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KINETIC ISOTOPE EFFECTS IN METHANE COUPLING ON A REDUCIBLE OXIDE CATALYST

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Kinetic isotope effects in methane activation on a reducible $Na/MnO_x/SiO_2$ catalyst have been investigated. The results show that there is a kinetic isotope effect for the formation of C_2 products but not for the formation of CO_x products. These observations conflict with kinetic measurements of the rate of formation of C_2 products which appear to show that the reaction is second order with respect to the methane partial pressure. It is concluded that the rate determining step is activation of the C–H (or C–D) bond and that the apparent second order kinetics is an artefact of the kinetic analysis. The absence of a kinetic isotope effect in the formation of carbon oxides is discussed.

1. Introduction

A vast amount of research has been performed in recent years on the oxidative coupling of methane [1-4]. Many different types of oxide catalyst have been found to be effective for this reaction. These fall into two types, those in which the oxide is irreducible, and those in which one of the components is reducible. In the latter category are oxides such as Li/NiO [5-7] and alkali-promoted MnO_x catalysts [8-12].

The mechanism of methane coupling has been studied particularly on irreducible oxides and there is good evidence in this case for a process in which methane molecules are activated by the catalyst and methyl radicals released into the gas phase [1,13-18]. Secondary reactions, in which two methyl radicals combine to give ethane, or in which a methyl radical is oxidized to CO or CO_2 may then take place quite far away from the catalyst surface. Thus, Lunsford et al. [4] have detected methyl radicals downstream from a catalyst bed using a matrix isolation technique.

The kinetics of the methane coupling reaction have been investigated by several groups. Often the reaction appears to be first order with respect to the methane partial pressure, and this has been interpreted as being consistent with a reaction in which the rate determining step involves breaking of the C–H bond [19–21]. On the other hand, Hatano and Otsuka [7] have reported that the rate of ethane production is second order in methane partial pressure on a Li/NiO catalyst, and concluded that the rate determining step is coupling of methyl radicals on the surface of the catalyst.

Evidence concerning whether C–H bond breaking is the rate determining step may be obtained from kinetic experiments in which CH_4 is replaced by CD_4. On a number of irreducible catalysts a clear kinetic isotope effect has been observed [22–27]. It is not clear whether a similar effect exists for reducible oxides. However, the observation of second order kinetics for methane coupling on a Li/NiO catalyst appears to argue against C–H bond breaking being rate determining in this particular case [7]. The purpose of the present work is to investigate whether there is a kinetic isotope effect on a reducible oxide catalyst for which measurements of the rate of formation of ethane suggest second order kinetics [28].

2. Experimental

(a) CATALYST PREPARATION

The catalyst used was a sodium pyrophosphate modified manganese oxide on silica sample similar to that described by Sofranko et al. [10], (hereinafter referred to as $Na/MnO_x/SiO_2$). This was prepared by wet impregnation of a previously acid washed silica (Davison, 57, nominal surface area 300 m^2 g^{-1}) with an aqueous solution of Mn(II) acetate and sodium pyrophosphate. Excess water was removed by rotary evaporation. the catalyst was dried at 200 ° C for 4 h and then calcined in air at 750 ° C for 17 h. The nominal loading of sodium pyrophosphate was 5% and the Mn loading was 15%.

(b) KINETIC MEASUREMENTS

A catalyst sample (40 mg) was placed in a silica glass reactor (5 mm I.D.; length, 25 cm) and held in place with glass wool plugs. The gases used were methane, air and nitrogen (B.O.C. > 99.99%) and these were used without further purification. The flow of reactants was controlled by Negretti flow controllers to give a total flow of 60 cm^3 min^{-1} and the methane/O_2 ratio was adjusted as required. The activity and selectivity of the catalysts was measured over a range of temperatures by sampling the products with a gas sampling valve and injection into a Perkin Elmer 8410 GC fitted with a 2 m Poropak QS column. Analysis of carbon monoxide and carbon dioxide was made possible by using a catalytic reactor in the gas chromatograph, which converted these products to methane for detection by FID. The response factors for the various products were taken from literature values. The carbon mass balance was correct to within 2%.

