Oxidative Coupling of Methane

I. Alkaline Earth Compound Catalysts

J. A. S. P. CARREIRO AND M. BAERNS[1]

Ruhr-University Bochum, P.O.B. 10 21 48, D-4630 Bochum, Federal Republic of Germany

The catalytic performance of oxides, sulfates, phosphates, carbonates, fluorides, and aluminates of Be, Mg, Ca, Sr, and Ba was studied for the oxidative coupling of methane to C_n hydrocarbons ($n \geq 2$). To compare the various catalytic compounds, normalized reaction conditions were applied: $T = 740°C$, $P_{CH_4}^{\circ} = 660$ mbar, $P_{O_2}^{\circ} = 80$ mbar, $P_{N_2}^{\circ} = 260$ mbar at a total pressure of 1 bar. C_{2+} selectivity increased from BeO (22%) via MgO (22 to 53%) and CaO (47 to 55%) to SrO and BaO (70 to 72%). Among different calcium compounds C_{2+} selectivity varied in the order CaO (47 to 55%), $CaSO_4$ (53%), Ca_2SiO_4 (43%), $CaAl_2O_3$ (18%), CaF_2 (14%), and $Ca_3(PO_4)_2$ (11%). Furthermore, the effect of catalyst preparation and operating conditions on coupling selectivity was investigated. The results are discussed on the basis of surface basicity of the catalysts. © 1989 Academic Press, Inc.

INTRODUCTION

In earlier work on oxidative coupling of methane to higher hydrocarbons the oxides of multivalent metals (e.g., Pb, Mn, Bi, Sn) were proposed as suitable catalytic materials (*1, 2*). The coupling selectivity of these oxides when supported on various carriers could be improved by the addition of alkali compounds (*3, 4*). Recent investigations have shown that basic compounds themselves are suited to oxidative methane coupling. Lunsford and co-workers reported that Li_2CO_3/MgO could be used as a suitable catalytic material (*5*). Pursuing this approach Aika and co-workers (*6, 7*) studied the catalytic properties of MgO doped with various main group and transition metal oxides; the highest C_{2+} selectivities were obtained with alkali-doped MgO. Also alkali-doped $BaCO_3$ and $SrCO_3$ catalysts resulted in high coupling selectivity and activity as observed by Aika *et al.* (*8*). Otsuka *et al.* (*9, 10*) who studied various rare earth metal oxides found that basic oxides like Sm_2O_2 and La_2O_3 were the most selective catalysts in this group; the authors achieved further improvement by doping Sm_2O_3 with alkali compounds (*11*). Similarly, as already mentioned above (cp. (*3, 4*)), doping of zinc oxide, manganese oxide, and other transition metal oxides with alkali compounds led to improved selectivities of these oxides when they were used as catalysts (*12, 13*); particularly, alkali chlorides were recommended in view of their known ability to affect dehydrogenation of ethane to ethylene.

Supplementing some earlier patent information (*14*), further results on the catalytic performance of various alkaline earth compounds are reported in the present paper. In particular, the methods of preparation and pretreatment of the catalysts before catalytic testing, as well as reaction conditions on the selectivity of the oxidative methane coupling reaction, are dealt with. Some preliminary suggestions are put forward to explain the different catalytic effects; no final elucidation of the various phenomena observed is, however, possible at present.

EXPERIMENTAL

Catalyst Preparation

Calcium oxide was prepared by decomposition of either calcium hydroxide or cal-

---

[1] To whom correspondence should be addressed.

cium carbonate. Magnesium oxide samples were obtained from magnesium hydroxide and $Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$; the different treatments to which these compounds were exposed prior to the catalytic experiments are described along with the respective results. Calcium silicate was prepared by adding deionized water to a suspension of calcium hydroxide in tetraethyl silicon ether, drying, and finally calcining the solid deposit at 800°C for 40 h. Calcium aluminate was obtained by the solid/solid reaction between CaO and alumina. SrO and BaO were prepared by thermal decomposition of $Sr(OH)_2 \cdot 8H_2O$ and $Ba(NO_3)_2$, respectively. The other alkaline earth compounds were used as commercially received. All alkaline earth compounds except BeO and BaO were used for the catalytic tests as cylindrical pellets (3 × 2 mm; pelletizing pressure 40–60 bar); BeO and BaO were used in particulate form (ca. 0.25 mm).

