Catalysis Letters 13 (1992) 143–152

Cation effects in the oxidative dehydrogenation of methane on sulphates

S. Sugiyama * and J.B. Moffat **

Department of Chemistry and Guelph-Waterloo, Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received 14 August 1991; accepted 8 January 1992

The oxidative coupling of methane has been studied on Mg, Ca, Sr and Ba sulphate. The conversions and selectivities are found to be dependent on the nature of the cation and to be approximately correlated with their electronegativities, thus implying that the C-H bond scission in CH_4, at least with these catalysts, is heterolytic, is rate determining, and further, that the formation of C_{2+} hydrocarbons is dependent, among other factors, on the concentration of methyl radicals.

Keywords: Methane; conversion; oxidative dehydrogenation; cations; sulphates

1. Introduction

While there is much yet to be learned concerning the oxidative dehydrogenation of methane there now seems to be general agreement that the principal function of the catalyst is the activation of methane [1] although the surface may also participate in the formation of CO_x [2]. This is not to say that purely gas phase processes do not occur. Various workers have shown that such gas phase processes may play a major role in the reaction scheme but there continues to be considerable discussion concerning the participation of the homogeneous and heterogeneous processes [3–8]. However, methyl radicals probably form on the surface of the catalyst rather than in the gas phase.

What is less clear, however, is the rate-determining step (RDS) in the process. A number of workers have performed experiments of various types which suggest that the C-H bond scission is rate determining [9–11] while at least one report attributes the RDS to exchange of lattice oxygen [1].

---

* Department of Chemical Science and Technology, The University of Tokushima, Minamijosanjima, Tokushima 770 Japan.

** To whom correspondence should be addressed.

The process by which methane is activated is also important in terms of our understanding of the function of the catalyst. Two possibilities exist: heterolytic and homolytic, the former presumably involving a perturbation of the electron density of the C-H bond of methane, the latter not. It should be noted, however, that dissociation of the C-H bond resulting from the perturbation of the bonding electron density does not preclude the formation of radical species. Although there is little or no direct evidence in support of either mechanism the heterolytic process appears to be favoured [12].

There is common acceptance of the formation of ethane by the recombination of methyl radicals [13]. This is not particularly surprising since many oxidation processes are free radical in nature. Direct evidence for the presence of methyl radicals in the MgO system for the conversion of methane has been shown [14].

If it is assumed [15] that the rate of production of ethane and ethylene (r_2) is proportional to the concentration of methyl radicals taken to the power of 2, while the rate of production of carbon monoxide and dioxide (r_1) is proportional to the concentration of methyl radicals, then

$$\frac{r_2}{r_1} \propto (\cdot \mathrm{CH}_3). \tag{1}$$

While this argument is grossly oversimplified it does provide us with an illustration of the importance of methyl radicals in the coupling process and hence of the importance of the catalyst as a means of generating these radical species.

There are a number of questions that may be asked concerning the relevant properties of the catalyst employed in this process. How does the composition of the catalyst influence the dissociation process? What elements are important? What is the nature of the active sites?

Although there is evidence [12] that adsorbed methane does not participate in the process by which C_2 hydrocarbons are formed, nevertheless methane must interact with the surface of the catalyst in order for dissociation of the C-H bond to occur. One-site as opposed to two-site interactions are undoubtedly to be preferred. If the one-site interaction is supposed to occur on surface oxygen atoms (there is strong evidence that oxygen is one of the elements required by the catalyst) it is then of interest to hold these in a fixed structural environment such as would be found in an anion such as sulphate and inquire as to the effect of the nature of the cation on the methane conversion process.

Earlier work from this laboratory has studied the effect of the addition to the feedstream of a small partial pressure of tetrachloromethane on the conversion of methane and selectivities to the various products with a variety of catalyst including alkali metal- and alkaline earth-oxides [16]. In general, enhancements of both the conversions and selectivities to C_2 hydrocarbons are observed. Since there is evidence that the beneficial changes from addition of TCM arise through its interaction with the catalyst further studies of such effects appear to be warranted.

