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The partial oxidation of methane to methanol: An approach to catalyst design

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Abstract

In this study a new approach for the design of catalysts for methane partial oxidation to methanol is outlined and results arising from this approach are discussed. The approach involves identifying metal oxide catalyst components which activate methane and oxygen, but do not readily destroy methanol, the desired product. A series of catalysts based on MoO_3 and WO_3 were prepared by impregnation with solutions containing the metal ions of the second component. The Cu/MoO_3 catalyst showed a selectivity advantage over the homogeneous gas phase oxidation in a reactor bed packed with quartz chips. In general, the WO_3 based catalysts were less effective for the production of methanol. Additionally, catalysts composed from physical mixtures of Ga_2O_3 and ZnO with MoO_3 were prepared. The Ga_2O_3/MoO_3 catalyst showed a maximum methanol yield greater than the homogeneous gas phase reaction over an inert bed of quartz particles. The increased methanol yield was attributed to a synergistic effect combining the beneficial reactivities of the MoO_3 and Ga_2O_3 component oxides. Comparison with data obtained from an empty reactor tube showed that none of the catalysts were as active or selective for methane partial oxidation to methanol. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The identification of catalysts showing high activity and selectivity for the direct partial oxidation of methane to methanol and formaldehyde is a major research aim. Many different catalyst systems have been investigated and varying degrees of success have been achieved, however, to date none have demonstrated outstanding performance [1,2]. Generally, catalysts operate under conditions where gas phase homogeneous reactions are more effective and the partial oxidation products are unstable. Based on the hydrogen balance current kinetic models predict a limiting selectivity of 67% methanol for the homogeneous process [3]. It is against this background that new approaches for the development of more effective catalysts are required. In this paper we describe an approach to design new catalysts for the demanding methane partial oxidation reaction. The approach which has been adopted is an attempt to combine components with known methanol combustion, methane activation and oxygen activation properties in the final catalyst formulation. The majority of catalysts used for methane partial oxidation are metal

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oxides and we have investigated the activation processes over a wide range of single metal oxides. The activation of the desired product, methanol, was probed by studying its oxidation and it is argued that a suitable catalyst component must not readily destroy methanol under reaction conditions. The activation of methane was investigated by studying the rate of methane/deuterium exchange. Oxygen activation was characterised by $^{16}O_2/^{18}O_2$ exchange, which has previously been extensively studied. Thus simplistically, it can be imagined that synergistic combinations may exist in which one component is principally responsible for methane activation and the other for oxygen activation/insertion. This type of approach is not without precedent, as one of the currently accepted views of the mode of operation of the bismuth molybdate SOHIO catalyst for propene oxidation and ammoxidation is that the bismuth component is responsible for hydrocarbon activation whilst the molybdenum component effects oxygen activation and insertion [4].

2. Experimental

Experiments to determine methanol stability were performed in a conventional microreactor with the catalyst held in a fused silica reactor tube. A methanol/oxygen/helium feed in the ratio 1/4/12, with a gas hourly space velocity (GHSV) in the region of 12 000 h^{-1} were used. Methanol stability was determined in the temperature range from 100°C to 520°C at atmospheric pressure.

A low dead volume isotope pulsing reactor was designed for methane/deuterium exchange studies. Exchange was monitored using a Varian GC and a Hiden quadrupole mass spectrometer. Studies were carried out at atmospheric pressure with a 1/1.2 methane/deuterium ratio and 700 h^{-1} gas hourly space velocity.

The exchange of $^{16}O_2/^{18}O_2$ isotopes with oxide surfaces has been extensively studied by Winter [5,6] and Boreskov [7] in the 1950s and 1960s. We have therefore utilised these results, concentrating on the work of Winter, although in general, agreement between the two research groups is excellent.

Catalytic activity for methane partial oxidation was studied in a fused silica lined stainless steel microreactor operator at 15 bar pressure. The reactant feed consisted of methane/oxygen/helium in the ratio 23/3/5 and a constant gas hourly space velocity of ca. 5000 h^{-1}. Product and reactant analysis was made using a Varian GC–MS.