(c) KINETIC ISOTOPE EXPERIMENTS

The kinetic isotope experiments were performed in a fixed bed quartz microreactor (I.D. 4 mm, length 25 cm), operated at atmospheric pressure, with a catalyst weight of 20 to 40 mg. The reaction conditions were typically $P(CH_4)$ or $P(CD_4) = 7.9$ kPa, $P(O_2) = 3.9$ kPa diluted in He with a total flow rate of 30 cm^3 min^{-1}.

For measuring the H/D isotopic effects, the mixture $CH_4/O_2/He$ was abruptly replaced by the equivalent $CD_4/O_2/He$ mixture and vice-versa. Gas analysis was made at the reactor outlet under steady-state conditions using automated gas chromatography (FID ant TCD detectors). The experiments were carried out at 750 ° C.

3. Results and discussion

Fig. 1 shows some results from the literature on the dependence of the rate of production of ethane from methane as a function of the partial pressure of methane, and compares these with some results obtained recently in one of our laboratories [28]. Fig. 1(a) shows that the rate of formation of ethane appears to be first order in methane on a Sm_2O_3 catalyst [21] and this is consistent with the observation of a kinetic isotope effect on catalysts of this type [22–27].

Fig. 1(b) shows the corresponding results obtained for a Li/NiO (reducible oxide) catalyst [7] and it appears that the order of reaction with respect to methane is higher than first order. A second order has been assumed in the original work [7] and this has been interpreted as evidence of a rate determining step in which two adsorbed methyl moities combine on the surface of the catalyst. We are not aware of any measurements using CD_4 which would show whether a kinetic isotope effect operates with a Li/NiO catalyst. If the reaction is second order with respect to methane there should be no kinetic isotope effect.

Fig. 1(c) shows some results obtained as part of the current work on a sodium promoted manganese oxide catalyst (also a reducible oxide system) [28]. The results appear to show a second order effect with respect to the partial pressure of methane, exactly equivalent to that reported by Hatano and Otsuka for a Li/NiO catalyst, as discussed above.

Table 1 shows the results obtained with our Na/MnO$_x$/SiO$_2$ catalyst in our kinetic measurements using CH_4 and CD_4 as reactants. Two points are clear from this work. First, there is a definite kinetic isotope effect in the rate of formation of ethane from methane. Second, there is no equivalent kinetic isotope effect in the reaction of methane to CO and CO_2. We shall consider these two points separately.

The existence of a kinetic isotope effect in the formation of ethane on our Na/MnO$_x$/SiO$_2$ catalyst indicates that the rate determining step is breaking of the C–H or C–D bond. This is not consistent with the results shown in fig. 1(c) which appear to show that the rate of formation of ethane is second order in methane partial pressure. However, as described elsewhere [28], it is possible to show that the kinetic results in fig. 1(c) are consistent with a first order reaction when account is taken of the need to regenerate the active centres.

The conclusion from the present work regarding the formation of ethane seems clear. A kinetic isotope effect is observed and this indicates that the rate determining step for our reducible oxide catalyst is C–H bond breaking, exactly the same as previously reported for irreducible oxide catalysts. Furthermore, since we observe an apparent second order with respect to the methane partial

