Investigation of reactivity and selectivity of methane coupling catalysts using isotope exchange techniques

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Received 2 October 1991; accepted 10 January 1992

The relationship between the activity and selectivity of four metal oxide catalysts for the oxidative coupling of methane has been compared with their basicity and their ability to effect the scission of C-H and O-O bonds. The rates of isotope exchange reactions (CH_4-D_2 and $^{16}O_2$-$^{18}O_2$) were used as a measure of catalyst's ability to activate both reactants. It is demonstrated that catalysts showing high C_2 selectivity in the oxidative coupling reaction activate methane strongly and oxygen weakly. The lack of direct correlation between the rates of methane conversion and bonds' activation indicates that the formation of the methyl radical cannot be explained by a simple, one-step mechanism.

Keywords: Oxidative methane coupling; deuterium exchange; oxygen exchange; basicity

1. Introduction

The oxidative coupling of methane has been a subject of intensive research [1,2] since it's discovery almost a decade ago [3,4]. This work resulted in elucidation of several important aspects of the reaction mechanism, and it is generally agreed that methyl radical formation occurs on the catalyst surface, followed by their dimerisation in the gas phase [5].

Subsequent experimental work carried out with CH_4/CD_4 mixtures provided direct evidence supporting this hypothesis [6,7]. The existence of significant primary H/D isotope effect indicates that the C-H bond cleavage is most likely the rate-limiting step, although some controversy still surrounds this issue [1].

The mechanism of the methyl radical formation is not well understood. Some workers believe that the interaction of the methane molecule with various forms of oxygen present on the catalyst surface leads to the homolytic abstraction of

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hydrogen. Several oxygen species have been proposed [4,8–13] as “active sites”: $[O_{ads}]$, $[O_{2ads}]$, $[O^-]$, $[O^2]$, $\{O_2^{2-}]$ and $[O_2^-]$. Others suggest [14–17] that the acid-base type of reaction is involved, where adsorbed methane dissociates heterolytically on the surface of the basic oxide, yielding H^+ and CH_3^-. In this scheme, a methyl radical is formed by subsequent subtraction of the electron from the unstable [18] methyl anion.

Another important aspect of the oxidative coupling reaction that warrants further investigation is the selectivity towards the formation of CO_x. It has been demonstrated that non-selective oxidation of the methane as well as the primary reaction products (ethane and ethylene) leads to the formation of carbon oxides [2]. However, factors that govern variation in selectivity between different catalytic systems still remain obscure. The objective of this work was to investigate the relationship between the reactivity of a series of metal oxide catalysts towards exchange of methane with deuterium and their activity for oxidative coupling of methane. A further objective was to compare the relative ability of these catalysts to activate methane and oxygen in order to identify factors governing the selectivity for C_2 and CO_x formation. Four catalysts spanning a wide range of activity and selectivity were chosen for this study: m-Sm_2O_3 (monoclinic), c-Sm_2O_3 (cubic), MgO and γ-Al_2O_3.

2. Experimental

REACTOR SYSTEM AND MATERIALS

An isotope switching fixed bed microreactor system similar to that described elsewhere [19] was used in all experiments. Flows of gases into the reactor was controlled by mass flow controllers (Brooks 5850 TR). A programmable temperature controller (RKC PS-962) allowed the reactor to be operated isothermally or in a temperature programmed mode. The exit gas analysis system consisted of a gas chromatograph (Shimadzu 8A instrument, TCD detector, Carbosphere 80/100 column 3.2 mm o.d., 1.5 m long) and quadrupole mass spectrometer (VG SX 200, enclosed source, triple filter, SEM detector) controlled by an IBM XT. BET surface areas of catalysts were measured using the nitrogen adsorption technique (Micromeritics ASAP 2400 apparatus), and the crystalline phase of samarium oxides was determined by XRD (Siemens Kristalloflex diffractometer).

The following materials were used as catalysts in this study: m-Sm_2O_3 (Molycorp, 96% pure, 1.8 m^2/g), c-Sm_2O_3 (prepared by CSIRO Division of Materials Science, > 97% pure, 8.5 m^2/g), MgO (Ajax Chemicals, analytical purity grade, 56 m^2/g) and γ-Al_2O_3 (Norton, high purity grade, 300 m^2/g). All gases used in this study were of high purity grade and were used without further purification.

