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Oxidative dehydrogenation of isobutane to isobutene by pyrovanadates, $M_2V_2O_7$, where M(II) = Mn, Co, Ni, Cu and Zn, and Co_2VO_4 and ZnV_2O_4: The effect of gold nanoparticles

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ABSTRACT

The pyrovanadates $M_2V_2O_7$, where M^{II} = Mn, Co, Ni, Cu and Zn, have been investigated for the oxidative dehydrogenation of isobutane from 300 to 450 °C, both with and without 5 wt% gold nanoparticles. Reduction of the pyrovanadate compounds was generally observed, yielding products that contained V(IV) and/or V(III), and depended on both M(II) and the presence of gold nanoparticles. The most stable pyrovanadate was $Ni_2V_2O_7$. Products identified by XRD were M_2VO_4, MVO_3, MV_2O_4, or V_2O_3. The conversion of isobutane always increased with temperature, reaching 11% and 16% in the absence and presence of gold nanoparticles, respectively, at 450 °C. Selectivities to isobutene were as high as 40–50%. Vanadium $2p_{3/2}$ XPS studies indicated that all catalysts exhibited surface V(V) and V(IV), while V(III) was present in those catalysts that generated V(III)-containing products. This suggests that catalytic activity depends on the rate of reoxidation of the lower oxidation states to V(V). Gold $4f_{7/2}$ XPS studies always indicated the presence of Au(0) and Au(I), and for some catalysts Au(III). The highest yields of isobutene correlate with the lowest Au(I) content. The reduction products $Co_2V^{IV}O_4$ and $ZnV^{III}_2O_4$ were compared in their activities with $Co_2V_2O_7$ and α-$Zn_2V_2O_7$. The reduced phase Co_2VO_4 proved to be a good catalyst, comparable to the best 5 wt% Au/$M_2V_2O_7$ compositions.

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1. Introduction

The oxidative dehydrogenation of small alkanes to generate alkenes represents an alternative approach to thermal pyrolysis and catalytic dehydrogenation processes. The latter, while used industrially, suffers from the requirement of high temperatures because of thermodynamic considerations, along with coke-induced deactivation of the catalyst. Oxidative dehydrogenation, which is thermodynamically favourable, does not have these disadvantages, and thus is a viable alternative. However, the selective oxidation or oxidative dehydrogenation of small hydrocarbons is a challenging area because the thermodynamically stable products of (deep) oxidation are CO_2 and H_2O [1–3]. As a consequence, many studies have been made of the selective oxidation of small hydrocarbons, using a variety of complex (e.g. ternary and quaternary) oxides, mixed oxides and supported catalysts. Of particular importance is the formation of isobutene from isobutane. Isobutene

is used industrially as a source material for the formation of methyl t-butyl ether (MTBE). This is used as an additive to petrol to replace lead-containing compounds [1–3]. Chromium oxides supported on oxide-based catalysts are used mainly for this purpose under oxygen-free conditions but, as pointed out above, this approach suffers from several disadvantages. Recently, several studies have been reported dealing with the development of improved chromium-based catalysts, including investigations of the oxide support, the presence of oxygen in the input stream and the inclusion of additives [1–6]. Other studies have involved the investigation of vanadium-, niobium- and molybdenum-based oxide catalysts, including combinations of these transition metals [7–10]. Many of the most active catalysts have been based around vanadium-containing oxide materials [11].

Takita and co-workers have studied the dehydrogenation of isobutane under both aerobic (i.e. oxygen supplied in the gas phase) and anaerobic conditions [10,12–14]. The latter process uses only lattice oxygen as the source of oxygen, with subsequent reduction of the oxide catalysts as isobutane is oxidized. The anaerobic studies were directed toward catalyst suitability for use in a thin layer reactor, with lattice oxygen ions diffusing through the catalyst bulk from the oxidant chamber to replenish the oxygen that is removed

