Methane partial oxidation to methanol over Ga_2O_3 based catalysts: use of the CH_4/D_2 exchange reaction as a design tool

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The CH_4/D_2 exchange reaction is used as an indication of methane activation over potential oxide catalysts; Ga_2O_3 exhibits an exchange rate over two orders of magnitude higher than other simple oxides and this approach leads to the identification of Ga_2O_3/MoO_3 as a selective catalyst for methane partial oxidation to methanol.

In recent years there has been considerable research attention directed to the identification of catalysts for the direct conversion of methane to more useful products. Most effort has been given to the oxidative coupling reaction,[1] but more recently there has been some success in the synthesis of catalysts active for the direct oxidation of methane to methanol.[2] At the high temperatures required to activate both methane and the oxidant, which in most cases is dioxygen, virtually all oxide surfaces display some activity[1] and hence the selection of suitable catalysts has been more on the basis of screening exercises than by scientific design. A number of approaches have been made concerning the identification of suitable catalysts[3] but, to date, none has proved to be useful in a predictive manner. We have now successfully addressed this problem and have used the CH_4/D_2 exchange reaction as an indication of methane activation over simple oxides, since the initial activation of methane and oxygen are key elementary steps in the overall oxidation process. The exchange reaction of methane and other hydrocarbons with deuterium has been extensively studied over many metals and is generally accepted to proceed *via* surface radical species.[4] However, the exchange reaction over oxides, which are the main components of oxidation catalysts, has received scant attention, and only minor attention has been given to γ-Al_2O_3,[5] chromium oxide gel,[6] La_2O_3,[7] TiO_2[8] and a range of oxides including MgO, CaO, SrO and BaO.[9] We have now made a detailed study of this reaction over simple oxides and in this communication we demonstrate the use of this reaction as a predictive catalyst design parameter.

Exchange experiments were carried out in a continuous flow microreactor and the origin of the oxide catalysts has been given previously.[10] Catalysts were tested in powdered form and were conditioned in the flow of methane and hydrogen at 540 °C for 2 h prior to testing. A methane : hydrogen ratio of 0.83 : 1 was utilised with a total gas hourly space velocity of 290 h^{-1}. The hydrogen flow into the reactor was then substituted *via* a switching valve with a carefully balanced flow rate of deuterium to minimise disruption in the flow. Pulses of deuterium (200 s duration) were introduced with methane to the catalyst. The exchange products were analysed on-line using a gas chromatograph mass spectrometer fitted with a quadrupole mass spectrometer unit. The empty silica reactor tube was shown to be inactive. Steady-state exchange rates were normally measured in the range 690–810 K. The rates for the most active oxides were measured at lower temperatures (Cr_2O_3, 640–720 K; ZnO, 620–670 K; Ga_2O_3, 560–600 K). All catalysts showed linear Arrhenius plots, with activation energies in the range 115–230 kJ mol^{-1}. The singly deuteriated species, CH_3D, was the major product in all cases, with CH_2D_2 being observed at high conversions. A comparison of a number of oxides is given in Fig. 1, which reports specific exchange activities at 773 K, obtained by extrapolation of the Arrhenius plots where necessary. The bulk oxides were studied by X-ray diffraction after use. Several formed hydroxide phases, including CaO, La_2O_3 and Nd_2O_3, whilst the oxides Fe_2O_3, Mn_2O_3 and V_2O_5 were reduced to the phases shown in Fig. 1. MoO_3 and WO_3 were also investigated, and formed oxygen-deficient shear structures such as $W_{25}O_{73}$; however, these were inactive for the exchange reaction.

Most noteworthy is that the rate of methane/deuterium exchange over gallium oxide is nearly two orders of magnitude higher than for any other oxide, with ZnO and chromia also showing high activity. Under our experimental conditions tantalum oxide, ceria and titania (Degussa P45, mixed anatase and rutile) showed the lowest measurable activity, while silica, niobia, Tb_4O_7 and Y_2O_3 were inactive. The results indicate that CH_3D was the primary product and the exchange process took place in a stepwise manner. This stepwise mechanism of exchange was also previously observed over Cr_2O_3,[5] and is very different from the simultaneous production of CH_3D, CH_2D_2, CHD_3 and CD_4 over metal catalysts. It is considered that the