TEMPERATURE PROGRAMMED DESORPTION OF CARBON DIOXIDE

A sample of the catalyst (50–100 mg) was placed in the reactor and supported by an alumina wool plug. The catalyst was conditioned in the flow of helium (650 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) at a temperature of 900°C for 1 h. After cooling to ambient temperature, the helium flow was switched to carbon dioxide (150 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) for 20 minutes. The reactor was subsequently purged with helium (250 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) for 10 minutes before ramping the temperature from ambient to 1000°C at 15°C/min. The appearance of carbon dioxide in the reactor effluent was monitored by the mass spectrometer operating in a single mass ($m/z = 44$) monitoring mode.

EXCHANGE OF METHANE WITH DEUTERIUM

The catalyst sample size and pretreatment were identical to those described above. A mixture of deuterium (3700 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) and methane (190 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) was passed over the catalyst at temperatures ranging from 600°C to 900°C. The reactor effluent was analysed by a combined GC and MS method. A sample of the reactor exit gas was injected into the gas chromatograph for product separation and quantitative analysis. The effluent from the TCD detector was then passed directly into the ion source of the mass spectrometer operating in a histogram scan mode. Specially developed software allowed the reconstruction of the ion chromatogram (RIC) and the mass spectra of the separated products. The isotopic composition of the products was then calculated using the least squares algorithm.

OXYGEN $^{16}O_2/^{18}O_2$ EXCHANGE

The procedure used for $^{16}O_2/^{18}O_2$ exchange was as follows. A flow of helium (3700 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) and two equal flows of $^{16}O_2$ (750 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$ each, coming from two separate gas lines) were mixed and passed over the catalyst (11 mg). The $^{16}O_2$ in one line was then replaced with an $^{18}O_2$ for a period of 60 seconds. The isotopic composition of oxygen in the reactor effluent was determined with the mass spectrometer by monitoring ions of $m/z = 32$, 34 and 36. The rates of $^{16}O/^{18}O$ formation were calculated after the concentrations of all three isotopic forms of oxygen in the exit gas reached a steady state.

EVALUATION OF CATALYSTS ACTIVITY

For a typical experiment, CH_4 (7500 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) and O_2 (1100 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) were passed over 10 mg of a conditioned catalyst at temperatures ranging from 600°C to 900°C. The composition of the reaction products was determined by GC analysis.

3. Results

The results of the temperature programmed desorption of carbon dioxide are presented in fig. 1. They show that the relative basicity of catalysts decreases in order m-Sm_2O_3 > c-Sm_2O_3 > MgO > γ-Al_2O_3. The presence of multiple maxima at different temperatures on the desorption curves for all catalysts except γ-Al_2O_3 indicates the existence of several types of basic sites of different strength. The temperatures of desorption of 50% of CO_2 are marked with broken lines.

Table 1 summarises the results of exchange experiments between deuterium and methane at various temperatures. The reaction rates were calculated in two ways: (i) - the rate of methane consumption, (i.e. the rate of formation of all deuterated methanes, $R[\text{-}CH_4]$) and (ii) - the rate of deuterium exchange expressed as $R[D] = R[CH_3D] + 2R[CH_2D_2] + 3R[CHD_3] + 4R[CD_4]$, which reflects the total number of C-H bond scissions occuring during the reaction. Due to very high activity of the c-Sm_2O_3 for the deuterium exchange, the reaction rates could only be measured up to the temperature of 850°C. Above that limit the degree of exchange was approaching 100% and the rates were affected by mass transport limitations.