Catalyst Testing and Characterization

The experimental equipment for catalyst testing was similar to that already described elsewhere (2). The quartz-made reactor having an inner diameter of 8 mm and a heated length of 15 cm has shown negligible catalytic activity under the reaction conditions applied. The reactants entered at the top and left at the bottom of the reactor. The catalyst pellets were placed in the middle of the heated zone. The length of the catalytic bed varied between 1 and 14 cm depending on the activity of the material used. The bottom of the reactor was filled with quartz granules. A 1-cm layer of quartz granules was also placed above the catalytic bed. Reactants and products were analyzed by gas chromatography using a Carbosieve SII column for separation of the permanent gases and a Porapak Q column for analyzing hydrocarbons. Formaldehyde was determined by using the liquid products collected in a cold trap applying the method of Norkus and Stul'gene (12).

To compare the catalytic performances of the various materials the following reference conditions were applied: $T = 740°C$, $P°_{CH_4} = 660$ mbar, $P°_{O_2} = 80$ mbar, $P°_{N_2} = 260$ mbar, and $P_{tot} = 1$ bar. The flow rate of the reactants was adjusted in such a way that conversion of oxygen was generally higher than 80%. Product selectivities are defined on the basis of percentage carbon converted.

BET surface areas were determined by the 1-point method before the use of the catalyst. Before this characterization the catalysts were pretreated for 1 h in nitrogen at 110°C. Phase compositions of some catalysts were determined by X-ray diffraction using a Guinier powder camera (Huber 621).

RESULTS

Activity and Selectivity

Results on activity and selectivity for the oxidative methane coupling reaction to C_{2+} hydrocarbons using alkaline earth compounds, i.e., alkaline earth oxides and various calcium compounds as catalysts are presented in Table 1.

Activity of the various catalysts can be deduced from the relationship between the modified reaction time W/F (weight of catalyst/volumetric flow rate) and the corresponding oxygen conversion. Since this relationship is, however, difficult to interpret when both variables change simultaneously, a rate constant k based on a pseudo-first-order reaction in oxygen was calculated for the rate of oxygen conversion as a measure of activity; as a first approximation any effect of methane could be neglected due to its large surplus.

The activity of alkaline earth oxides decreased in the sequence CaO > MgO > BaO, BeO, SeO. Although SrO and BaO appeared rather attractive from a selectivity point of view (see below) they were not chemically stable during the oxidative coupling of methane: extended exposure to H_2O vapor formed during oxidative methane conversion resulted in the formation of

TABLE 1

Catalytic Activity and Selectivity S of Alkaline Earth Compounds

Catalyst	S_{BET}[e] (m^2/g)	W/F[f] $(g \cdot s/ml)$	A/F[g] $(10^4 s/cm)$	X_{O_2} (%)	k[h] $(ml/g \cdot s)$	S_{C_2}[i] (%)	$S_{C_{3+}}$ (%)	$S_{C_{2+}}$[j] (%)	S_{CO} (%)	S_{CO_2} (%)	C_2^-/C_2	S_{H_2} (%)
BeO	n.dtd.	31.09	—	99	0.15	22	0.2	22	32	46	0.63	0.8
BeSO$_4$	n.dtd.	11.48	—	86	0.2	6	—	6	61	33	0.21	1.4
MgO[a]	24.4	0.21	5.1	93	13	45	1.8	47	16	37	0.63	6.8
MgO[b]	36.8	0.58	21.0	95	5	22	0.1	22	27	51	0.57	8.6
MgSO$_4$	0.7	45.57	31.9	55	0.02	43	4.6	48	36	16	1.83	2.9
CaO[c]	7.6	0.17	1.3	100	$\geq$40	46	1.2	47	4	49	0.43	0.3
CaO[d]	6.3	0.13	0.8	94	22	52	3.2	55	13	32	0.54	1.6
CaSO$_4$	0.1	4.90	0.5	53	0.15	50	2.6	53	3	44	0.79	1.0
Ca$_3$(PO$_4$)$_2$	5.7	1.57	8.9	96	2	11	—	11	28	61	0.31	1.0
Ca$_2$SiO$_4$	9.2	0.20	1.8	100	$\geq$35	42	1.2	43	3	54	0.39	0.2
CaAl$_2$O$_4$	32.2	0.14	4.5	84	0.4	18	—	18	28	54	0.26	1.3
CaF$_2$	0.1	3.30	0.3	98	1.2	14	0.1	14	13	73	0.39	1.5
SrO	0.1	23.09	2.3	88	0.1	64	7.6	72	3	25	1.32	—
SrCO$_3$	n.dtd.	2.99	—	64	0.3	40	0.3	40	9	51	0.43	2.1
SrSO$_4$	0.8	24.52	19.6	100	$\geq$0.3	7	—	7	1	92	0.61	0.7
BaO	n.dtd.	14.48	—	98	0.3	63	7.2	70	—	30	0.95	0.5
BaSO$_4$	n.dtd.	16.95	—	20	0.01	34	—	34	35	31	0.39	6.0