In the present work a series of sulphates of the alkaline-earth elements, Mg, Ca, Ba and Sr are studied both in the presence and absence of TCM to determine the influence of the cation on the properties of the catalyst as evidenced from the conversion of methane and selectivities to the various products.

2. Experimental

All of the solids examined as catalysts were of high purity and were employed without further purification. $MgSO_4$ (99.99%, surface area 0.8 m^2/g), $CaSO_4$ (99.99%, 0.2 m^2/g), $BaSO_4$ (99.999%, 0.3 m^2/g) were purchased from Aldrich and $SrSO_4$ (99.999%, 0.2 m^2/g) from Johnson Matthey.

The catalytic experiments were performed in a fixed-bed continuous flow reactor operated under atmospheric pressure. The reactor consisted of a 9 mm I.D. and 35 mm in length quartz tube sealed at each end to 4 mm I.D. quartz tubes to produce a total length of 20 cm. The catalyst was held in place in the enlarged portion of the reactor by two quartz wool plugs. The reactor was designed to minimize the free volume in the hottest zone to reduce the contribution of noncatalytic homogeneous reactions. In those experiments in which carbon tetrachloride was added the additive was introduced to the main flow of reactants (CH_4, O_2 and diluent helium) by saturating a separate stream of helium with CCl_4 at 0°C. In all experiments, the temperature of the catalyst was raised to 775°C while maintaining a continuous flow of helium and was then conditioned at this temperature under a 25 ml/min. flow of molecular oxygen for 1 hour. Then the reactor was purged with helium and the temperature of the reactor was adjusted to the reaction temperature before introduction of the reactant gas mixture consisting of methane, oxygen, and helium (total flow rate of 30 ml/min). The reactor was charged with 1.4 g of catalyst.

The reactants and products were analyzed with an on-stream HP 5880 gas chromatograph equipped with a TC detector and integrator. Two columns, one Porapak T (18 ft. × 1/8 in) the other Molecular Sieve 5A (35 cm × 1/8 in) were employed in the analyses.

Blank experiments conducted with CH_4 absent from the feed ($O_2 + He + CCl_4$) indicated that CCl_4 undergoes oxidation producing CO and CO_2. The data reported were corrected by running duplicate experiments with CH_4 absent under otherwise identical sets of process variables.

3. Results and discussion

In the absence of tetrachloromethane (TCM) the products were CO, CO_2, C_2H_2, C_2H_4, C_2H_6 and C_3H_6, together with unconverted CH_4 and O_2. Water