Several workers have shown that the exchange between hydrocarbons and deuterium catalysed by metal oxides proceeds via carbanionic intermediate, and thus involves heterolytic dissociation of an adsorbed molecule on the surface of the solid [20,21]. On the basis of the binominal distribution of deuterated methanes it has also been proposed that the exchange reaction over metal oxides is predominantly sequential [22]. Our results remain in agreement with such a reaction scheme, except for the m-Sm_2O_3, which shows an unusual

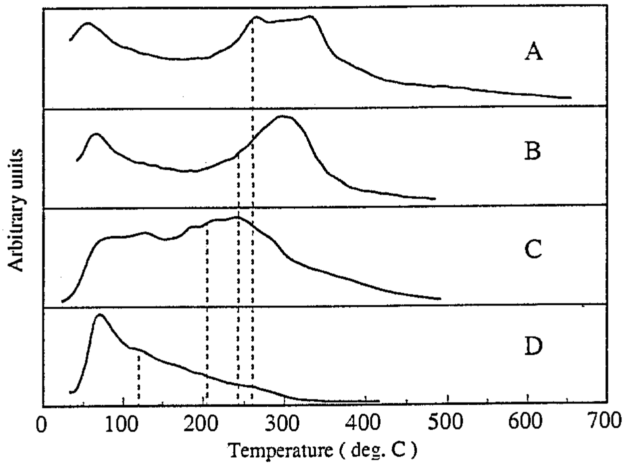

Fig. 1. Carbon dioxide temperature programmed desorption profiles. Numbers in parentheses refer to the temperatures of desorption of 50% of CO_2. A) m-Sm_2O_3 (265°C); B) c-Sm_2O_3 (244°C); C) MgO (206°C); D) γ-Al_2O_3 (120°C).

Table 1
Activity of catalysts in CH_4-D_2 exchange reaction

Catalyst	Temp. (°C)	R[-CH_4]	Composition of exchanged CH_4 (%)				R[D]
			CH_3D	CH_2D_2	CHD_3	CD_4	
m-Sm_2O_3	700	6.74	100.0	0.0	0.0	0.0	6.7
	750	11.6	79.8	0.0	0.0	20.2	18.6
	800	17.2	85.4	0.0	0.0	14.6	24.8
	850	29.9	87.5	0.0	0.0	12.5	41.1
	900	59.9	82.1	10.0	0.0	7.9	79.6
c-Sm_2O_3	700	18.7	100.0	0.0	0.0	0.0	18.7
	750	49.5	82.1	17.9	0.0	0.0	58.4
	800	83.7	55.4	32.7	11.8	0.0	130.9
	850	101.1	50.3	31.2	13.5	5.0	175.1
MgO	700	16.8	100.0	0.0	0.0	0.0	16.8
	750	36	94.3	5.7	0.0	0.0	38.0
	800	53.5	81.3	16.5	2.3	0.0	64.7
	850	58.1	77.8	18.7	3.5	0.0	73.0
	900	68.7	74.8	21.0	4.2	0.0	88.9
γ-Al_2O_3	700	–	100.0	0.0	0.0	0.0	–
	750	2.53	100.0	0.0	0.0	0.0	2.5
	800	5.24	100.0	0.0	0.0	0.0	5.2
	850	10.1	100.0	0.0	0.0	0.0	10.1
	900	24.3	90.3	9.7	0.0	0.0	26.7
Blank	800	4.06	100.0	0.0	0.0	0.0	4.1
	850	4.22	100.0	0.0	0.0	0.0	4.2
	900	9.47	100.0	0.0	0.0	0.0	9.5

distribution of CH_3D and CD_4 (see table 1). This result is difficult to explain. In our previous work, we identified the existence of the pool of strongly adsorbed methane on the surface of m-Sm_2O_3 under the conditions of oxidative methane coupling [19]. This observation was confirmed recently by others [23]. It is possible that the multiple exchanges occur on sites where methane is strongly adsorbed, resulting in a peculiar isotopic distribution. Some credence is given to this speculation by the fact that the relative amount of CD_4 formed decreases at higher temperatures, where the adsorption of methane on the catalyst surface can be expected to be weaker.

The results of the oxygen exchange experiments are presented in table 2. The rates of oxygen exchange (R[O]) were calculated as twice the rates of $^{16}O/^{18}O$ formation and are therefore directly proportional to the number of O-O bond scissions that occurred during the reaction. For all catalysts studied the steady concentrations of all isotopic forms of oxygen in the exit gas was reached within seconds.