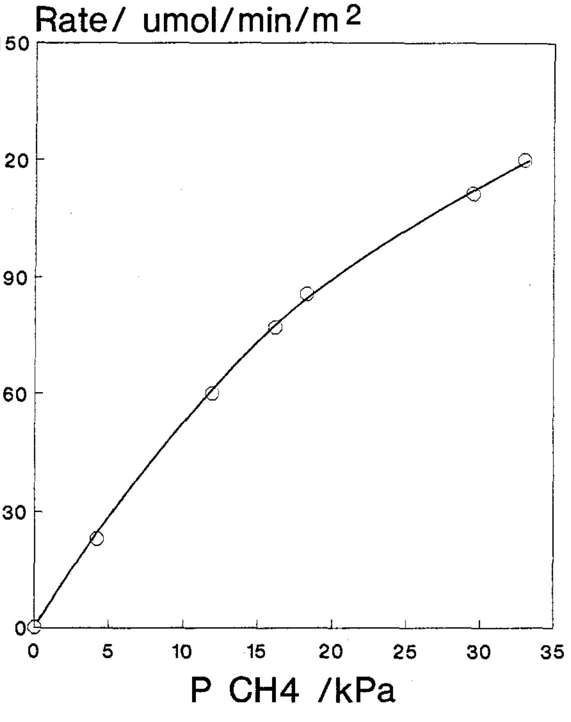

Fig. 1(a). The rate of formation of ethane as a function of methane partial pressure on Sm_2O_3, after ref. [21].

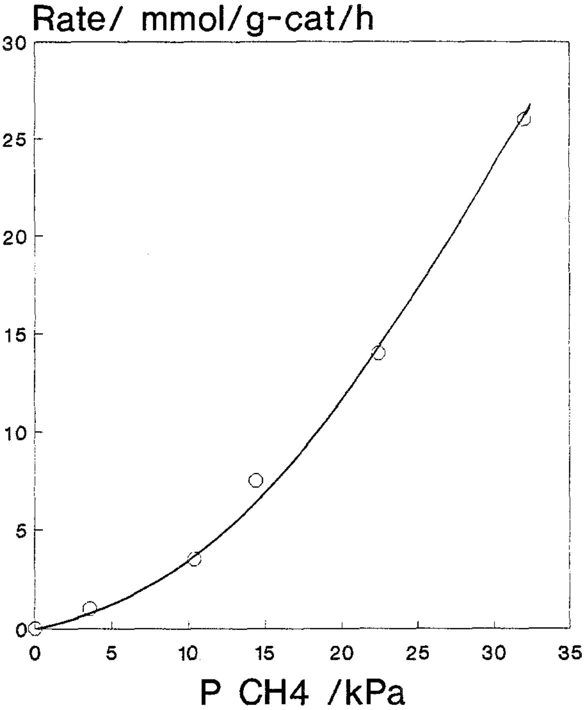

Fig. 1(b). The rate of formation of ethane as a function of methane partial pressure on a Li/NiO catalyst, after ref. [7].

pressure, similar to that reported by Otsuka et al. for Li/NiO, we are inclined to suggest that a similar interpretation may be applied to their results. A kinetic isotope effect may well be found for a Li/NiO catalyst also. Recently, Tong and Lunsford [29] have also produced evidence that the mechanism of ethane formation on a $LiNiO_2$ catalyst involves coupling of gas phase methyl radicals.

Finally, the fact that no equivalent kinetic isotope effect is observed for the conversion of methane into CO and CO_x requires some comment. One possible explanation for this is that on these reducible oxide catalysts there are two quite distinct types of site; one of which activates methane to release methyl radicals; the other activates methane but the methyl moiety formed is trapped in a strongly adsorbed state where it is much more likely to be oxidized rather than be released into the gas phase. A similar suggestion concerning the existence of two different types of active site has been made, for example, by Hatano and Otsuka. They have concluded that deep oxidation of methane occurs at NiO sites in their Li/NiO catalyst. Our results would be consistent with a model in which methane is fully oxidized on MnO_x sites. The activation of methane to release a methyl radical into the gas phase could occur at a Na-modified MnO_x site.

The existence of two quite different types of site is consistent with a number of other features of methane activation over this type of reducible oxide catalyst.