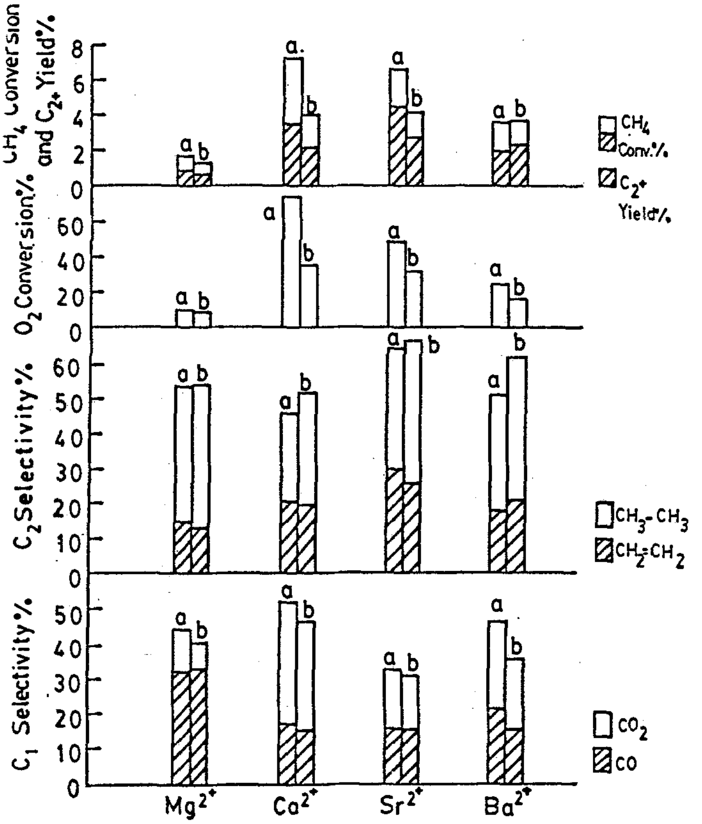

Fig. 1. Comparison of the conversions and selectivities for Mg, Ca, Sr and Ba sulphates. Reaction temperature 835°C, $W = 1.4$ g, $CH_4 = 8.5$ ml/min (215 Torr), $O_2 = 1.2$ ml/min (30.4 Torr), Total flow 30.0 ml/min. a: 0.5 hr-on-stream; b: 6 hr-on-stream.

was also produced but is not reported here. With a CH_4/O_2 feed ratio of 7/1 at a reaction temperature of 835°C strontium sulphate produced the highest selectivity to C_2 hydrocarbons (fig. 1). However, the conversion on both the calcium and strontium sulphates decreases markedly during 6 hours time-on-stream. The lowest conversion is found with the magnesium-based catalyst.

The most evident effect of the continuous addition of TCM to the feedstream is observed with the conversions (fig. 2). With all of the catalysts the conversions with TCM present at 30 min on-stream are approximately twice those observed under similar conditions in the absence of TCM. However, after 6 hours on-stream the conversions had deteriorated to values approximately equal to those observed under the same conditions but in the absence of TCM although the selectivities remained approximately the same during this time. While the C_2 selectivities were highest on the strontium-based catalysts in the absence of TCM, in its presence these selectivities are now highest with calcium sulphate. However, while with no TCM in the feedstream the quantities of C_2H_4 and

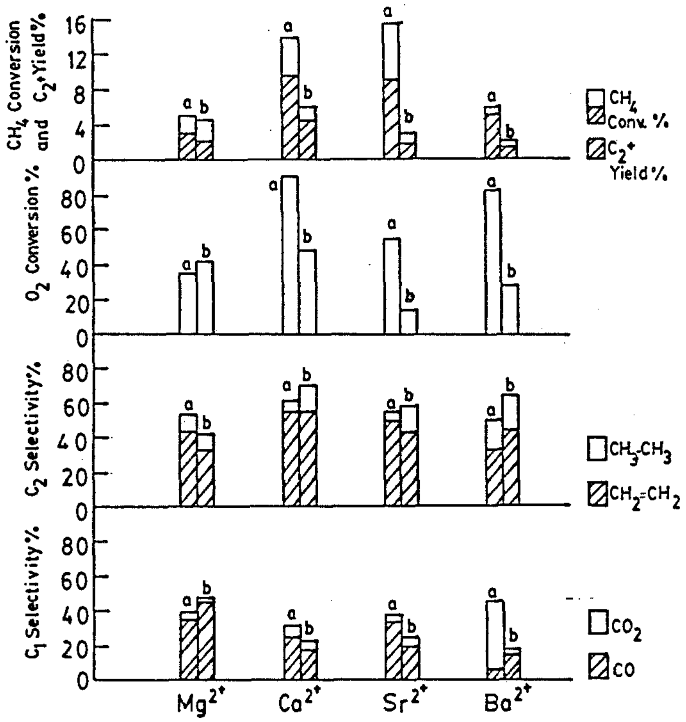

Fig. 2. Comparison of the conversions and selectivities for Mg, Ca, Sr and Ba sulphates. Same conditions as in fig. 1 except including 1.2 ml/min (1.3 Torr) TCM.

C_2H_6 found in the product are approximately equal, when TCM in present, the C_2 product is primarily ethylene with all the catalysts under study.