Table 2
Comparison of $^{16}O_2/^{18}O_2$ exchange rates

Temp. (°C)	Rates of formation of $^{16}O^{18}O$ ($\mu mol \cdot g^{-1} \cdot s^{-1}$)				
	m-Sm_2O_3	c-Sm_2O_3	MgO	γ-Al_2O_3	Blank
600	40.2	230.5	148.4	17.4	–
650	50.6	541.0	296.9	27.3	–
700	81.1	972.7	556.6	65.2	–
750	157.7	1351.5	855.5	160.6	–
800	315.5	1570.3	1103.5	318.9	20.3
850	504.5	1669.9	1279.2	451.5	27.1
900	677.1	1726.5	1417.9	542.4	40.6

The rates of D_2/CH_4 exchange (R[D]) and the $^{16}O/^{18}O$ exchange (R[O]) as described above provide a convenient measure of the ability of catalysts to dissociate methane and oxygen. It should be noted that while R[D] expresses simply the ability of the catalyst to heterolytically dissociate methane, the R[O] does not refer to any particular form of active oxygen which may constitute an intermediate in the exchange reaction.

The activities and selectivities of the catalysts for the oxidative methane coupling reaction are presented in table 3. The comparison of the rates of methane conversion (table 3) with their carbon dioxide desorption profiles (fig. 1) shows that the catalysts' activity in most cases parallels their basicity, which is in agreement with the results published by other workers [14,17,24]. As mentioned before, the choice of catalysts used in this study ensured that both their characteristics (e.g. basicity, surface areas) and activities in isotope exchange and oxidative coupling span over a wide range to facilitate the identification of factors determining their performance.

4. Discussion

The correlation of the results of isotope exchange experiments with catalysts' activity and selectivity data obtained under the conditions of an oxidative methane coupling reaction has to be approached with caution. The major difference between both sets of conditions was the absence of carbon dioxide and water during the exchange experiments. Both these products are capable of altering the catalytic activity of metal oxides by hydroxylation of the surface and CO_2 adsorption or carbonate formation [25].

However, our previous studies have shown that at 700°C there is no significant adsorption of CO_2 on the surface of a SM_2O_3 catalyst working under oxidative coupling conditions [19]. This is consistent with the carbon dioxide temperature programmed desorption profiles for both cubic and monoclinic

Table 3
Comparison of catalysts activity and selectivity in oxidative methane coupling

Catalyst	Temp. (°C)	Reaction rates (μmol·g^{-1}·s^{-1})						Conversion (%)		Selectivity (%)
		Consumption		Formation						
		-CH_4	-O_2	C_2H_4	C_2H_6	CO	CO_2	CH_4	O_2	C_2
m-Sm_2O_3	600	36.3	24.6	0.0	0.0	18.6	17.7	0.5	2.2	0.0
	650	91.7	87.0	0.0	8.1	38.4	37.1	1.2	7.9	17.7
	700	188.5	163.6	5.8	29.5	59.8	58.1	2.5	14.9	37.5
	750	326.2	251.2	21.3	66.3	74.7	76.3	3.3	22.8	53.7
	800	588.9	430.0	67.6	124.5	99.0	105.7	7.9	39.1	65.2
	850	748.7	564.0	95.7	150.6	123.7	132.4	10.0	51.3	65.8
	900	877.7	694.3	112.8	164.2	158.9	164.8	11.7	63.1	63.1
c-Sm_2O_3	600	126.0	224.3	0.0	0.0	32.0	94.0	1.7	20.4	0.0
	650	447.2	467.3	24.4	73.5	65.6	185.8	6.0	42.5	43.8
	700	683.1	702.1	46.9	130.5	62.6	265.7	9.1	63.8	51.9
	750	986.0	910.0	77.0	188.0	216.3	343.2	13.1	82.7	53.8
	800	1323.0	1082.5	170.0	245.0	274.0	254.3	17.6	98.4	62.7
	850	1333.0	1100.0	137.0	215.0	334.1	276.3	17.8	100.0	52.8
	900	1337.0	1100.0	108.0	157.0	351.3	255.4	17.8	100.0	39.6
MgO	600	15.8	13.6	0.0	0.0	15.8	0.0	0.2	1.2	0.0
	650	52.1	54.3	0.0	4.7	37.5	5.2	0.7	4.9	18.0
	700	83.0	91.6	0.0	5.0	62.2	10.8	1.1	8.3	12.0
	750	104.3	109.6	0.0	7.4	75.1	14.4	1.4	10.0	14.2
	800	127.1	118.8	0.0	13.0	83.7	17.4	1.7	10.8	20.5
	850	141.5	117.3	4.3	17.4	79.2	18.9	1.9	10.7	30.7
	900	164.0	154.6	5.8	22.8	81.6	25.2	2.2	14.0	34.9
γ-Al_2O_3	600	14.8	19.9	0.0	0.0	9.4	5.4	0.2	1.8	0.0
	650	30.0	33.9	0.0	0.0	19.0	11.0	0.4	3.1	0.0
	700	48.0	66.0	0.0	0.0	32.0	16.0	0.6	6.0	0.0
	750	66.0	76.3	0.0	4.5	36.0	21.0	0.9	6.9	13.6
	800	98.0	116.8	0.0	7.0	51.0	33.0	1.3	10.6	14.3
	850	183.4	161.1	4.8	17.6	92.1	46.5	2.4	14.6	24.4
	900	226.2	210.8	12.8	25.3	83.0	67	3.0	19.2	33.7

