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The complete oxidation of isobutane over CeO_2 and Au/CeO_2, and the composite catalysts MO_x/CeO_2 and $Au/MO_x/CeO_2$ ($M^{n+} = Mn$, Fe, Co and Ni): the effects of gold nanoparticles obtained from *n*-hexanethiolate-stabilized gold nanoparticles

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ABSTRACT

The complete oxidation of isobutane has been studied over CeO_2 and Au/CeO_2, as well as the composite catalysts MO_x/CeO_2 and $Au/MO_x/CeO_2$, where M = Mn, Fe, Co and Ni, using a range of CeO_2 surface areas. The catalytic ability of CeO_2 depended on the specific surface area, and the addition of gold always increased activity. Similarly, addition of MO_x to CeO_2 (M:Ce = 1:10) increased catalytic activity, and there was a synergic interaction between the MO_x and CeO_2 phases. For $Au/MO_x/CeO_2$ catalysts the presence of gold nanoparticles did not affect the initial reaction temperature or that for 100% conversion, or the apparent activation energy compared to MO_x/CeO_2 catalysts. The rate determining step in these reactions is suggested to be C—H bond activation. This was supported by TG/DTA studies under 10% H_2 in N_2 that showed there was no correlation between the catalysis results and the temperature of initial mass loss of lattice oxygen. Gold nanoparticles (5 wt%) were introduced by adsorption and subsequent thermolysis of preformed *n*-hexanethiolate-stabilized gold nanoparticles. STEM and XRD studies showed that the average size of the gold nanoparticles depended on the surface area. Introduction of gold nanoparticles by this method introduces a small amount of sulfur as adsorbed sulfate, but this did not have any major poisoning effect on isobutane oxidation. Gold $4f_{7/2}$ XPS studies on $Au/MO_x/CeO_2$ showed that the only common gold species was Au(0), suggesting that higher oxidation states were not important in the oxidation, while Ce $3d_{5/2}$ studies established the presence of Ce(III) in addition to Ce(IV), indicating their involvement in the Mars-van Krevelen mechanism, including possible participation in reoxidation of reduced MO_x.

1. Introduction

Although bulk gold metal is not catalytically active, it is well established that gold becomes active when finely divided in the form of nanoparticles [1–3]. In 1987, Haruta et al. reported that when gold is well dispersed in the form of nanoparticles on a metal oxide substrate, it exhibits a high catalytic activity for the oxidation of CO below room temperature, even as low as −70 °C [4,5]. This report promoted the study of the catalytic behaviour of gold nanoparticles for industrial and environmental applications. When deposited on both metal and non-metal oxide supports, gold nanoparticles display a range of unique activities for a number of reactions, including low temperature oxidations (such as CO), the partial or complete oxidation of hydrocarbons and other organic compounds, the hydrogenation of carbon oxides, and even the water–gas shift reaction [3,6–29]. Most studies dealing with the complete oxidation of small hydrocarbons have concentrated on methane using a variety of metal oxides [10–17], although the oxidation of ethane, propane and propene have also received attention [10,18–22]. Other studies have dealt with the control of volatile organic compounds (VOCs) from an environmental perspective and have involved the complete oxidation of aromatics (e.g. benzene and toluene), as well as functionalised organic compounds (alcohols, aldehydes, ketones, etc.) [23–29].

Several approaches may be used to deposit gold onto metal and non-metal oxides. The most common are co-precipitation and deposition-precipitation using chloroauric acid, $HAuCl_4$, as the source of gold, followed by calcination at higher temperatures [30].

