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Designing oxidation catalysts

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Abstract

A simplified approach is described for the design of oxidation catalysts. It is based on three components and for selective oxidation the approach involves identifying catalysts that (a) do not catalyse the oxidation of the required product under the reaction conditions to be tested, (b) activate the oxidant and (c) activate the substrate. This approach is initially demonstrated to identify components of novel methane oxidation catalysts for the formation of methanol. The approach seeks to identify oxides that are capable of activating methane and oxygen, but do not destroy methanol, the desired product. From the perspective of methanol stability the oxides MoO_3, Nb_2O_5, Ta_2O_5 and WO_3 all produced high methanol conversion, however, high selectivities towards formaldehyde and dimethylether were obtained, with only low levels of carbon oxides throughout the range of conversions. The products formaldehyde and dimethylether were desirable by-products from a methane partial oxidation process, hence these oxides are considered to be suitable catalyst components. The activation of oxygen was probed using the $^{16}O_2/^{18}O_2$ exchange reaction. The activation of methane has been probed by the exchange reaction with deuterium under non-oxidative conditions. The most active catalyst was Ga_2O_3 which exhibited normalised exchange rates several orders of magnitude greater than the other catalysts.

On the basis of these results we tested a simple two component oxide catalyst for methane partial oxidation based on a Ga_2O_3/MoO_3 physical mixture, which showed an increased methanol yield compared with the homogeneous gas phase reaction in the reactor tube packed with quartz chips. The increased methanol yield has been attributed to the development of a co-operative effect between the Ga_2O_3 and MoO_3 oxide phases.

The design approach has also been extended to the design of total oxidation of hydrocarbons for VOC destruction using benzene as a model VOC. In this case the design approach seeks to identify catalysts that can activate the substrate and the oxidant and also destroy the possible partial oxidation products. This approach is used to demonstrate that uranium oxide catalysts are extremely active for the oxidation destruction of hydrocarbons and chlorohydrocarbons. The degree of success from this approach indicates the validity of this novel approach in both the identification of selective and total oxidation catalysts.

Keywords: Oxidation; Catalysts; Methanol; VOC destruction

1. Introduction

The design of oxidation catalysts has, for a long time, been the aim of both industrial and academic researchers. Oxidation is one of the main pathways for the activation of raw materials that are readily available to the chemical industry. A number of commercial oxidation catalysts have been identified and these include both partial and total oxidation catalysts. A number of catalysts have been identified as the result of careful, but time consuming, screening exercises in

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which a large number of formulations are tested. Sometimes catalysts are identified from a chance observation. Both approaches are equally valid when the desired result is achieved. However, the scientific design of catalysts is a topic of immense interest for catalytic researchers and in this paper a simplified design approach is described and exemplified. It is based on three components and for selective oxidation the approach involves identifying catalysts that

(a) do not catalyse the oxidation of the required product under the reaction conditions;
(b) activate the oxidant;
(c) activate the substrate.

This approach is initially demonstrated to identify components of novel methane oxidation catalysts for the formation of methanol. The approach seeks to identify oxides that are capable of activating methane and oxygen, but do not destroy methanol, the desired product. The activation of oxygen was probed using the $^{16}O_2/^{18}O_2$ exchange reaction. The activation of methane has been probed by the exchange reaction with deuterium under non-oxidative conditions.

The design approach has also been extended to the design of total oxidation of hydrocarbons for VOC destruction. In this case the design approach seeks to identify catalysts that can activate the substrate and the oxidant and also destroy the possible partial oxidation products. This approach is used to demonstrate that uranium oxide catalysts are extremely active for the oxidation destruction of hydrocarbons and chlorohydrocarbons.