A series of catalysts based on MoO_3 and WO_3 were prepared, a second component was added by impregnation of the base oxides to incipient wetness with metal salt solutions. The catalysts produced were denoted as M/MoO_3 and M/WO_3 with a molar ratio of impregnating metal to base oxide of 25 mol%. The resultant materials were dried at 110°C for 2 h, ground and calcined at 560°C for 4 h before use. Catalysts consisting physical mixtures of Ga_2O_3 and ZnO with MoO_3 were also prepared. These catalysts were denoted Ga_2O_3/MoO_3 and ZnO/MoO_3 and were prepared by grinding the oxides in a 1/1 Mo/M, (where M=Ga or Zn), molar ratio in a large mortar and pestle for 20 min. The resulting finely divided powder was calcined in a fused silica boat in static air at 650°C for 3 h. The calcined sample was ground for a further 20 min before use. The single oxides tested were used as supplied by Aldrich [8].

3. Results and discussion

The wide range of oxides screened exhibited vastly differing reactivities for methanol oxidation. In order to assess the stability of methanol over the candidate oxides the materials were ranked according to the temperature at which 30% of the methanol in the reactor feed was converted to carbon oxides [8]. Methanol was most stable over the oxides MoO_3, WO_3, Nb_2O_5, Ta_2O_5 and Sb_2O_3, whilst it was readily destroyed by CuO and Cr_2O_3. With the exception of Sb_2O_3 the conversion of methanol over these catalysts was relatively high, however, high selectivity to the partially oxidised products formaldehyde and dimethylether were observed. These products were not considered wholly undesirable by-products during a methane oxidation process. The full results from methanol oxidation studies have been discussed previously [8].

The methane/deuterium exchange rates have been previously published [9]. The exchange operated via a sequential mechanism and the primary product was CH_3D. The most active oxide for the exchange reaction was Ga_2O_3, showing a rate several orders of magnitude greater than all other materials. ZnO also exhibited high activity for the exchange reaction and it is interesting to note that both elements show high activity for alkane activation, such as aromatisation processes of short chain alkanes, in combination with MFI type zeolites [10]. The exchange may take place by a single or combination of mechanisms, not all of which are relevant to methane partial oxidation, however, the general reactivity towards alkane activation is valid.

The exchange of gaseous oxygen isotopes with metal oxides is a technique which has been extensively studied. We have not repeated these studies as a large library of data already exists, therefore, we have utilised these data in our catalyst design process, particularly concentrating on the studies published by Winter [5,6]. The exchange reactions may take place by one, or a combination, of reaction mechanisms. Homomolecular exchange (R_0) is exchange catalysed by the oxide surface, but does not involve exchange with oxygen of the oxide lattice. Exchange of lattice oxygen with the gas phase can also take place via mechanisms denoted as R_1 and R_2 which are numbered in accordance with the number of lattice oxygen species participating in the exchange process. The oxides MoO_3, V_2O_5 and WO_3 showed exchange of the whole of the lattice oxygen with the gas phase. The diffusion of oxygen throughout the lattice of these solids was faster than the surface exchange, which was therefore the rate determining process. The exchange mechanism for these oxides operated by a combination of R_1 and R_2 processes. For use in this study the process of oxygen exchange over these oxides was called R_3. A broad range of oxygen exchange activity spanning many orders of magnitude was observed [5]. The most active oxide was CuO followed closely by Mn_2O_3, whilst SiO_2 and GeO_2 were inactive.

The catalysts prepared and tested for methane partial oxidation have been formulated on the basis of the previously described results for the activation of methane and oxygen and the destruction of methanol. The oxides MoO_3 and WO_3 were selected as base oxides for catalyst formulation for several reasons. Firstly, methanol was relatively stable over both oxides, and selective oxidation products, mainly formaldehyde, were predominant. MoO_3 and WO_3 also show moderate activity for heterolytic oxygen exchange which operates by an R_3 type mechanism involving complete exchange of the bulk lattice oxygen with the gas phase. This indicates that oxygen mobility throughout the lattice is a facile process, the lability of such oxygen is an important concept for selective oxidation catalysts [11]. The virtual mechanism developed by Dowden et al. [12] for methane partial oxidation has also suggested that MoO_3 should demonstrate oxygen insertion ability by virtue of its n-type semiconductivity. Molybdenum trioxide has been extensively studied for methane partial oxidation in unsupported [13] and supported form [14,15] and in conjunction with additional catalyst components [16]. Tungsten trioxide has been less well studied than MoO_3 for methane partial oxidation, but it has been recommended for inclusion in methane partial oxidation catalyst formulation [12] and has shown relatively high activity for the production of formaldehyde from methane at atmospheric pressure and 685°C [17].