[a] Prepared from Mg$_5$(OH)$_2$(CO$_3$)$_4 \cdot$ 4H$_2$O.

[b] Prepared from Mg(OH)$_2$.

[c] Prepared from CaCO$_3$.

[d] Prepared from Ca(OH)$_2$.

[e] S_{BET}; specific surface area.

[f] Weight of catalyst W/volumetric flow rate F.

[g] $A = W \cdot S_{BET}$.

[h] k, rate constant ($\ln(1 - X) = -k(W/F)$).

[i] C$_2$H$_6$ + C$_2$H$_4$.

[j] Total hydrocarbons $n \geq 2$.

the respective hydroxides and successively of hydrated hydroxides having melting points below the reaction temperature applied. This undesired hydration reaction could not be avoided. Furthermore, carbonates were formed. X-ray diffraction analysis of the SrO catalyst after exposure to the catalytic reaction showed the following phase composition: Sr(OH)$_2$ $\cdot$ H$_2$O, Sr(OH)$_2$, SrCO$_3$, and SrO. Tentatively it may be assumed that liquid hydroxides are stabilized in a solid carbonate matrix similarly to supported-liquid-phase catalysts. Since this behavior of SrO and BaO catalysts was detrimental to catalyst operation over an extended period of time these cata-

lysts were not included in any further studies. The activity of the various calcium compound catalysts decreased in the order

$$CaO > Ca_2SiO_4 > CaAl_2O_4 > Ca_3(PO_4)_2$$
$$> CaF_2 > CaSO_4.$$

(A similar pattern was also observed when using the surface area instead of the mass of the catalyst as reference for activity comparison.)

Among the various alkaline earth compounds the sulfates were, in general, rather inactive compared to the respective oxides.

The C$_{2+}$ as well as C$_{3+}$ selectivity was lowest for BeO and highest for SrO and BaO:

Oxide	BeO	MgO	CaO	SrO	BaO
$S_{C_{2+}}$ (%)	22	22–53	47–55	72	70
$S_{C_{3+}}$ (%)	0.2	0.1–1.8	1.2–3.2	7.6	7.2

Different selectivities of the alkaline earth oxide catalysts for the same bulk oxide were obtained depending on the method of preparation and the conditions of subse-

quent pretreatment; these phenomena are dealt with separately in the two following subsections. For MgO and CaO which were prepared from different precursor compounds the upper and lower limits of selectivity have been given in Table 1.

The C_{2+} selectivities of calcium compound catalysts varied between 11 and 55%:

Compound	CaO	$CaSO_4$	Ca_2SiO_4	$CaAl_2O_4$	CaF_2	$Ca_3(PO_4)_2$
$S_{C_{2+}}$ (%)	47–55	53	43	18	14	11

Among the alkaline earth sulfates $MgSO_4$ and $CaSO_4$ were as selective as the respective oxides, while $BeSO_4$, $SrSO_4$, and $BaSO_4$ resulted in significantly lower C_{2+} selectivities.