Increases in reaction temperature from 775 to 835°C with strontium sulphate after 30 min on-stream and TCM present in the feed produced no unexpected results (fig. 3). The conversion of CH_4 increased from 4 to 16% while the selectivities to C_2 and CH_3Cl decreased from 76% to 57% and from 8 to 3%, respectively. However, a comparison of results after 6 hours on-stream and TCM again present showed significant differences. While the conversion of CH_4 increased as the temperature increased up to 800°C, a precipitous drop in conversion occurred at the higher temperature of 835°C. After 6 hours on-stream, the selectivities to C_2 and CH_3Cl increase and decrease, respectively, with increase in temperature to 800°C, the latter from 13 to 3% approximately. However, with the further increase in temperature to 835°C, the selectivity to C_2 hydrocarbons and CH_3Cl decreases and increases, respectively, the latter to 13%.

Semiquantitatively similar effects were observed with $CaSO_4$ on increasing the temperature from 700 to 835°C (not shown). However, with this catalyst the discontinuity was observed between 750 to 775°C. In contrast such discontinuities were not evident with either $BaSO_4$ or $MgSO_4$. It is of interest that the

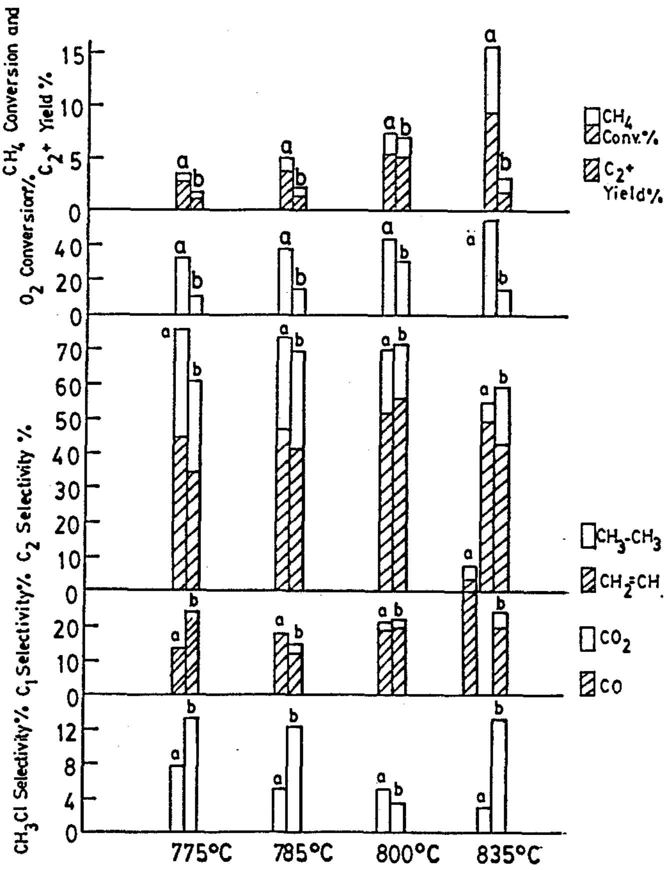

Fig. 3. Reaction temperature effect with $SrSO_4$. Same conditions as in fig. 2.

temperature of the discontinuity with $CaSO_4$ and $SrSO_4$ correspond to the melting points of $CaCl_2$ and $SrCl_2$ (772 and 873°C, respectively), although such a species on $SrSO_4$ after reaction at 835°C could not be detected by X-ray diffraction.

The effect of increases in the flow rates of methane and of oxygen was investigated on $SrSO_4$ (fig. 4). At an oxygen flow rate of 1.2 ml/min, an increase of the CH_4 flow rate decreases the CH_4 conversion and increases the selectivity to C_2 hydrocarbons. Increase in the time on stream from 30 min to 6 hr decreases the CH_4 conversion but at a CH_4/O_2 ratio of 1 the selectivity increases. At a CH_4 flow rate of 8.5 ml/min, a decrease in oxygen flow rate has relatively little effect on either the CH_4 conversion or selectivity to C_2 hydrocarbons, although the values of the former are relatively small (3–5%). Under conditions of high CH_4/O_2 ratio deactivation of the catalyst was not observed.