A range of components have been added to the base oxides to produce the final catalysts. These components are the oxides of gallium, vanadium, iron, cobalt and copper. Gallium oxide, Ga_2O_3, was selected for its high activity for methane activation demonstrated by the deuterium exchange studies, ZnO was also selected for the same reason. V_2O_5 has been reported to possess a heterolytic oxygen exchange mechanism similar to MoO_3 and WO_3 [5]. It is also a well-known oxidation catalyst which has been studied for methane partial oxidation in supported form [18], V^{5+} has also been predicted to exhibit dehydrogenation and oxygen insertion properties which are important factors identified by Dowden et al. [12] for selective methane oxidation in his virtual mechanism.

Iron is selected for several reasons, firstly in our design approach Fe_2O_3 shows mid range activity for oxygen exchange and methanol stability. The methane/deuterium exchange rate over iron oxide was one of the lowest measured although the oxide was reduced from Fe_2O_3 to Fe_3O_4 during use. In the literature iron oxide is also an important component of many methane partial oxidation catalysts, its use in catalyst formulation is diverse and examples of the types of systems used are $MoO_3/Fe_2O_3/SiO_2$ [19], Cu/Fe/ZnO [20], Fe-sodalite [21], Cu/Fe/ZSM-5 [22], $(MoO_3)_3{\cdot}Fe_2O_3$ [23], FeNbO [24] and Fe/SiO_2 [25].

Cobalt oxide, Co_3O_4, showed intermediate performance for methanol stability, it has been reported to show very high activity for homomolecular oxygen exchange [7] and unstable during studies to determine heterolytic oxygen exchange [5]. It is also interesting to include Co_3O_4 in the study as generally it is recognised as one of the most active oxides for combustion reactions [26]. The last component used for catalyst preparation is CuO. Copper oxide has the highest oxygen exchange rate and readily destroyed methanol to carbon oxides. Dowden et al. [12] have suggested that Cu^{2+} is a good component for methane activation due to its dehydrogenation activity. Copper has also been reported to be an effective catalyst component particularly in conjunction with iron [20,22] and also in other systems such as $CuO{\cdot}MoO_3$ [16].

It is important to consider the activity of catalytic methane oxidation with respect to the homogeneous gas phase oxidation. The homogeneous gas phase oxidation was investigated in the empty reactor tube and a reactor packed with a quartz bed (Table 1).

Table 1
Results for methane oxidation

Catalyst	Temperature (°C)	CH_4 conversion (%)	Selectivity (%)					CH_3OH *per pass* yield
			CH_3OH	HCHO	CO	CO_2	C_2H_6	
MoO_3	450	0.3	11	—	72	17	—	0.04
	500	1.2	—	—	73	23	2	0
Cu/MoO_3[a]	450	0.6	19	14	60	7	—	0.11
	500	4.2	—	—	40	59	1	0
Co/MoO_3[a]	450	0.5	14	—	47	39	0	0.07
	500	2.9	—	—	62	36	2	0
Fe/MoO_3[a]	450	0.5	14	—	69	17	—	0.07
	500	3.9	—	—	65	33	2	0
V/MoO_3[a]	450	0.6	—	—	79	21	—	0
	500	0.6	—	—	68	28	4	0
Ga/MoO_3[a]	450	1.3	10	—	77	13	—	0.13
	500	3.2	—	—	69	30	1	0
WO_3	450	0.5	6	—	18	76	—	0.03
	500	0.4	—	—	33	67	—	0
Cu/WO_3[a]	450	0.3	—	—	—	100	—	0
	500	0.4	—	—	25	75	—	0
Co/WO_3[a]	450	1.2	—	—	53	47	—	0
	500	0.4	tr.	—	39	61	—	0
Fe/WO_3[a]	450	0.2	tr.	—	33	67	—	0
	500	0.6	tr.	—	74	26	—	0
V/WO_3[a]	450	0.8	16	—	60	24	—	0.08
	500	1.2	—	—	83	15	2	0
Ga/WO_3[a]	450	0.4	11	—	16	73	—	0.04
	500	1.8	—	—	85	15	—	0
Ga_2O_3/MoO_3[b]	455	3.0	22	—	50	27	1	0.66
	500	3.1	—	—	62	33	5	0
ZnO/MoO_3[b]	450	0.4	—	—	26	74	—	0
	500	3.6	—	—	64	44	2	0
Ga_2O_3	450	1.5	3	—	27	68	2	0.05
	500	3.1	—	—	28	70	2	0
Quartz packing	450	0.4	—	—	68	32	—	0
	475	3.5	15	—	70	13	2	0.53
	500	3.5	15	—	68	17	3	0.44
Empty tube	450	8.1	29	—	63	7	1	2.34
	500	8.0	19	—	68	7	6	1.52