forms of Sm_2O_3 (fig. 1), where all CO_2 desorbes below 600°C. Considering that carbon dioxide desorption from the surface of MgO and γ-Al_2O_3 occurs at even lower temperatures, no significant poisoning can be expected. This conclusion has been confirmed by results published by Peil et al. [26].

Despite the above uncertainties, the comparison of the isotope exchange and the oxidative coupling results provides valuable information about some mechanistic aspects of the latter reaction. As mentioned before, while the scission of the C-H bond has been shown to be the rate limiting step in the oxidative coupling reaction in some catalytic systems [14,27–29], the mechanism of methyl radical formation still remains unclear.

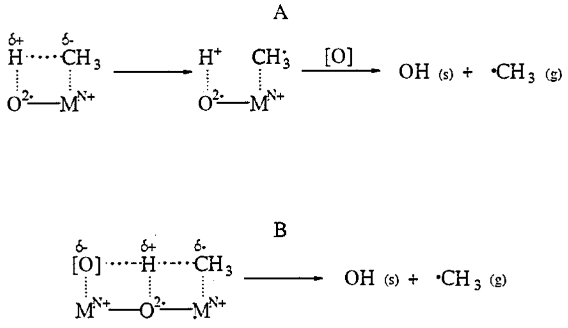

Fig. 2. Schematic of proposed mechanisms of methyl radical formation.

Two different routes have been proposed for the formation of the methyl radical. The first involves the subtraction of the proton from methane molecule on the basic site, leading to the formation of methyl anion [14–17]. Subsequent transfer of the electron from the methyl anion and the proton to the oxygen results in the formation of methyl radical and water via an OH intermediate (fig. 2A).

In this scenario, the activation of methane in both the oxidative coupling reaction and the deuterium exchange involves the same initial step, i.e. heterolytic scission of the C-H bond. The rate of methane conversion in the coupling reaction can therefore be expected to correlate with the catalyst's ability to effect such scission as measured by the rates of deuterium exchange.

The comparison of the results (tables 1 and 3) shows that no such correlation exists. For example, the rates of deuterium exchange over MgO are marginally higher than over m-Sm_2O_3, and yet the rates of methane conversion under oxidative coupling conditions are much higher over the latter catalyst. Conversion of methane over γ-Al_2O_3 is higher than over MgO at temperatures above 800°C, while deuterium exchange is faster over MgO. Comparison of the methane conversion rates with R[D] for all catalysts at temperatures from 700°C to 900°C is shown in fig. 3. If both reactions proceeded via heterolytic dissociation of methane, the data points for all catalysts would be expected to fall on one line. The fact that different dependence is seen for each catalyst suggests that there is no common mechanism for both reactions.