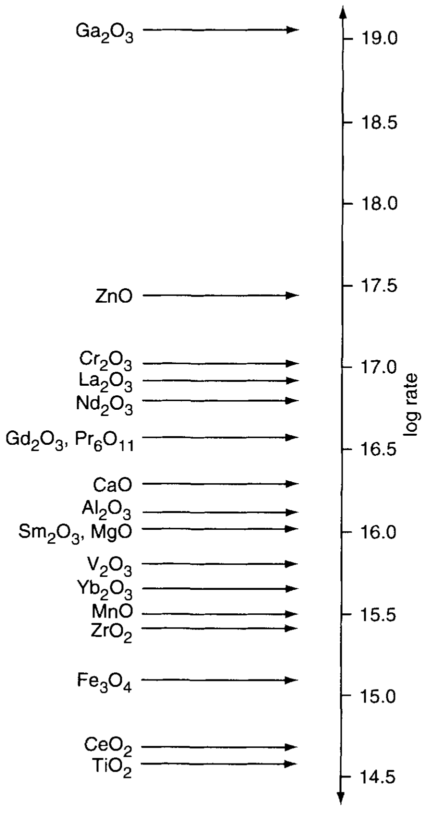

Fig. 1 Specific rates of the methane/deuterium exchange reaction over the indicated oxides at 773 K, in logarithmic form

Table 1 Results of methane oxidation experiments at 728 ± 5 K (measurements were made at 15 bar with $CH_4 : O_2 : He$ ratios of 23 : 3 : 5 at GHSV = 5000 h^{-1})

		Selectivity (%)				
Catalyst	Methane conversion (%)	CH_3OH	CO	CO_2 CO_2	C_2H_6	Relative methanol yield (per pass)
Quartz chips	0.1	—	—	100	—	—
Ga_2O_3	1.5	3	27	68	2	5
MoO_3	1.0	7	75	18	—	7
Ga_2O_3/MoO_3	3.0	22	50	27	1	66

mechanism of exchange over the more basic oxides proceeds *via* an anionic intermediate[8] and this accounts for the significant differences between metals and oxides for this reaction.

The high activity demonstrated by Ga_2O_3 and ZnO is of significance since both these oxides are the preferred catalysts components together with H-ZSM-5 for the aromatisation of propane and butane in the Cyclar process.[11] The identification of the high CH_4/D_2 exchange rate gives some background to the origin of their catalytic efficacy since Ga_2O_3 and ZnO are considered to play a key role in the initial activation of the alkane by polarising a C–H bond.[12] On the basis of these findings we considered that Ga_2O_3 could be a useful component of selective methane oxidation catalysts. Previously we have studied the stability of methanol towards oxidation at elevated temperatures over oxides and have shown that a correlation exists between the rate of methanol oxidation and the rate of its $^{18}O_2/^{16}O_2$ exchange reaction.[10] From these studies we identified MoO_3 as an oxide for which methanol was reasonably stable, but was known to activate dioxygen.[13] To test the hypothesis that Ga_2O_3 would improve methane activation when used as a catalyst component, a physical mixture of Ga_2O_3 and MoO_3 (mole ratio 1 : 1) was prepared by grinding the oxides together followed by calcination [650 °C, 3 h]. X-Ray diffraction analysis and other characterisation methods did not indicate that any significant changes in the oxides had occurred on calcination. Ga_2O_3, MoO_3 and the Ga_2O_3/MoO_3 physical mixture were then used separately as methane oxidation catalysts in a silica-lined stainless-steel microrector at 15 bar using a reaction mixture of $CH_4 : O_2 : He = 23 : 2 : 5$ with a total gas hourly space velocity of 5000 h^{-1}. The experimental results are shown in Table 1 and it is clear that although both Ga_2O_3 and MoO_3 exhibit low methanol selectivities, the Ga_2O_3/MoO_3 physical mixture significantly enhances the rate of methanol formation. In this way the simple physical mixture of the two oxides has combined beneficially the characteristics of both oxides.

At this stage we have made no attempt to optimise the use of Ga_2O_3 as a catalyst component, but it is clear that the incorporation of Ga_2O_3, and possibly also ZnO and Cr_2O_3, in catalyst formulations could lead to the design of novel high activity catalysts for the partial oxidation of methane.

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