$CH_4/O_2/He=23/3/5$, 15 bar, GHSV=5000 h^{-1}.

[a] Prepared by impregnation.

[b] Prepared by physical mixture.

Comparison with the quartz bed is especially valuable for the evaluation of catalyst performance as quartz is generally accepted as inert for the reaction and the use of equivalent bed volume and sieving fraction means that residence times and heating profiles will be similar. In the empty reactor tube both methane conversion and methanol selectivity are greater than the quartz bed. This trend in conversion can be related to the residence time within the reactor heated zone which is lower for the quartz chips since the void volume is reduced. Generally, it would be expected that methanol selectivity would be higher at lower conversion, however, the partial pressure of oxygen and the increased heated surface area within the quartz bed may favour methanol combustion, thus reducing selectivity. Carbon monoxide is the predominant product in both cases showing selectivity in excess of 60%. In the literature it is frequently the case that methane oxidation in the empty reactor tube is used for comparison with catalytic data. However, we consider the comparison with the inert quartz bed is a more valid scientific comparison against which catalyst performance should be judged.

The results for methane oxidation over the molybdenum oxide series of catalysts prepared by impregnation are presented in Table 1. Selectivity to methanol was shown by all the MoO_3 based catalysts and MoO_3 with the exception of V/MoO_3. The order of methanol selectivity at 450°C was

$$\begin{aligned}&Cu/MoO_3 > Fe/MoO_3 > Co/MoO_3\\&\qquad > Ga/MoO_3 > MoO_3.\end{aligned}$$

The selectivity comparison at 450°C is made at different levels of methane conversion, which may have an influence on methanol selectivity, however, conversions were broadly similar in magnitude. The major product under these conditions was CO. The Cu/MoO_3 catalyst also produced formaldehyde with a selectivity of 14%, resulting in a combined C_1 oxygenate selectivity of 33%, which was over twice that of Fe/MoO_3. None of the other molybdenum catalysts tested produced formaldehyde.

The MoO_3 impregnated catalysts showed low conversion (<0.2%) at 400°C, comparison of methane conversion at 450°C revealed the following order:

$$\begin{aligned}&Ga/MoO_3 > MoO_3 > V/MoO_3 \approx Cu/MoO_3\\&\qquad > Co/MoO_3 \approx Fe/MoO_3.\end{aligned}$$

The addition of gallium to the MoO_3 base oxide increased the methane conversion and is consistent with the high activity of Ga_2O_3 to activate methane. The addition of vanadium, copper, cobalt and iron suppressed methane conversion relative to MoO_3.

Comparison with the homogeneous gas phase oxidation over the quartz material shows that at 450°C the molybdenum oxide based catalysts increased methane conversion, and with the exception of V/MoO_3, they also increased the selectivity towards methanol. Above 450°C the quartz bed was more active and produced higher methanol selectivity than any of the MoO_3 systems. Nevertheless, the combined selectivity for methanol and formaldehyde over the Cu/MoO_3 catalyst at 450°C was greater, albeit at lower conversion, than the quartz bed or the empty reactor tube. It is clear by comparison with the quartz bed data that gas phase reactions become dominant above 450°C and any selectivity advantage offered by the catalyst is lost. It is also evident that any validity of the design approach is lost once the influence of surface heterogeneous reactions are diminished.

Characterisation of the catalysts by X-ray diffraction indicated that the MoO_3 catalysts impregnated with copper, cobalt and iron salts formed mixed phases. These were $CuMoO_4$, $CoMoO_4$, $Fe_2Mo_{3-5}O_{12-15}$ and $Fe_2(MoO_4)_3$, respectively. The catalyst impregnated with gallium and vanadium showed no detectable formation of any mixed phases and the predominant phase was MoO_3.