The second step in this mechanism is the transfer of the electron from a methyl anion to the oxygen. The literature data indicates that the methyl anion is very unstable [18], so that electron transfer is unlikely to be the limiting step in this reaction sequence. The lack of relationship between the rates of deuterium exchange and the rates of methane conversion clearly demonstrates that the ability of the catalyst to heterolytically dissociate a methane molecule does not explain its activity in the oxidative coupling reaction.

The second proposed mechanism for the methyl radical formation involves the formation of a transition complex consisting of the adsorbed methane

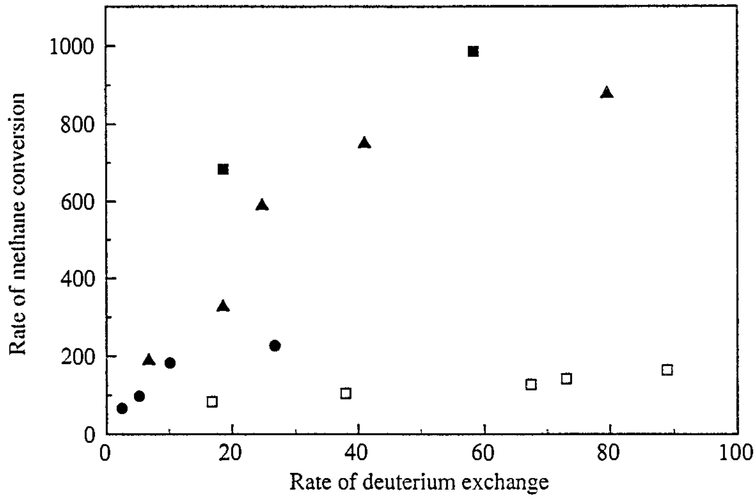

Fig. 3. Comparison of the rates of deuterium exchange and methane conversion. All rates expressed in $\mu mol \cdot g^{-1} \cdot s^{-1}$. ▲-m-$Sm_2O_3$; ■-c-$Sm_2O_3$; □-MgO; ●-$\gamma$-$Al_2O_3$.

molecule and the surface oxygen [4,8–13] (fig. 2B), which subsequently dissociates yielding methyl radical and water (or its precursor, e.g. OH). In this case the rate of methane conversion $R[-CH_4]$ under the oxidative coupling conditions can be expected to correlate with the ability of the catalyst to activate oxygen as measured by the rates of the O-O bond scission, (R[O]). Such correlation could be expected to be more pronounced under the conditions of high oxygen conversion, i.e. where the methane conversion rate may be limited by the availability of oxygen [30].

No such correlation can be found (see tables 2 and 3). While m-Sm_2O_3 and γ-Al_2O_3 show similar rates of oxygen activation, methane conversion over m-Sm_2O_3 is faster by almost an order of magnitude. High oxygen activation is found for MgO, and yet is shows the lowest methane conversion rates amongst all catalysts tested. Comparison of the methane conversion rates with R[O] for all catalysts at temperatures from 600°C to 900°C is shown in fig. 4. As in the case of deuterium exchange, no consistent relationship between oxygen activation and methane conversion can be found.

Considering that this mechanism proposes the formation of a transition complex consisting of methane and oxygen, a correlation between $R[-CH_4]$ and both R[D] and R[O] may also be expected. This view is supported by the fact that several kinetic expressions derived for various catalytic systems show that the rate of methane conversion is dependent on the partial pressures of CH_4 and O_2 [31–33]. An attempt to find the relationship between both the activation of oxygen (R[O]) and methane (R[D]) and the rates of methane conversion has also been unsuccessful.

The above results clearly indicate that the mechanism of methyl radical formation can not be explained *alone* by the ability of the catalyst's surface to