Most of the selectivity data have been obtained at oxygen conversions of 85 to 100% corresponding to methane conversions of approximately 8 to 15% depending on product distribution. Within this range of conversion the selectivity of hydrocarbon formation can be considered independent from oxygen conversion as has been shown elsewhere (22); also at lower oxygen conversions this argument is applicable as a first approximation.

Almost all the catalysts resulted in the formation of CO as well as CO_2, in addition to some hydrogen. There is, however, no final explanation yet for their different proportions obtained with the various catalysts. (The selectivity S_{H_2} being a measure for hydrogen formation is the proportion of hydrogen observed compared to the total hydrogen contained in the methane converted.) The ratio of ethylene to ethane is presumably only slightly affected by the different catalysts but it increases with contact time. Tentatively, this may be understood as an indication that ethylene is mainly formed noncatalytically from ethane in a subsequent homogeneous gas-phase reaction.

Preparation of MgO and CaO

The catalytic properties of MgO and CaO were significantly affected by the precursor used for preparation (cp. Table 1). MgO obtained from $Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$ was much more selective than MgO from $Mg(OH)_2$; CaO prepared from $Ca(OH)_2$ was more selective than CaO from $CaCO_3$.

The conditions of precursor transformation to MgO and CaO respectively, i.e., temperature and gas-phase composition, also showed an influence on the C_{2+} selectivity as can be concluded from the results of Table 2. The most selective magnesium oxide was obtained when magnesium hydroxycarbonate was decomposed without previous drying in the presence of methane and air (reaction atmosphere) at 600°C and then the temperature was raised from 600°C to the final reaction temperature of 740°C (catalyst M-1). Reasonable C_{2+} selectivity was also achieved when magnesium hydroxycarbonate was decomposed under standard reaction conditions at 740°C (catalyst M-2). The effect of the precursor ($CaCO_3$ and $Ca(OH)_2$) and its treatment was less marked for the calcium oxide than for the magnesium oxide catalyst. Incipient-wetness impregnation of the magnesium hydroxycarbonate, which was used as precursor for MgO, with ethanol or distilled water as hydroxylic solvent also affected

TABLE 2

Effect of Preparation and Calcination Conditions on the Activity (for Definition See Table 1) and Selectivity S of MgO (M-) and CaO (C-) Catalysts

Catalyst	S_{BET} (m²/g)	W/F (g · s/ml)	A/F (m² · s/ml)	X_{O_2} (%)	k (ml/g · s)	$S_{C_{2+}}$ (%)	S_{CO} (%)	S_{CO_2} (%)	$C_2^=/C_2$	S_{H_2} (%)
M-1	23.6	0.19	4.5	94	15	53	10	37	0.64	2.4
M-2	24.4	0.21	5.1	93	13	47	16	37	0.63	6.0
M-3	21.5	0.82	17.6	96	4	41	11	48	0.63	2.3
M-4	36.8	0.58	21.3	95	5	22	27	51	0.57	8.6
C-1	7.6	0.17	1.3	100	≥40	47	4	49	0.43	2.9
C-2	6.3	0.13	0.8	94	22	55	13	32	0.54	4.6
C-3	5.6	0.71	4.0	100	≥10	46	9	46	0.57	4.3

Note: M-1, decomposition of magnesium hydroxicarbonate (pellets) at 600°C under standard reaction atmosphere. M-2, decomposition of magnesium hydroxicarbonate (pellets) under standard reaction conditions. M-3, decomposition of magnesium hydroxicarbonate (powder) in air at 800°C. M-4, decomposition of Mg(OH)₂ (pellets) under standard reaction conditions. C-1, decomposition of CaCO₃ (pellets) under standard reaction conditions. C-2, decomposition of Ca(OH)₂ (pellets) under standard reaction conditions. C-3, decomposition of Ca(OH)₂ (powder) in air at 800°C.

the selectivity. This kind of pretreatment led to a significant decrease in C_{2+} selectivity as illustrated in Table 3. The effect was more pronounced when the precursor was calcined in air after impregnation with the solvent.

