytic selectivity and/or activity has recently been evidenced by two means: either by changing the nature of the exposed crystalline face on a MgO catalyst (*9*) or by modifying the crystal structure of a system (e.g., passing from monoclinic to cubic Sm_2O_3) (*10*). This activity change has been interpreted as a variation of the lattice oxygen mobility or of the ease of oxygen vacancy formation. For our part, another means to study the influence of the lattice oxygen mobility on the catalytic activity would be to modify the nature of the crystal components keeping the structure unchanged. This method of investigation needs, in our opinion, the use of a crystalline compound containing at least two elements A and B for which many combinations of A and B are possible. A family of compounds of well defined structure, namely, $A_2B_2O_7$ (the pyrochlore system), has been chosen. The interest of these systems has been proved recently by Lewandowski *et al.* (A = Bi and B = Sn) (*11*) and

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by Ashcroft *et al.* (A = rare earths, B = Sn (*12*). Systems for which B = Ti, Zr, Sn, and A = different rare earths (La, Sm, Gd, . . .) have been studied in our laboratory (*13, 14*).

In the present work, after the analysis of the catalytic properties of these systems, a method to evaluate the element–oxygen binding force by computing the A–O and B–O bond energies is proposed. These bond energies should be directly related to the activity toward C_2 hydrocarbon formation and to the possibility of oxygen vacancy or/and adsorption site formation. The evaluation of this force should allow (for a system with unchanged crystal structure) a better insight into the role of oxygen in methane oxidative coupling.

EXPERIMENTAL

The $Ln_2Ti_2O_7$ and $Ln_2Zr_2O_7$ pyrochlores (Ln = lanthanide rare earth) have been prepared by the sol–gel method starting from the rare earth oxide and from Ti or Zr isopropionate solutions (purchased from Strem Chem.) (*15*). The $Ln_2Sm_2O_7$ pyrochlore has been prepared in the same manner except for the *in situ* formation of the tin propionate from a chlorinated precursor. This leads to a translucent solid precursor which is then submitted for 2 h to a heat treatment at temperatures between 973 and 1073 K, depending on the nature of the pyrochlore. The structure of the oxides has been determined before and after catalytic reaction by X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy and results are compared with the published data (*16*).

The activity and selectivity of the various samples were determined in a fixed bed quartz reactor (6.6 mm ID) under the following conditions: catalyst weight, 0.67 g; inlet temperature, 873–1023 K; feed gas partial pressures, 0.133 atm CH_4, 0.0665 atm O_2, and 0.8 atm He; gas flow, 4.5 liter h^{-1} (g catalyst)$^{-1}$ (STP); CH_4/O_2 ratio = 2. O_2; CH_4, H_2 gas were introduced through a mass flow metering device. More details are given in Ref. (*17*). Methane conversion (α_T) was calculated as the number of transformed CH_4 moles × 100 divided by the number of CH_4 moles introduced. Selectivity in product (*i*) is defined as number of CH_4 moles transformed into product (*i*) × 100/number of transformed CH_4 moles. C_2 yield is given by the ratio of CH_4 conversion to the (C_2H_4 + C_2H_6) selectivity × 100.

RESULTS

(*a*) *Stability of the Pyrochlores*

Pyrochlore oxide structures are stable at high temperature. XRD measurements performed before and after the catalytic reaction show the same pyrochlore species (e.g., $Sm_2Sn_2O_7$; Figs. 1a, 1b). Under our experimental conditions, that is, using helium as a diluent gas, the relative decrease of C_2 yield is only equal to 20% after 5 days on line (Fig. 2). No further change, neither in activity nor in selectivity, is observed in the 5 following days. It must be noted that the catalyst is kept at 400°C under helium overnight and that this treatment does not change its properties. The maximum CH_4 conversion was 40.4% with a C_2 (C_2H_4 + C_2H_6) selectivity of 48.8%, which means a maximum C_2 yield of 19.7%. When methane is used alone without oxygen the conversion decreases quickly. The initial activity and selectivity is rapidly restored by returning to the initial (CH_4, O_2, He) mixture. This catalyst tested in the conditions of Ashcroft *et al.* (*12*) (CH_4/O_2 = 2; without