2. Methane partial oxidation to methanol

The direct partial oxidation of methane to methanol would offer considerable economic advantages over the current two stage process, by-passing the costly steam reforming step. Such a process would also facilitate the utilisation of the vast natural gas reserves which are often located in remote and inhospitable areas. The partial oxidation of methane to methanol has received considerable research attention and although appearing a relatively simple transformation the development of efficient catalysts has met with little success [1]. One of the major challenges encountered with methane oxidation in many heterogeneous systems is the high temperatures required to activate the methane molecule, the use of such temperatures often leads to the production of deep oxidation products which are more thermodynamically stable products compared to methanol.

In the present study a novel approach for the scientific design of new methane partial oxidation catalysts has been adopted. This approach has studied the activation of methane and oxygen on single metal oxides and the stability of methanol over the same oxides. By studying these interactions the suitability of single oxides for inclusion as components in methane oxidation catalysts can be assessed.

Experiments to determine methanol stability were carried out in a conventional liquid feed microreactor with a fused silica reactor tube. The reaction conditions used 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}. Methanol stability was determined in the temperature range from 100°C to 500°C at atmospheric pressure. Product analysis was performed on-line using a Varian GC–MS system.

A low dead volume isotope pulsing reactor was designed for methane/deuterium exchange studies. Under normal operation methane and hydrogen (1/1) were passed over the catalyst held in a fused silica reactor tube. The hydrogen supply was then switched to deuterium and the exchange reaction monitored using a mass spectrometer. Studies were carried out using a gas hourly space velocity of 700 h^{-1}.

The exchange of $^{16}O_2/^{18}O_2$ isotopes with oxide surfaces has been extensively studied by Winter [2] and Boreskov [3]. These results have been utilised, concentrating on the work of Winter [2], although in general agreement between the two research groups is excellent.

Catalytic activity for methane partial oxidation was studied in a silica lined stainless steel microreactor maintained at 15 bar pressure. The reactant feed consisted of methane/oxygen/helium in the ratio 23/2/5 and experiments were conducted at a constant gas hourly space velocity of ca. 5000 h^{-1}.

A ranking order for the stability of methanol over candidate oxides was produced, this was based on the temperature at which 30% of the methanol feed was converted to carbon oxides [4], this is illustrated in Fig. 1. The majority of oxides tested totally combusted methanol below 400°C. Over the oxide