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during reaction of the catalyst with isobutane in the reactant chamber. Survey studies were made of a wide range of binary and ternary oxides. Under aerobic conditions (75 mol% isobutane, 5 mol% oxygen and 20 mol% nitrogen) the most active catalysts were V_2O_5, the pyrovanadate $Cu_2V_2O_7$, and CaV_2O_6. Indeed $Cu_2V_2O_7$ was more active than V_2O_5 below 350 °C, although the latter proved to be more active at 400 °C and above. Species such as $LaVO_4$, $BiVO_4$ and MgV_2O_6 were less active, while oxide species based around niobium, tantalum and molybdenum showed the lowest activity. Other studies under aerobic conditions have included the pyrovanadate $Mg_2V_2O_7$ [13], along with MgV_2O_6, and more extensive studies on $Cu_2V_2O_7$, as well as CuV_2O_6, $Cu_3V_2O_8$ and $Cu_5V_2O_{10}$ [14]. The pyrovanadate $Cu_2V_2O_7$ and CuV_2O_6 were found to be the most active catalysts, along with V_2O_5, while $Cu_3V_2O_8$ and $Cu_5V_2O_{10}$ exhibited lower catalytic activity. However, while Cu(II) and Mg(II) as counter cations have been well studied for pyrovanadate, there have been no studies with other transition metal counter cations, which may potentially show improved catalytic activity.

Supported gold nanoparticles have been shown to be highly active in the oxidation of CO to CO_2, even under sub-ambient conditions (as low as −70 °C) [15,16]. They are also active in the complete oxidation (combustion) of small hydrocarbons, such as methane and propane [17–21], as well as other volatile organic compounds (e.g. aromatics, alcohols, aldehydes, ketones, etc.) [22–25], when used in conjunction with various oxide catalysts and supports. Furthermore, when deposited on a range of metal oxides, gold nanoparticles have been shown to exhibit a unique activity and selectivity in a variety of reactions. In addition to the above reactions, these include the partial oxidation of hydrocarbons (such as propene epoxidation), the hydrogenation of carbon oxides, the reduction of NO, and even the water gas-shift reaction [26–30]. However, to our knowledge, there are no studies reported on the effect of gold nanoparticles for oxidative dehydrogenation under milder temperature conditions that do not lead to complete oxidation of the parent small hydrocarbon.

In the present study we have investigated the oxidative dehydrogenation of isobutane to isobutene using a selection of transition metal pyrovanadates, $M_2V_2O_7$, where M(II) = Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}, as potential catalysts, under isobutane-rich conditions (50 mol% isobutane, 2.5 mol% oxygen, 47.5 mol% nitrogen) from 300 to 450 °C. As noted above, pyrovanadates have been shown to be one of the most active catalyst formulations for the oxidative dehydrogenation of isobutane to isobutene, and $Cu_2V_2O_7$ was included to enable comparisons with previous studies on this compound under the reaction conditions used in the present study. Also, the effect of gold nanoparticles (at a loading of 5 wt%) has been studied as regards the potential enhancement of the oxidative dehydrogenation of isobutane. In the present study the gold nanoparticles were obtained by the initial formation of n-hexanethiolate-stabilized gold nanoparticles, which were then completely adsorbed onto the catalyst surface from an n-hexane solution using the approach of Zheng and Stucky [31]. Following isolation, the resulting solids were thermolysed at 340 °C for 1 h in air to generate the gold nanoparticles and remove the organo- and/or organosulfur-thermolysis products, with minimum adsorption of sulfur-containing species on the catalyst surface [32–34].
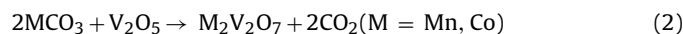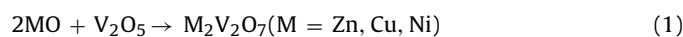
2. Experimental

2.1. Materials

Manganese(II) carbonate (Aldrich, 99.9+%), cobalt(II) carbonate (Aldrich, 99.998%), cobalt(II) oxide (Alfa Aesar, 95%), nickel(II) oxide (black, Univar, analytical reagent), copper(II) oxide (Ajax, 97% min.), zinc(II) oxide (May & Baker, >99%), vanadium(III)

oxide (Strem, 95%), vanadium(IV) oxide (Strem, 99+%), vanadium(V) oxide (Merck, >99%), chloroauric acid ($HAuCl_4 \cdot 3H_2O$, Sigma–Aldrich, ≥49.0% Au), tetra-n-octylammonium bromide ($C_{32}H_{68}NBr$, Sigma–Aldrich, 98%), sodium borohydride (Merck), n-hexanethiol ($CH_3(CH_2)_5SH$, Sigma–Aldrich, 95%), toluene (Merck, ACS reagent), methanol (Lab-scan, AR grade) and n-hexane (Merck) were obtained from the listed sources and were used as received. The gases used for the catalysis studies were nitrogen (BOC Gases, Ultra High Purity), oxygen (BOC Gases, High Purity), isobutane (BOC Gases, Instrument Grade) and isobutene (calibration standard) (Sigma–Aldrich, 99%). For the TG/DTA studies under reducing conditions, 10% H_2 in N_2 (Coregas) was used.