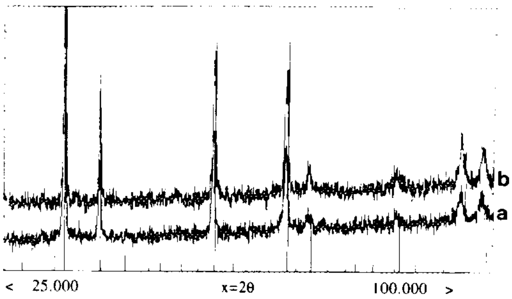

FIG. 1. X-ray diffraction pattern of $Sm_2Sn_2O_7$ (a) before catalytic test, and (b) after catalytic test.

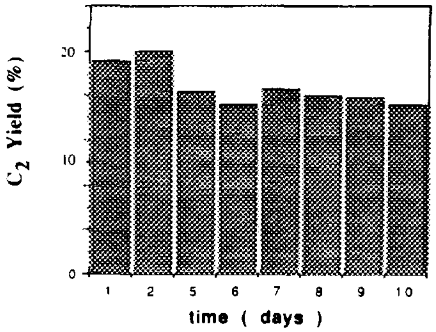

FIG. 2. Variation of C_2 yield versus reaction time at 973 K for $Sm_2Sn_2O_7$.

helium dilution) proved to be less stable and to lose tin within a few hours.

(*b*) *Effect of the Temperature on Reactivity and Selectivity*

The methane conversions obtained on $Ln_2B_2O_7$ (B = Ti, Zr, Sn) pyrochlores at 973 K are represented in Fig. 3. The ethane and ethene selectivities at 873 and 973 K are given in Table 1.

For Ti pyrochlores, the methane conversion (α_T = 30%) does not change significantly between 873 and 1073 K. The oxygen conversion is always higher than 98.3% in this temperature region. Oxidative reaction is the major process occurring on the catalysts belonging to this family, and this does not really change with the nature of the rare earth. In fact, titanium-based catalysts are very oxidizing systems and give a total oxygen conversion for a temperature higher than 873 K. The low CO_2/CO ratio indicates that the competing water–gas shift reaction which gives CO and hydrogen plays a significant role.

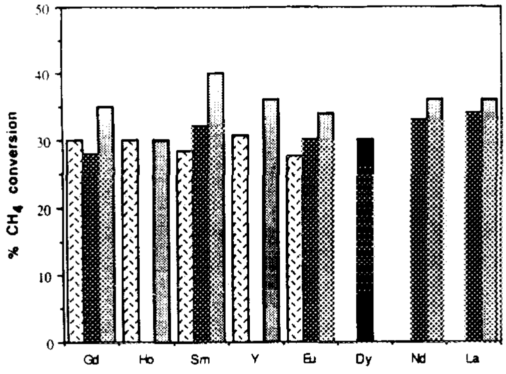

FIG. 3. CH_4 conversion as a function of the rare earth and cocation in $A_2B_2O_7$ systems at 973 K: ▨ $Ln_2Ti_2O_7$, ■ $Ln_2Zr_2O_7$, and ▩ $Ln_2Sn_2O_7$.

TABLE 1

C_2 Selectivities for $A_2B_2O_7$ Structures at 873 K and 973 K

Rare earth (Ln)	C_2 selectivity (%)					
	Ti pyrochlore		Zr pyrochlore		Sn pyrochlore	
	873 K	973 K	873 K	973 K	873 K	873 K
Gd	3.2	6.2	10.2	15.6	26.5	42.8
Ho	0.0	0.0	—	—	12.0	26.2
Sm	1.7	10.0	15.9	22.1	40.4	48.8
Y	0.0	3.4	—	—	26.6	45.3
Eu	2.3	8.7	20.5	23.7	22.7	41.3
Dy	—	—	14.3	16.0	—	—
Nd	—	—	3.5	10.8	17.3	43.6
La	—	—	28.1	33.6	25.0	42.8