The results for methane oxidation over the tungsten oxide catalysts prepared by impregnation are also shown in Table 1. Selectivity towards methanol was also shown by some of the tungsten oxide based catalysts, the order of methanol selectivity at 450°C is given by

$$V/WO_3 > Ga/WO_3 > WO_3$$

The methanol selectivity over V/WO_3 was 16%, this decreased to zero at 500°C, but increased to 5% at 550°C. The catalysts Co/WO_3, Cu/WO_3 and Fe/WO_3 did not show any methanol selectivity at 450°C. Comparison with the quartz bed shows that the catalysts V/WO_3, Ga/WO_3 and WO_3 showed a selectivity advantage at 450°C but this was no longer the case when the reaction temperature was increased to 500°C. Comparison of the reactivity of the empty reactor tube showed that there was no advantage in using any of the tungsten oxide based catalysts. Methane conversion over the WO_3 based catalysts were broadly similar to those over the MoO_3 catalysts, although in general terms the WO_3 catalysts exhibit lower selectivity to methanol. The product distributions from WO_3 catalysts were also different from the MoO_3 catalysts, particularly at lower temperatures as the WO_3 catalysts showed higher CO_2 selectivity. The influence of reaction temperature on CO and CO_2 selectivity was opposite over the two catalyst systems, as generally CO_2 selectivity decreased with increasing temperature over WO_3 whilst it increased over MoO_3 catalysts. The origin of these effects are not clear but it may be that the water gas shift reaction is more significant in the presence of WO_3. The CO_2 selectivity over Cu/MoO_3 and Co/MoO_3 were also relatively high and it is possible that sequential CO oxidation takes place readily, especially as the oxides CuO and Co_3O_4 are the most active for the oxidation of CO to CO_2 [27]. Another general difference between the WO_3 and MoO_3 catalyst is that the WO_3 catalysts did not produce any higher C_2 hydrocarbons, with the exception of Ga/WO_3 at 550°C.

Powder X-ray diffraction studies of the catalysts showed that the cobalt and iron impregnated WO_3 catalysts formed the mixed oxide phases, $CoWO_4$ and $FeWO_4$ (Ferberite). The catalysts containing copper, vanadium and gallium exhibited only diffraction peaks from WO_3, which was identified with monoclinic and triclinic crystal systems.

In terms of activity, it is difficult to rationalise methane conversion in relation to the probe reactions. Furthermore, the differences in relative orders of activity between the MoO_3 and WO_3 catalyst series provides further difficulties to rationalise the data. This may be a consequence of the mixed phase formation which has been identified for many of the impregnated systems.

The activity of the catalysts for methane oxidation prepared by impregnation of the MoO_3 and WO_3 base oxides are somewhat disappointing. We have also prepared dual component catalysts by physically mixing Ga_2O_3 with MoO_3 and ZnO with MoO_3. This method of catalyst preparation was adopted as it envisaged that a greater degree of control over the final structure can be retained compared to catalysts prepared by impregnation. There is also precedent for the preference of this catalyst preparation method as MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts prepared by a physical mixing in a ball mill were more selective for methane partial oxidation than analogous catalysts prepared by impregnation of the SiO_2 [28].

Characterisation of the physically mixed catalyst by powder X-ray diffraction showed no detectable formation of a mixed phase for the Ga_2O_3/MoO_3 catalyst whilst the phase $ZnMoO_4$ was identified from the ZnO/MoO_3 mix.