2.2. Preparation of $M_2V_2O_7$, where M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}

The pyrovanadates, $M_2V_2O_7$, were prepared by the solid-state reactions of stoichiometric amounts of the respective powdered oxides or carbonates according to the equations given below:

$$2MO + V_2O_5 \rightarrow M_2V_2O_7 (M = Zn, Cu, Ni) \qquad (1)$$

$$2MCO_3 + V_2O_5 \rightarrow M_2V_2O_7 + 2CO_2 (M = Mn, Co) \qquad (2)$$

For each compound a metal oxide or carbonate was combined with V_2O_5 and thoroughly ground until a homogenous mixture was obtained. The resulting powders were then pressed into pellets and heated in platinum crucibles in air under the conditions indicated below. Both $Co_2V_2O_7$ and $Ni_2V_2O_7$ have only one polymorph and the pellets were heated at 650 °C for 67 and 65 h, respectively [35,36]. However, $Mn_2V_2O_7$, $Cu_2V_2O_7$ and $Zn_2V_2O_7$ each have two structural forms (the low temperature α-form and the high temperature β-form) [37–42]. Accordingly, the pressed pellets for $Mn_2V_2O_7$ and $Cu_2V_2O_7$ were heated at 800 and 600 °C for 13 and 9 days, respectively, to obtain the high temperature β- and low temperature α-forms, respectively (note that low temperature α-$Mn_2V_2O_7$ transforms to β-$Mn_2V_2O_7$ at 23 °C [37], while the $Cu_2V_2O_7$ α → β transformation occurs at 710 °C [40]). The pellets for $Zn_2V_2O_7$ were heated at 925 °C for 1 h (above the melting point of $Zn_2V_2O_7$, which is 877 °C), followed by a temperature reduction of 5 °C every 15 min until 750 °C and then quenched so that the α-form was obtained. The α-form of $Zn_2V_2O_7$ transforms into the β-form at 615 °C [41]. Thus for $Mn_2V_2O_7$, $Cu_2V_2O_7$ and $Zn_2V_2O_7$ the forms synthesised were the β-, α- and α-forms, respectively, which are the thermally stable forms within the temperature range used for the catalysis studies (300–450 °C). X-ray powder diffraction (XRD) was used to confirm the forms and purities of the five pyrovanadates (PDF files – α-$Mn_2V_2O_7$: 00-052-1265; β-$Mn_2V_2O_7$: 01-089-0483; $Co_2V_2O_7$: 01-070-1189; $Ni_2V_2O_7$: 01-070-1190; α-$Cu_2V_2O_7$: 01-070-0831; α-$Zn_2V_2O_7$: 01-070-1532).

2.3. Preparation of $Co_2V^{IV}O_4$ and $ZnV^{III}_2O_4$

Both Co_2VO_4 and ZnV_2O_4 were prepared using the procedures described by Rogers et al. [43], Bernier et al. [44] and Ebbinghaus et al. [45]. The relevant combinations of the oxides CoO, V_2O_3 and V_2O_5, or ZnO and V_2O_3, were combined in the appropriate stoichiometric amounts and thoroughly ground together using an agate mortar and pestle in a glove box (Vacuum Atmospheres HE Series Dri-Lab with an HE-493 dry-train) under a dried argon atmosphere. The oxide mixtures were then pressed into pellets. The pellets were heated at 800 and 900 °C, respectively, for 3 days in sealed, evacuated quartz tubes. On cooling, the pellets were powdered and reground in the argon-filled glove box and repressed into pellets. Heating at the above temperatures in evacuated quartz tubes for a further 3 days resulted in pure Co_2VO_4 and ZnV_2O_4 as established

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