On Zr pyrochlores (Fig. 3), the same results for methane and oxygen conversions as on Ti pyrochlores were found (α_T = 30%; α_T = 98.5% for oxygen), but the C_2H_4 + C_2H_6 selectivity was higher. The highest selectivity for each catalyst varied from 18.4 for Dy to 33.6 for La. It must be noted that the highest selectivity is observed at different temperatures (923, 973, and 1023 K), depending on the pyrochlore. The nature of the rare earth influences the selectivity but not the activity. Three systems (Sm, Eu, and La) give the best yields. The water–gas shift reaction is less important in the case of the Zr pyrochlores than on the titanium based ones.

The Sn pyrochlore family appears to be different from the previous two cases. The activity increases with the reaction temperature and the optimum is observed at 973 K on most catalysts. In the same way the oxygen conversion increases with temperature (60% at 873 K, 100% at 973 K). Sn pyrochlores give much higher selectivities than do the Ti and Zr families (10.0, 22.2, and

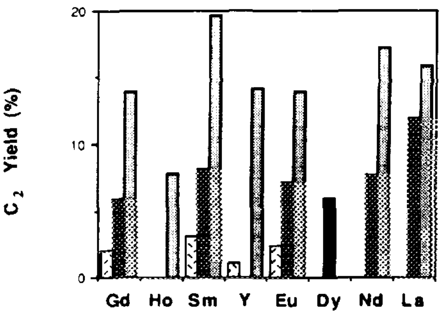

FIG. 4. C_2 yield as a function of the rare earth and cocation in $A_2B_2O_7$ systems in 973 K: ▨ $Ln_2Ti_2O_7$, ■ $Ln_2Zr_2O_7$, and ☐ $Ln_2Sn_2O_7$.

48.8% at 973 K for $Sm_2Ti_2O_7$, $Sm_2Zr_2O_7$ and $Sm_2Sn_2O_7$, respectively). At this temperature, the highest selectivity for all Sn pyrochlores was observed. The CO_2/CO ratio is always high, indicating that the water–gas shift reaction is almost not working. The changes in $C_2/C_2^=$-ratio (ethane/ethylene) versus the reaction temperature are the same whatever the nature of the pyrochlore. The decrease of this ratio versus the temperature leads to a limiting value situated between 0.5 and 1, in agreement with the increased thermodynamic stability of C_2H_4 versus C_2H_6 when the temperature is increased. A high C_2 selectivity is obtained by enhancing the CH_4/O_2 ratio from 2 to 5. For example, for $La_2Zr_2O_7$ the selectivity is increased from 33.6 to 43.7% and for $Sm_2Sn_2O_7$ from 48.8 to 60.3. This selectivity enhancement is obtained at the expense of the conversion, which shows a decreased yield (11.4 to 6.2% for $La_2Zr_2O_7$, and 19.7 to 11.5 for $Sm_2Sn_2O_7$).

Concerning the Sn pyrochlores, the nature of the rare earth has a relatively important effect on the methane conversion activity, as well as on the C_2 selectivity. The best system is $Sm_2Sn_2O_7$ both for the methane activity and C_2 selectivity, leading thus to a high C_2 yield (19.7) (Fig. 4). This yield places this catalytic system among the best in methane activation. It is closely followed by Nd-, and La–Sn pyrochlores.

For all rare earths the C_2 yield increases in the following way: Ti < Zr < Sn. The nature of the cocation plays here a preponderant role in the C_2 yield variation. The yield is enhanced by a factor of 4 when passing from Ti to the Sn pyrochlore. It appears clearly that for the $A_2B_2O_7$ pyrochlores the nature of the cocation B is much more important than the change of the rare earth (cocation A) (Fig. 4).