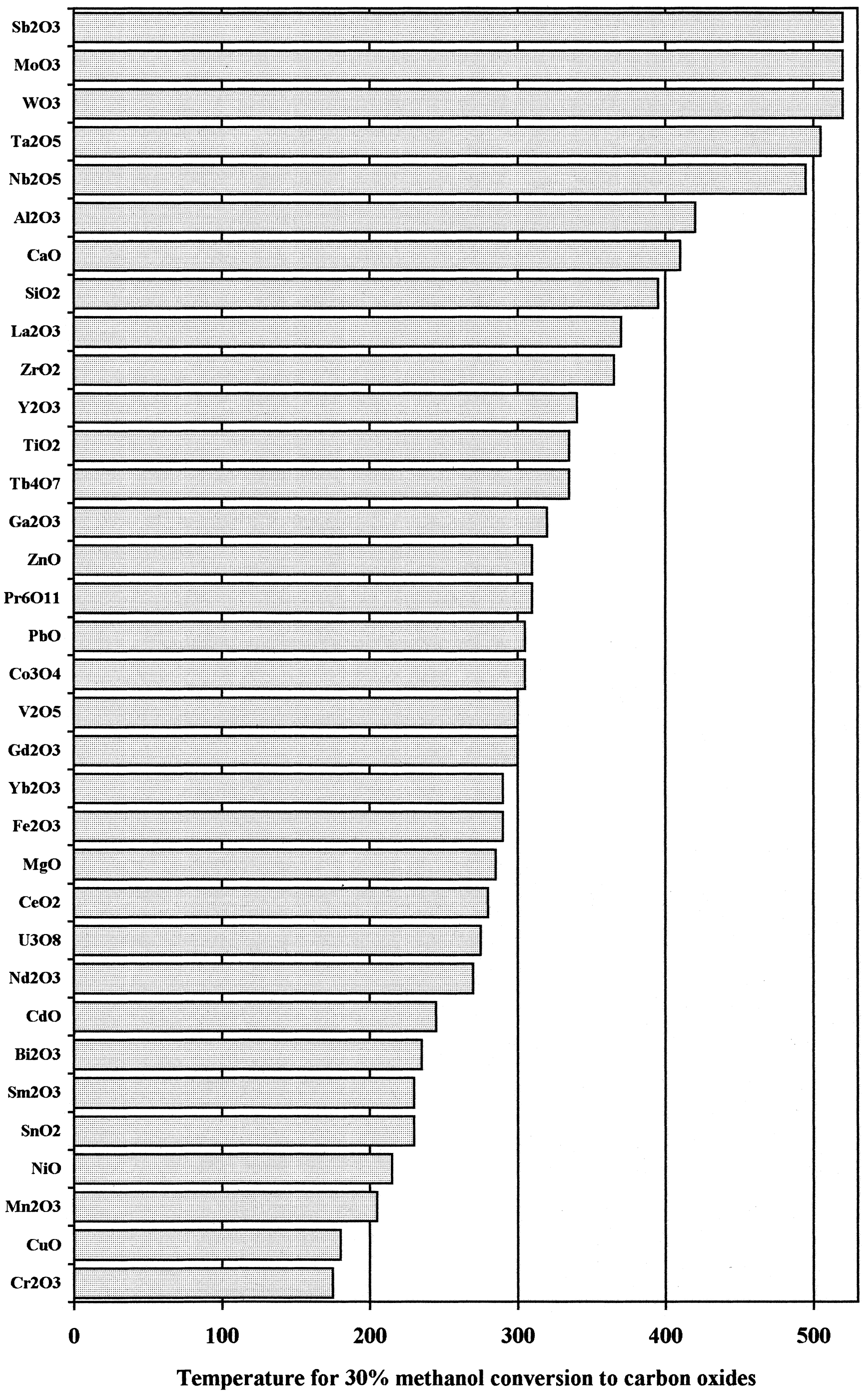

Fig. 1. Ranking for methanol stability based on the temperature at which 30% methanol feed was converted to carbon oxides (methanol/O_2/He=1/4/12, 12 000 h^{-1}).

Sb_2O_3 methanol showed exceptional stability as only 3% methanol conversion was exhibited at 500°C. The oxides MoO_3, Nb_2O_5, Ta_2O_5 and WO_3 were all at high temperatures in the methanol stability ranking. These oxides all showed high methanol conversion however, major reaction products were formaldehyde and dimethylether which are desirable by-products from a methane partial oxidation process.

A ranking order for oxygen activation based on the oxygen exchange data of Winter [2] and Boreskov [3] is shown in Fig. 2. These data exclude MoO_3 for which oxygen exchange reaction is extremely rapid but occurs mainly via exchange of the bulk oxygen rather than just the surface oxygen. Comparison of the methanol stability results with the surface oxygen exchange activity of the oxides showed that a correlation was evident [4]. This correlation, albeit weak, can be expected to be important for the ultimate design of methane partial oxidation catalysts.

The pattern of activity for the activation of methane based on the CH_4/D_2 exchange reaction, at 500°C normalised for surface area effects is shown in Fig. 3.

The most active catalyst by a considerable margin was Ga_2O_3 which showed an exchange rate several orders of magnitude greater than any other oxide. ZnO also showed high activity for the exchange reaction. It is interesting to note that these two oxides are recognised for their high activity in other processes involving hydrocarbon activation [5]. For all the oxides included in Fig. 2 the exchange process took place in a stepwise manner. CH_3D was the primary product whilst traces of CH_2D_2 were detected at higher rates of exchange. The oxides MoO_3, Nb_2O_5, Ta_2O_5 and WO_3 were all reduced under reaction conditions and were inactive or showed very low activity for the exchange reaction.