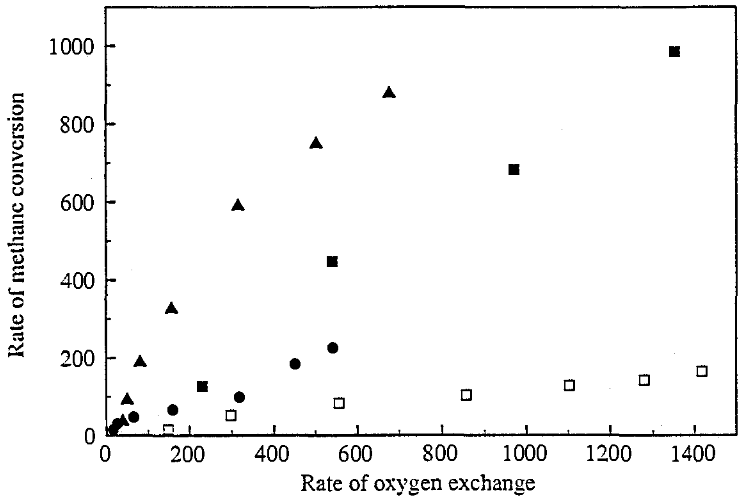

Fig. 4. Comparison of the rates of deuterium exchange and methane conversion. All rates expressed in $\mu mol \cdot g^{-1} \cdot s^{-1}$. ▲-m-$Sm_2O_3$; ■-c-$Sm_2O_3$; □-MgO; ●-$\gamma$-$Al_2O_3$.

dissociate either methane or oxygen, or both. This is not to say that the above factors do not play a role at all and can be discounted altogether. For example, most known oxidative coupling catalysts are strongly basic. This strongly suggests that either adsorption or dissociation of weakly acidic methane on the surface (or both) are an important part of the sequence leading to the radical formation.

It can only be speculated that methyl are formed in a sequence of steps, and perhaps require some very specific active sites, where other properties of the surface also play an important role. These properties may include, for example, lattice defects, distance between the metal and oxygen in the lattice, specific geometry of the site on which both reactants are adsorbed in particular configuration or the presence of some specific activated form of oxygen. Identification of these factors is beyond the scope of the techniques used in this study.

Considering the wide variety of materials of vastly different composition and structure [1,2] which have been found during the past ten years as being capable of catalysing the oxidative coupling reaction, it may well be true that several types of sites exist. Their common feature would be the ability to effectively catalyse the sequence of steps leading to the radical formation.

Another important aspect of the oxidative coupling reaction is selectivity towards the formation of C_2 hydrocarbons. It has been demonstrated by several workers that the selectivity of catalysts increases with their basicity. This issue can be discussed in terms of the ability of the catalyst surface to activate weakly acidic methane and weakly basic oxygen. The activation of methane can be expected to occur on an electron-rich (basic) sites, initiating a series of steps leading to the formation of gas-phase methyl radicals, resulting in the formation of C_2 products. The oxygen would be activated on an electron-deficient (acidic)

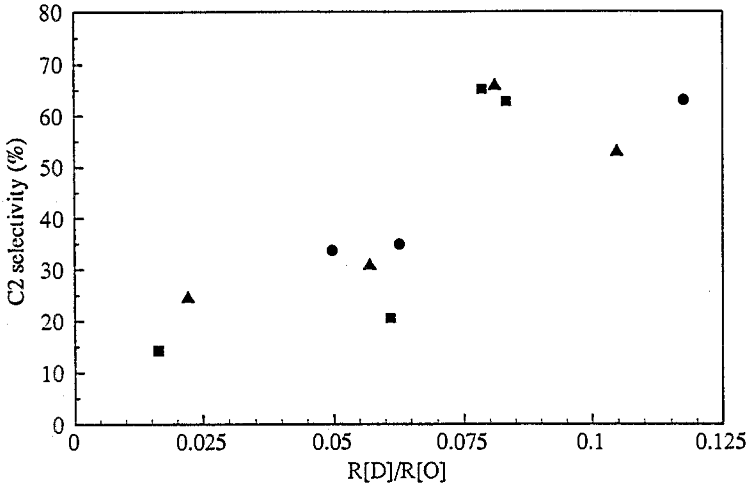

Fig. 5. Comparison of the selectivity towards C_2 formation in oxidative coupling reaction with the relative ability of the catalyst to activate methane and oxygen expressed as R[D]/R[O]. ■-800°C; ▲-850°C; ●-900°C.

sites, facilitating the nonselective oxidation of the methane and the coupling products (ethane and ethylene), thus giving rise to the deep oxidation products (CO_x). This is consistent with recently published observation that the acidic sites on the catalysts surface adversely affect C_2 selectivity [17].