DISCUSSION

Winter's studies (*6*, *18*) on oxygen adsorption on a wide variety of oxides have shown that the mechanism of oxygen exchange between the gas phase and lattice passes through an O^- species on rare earth oxides. Recent results have confirmed the importance of these species in the oxidative coupling of methane and evidence the importance of the crystal structure. Depending on the structure, the ability to extract an oxygen from the structure to form a surface vacancy changes. This vacancy seems to be necessary for the exchange of oxygen between the gas phase and the lattice, as well as for the bonding of methane to the surface. It becomes essential to quantify, for a given crystal system, the energy required to extract an oxygen in order to relate it to the oxidative methane coupling activity. Therefore for each member of an $A_2B_2O_7$ pyrochlore system the A–O and B–O bond energies have been calculated.

The pyrochlore structure is constituted by an elementary cubic system in which each element A (rare earth) is surrounded by 8 oxygens and each element B (cocation Ti, Zr, Sn) by 6 oxygens. This structure can be derived from the fluorite structure ($A_2B_2O_8$) on the basis that one out of eight of the negative ions is lacking (*19*). Henry's method (*20*) is used to derive the bond energies from the mean cation–oxygen distance calculated by Poix's invariant method (*21*). For each element, the Coulombic energy is given by the following formula:

the oxidative coupling of methane. The diversity of the pyrochlores prepared by a mild method and their wide stability range, especially in our catalytic conditions, have enabled us to study the activity and selectivity of the methane/oxygen reaction, as well as to have an insight into the fundamentals of this reaction.

$Sm_2Sn_2O_7$ exhibits the highest C_2 yield among the systems studied (20% at 973 K) and competes well with the best systems for which there are published data. A good correlation between C_2 yield and the cocation B–O bond energies has been found for these pyrochlores. This relation suggests that oxygen vacancies are directly involved in the reaction. Other oxides of well defined structures will be prepared in the near future in order to study the methane oxidation versus the oxygen environment (number of neighbour oxygens, energy, nature of the elements, oxidation states).

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Reduction of Acetophenones over Pd/AlPO$_4$ Catalysts. Linear Free Energy Relationship (LFER)

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We studied the reduction of variously substituted acetophenones over Pd/AlPO$_4$, Pd/AlPO$_4$–SiO$_2$, and Pd/SiO$_2$ catalysts containing 3% Pd by weight. After the catalysts were characterized texturally and kinetically, they were used to reduce the different acetophenones at various temperatures under the same reaction conditions. The results correlate with the Hammett equation quite well, and the reaction was found to feature different sensitivity to electron-withdrawing ($0.05 < \rho < 0.20$) and electron-releasing substituents ($0.76 < \rho < 1.37$). On the other hand, a compensating effect was also found to occur, so the reaction mechanism can be assumed to be the same for every substrate. The reductions probably do not take place via enol forms of the acetophenone. The reaction rate decreases with increasing solvent polarity. © 1993 Academic Press, Inc.

INTRODUCTION

Reductions of carbonyl compounds are of great interest to and widely used in organic chemistry. Such is the case with Wolff–Kishner and Clemensen reductions, whereby a carbonyl group is transformed into a methylene function by using hydrazine in a basic medium or zinc amalgam in hydrochloric acid, respectively, and the use of metal hydrides to convert aldehyde and ketones into their corresponding alcohols (*1*), and of alkali metals in ammonia to transform the carbonyl group into a methylene radical (*2*). Depending on the type of reductant used, the carbonyl function can be converted into a hydroxyl or methylene group as required. The hydrogenation of α,β-unsaturated carbonyl compounds can be effected quite selectively on the carbon–carbon double bond or the carbon–oxygen bond (*3*, *4*). Carbonyl compounds can also be reduced with dihydrogen under homogeneous (*5*) or heterogeneous catalysis (*6*), as well as by hydrogen transfer. The most interesting asset of this process is the possibility of changing the selectivity toward the alcohol or the saturated hydrocarbon by changing the catalyst structure or the way in which the hydrogenation is performed (*8*, *9*).