A correlation has been established between the exchange activity and the ionic radii of the lanthanide sesquioxides. It has been established that the basicity of the lanthanide oxides decreased in a gradual manner as the 3+ metal ionic radius decreased [6]. Thus the relationship observed indicates that the exchange rates were related to the strength of basic sites on the oxide surface and is consistent with methane activation by the abstraction of H^+ to form a surface methyl anion.

The results discussed above were used as a guide for the selection of suitable methane oxidation catalyst components. The best of a very limited set of catalysts tested so far is a physical mixture of Ga_2O_3 and MoO_3. Ga_2O_3 was selected for the ability to activate methane whilst MoO_3 was selected for two reasons. Firstly, the major product from methanol oxidation was formaldehyde, produced with 97% selectivity at 500°C, the balance of products were carbon oxides. Secondly, the mechanism of oxygen exchange identified by Winter [2] was of R_3 type. This type of mechanism involved exchange with the whole of the lattice oxygen, not merely the surface layer indicating that the mobility of oxygen throughout the oxide lattice was a facile process. The lability of lattice oxygen is an important concept in selective oxidation reactions, particularly with respect to the Mars van Krevelan mechanism, in which lattice oxygen is the active oxygen insertion species.

The results of methane oxidation studies are shown below for Ga_2O_3/MoO_3, Ga_2O_3, MoO_3 and the reactor tube packed with quartz chips (Table 1).

The Ga_2O_3/MoO_3 catalyst produced the highest maximum yield of methanol which was approximately 25% greater than that over the quartz chips, the maximum from the quartz chips bed was observed at 500°C, 45°C higher than for the oxide catalysts.

Table 1
Results from methane oxidation studies[a]

Catalyst	Temperature (°C)	CH_4 Conversion (%)	Selectivity (%)				Relative per pass CH_3OH yield[b]
			CH_3OH	CO	CO_2	C_2H_6	
Quartz chips	455	0.1	–	–	100	–	–
	500	3.5	15	70	13	2	53
Ga_2O_3	455	1.5	3	27	68	2	5
MoO_3	455	0.3	13	69	18	–	4
Ga_2O_3/MoO_3	455	3.0	22	50	27	1	66

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

[b] Relative per pass CH_3OH yield=CH_4 conversion×CH_3OH selectivity.