The results of methane oxidation by the physically mixed catalysts and Ga_2O_3 are presented in Table 1. The Ga_2O_3/MoO_3 catalyst produced the highest maximum yield of methanol which was greater than that over the quartz packing by approximately 25%. The maximum methanol yield from the quartz packing was observed at 500°C, 45°C higher than for the oxide catalysts. Comparison with the activity of the empty reactor tube showed that methanol yields were higher in the absence of any packing, indicating that homogeneous gas phase reactions were important for methanol production. However, as discussed previously, we consider that the catalytic activity should be considered against the homogeneous methane oxidation activity of the quartz chips bed. $ZnMoO_4$ did not produce any methanol under the conditions used in these studies. The methanol yields over MoO_3 and Ga_2O_3 were also very low in comparison to the quartz packing and Ga_2O_3/MoO_3 catalyst. Methane oxidation over MoO_3 showed that the oxide was relatively selective for methanol, whilst Ga_2O_3 was more active, showing a much higher methane conversion. These observations are consistent with the high activity for methane activation of Ga_2O_3, as discussed previously in relation to methane/deuterium exchange, and the oxygen exchange mechanism and the selective oxidation function exhibited by MoO_3 during methanol oxidation studies. Both of these aspects were beneficially combined for methane partial oxidation by the physically mixed Ga_2O_3/MoO_3 system. These benefits were the high activity of Ga_2O_3 and the selective oxidation function of MoO_3. The increased yield of methanol over the homogeneous gas phase reaction in the quartz packed reactor suggests that there was the development of a synergistic effect between the two phases. Such an effect can be envisaged by considering the bifunctional nature of the catalyst.

The Ga_2O_3 component could provide the methane activation function to produce a surface methyl activated species. Such species have been identified by infrared spectroscopy and their mobility on catalyst surfaces confirmed [29]. Surface methyl species can migrate to sites on the MoO_3 phase responsible for oxygen insertion, subsequently leading to the formation of methanol. The intimate mix of the two component oxides provides many phase boundaries at which these processes can operate. The exact nature of the oxygen insertion sites on MoO_3 is unclear, however, M=O species on MoO_3 surfaces have been proposed as active sites for methane partial oxidation to formaldehyde at atmospheric pressure [30]. The same type of M=O sites have also been proposed as important for other selective oxidation reactions [31]. The migration of the surface methyl species to this site could lead to the insertion of oxygen to form a surface methoxy species. The desorption of this species to the gas phase may then be a relatively facile process as the diffusion of oxygen throughout the MoO_3 lattice to regenerate the surface M=O site would be rapid [5]. The regeneration of such surface sites by bulk lattice oxygen has been previously proposed for selective methane oxidation on MoO_3 [30]. The production of methanol from a methoxy precursor has also been proposed as an important mechanistic step by other research groups [32,33]. The production of methanol from the methoxy species can subsequently take place either via the release of the methoxy radical to the gas phase or via a surface reaction by abstraction of a surface hydrogen source followed by desorption of the product. Co-operative effects in catalysis have often been attributed to the formation of a new phase which is more active or selective than the individual phases [34]. Characterisation of the Ga_2O_3/MoO_3 catalyst by powder X-ray diffraction and X-ray photoelectron spectroscopy before and after use did not reveal any evidence for the formation of a new mixed oxide phase.

Homogeneous gas phase reactions are clearly important for the production of methanol during methane oxidation. Under the conditions for maximum methanol per pass yield over Ga_2O_3/MoO_3 the quartz packing only showed trace methane conversion with no selectivity to methanol. It is difficult to assess the contribution, if any, of gas phase reactions in the presence of the Ga_2O_3/MoO_3 catalyst which may to some extent initiate gas phase reactions at a lower temperature. It is clear however, that the catalyst plays an important role in producing the increased methanol yield at lower temperatures.

4. Conclusions

Catalyst systems based on MoO_3 and WO_3 prepared by impregnation with copper, cobalt, iron, vanadium and gallium were prepared and tested for methane partial oxidation to methanol. In general, the MoO_3 based catalysts showed better performance than the WO_3 materials. Comparison with the homogeneous gas phase reaction in a quartz packed reactor showed that the Cu/MoO_3 catalyst had a selectivity advantage for methanol production at 450°C and the combined selectivity to methanol and formaldehyde was greater than the homogeneous reaction in an empty reactor tube.

In an extension of the approach catalysts were prepared by physically mixing the oxide components, these were Ga_2O_3/MoO_3. The ZnO/MoO_3 catalyst formed the mixed oxide phase $ZnMoO_4$ after calcination, whilst no mixed phase formation was observed for the Ga_2O_3/MoO_3 catalyst. The Ga_2O_3/MoO_3 catalyst which has been developed from the design approach has shown an increased yield of methanol when compared to the homogeneous gas phase oxidation of methane in a quartz packed reactor. This increased yield has been attributed to a co-operative effect which can be explained from results of the individual activation steps. The results presented in the present study emphasise the validity of the approach that has been adopted. However, comparison with the homogeneous reaction in the empty reactor tube showed that the use of any catalyst was deleterious [35].

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