Generally speaking, the reaction mechanisms proposed so far to account for the reduction of carbonyl compounds with hydrogen–metal systems are of the Horiuti–Polanyi type (*10*). The hydrogen atoms adsorbed on the metal, after dissociation, reduce the adsorbed carbonyl compounds stepwise. However, there is no universal agreement as to the nature of the active sites involved. While the sites where the aldehyde or ketone is converted into the alcohol, and this last in turn is transformed into the saturated compound, might be the same, the occurrence of sites of different nature on the edges and at the apices of the crystals (*11*, *12*) could be indicative of a different catalytic behaviour of the sites in question in hydrogenation and hydrogenolysis reactions.

The reduction mechanism supposedly involves the attack of the carbonyl compound by hydride ions and protons successively generated on the catalyst surface by adsorption of hydrogen atoms at high and low

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electron density sites, respectively (*13, 14*). This mechanism is inspired by that widely accepted for the reduction of metal hydrides, the first step of which involves the attack of a hydride ion on the carbonyl compound.

Alternatively, the reduction could take place via the enol form of the carbonyl compound in equilibrium with the oxo form. In this respect, Teratani *et al.* (*15, 16*) studied the deuteration of 1-cyclohexenyl methyl ether and cycloalkanones over different catalysts and arrived at different conclusions depending on the catalyst used. With Ru, Os, Ir, and Pt catalysts, the addition of two deuterium atoms to the carbonyl group was the prevailing processes, whereas with Pd and Rh catalysts, the deuterium atoms incorporated themselves at positions C_2 and C_6. On the other hand, Acke and Anteunis (*17*) detected enol intermediates and charged semihydrogenated species on the basis of which they accounted for the formation of alkanes, alcohols, and ethers.

One way of approaching the reaction mechanism proposed for the reduction of a series of homologous compounds is to determine whether the reaction features a linear free energy relationship—the equations most widely used in this respect on account of their simplicity are those of Brönsted, Taft and Hammett (*18*)—and is subjected to a compensating effect.

Linear free energy relationships for a given process can also be derived from the Hammet equation in the form

$$\log k/k_0 = \rho\sigma$$

where k is the rate constant of the process, k_0 the same constant for the reference compound, ρ the specific rate, and σ the electronic contribution from the substituent (*19*).

The so-called "compensating effect" is one other of such models and can be derived from the Arrhenius equation in the form

$$\log A = B + eE_a,$$

where B and e are two characteristic constants of the group of reactions and/or catalysts concerned. In the event that changes in one of these parameters result in concomitant changes in the other, the process is said to be subject to a "compensating effect." This phenomenon was first reported by Constable in 1925 (*20*) in relation to the hydrogenation of ethanol over copper catalysts and has since been studied by a number of authors (*21, 22*).

In this work we studied the reduction of variously substituted acetophenones in order to determine, irrespective of the reaction mechanism involved, whether all arylketones are reduced via a similar reaction pathway over Pd catalysts supported on aluminium orthophosphate and related systems. The solids used in this work ($AlPO_4$ and $AlPO_4$–SiO_2) have been employed by Marinas and co-workers since 1970 in different organic processes taking place via carbonium ions (*23*), and later as supports for metals such as Ni, Pd, Pt, and Rh. These catalysts have been applied to the reduction of organic substances such as alkenes (*24*), alkynes (*25*), xylenes (*26*), aromatic nitro compounds (*27*), etc., both by classical hydrogenation and by hydrogen transfer, with excellent results in every case.

EXPERIMENTAL

Supports

The substances used as supports were pure silica, pure aluminium orthophosphate and mixed 80 : 20 w/w SiO_2–$AlPO_4$ systems that were gelled in different media (*28*).

Synthesis of support F72. In a 100-ml beaker place 3.56 g of SiO_2 (Merck ref. 7734) and 30 ml of distilled water. Then add 3.4 ml of 85% w/w H_3P_4 and 1.7 g of $AlCl_3 \cdot 6H_2O$, and stir the mixture for 30 min. Next, immerse the beaker in a bath at 273 K and add 0.1 *M* NH_4OH dropwise to Ph 6.9. Allow the gel thus formed to stand for 24 h and then filter and air-dry it. Finally, calcine at 923 K for 3 h.