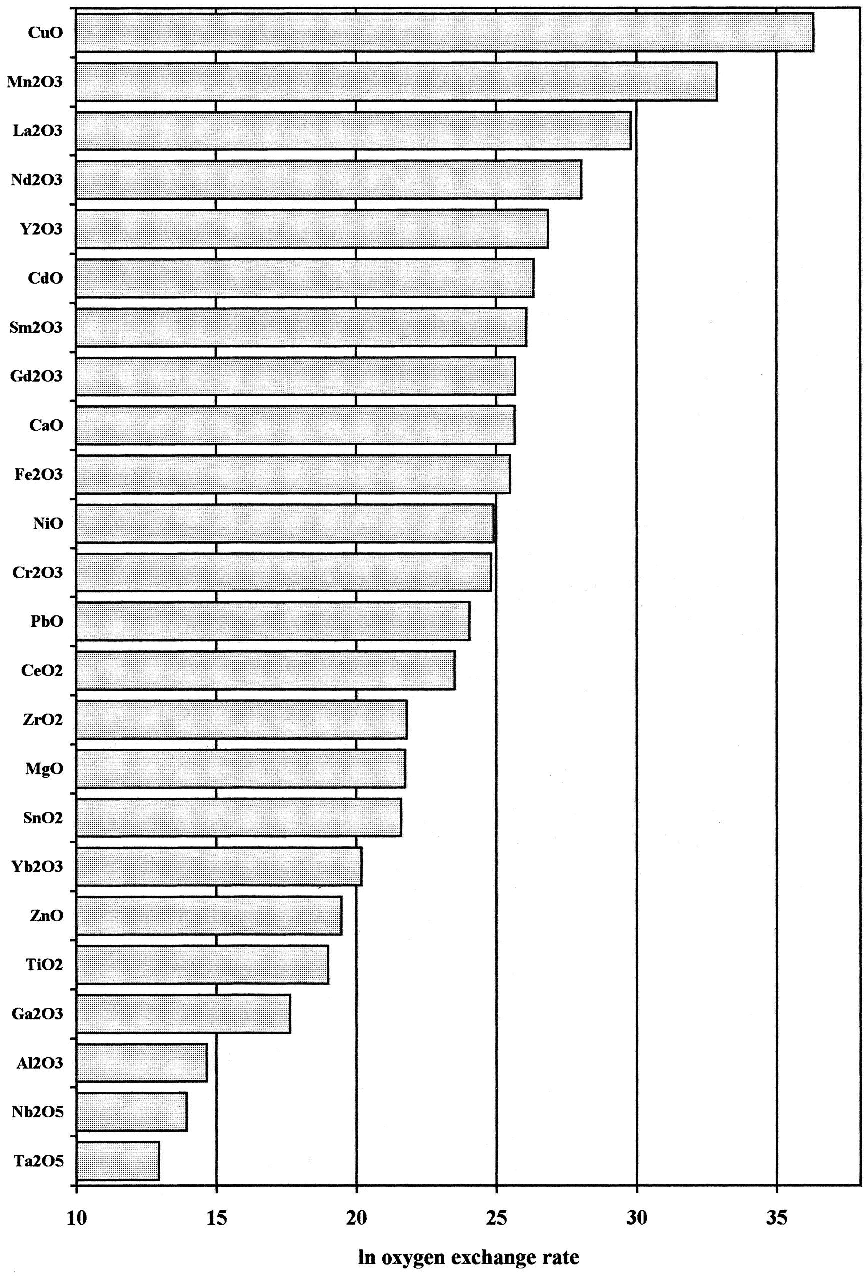

Fig. 2. Ranking for the activation of oxygen based on the $^{16}O_2/^{18}O_2$ exchange reaction at 350°C.

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, in the present study we consider that the catalytic activity should be considered against the homogeneous methane oxidation activity of the quartz chips bed. This comparison provides a more valid comparison as residence time in the heated zone of the reactor and the heat transfer throughout the

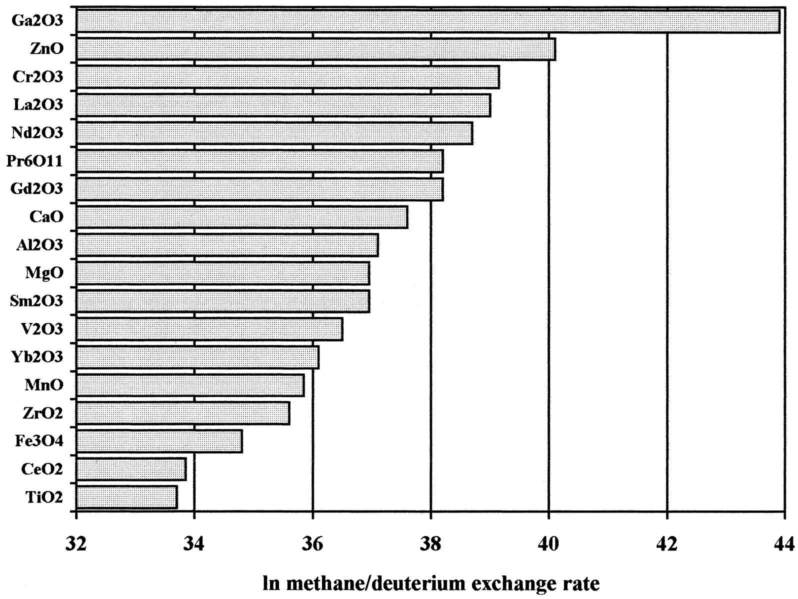

Fig. 3. CH_4/D_2 surface area normalised exchange rates at 500°C (CH_4/D_2=1300 h^{-1}).

catalyst bed will be similar, although the pore volumes may differ slightly.