Activity was also affected by the pretreatment conditions (cp. Tables 2 and 3); this was most probably due to a change of surface area during catalyst operation.

Operating Conditions

The effect of the reaction temperature and of the molar ratio of methane to oxygen at the reactor inlet on activity and selectivity is illustrated in Tables 4 and 5; the relationship was investigated for the MgO catalysts only.

When the reaction temperature was increased from 600 to 740°C, C_{2+} and ethylene selectivity, the latter expressed by the ratio of C_2H_4 to C_2H_6, increased markedly (cp. Table 4). Since the increase in activity was only small between 700 and 740°C (cp. Table 4) it may be assumed that mass transport limitation prevailed; this proposition, however, was not studied in more detail.

The decrease of the methane/oxygen ra-

TABLE 3

Activity (for Definition See Table 1) and Selectivity S of Differently Pretreated MgO

Catalyst	S_{BET} (m²/g)	W/F (g · s/ml)	A/F (m² · s/ml)	X_{O_2} (%)	k (ml/g · s)	$S_{C_{2+}}$ (%)	S_{CO} (%)	S_{CO_2} (%)	$C_2^=/C_2$	S_{H_2} (%)
M–2	24.4	0.21	5.1	93	13	47	16	37	0.63	6.8
M–5	18.3	0.48	8.8	77	3	34	24	42	0.54	7.9
M–6	17.1	0.49	8.4	89	4.5	34	22	44	0.62	7.6
M–7	24.8	0.22	5.5	90	10	42	15	43	0.63	3.0

Note: M-2, no pretreatment. M-5, impregnated with ethanol; drying, 22 h, 130°C (20 mbar); calcination 4 h, 600°C. M-6, impregnated with water; drying, 22 h, 130°C (20 mbar); calcination 4 h, 600°C. M-7, impregnated with water; drying, 22 h, 130°C (20 mbar).

TABLE 4

Effect of Reaction Temperature on Activity (for Definition See Table 1) and
Selectivity S of the MgO Catalyst M-1 ($P^\circ_{CH_4}$ = 0.64 bar; $P^\circ_{O_2}$ = 0.078 bar)

T_R (°C)	W/F (g · s/ml)	X_{O_2} (%)	k (ml/g · s)	$S_{C_{2+}}$ (%)	S_{CO} (%)	S_{CO_2} (%)	$C^=_2/C_2$	S_{H_2} (%)
600	1.08	93	2.5	2	8	90	0.08	4.1
650	0.43	97	8.2	18	19	63	0.30	5.8
700	0.20	91	12.0	40	15	45	0.46	5.9
740	0.19	94	14.8	53	10	37	0.64	2.4

tio affected the C_{2+} selectivity only slightly (cp. Table 5); i.e., the lower methane/oxygen ratio resulted in higher C_{2+} yields due to higher methane conversions. There was expectedly no effect on activity. (The results are similar for both MgO catalysts either from magnesium hydroxicarbonate or from magnesium hydroxide.)

Adding water to the reactant mixture (methane and air) when using a CaO catalyst did not affect significantly the coupling selectivity to C_{2+} hydrocarbons. There was, however, a significant increase in hydrogen selectivity when the water partial pressure was increased (cp. Table 6). Activity was slightly decreased by the presence of water vapor but this effect was inside the limits of experimental accuracy.

DISCUSSION

C_{2+} selectivities of alkaline earth oxides increase from BeO to BaO; bulk basicity of these materials increases concomitantly

(14). This result confirms previous assumptions that basicity of the catalytic materials is favorable for high selectivities (3, 19). Surface basicity, however, may not necessarily correspond fully to bulk basicity; this may explain the different C_{2+} selectivities observed for MgO as well as for CaO catalysts when methods of preparation and pretreatment conditions of the catalysts varied (cp. Table 2). In this context it is interesting to note that catalytic properties of MgO have also been reported to be particularly sensitive to conditions of preparation and pretreatment for other reactions (15, 16). This proposition is supported with respect to MgO by results indicating that this compound may exist even at high temperatures in different surface morphologies, i.e., different crystal planes are exposed to various degrees (17, 18); hence different acid/base properties are to be expected as catalyst preparation varies.