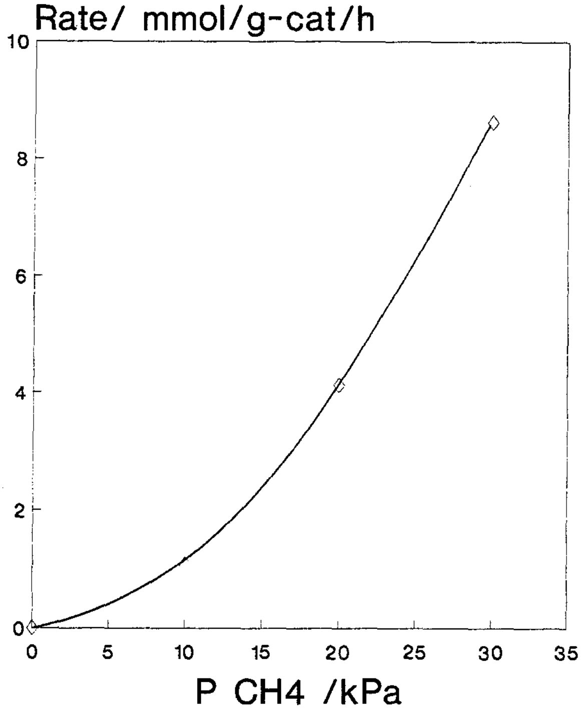

Fig. 1(c). The rate of formation of ethane as a function of methane partial pressure on a $Na/MnO_x/SiO_2$ catalyst, after ref. [28].

First, it is well established [30–32] that chlorine on the surface of Na/MnO_x severely inhibits total oxidation but has little effect on ethane formation. Furthermore, recent studies by Lambert and co-workers have indicated that in the presence of both alkali and chlorine a new type of surface oxygen species is created on a MnO_x surface [33]. Earlier work on chromium oxide from the same group had shown that chlorine eliminated one form of surface oxygen [34]. These experiments show that chlorine and/or alkali modify the surface of reducible oxides and could well explain the kinetic results observed in the present work.

An alternative model which would explain our kinetic results is one in which there is a single type of site, the character of which is modified when the temperature is increased. For example, a site at which adsorbed oxygen is in equilibrium with gas phase oxygen could function as a nonselective methane activation site (giving CO_2) when oxygen is adsorbed, but as a selective methane activation site (giving CH_3) when no oxygen is adsorbed at the site. The only substantial difference between the two models is in the detailed description of the two types of site.

In summary, this work has established that there is a kinetic isotope effect in the formation of ethane from methane over a reducible oxide catalyst. This shows that the rate determining step is C–H bond breaking and that the reaction is first

Table 1
The rate of reaction of CH_4 and CD_4 on a $Na/MnO_x/SiO_2$ catalyst at 750 °C

Reactant	t/h [a]	C_{CH_4} [b]	C_{O_2} [c]	S_{C_2} [d]	R_{CH_4}/R_{CD_4} [e]	$R_{C_2H_6}/R_{C_2D_6}$
CD_4 [g]	3.2	7.9	24.3	5.6		
					1.12	1.19
CH_4	3.8	8.9	22.9	5.9		
					1.15	1.29
CD_4	4.2	7.7	22.5	5.3		
					1.13	1.36
CH_4	4.8	8.8	22.4	6.3		
					1.18	1.34
CD_4	5.3	7.4	22.5	5.6		
					1.17	1.37
CH_4	5.9	8.7	22.4	6.3		
CD_4 [h]	6.0	12.1	37.5	3.1		
					1.06	1.49
CH_4	6.4	13.0	42.3	4.3		
					1.12	1.47
CD_4	6.8	11.5	37.4	3.3		
					1.13	1.53
CH_4	7.0	13.2	42.8	4.4		
					1.01	1.55
CD_4	7.5	12.9	32.8	2.9		
					1.00	1.61
CH_4	8.8	13.1	43.7	4.6		

[a] Time on stream.
[b] Total conversion of methane (%).
[c] Total conversion of oxygen (%).
[d] Selectivity to ethane.
[e] Ratio of rate of conversion of CH_4 and CD_4 to combustion products ($CO+CO_2$).
[f] Ratio of rate of conversion of CH_4 and CD_4 to ethane.
[g] Experiments performed on a fresh 20 mg sample of catalyst.
[h] Experiments performed on a used 40 mg sample of catalyst.

order in methane partial pressure. Kinetic results which appear to show a higher order in methane need to be interpreted in the light of this information.