The methanol yields over MoO_3 and Ga_2O_3 were very low in contrast to the dual oxide catalyst. Comparison of the methane oxidation results for MoO_3 and Ga_2O_3 shows that MoO_3 is more selective for methanol production whilst Ga_2O_3 is more active, showing a higher methane conversion. These observations are consistent with the high activity for methane activation over Ga_2O_3 and the oxygen exchange mechanism and the selective oxidation function exhibited by MoO_3 during methanol oxidation studies.

It should be noted that the principles of this design approach have been demonstrated using a very simple method for the catalyst preparation based on physically mixing the two component oxides. 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. It is therefore feasible that the effect is due to the interaction between the two oxides in a form of contact synergy. 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 [7].

3. Total oxidation of benzene

The reduction of emissions of volatile organic compounds (VOCs) from chemical installations is becoming increasingly important. VOCs are a wide ranging class of compounds commonly occurring in commercial waste streams and constitute a major source of air pollution. Several VOC abatement technologies have been proposed, these include thermal oxidation and catalytic oxidation [8]. Thermal oxidation is carried out at high temperature, typically >1000°C, and is relatively insensitive to space velocity and to the composition and concentration of the waste gases. Whereas, catalytic oxidation involves combustion at lower temperatures, typically 400–600°C, but is greatly affected by space velocity, waste gas composition and concentration. In general, it is expected that catalytic VOC destruction efficiency will increase with increased temperature and decreased space velocity [9]. The lower temperatures required for catalytic combustion results in a lower fuel demand and can therefore be more cost effective than a thermal oxidation process. The catalytic process also exerts more control over the reaction products and is less likely to produce toxic by-products, such as dioxins, which may be

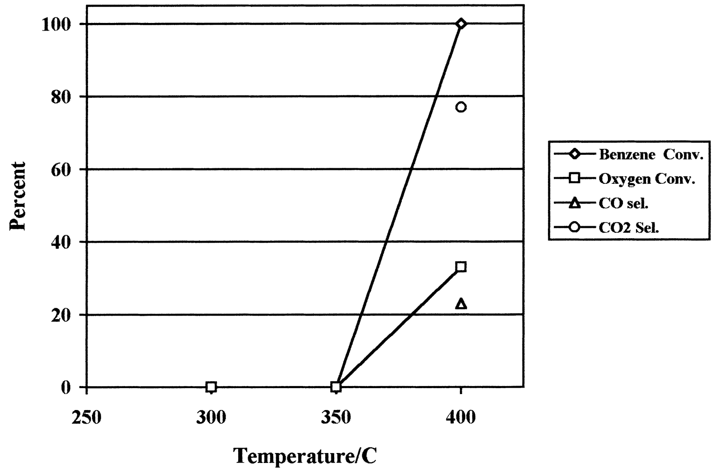

Fig. 4. Benzene conversion using U_3O_8 (1% benzene in air, 70 000 h^{-1}).

produced by thermal combustion. A combination of the two methods has been proposed and it is claimed that this process gives increased VOC destruction efficiency [10].

Catalytic oxidation using an air oxidant therefore provides a convenient route for VOC destruction. The relative ease of destruction of VOCs by catalytic oxidation varies according to the class of compound and follows the general order, alcohols>aldehydes>aromatics>ketones>acetates>alkanes>chlorinated alkanes [10]. Various catalysts have been proposed and these fall into two broad categories, noble metals and metal oxides [11,12]. Noble metal catalysts, which are often supported, show high intrinsic combustion activity, however, they are relatively expensive, susceptible to poisoning even at low levels and in some cases show poor stability [12]. The oxides of cobalt, copper, chromium, manganese and nickel have all been used for VOC destruction [13–15] and it would be expected that oxide catalysts could tolerate higher levels of poisons, however, the activity shown by these oxides is generally lower than noble metal catalysts. It is therefore evident that if high activity oxide catalysts can be developed for VOC destruction these will be preferred.