The effect of on-stream times up to 6 hours is illustrated for $SrSO_4$ in fig. 5. As noted earlier in this report the conversion decreases after approximately 1

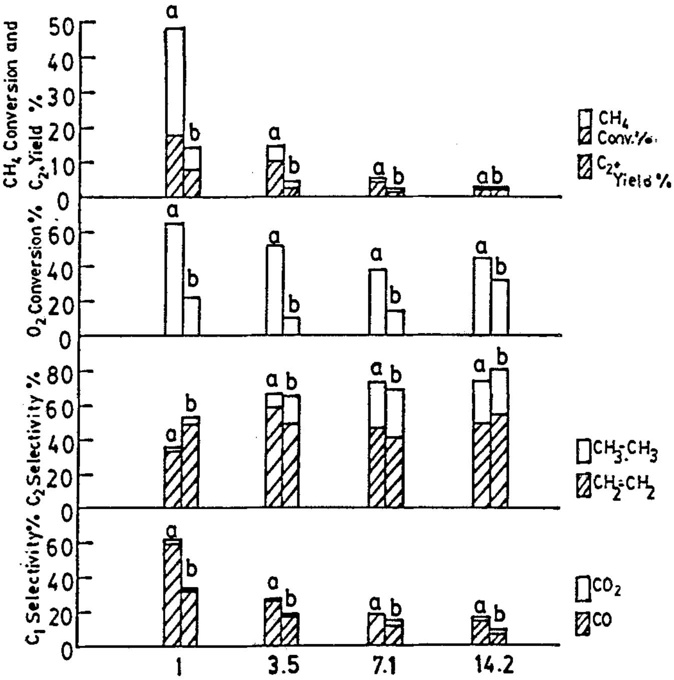

Fig. 4. Comparison of the conversion and selectivities on $SrSO_4$ for various CH_4/O_2 ratios. Conditions same as in fig. 3 except reaction temperature is 785°C.

$$\frac{CH_4}{O_2}=\frac{1.2}{1.2};\ \frac{4.2}{1.2};\ \frac{8.5}{1.2};\ \frac{8.5}{0.6};\ \frac{(\mathrm{ml/min})}{(\mathrm{ml/min})}.$$

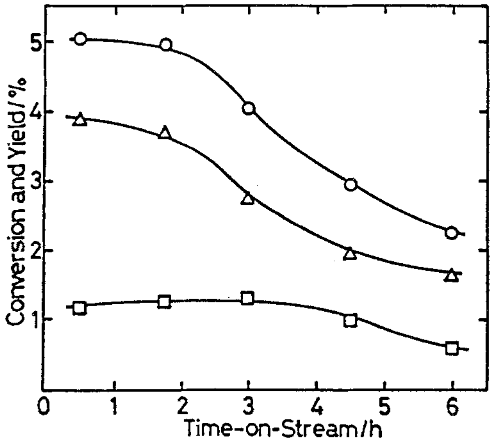

Fig. 5. Conversion and yields on $SrSO_4$ for various times-on-stream in the presence of TCM in the feedstream. Reaction temperature 785°C; other conditions as in fig. 2.

CH_4 conversion (○); C_{2+} yield (△); C_2 yield (□).