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References

[1] J.S. Lee and S.T. Oyama, Catal. Rev. Sci. Eng. 30 (1988) 249.
[2] K. Otsuka, Sekiyu Gakakaishi (J. Jap. Petr. Soc.) (1987) 30.
[3] G.J. Hutchings, M.S. Scurell and J.R. Woodhouse, Chem. Soc. Rev. 18 (1989) 251.
[4] J.H. Lunsford, Catalysis Today 6 (1990) 235.
[5] K. Otsuka, Qin Liu, M. Hatano and A. Morikawa, Chem. Lett. (1986) 903.
[6] K. Otsuka, Qin Liu and A. Morikawa, Inorg. Chim. Acta 118 (1986) L23.
[7] M. Hatano and K. Otsuka, J. Chem. Soc., Faraday Trans. I, 85 (1989) 199.
[8] J.A. Sofranko, J.J. Leonard and C.A. Jones, J. Catal. 103 (1987) 302.
[9] C.A. Jones, J.J. Leonard and J.A. Sofranko, J. Catal. 103 (1987) 311.
[10] J.A. Sofranko, J.J. Leonard and C.A. Jones, A.M. Gaffney and H.P. Withers, Catal. Today 3 (1988) 127.
[11] R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 43 (1988) 105.
[12] R. Burch, S. Chalker, G.D. Squire and S.C. Tsang, J. Chem. Soc., Faraday Trans. 86 (1990) 1607.
[13] J.B. Kimble and J.H. Kolts, Energy Progress 6 (1986) 226.
[14] T. Ito and J.H. Lunsford, Nature (London) 314 (1985) 721.
[15] T. Ito, J.-X. Wang, C.-H. Lin and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 5062.
[16] C.-H. Lin, J.-X. Wang and J.H. Lunsford, J. Catal. 111 (1988) 302.
[17] D.J. Driscoll, W. Martin, J. Wang and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 58.
[18] D.J. Driscoll and J.H. Lunsford, J. Phys. Chem. 89 (1985) 4415.
[19] J.A. Roos, S.J. Korf, R.H.J. Veehof, J.G. Van Ommen and J.R.H. Ross, Appl. Catal. 52 (1989) 131.
[20] V.T. Amorebieta and A.J. Cloussi, J. Phys. Chem. 92 (1988) 4576.
[21] K. Otsuka and K. Jino, Inorganica Chimica Acta 121 (1986) 237.
[22] C.A. Mims, R.B. Hall, K.D. Rose and G.R. Myers, Catal. Lett. 2 (1989) 361.
[23] N.W. Cant, C.A. Lukey, P.F. Nelson and R.J. Tyler, J. Chem. Soc., Chem. Commun. (1988) 766.
[24] P.F. Nelson, C.A. Lukey and N.W. Cant, J. Catal. 120 (1989) 216.
[25] K. Otsuka, M. Inaida, Y. Wada, T. Komatsu and A. Morikawa, Chem. Lett. (1989) 1531.
[26] A. Ekstrom and J.A. Lapszewicz, J. Amer. Chem. Soc. 111 (1989) 8515.
[27] C. Mirodatos, A. Holmen, R. Mariscal and G.A. Martin, Catalysis Today 6 (1990) 601.
[28] R. Burch and S.C. Tsang, J. Chem. Soc., Faraday Trans I, accepted.
[29] Y. Tong and J.H. Lunsford, J. Chem. Soc., Chem. Commun. (1990) 792.
[30] R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 46 (1989) 69.
[31] R. Burch, E.M. Crabb, G.D. Squire and S.C. Tsang, Catal. Lett. 2 (1989) 249.
[32] R. Burch and S.C. Tsang, Appl. Catal., submitted.
[33] G.D. Moggridge, J.P.S. Badyal and R.M. Lambert, J. Phys. Chem. 94 (1990) 508.
[34] J. Foord and R.M. Lambert, Surf. Sci. 169 (1986) 327.