Uranium oxides have previously been used as catalysts both in pure form and as catalyst components. The oxide U_3O_8 was shown to have appreciable activity for the oxidation of CO by molecular oxygen [16]. Whilst uranium oxides have also been used as major catalyst components in dual oxide systems, such as uranium-antimony for propylene ammoxidation [17,18] and uranium–bismuth catalysts for oxidative demethylation [19]. In the studies concerning methanol stability (Fig. 1) it was found that U_3O_8 was one of the most active materials for oxidative destruction of methanol. In view of this, uranium oxides were selected as the basis for the design of novel VOC destruction catalysts [20] and this is exemplified in this paper using benzene as a model VOC.

The destruction of benzene was primarily investigated over unmodified U_3O_8, initial catalytic activity was observed at 380°C with trace benzene conversion. The conversion increased steeply as the temperature was raised, showing 100% at 400°C (Fig. 4). The sole reaction products were the carbon oxides CO and CO_2, produced with selectivities of 27% and 73%, respectively. The steeply rising conversion can be attributed to the increase in the temperature of the catalyst bed during the highly exothermic benzene combustion reaction ($\Delta H_{298}=-3302$ kJ mol^{-1}). The temperature of the gas stream close to the exit from the catalyst bed was consistently in the region of 30°C higher than the reactor furnace temperature when the catalyst showed high conversion.

A hysteresis effect was evident for the catalytic activity when the reaction temperature was decreased from 400°C. Decreasing the temperature to 350°C resulted in a slight drop in benzene conversion to 95% whilst the CO and CO_2 product selectivities remained approximately constant. When the temperature was decreased further to 300°C the catalyst was inactive.

A comparison of the U_3O_8 combustion activity was made with Co_3O_4, a known highly active combustion catalyst for the destruction of benzene and other organic substrates [21]. Co_3O_4 was active at 350°C, 50°C lower than U_3O_8, benzene conversion increased with temperature but even at 450°C it was only 90%. Although Co_3O_4 was less active than U_3O_8 the former catalyst showed the advantage of 100% selectivity towards CO_2, the preferred product.

Although high catalyst activity for benzene destruction was observed with U_3O_8, the problem that concerned the selectivity to CO remained. Ideally in the designed catalyst the conversion of CO should be >95% and it is apparent that unmodified U_3O_8 catalysts do not achieve this goal. It was therefore decided to use the catalyst design approach to provide a solution to investigate modified U_3O_8 catalysts since it was considered feasible that the addition of a second catalyst component could aid in the enhancement of the oxidation of CO to CO_2. A range of mixed oxide catalysts supported on silica were prepared [22] and these were evaluated for CO oxidation and the ranking order is shown in Fig. 5. The results obtained suggested that the Cu/U/SiO_2 catalyst would be the preferred catalyst to secure both high activity for benzene destruction together with high selectivity to CO_2.

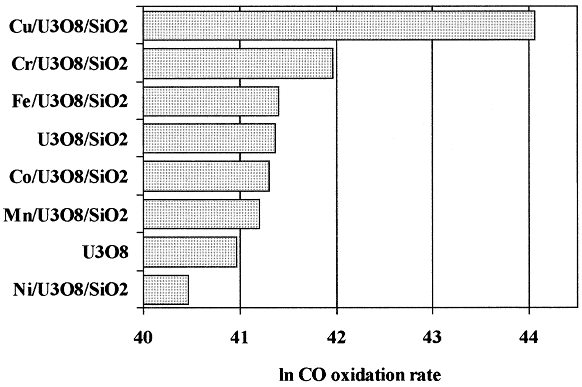

Fig. 5. CO oxidation rate over modified U/SiO_2 catalysts at 500°C.