If the above hypothesis is valid, a highly selective catalyst should be able to activate methane strongly and oxygen weakly. The ratio of the rates of deuterium and oxygen exchange reactions (R[D]/R[O]) provides a direct measure of the relative ability of the catalyst surface to activate both molecules. The drawback of using R[D]/R[O] ratio stems from the fact that being a quotient of two experimentally determined quantities its value can be biased with a considerable error. Further distortion can be caused by the contribution of the gas phase reactions, as the R[D]/R[O] ratio reflects only the characteristics of the catalyst. Despite these uncertainties, a good correlation between R[D]/R[O] ratio and C_2 selectivity has been found (fig. 5). It is important to stress that this correlation was obtained for four catalysts at temperatures ranging from 800°C to 900°C, for methane conversions ranging from 1.3% to 17.8% and oxygen conversions ranging from 10.6% to 100.0%.

The link between the basicity and C_2 selectivity can therefore be interpreted in terms of strong activation of methane and weak activation of oxygen. For an acidic surface (e.g. γ-Al_2O_3) the opposite is true, making it a good oxidation (combustion) catalyst. This is illustrated (Figure 6) by the dependence between the R[D]/R[O] (measured at 800°C) and the catalysts' basicity, expressed in terms of the temperature of desorption of 50% of CO_2. Similar dependence exists for other temperatures.

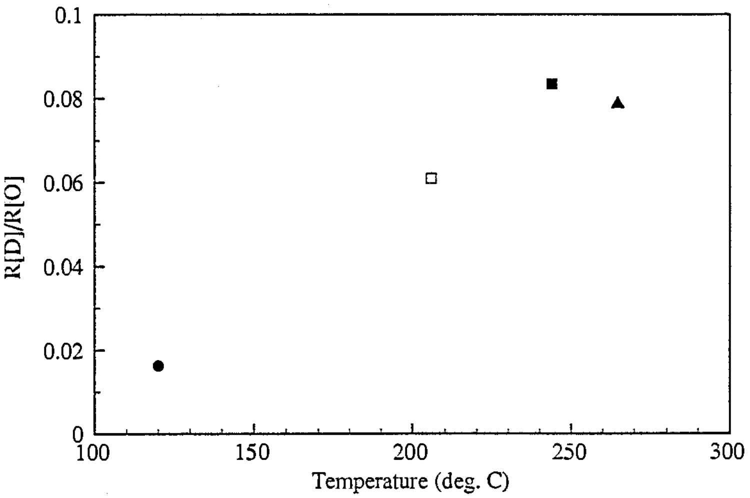

Fig. 6. Dependence of the R[D]/R[O] measured at 800°C and the basicity of the catalyst expressed as the temperature of desorption of 50% of CO_2 in TPD experiments. ▲-m-Sm_2O_3; ■-c-Sm_2O_3; □-MgO; ●-γ-Al_2O_3.

The above results provide a valuable insight into the mechanism of the oxidative methane coupling and explain the link between the basicity of the catalyst surface, activation of the reactants and the selectivity towards formation of C_2 products.

5. Conclusions

The following conclusions can be drawn from studying the relationship between the ability of catalysts to activate methane and oxygen and their performance in an oxidative coupling reaction:

1. Methane conversion in an oxidative coupling reaction does not correlate with the ability of the catalyst surface to dissociate either methane or oxygen or both.

2. Formation of the methyl radicals cannot be explained by a simplistic mechanism involving either heterolytic dissociation of methane on the catalyst surface or its interaction with oxygen. It is more likely that a multi-step mechanism or specific characteristics of the active site are involved.

3. Selectivity to C_2 hydrocarbons can be explained by the relative activation of methane and oxygen on the catalyst surface. As methane is weakly acidic and oxygen weakly basic, the ratio of the activation rates is high over basic catalysts. This explains the relationship between basicity and selectivity of the oxidative coupling catalysts.

Acknowledgment

The authors wish to thank Mrs. Jan R. Chipperfield for providing the surface area measurements and XRD spectra of samarium oxides.

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