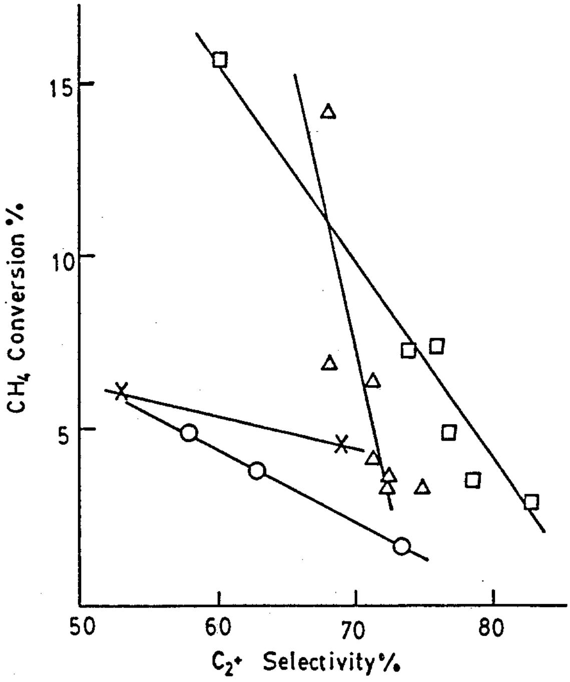

Fig. 6. Relationship between conversion and selectivities for Mg, Ca, Sr and Ba sulphates. Conditions same as in fig. 2 except data collected at 0.5 hr-on-stream. $MgSO_4$(○), $CaSO_4$(△), $SrSO_4$(□), $BaSO_4$(X).

hour on stream. However the C_{2+} selectivities remain approximately constant during this time.

As expected, the selectivity increases as the conversion decreases for each of the catalysts studied (fig. 6). However, the rates of such changes are evidently dependent on the sulphate being examined. With calcium sulphate the selectivity changes relatively little (68 to 73%) as the conversion decreases from 14 to 4%. In contrast, for a decrease in conversion from 5 to 2% observed with the magnesium catalyst, the selectivity changes from 58 to 73%.

In earlier work [16] experiments on oxides which had been exposed to TCM prior to use in the conversion of CH_4 and where TCM was subsequently absent from the feedstream provided evidence for the interaction of TCM with the catalyst, although not precluding the participation of TCM in a gas phase process. In the present work the effect of the presence of TCM in the feedstream on the conversions and selectivities observed with alkaline earth sulfates is quite different from that found earlier on the oxides [16] and phosphates [17]. Thus the present observations together with those reported earlier provide further evidence for the interaction of TCM with the catalyst, although at this time the nature of any species formed is not yet known.

As noted in the introduction the principal function of the catalyst is generally believed to be associated with the activation of methane. The dependence of