There is no definite selectivity pattern for

TABLE 5

Effect of Methane/Oxygen Ratio on Activity (for Definition See Table 1), Selectivity S,
and Yield Y on MgO Catalysts M-3 and M-4 at T = 740°C

Catalyst	$P^\circ_{CH_4}$ (bar)	$P^\circ_{O_2}$ (bar)	CH_4/O_2	W/F (g · s/ml)	X_{O_2} (%)	k (ml/g · s)	X_{CH_4} (%)	$S_{C_{2+}}$ (%)	$Y_{C_{2+}}$ (%)	$C^=_2/C_2$
M-4	0.64	0.078	8.2	0.58	95	5.2	10	22	2.1	0.57
M-4	0.47	0.116	4.1	0.58	96	5.5	19	21	3.9	0.94
M-3	0.64	0.078	8.2	0.82	96	3.9	11	41	4.4	0.63
M-3	0.47	0.115	4.1	0.87	97	4.0	20	37	7.5	0.97

Note: M-4, prepared from magnesium hydroxide. M-3, prepared from magnesium hydroxycarbonate.

TABLE 6

Effect of Water Partial Pressure on Activity (for Definition See Table 1)
and Selectivity S of CaO Catalyst C-3 ($P^\circ_{CH_4}$ = 0.52 bar; $P^\circ_{O_2}$ = 0.058 bar;
T_R = 740°C)

P_{H_2O} (°C)	W/F (g · s/ml)	X_{O_2} (%)	k (ml/g · s)	$S_{C_{2+}}$ (%)	S_{CO} (%)	S_{CO_2} (%)	$C_2^=/C_2$	S_{H_2} (%)
0	0.17	98	23	54	11	35	0.45	0.69
116	0.17	96	19	54	10	36	0.45	0.73
199	0.17	96	19	55	9	36	0.39	1.03

the other alkaline earth metal compounds as may be derived from Table 1. C_{2+} selectivities of the sulfates of beryllium and strontium were very low (6 and 7%, respectively) while those of magnesium (48%), calcium (53%), and barium (34%) were comparatively high. For Mg, Ca, and Ba activity, represented by oxygen conversion and the respective residence time or by the pseudo-first-order rate constant the selectivity is lower for the compounds (salts) than for the respective oxides. With respect to product distribution, it appears, in general, that all alkaline earth metal compounds (salts) show a lower selectivity than the respective oxides which is certainly due to a decrease in the concentration of basic sites on the surface.

No final evaluation of the different activities of the various alkaline earth compounds seems possible at present; the activity is most probably affected not only by the specific surface area but also by its ability to interact with water vapor and carbon dioxide as has been recently shown for the Li_2O/MgO system when used as a catalyst for the oxidative coupling of methane (20). In this study only the effect of water vapor on the performance of a CaO catalyst was investigated. There was no significant change in C_{2+} selectivity; however, the amount of hydrogen formed during the reaction increased with increasing vapor pressure of water, which may be taken as an indication that the water gas shift reaction plays a role and that it is catalyzed by the alkaline earth compounds. For BaO and

SrO there was an additional influence of water as outlined above, leading to liquid hydroxide and hydrate formation.

Participation of bulk lattice oxygen of the alkaline earth compounds in the reaction is most probably rather insignificant. This may explain the lower sensitivity of these materials to variations of oxygen partial pressure and the methane/oxygen ratio respectively compared to multivalent oxide catalyst (2–4, 14, 21). It is shown that the CH_4/O_2 ratio only slightly affects C_{2+} selectivity of MgO; this is different for multivalent metal oxide catalysts (cp. the cited references). This phenomenon may be related to the fact that lattice oxygen species of the alkaline earth metal oxides which are regenerated by dissociative adsorption of oxygen on the catalytic surface are not readily inserted into a C–H bond leading to nonselective oxidation.