These catalysts were then examined for benzene destruction and the results are given in Fig. 6. The benzene conversion over U/SiO_2 was 100% at 400°C, CO and CO_2 were produced with selectivities of 27% and 73%, respectively. The activity of the U/SiO_2 catalyst was observed to be similar to U_3O_8. The addition of cobalt to the U/SiO_2 system depressed the benzene conversion relative to the undoped catalyst. The conversion over Co/U/SiO_2 at 400°C was 91%, increasing steadily with temperature and reaching 100% at 500°C. The CO and CO_2 selectivities

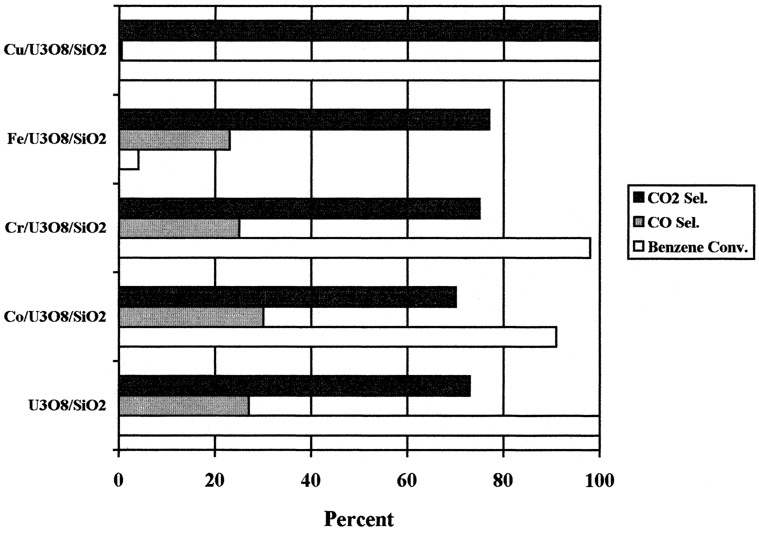

Fig. 6. Benzene conversion over modified U/SiO_2 catalysts at 400°C.

were not drastically affected by the addition of the cobalt component. The activity of the Cr/U/SiO_2 catalyst was similar in many respects to Co/U/SiO_2 as benzene conversion over Cr/U/SiO_2 was also slightly suppressed. At 500°C the Cr/U/SiO_2 catalyst did not completely destroy benzene, as a trace quantity was still present in the reactor effluent. The CO and CO_2 selectivities were again not affected by the addition of chromium. Doping U/SiO_2 with iron suppressed the benzene conversion drastically as the conversion was only 4% at 400°C. However, the benzene conversion did increase significantly to 100% at 500°C. CO and CO_2 selectivities were similar to Co/U/SiO_2 and Cr/U/SiO_2. The addition of copper did not decrease the conversion of benzene when compared to the U/SiO_2 system as the conversion was 100% at 400°C. As expected from the catalyst design studies, the addition of copper had an extremely beneficial effect on the product distribution, as the selectivity towards CO_2 was increased across the entire temperature range. The CO_2 selectivity over the Cu/U/SiO_2 catalyst was at least greater than 99%, with only trace quantities of CO detected at 400°C and 450°C.

4. Conclusions

A simplified catalyst design approach has been described and exemplified for both partial and total oxidation. For the oxidation of methane to methanol the design methodology has been used to show that a Ga_2O_3/MoO_3 catalyst gives an increased yield of methanol when compared to the homogeneous gas phase oxidation of methane in a quartz chips packed reactor. This increased yield has been attributed to a co-operative effect which can be explained from results of the individual activation steps. In addition, using benzene as a model VOC, the design approach has been used to improve the CO_2 selectivity of U_3O_8 by the addition of Cu. In this case the Cu/U/SiO_2 catalyst is shown to give a CO_2 yield of over 99%. Overall the results presented emphasise the validity of the approach that has been adopted in the simplified design procedure for heterogeneous catalysts.

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