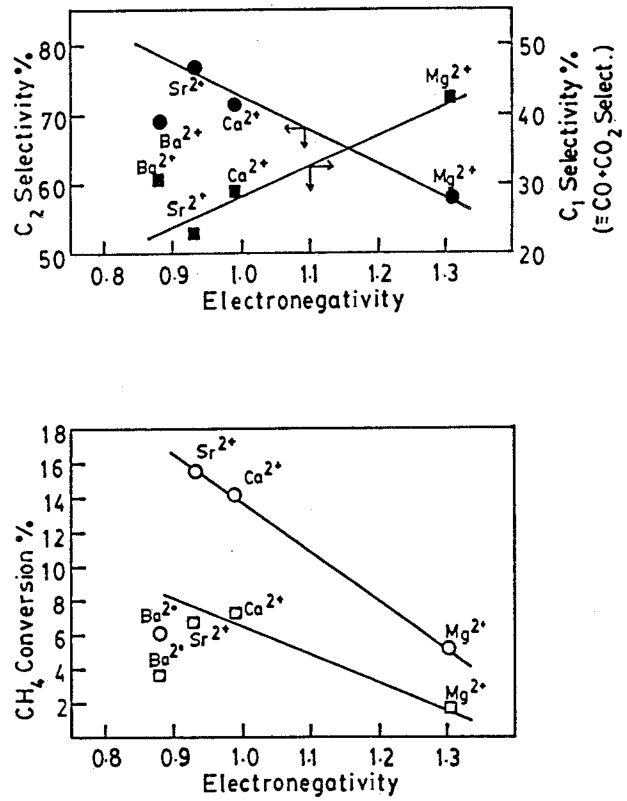

Fig. 7. Correlation of conversions and selectivities with electronegativity of the cations. Upper figure: Data correspond to 4–5% CH_4 conversions and 0.5 hr-on-stream in the presence of TCM. Electronegativities are those of Pauling. Reaction temperatures: $MgSO_4$ (835°C), $CaSO_4$ (750°C), $SrSO_4$ (785°C), $BaSO_4$ (800°C). C_{2+} selectivity (●); $C_1(CO+CO_2)$ selectivity (■). Lower figure: CH_4 conversion (835°C) with TCM (○) or without TCM (□).

both the conversion and selectivity on the electronegativity of the cation as observed in the present work appears to support this contention (fig. 7). The selectivity to C_{2+} hydrocarbons and the conversion of methane both increase as the electronegativity of the cation decreases. The perturbation of the electron density of the anion by neighbouring cations presumably decreases with decrease in the electronegativity of the cation and consequently the effective charge on the oxygen atoms of the sulfate anion should be higher for cations of lower electronegativity. This appears to be consistent with the ability of the oxygen atoms to assist in the dissociation of a C-H bond by perturbation of the electron density and the subsequent scission of the bond. These results may also be viewed as providing evidence in support of a heterolytic dissociation of the C-H bond of methane but this is, of course, not definitive. The increase in selectivity with decreasing electronegativity and the expected reciprocal relationship between the latter and the charge density on the anion and hence the facility for C-H bond dissociation also provides support, albeit indirect, for the suggested relationship between methyl radical concentrations and rates of C_{2+} hydrocarbon formation as expressed in eq. [1]. Finally the present results provide indirect evidence for C-H bond scission as the rate determining step.

Acknowledgement

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

References

[1] A. Ekstrom and J.A. Lapszewicz, J. Am. Chem. Soc. 110 (1988) 5226.
[2] P.F. Nelson and N.W. Cant, J. Phys. Chem. 94 (1990) 3756.
[3] G.S. Lane and E.E. Wolf, J. Catal. 113 (1988) 144.
[4] D.J.C. Yates and N.E. Zlotin, J. Catal. 111 (1988) 317.
[5] G.A. Martin, A Bates, V. Ducarme and C. Mirodatos, Appl. Catal. 47 (1989) 287.
[6] M. Hatano, P.G. Hinson, K.S. Vines and J.H. Lunsford, J. Catal. 124 (1990) 557.
[7] D.J.C. Yates and N.E. Zlotin, J. Catal. 124 (1990) 562.
[8] Z. Kalenik and E.E. Wolf, J. Catal. 124 (1990) 566.
[9] O.V. Buevskaya, A.I. Suleimanov, S.M. Aliev and V.D. Sokolovskii, React. Kinet. Catal. Lett. 33 (1987) 223.
[10] V.T. Amorebieta and A.J. Colussi, J. Phys. Chem. 92 (1988) 4576.
[11] N.W. Cant, C.A. Lukey, P.F. Nelson and R.J. Tyler, J. Chem. Soc., Chem. Commun. (1988) 766.
[12] A. Ekstrom and J.A. Lapszewicz, J. Chem. Soc., Chem. Commun. (1988) 797.
[13] P.F. Nelson, C.A. Lukey and N.W. Cant, J. Phys. Chem. 92 (1988) 6176.
[14] D.J. Driscoll and J.H. Lunsford, J. Phys. Chem. 89 (1985) 4415.
[15] J.A. Roos, S.J. Korf, R.H.J. Veehof, J.G. Van Ommen and J.R.H. Ross, Appl. Catal. 52 (1989) 131.
[16] S. Ahmed and J.B. Moffat, J. Catal. 125 (1990) 54, and references contained therein.
[17] T. Ohno and J.B. Moffat, Catal. Lett. 9 (1991) 23.