The improvement of C_{2+} selectivity with increasing temperature (cp. Table 4) must certainly be attributed to different activation energies of the selective and nonselective reaction channel; i.e., the nonselective channel (lower activation energy) is favored at lower temperature while the opposite is true for the selective channel. The appreciable H_2 formation at 600 to 700°C compared to 740°C may tentatively be explained by assuming that the nonselective path occurs via a methoxy species; this species might then be converted to a surface formaldehyde species which decomposes subsequently to H_2 and CO.

The approach presented in this study us-

ing only one-component catalysts was helpful for specifying some relevant factors affecting catalytic performance. However, the catalytic materials with high basicity and, hence, high selectivity, i.e., SrO and BaO, appear not to be applicable in practice because their interaction with water vapor results in liquid hydroxides. Materials of high basicity similar to SrO and BaO without having the aforementioned shortcomings can be prepared by incorporation of alkali compounds into the surface of stable alkaline earth oxides like MgO and CaO; this will be dealt with in a subsequent paper (23).

ACKNOWLEDGMENTS

REFERENCES

1. Keller, G. E., and Bhasin, M. M., *J. Catal.* **73**, 9 (1982).
2. Hinsen, W., and Baerns, M., *Chem. Ztg.* **107**, 223 (1983).
3. Hinsen, W., Bytyn, W., and Baerns, M., *in* Proceedings, 8th International Congress on Catalysis, Berlin, 1984." Dechema, Frankfurt-am-Main, 1984.
4. Baerns, M., and Bytyn, W., Canadian Patent 458,797 (July 12) 1984/August 25, 1987).
5. Ito, T., Wang, J. X., Lin, C. H., and Lunsford, J. H., *J. Amer. Chem. Soc.* **107**, 5062 (1985).
6. Moriyama, T., Takasaki, N., Iwamatsu, E., and Aika, K. I., *Chem. Lett.*, 1165 (1985).
7. Iwamatsu, E., Moriyama, T., Takasaki, N., and Aika, K. I., *J. Chem. Soc. Chem. Commun.*, 19 (1987).
8. Aika, K. I., Moriyama, T., Takasaki, N., and Iwamatsu, E., *J. Chem. Soc. Chem. Commun.*, 1210 (1986).
9. Otsuka, K., Jinno, K., and Morikawa, A., *Chem. Lett.*, 499 (1985).
10. Otsuka, K., Jinno, K., and Morikawa, A., *J. Catal.* **100**, 353 (1986).
11. Otsuka, K., Liu, Q., Hatano, M., and Morikawa, A., *Chem. Lett.*, 467 (1986).
12. Otsuka, K., Liu, Q., Hatano, M., and Morikawa, A., *Chem. Lett.*, 903 (1986).
13. Otsuka, K., and Komatsu, T., *Chem. Lett.*, 1955 (1986).
14. Baerns, M., Carreiro, J., and Bytyn, W. German Patent Appl. DEOS 3534530 A1 (September 27, 1985).
15. Norkus, P. K., and Stul'gene, S. P., *Zh. Anal. Khim.* **23**, 103 (1968).
16. Duffy, J. A., and Ingram, M. D., *J. Non-cryst. Solids* **21**, 373 (1976).
17. Boudart, M., Delbouille, A., Derouane, E. G., Indovina, V., and Walters, A. B., *J. Amer. Chem. Soc.* **94**, 6622 (1972).
18. Hattori, H., Shimazu, K., Yoshi, N., and Tanabe, K., *Bull. Chem. Soc. Japan* **49**, 969 (1976).
19. Carreiro, J. A. S. P., and Baerns, M., *React. Kinet. Catal. Lett.* **35**, 349 (1987).
20. Korf, S. J., Roos, J. A., de Bruijn, N. A., van Ommen, J. G., and Ross, J. R. H., *J. Chem. Soc. Chem. Commun.*, 1432 (1987).
21. Bytyn, W., and Baerns, M., *Appl. Catal.* **28**, 199 (1986).
22. Carreiro, J. A. S. P., Ph.D. thesis, Ruhr-University Bochum, 1986.
23. Carreiro, J. A. S. P., and Baerns, M., *J. Catal.*, in press.