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Other methods include co-sputtering, chemical vapour deposition and solvated metal atomic dispersion [2,6,31]. In general, these methods lack control over the actual size of the gold nanoparticles that are deposited on the support. An alternative approach involves the adsorption of previously formed *n*-alkanethiolate-stabilized gold (*n*-C_nSAu) nanoparticles from an aprotic solvent, followed by isolation and calcination at higher temperatures to remove the *n*-alkanethiolate ligands, as described by Zheng and Stucky [32]. Similar approaches have been used for the introduction of gold nanoparticles on TiO_2, titania aerogels and CeO_2 as support media [8,33–35]. Also, functionalised *n*-alkanethiols, such as mercaptoalkanoic acids can be used to stabilize gold nanoparticles [36], which have groups (e.g. —OH) that have greater attraction to the oxide surface. Advantages of this approach include the deposition of an exact amount of gold on an oxide surface as the gold content of the *n*-C_nSAu (or functionalised *n*-C_nSAu) nanoparticles can be determined by a prior thermogravimetric analysis, while transmission electron microscopy allows the average particle size and size range to be determined for the parent nanoparticles [37]. Adsorbed *n*-C_nSAu nanoparticles thermally decompose at high temperatures, although longer chain thiols require higher temperatures for the removal of their resulting organo and organosulfur decomposition/oxidation products because of strong adsorption onto the metal oxide surface [37]. Thus *n*-hexanethiolate as a ligand has been found to be suitable for this purpose, with complete volatilisation of organic decomposition products generally occurring by 340 °C. This procedure does, however, leave some sulfur as adsorbed sulfate on the oxide surface, which can have a detrimental effect on substrate oxidation such as the oxidation of CO [38]. Tai et al. have shown in their studies of the oxidation of CO with gold nanoparticles that adsorbed sulfate can be removed from titania-coated silica by heating above 600 °C in air, or at 400 °C in an H_2/Ar atmosphere, the latter presumably the result of formation of volatile lower oxidation state sulfur-oxygen compounds, such as SO_2 [38]. A similar result was obtained by Almukhlifi and Burns in their study of the oxidative dehydrogenation of isobutane to isobutene in the presence of gold nanoparticles, which was performed under reducing conditions [39].

Several studies of the effects of gold nanoparticles on the complete oxidation of small hydrocarbons using catalytically active transition metal oxides as a support have been reported. Waters et al. synthesised Au/metal oxide catalysts using co-precipitation involving Na_2CO_3 and found that complete oxidation of methane followed the sequence $Au/Co_3O_4 > Au/NiO > Au/MnO_x > Au/Fe_2O_3$, with Au/CeO_x unreactive under the reaction conditions [11]. Choudhary et al. prepared Au/metal oxide catalysts using deposition-precipitation with urea to adjust solution pH, and found that for methane oxidation, the sequence followed the order $Au/Fe_2O_3 > Au/MnO_2 > Au/Al_2O_3 \sim Au/CeO_2 \sim Au/CoO_x > Au/Ga_2O_3 > Au/MgO > Au/TiO_2$ [17]. Differences likely relate to the synthetic method used and to the sizes of the gold nanoparticles.

Nieuwenhuys and co-workers have used an alternative approach in their studies of methane oxidation involving the support of transition metal oxides (MO_x) on high surface area γ-Al_2O_3, with the gold nanoparticles introduced by deposition-precipitation using urea [14,15]. These catalysts have multicomponent compositions of the type $Au/MO_x/\gamma$-Al_2O_3, where M = Cr, Mn, Fe, Co, Ni, Cu and Zn. In two studies Niewenhuys and co-workers showed that different effects from the gold nanoparticles were obtained depending on the order of addition of the MO_x component and gold nanoparticles to the γ-Al_2O_3 support. The gold nanoparticles were found to always enhance catalytic activity, but in one study the MO_x phase was found to enhance the oxidation of methane, while in the other the presence of MO_x generally did not affect the catalytic activity compared to the parent Au/γ-Al_2O_3 catalyst. In both studies the gold nanoparticle size depended on the MO_x component, and there were some significant variations in particle size following reaction. This results because complete oxidation of methane occurs at high temperatures ($\lesssim$700 °C) and aggregation of gold nanoparticles is known to accelerate markedly above 400 °C [40].

Solsona et al. investigated the complete oxidation of propane, as well as methane and ethane, over several Au/MO_x supports where $MO_x = Co_3O_4$, Mn_2O_3, CuO, Fe_2O_3 and CeO_2 [18]. The catalysts were prepared by co-precipitation. Other studies included Au/TiO_2, formed by deposition-precipitation, and Au/CoO_x and Au/MnO_x, by impregnation. The presence of gold generally resulted in a significant increase in catalytic activity relative to the parent MO_x catalysts, and the most active catalyst was Au/Co_3O_4. Also, the complete oxidation of propane has been studied using an Au/MnO_x/TOS catalyst, where TOS represents a triple oxide support consisting of CeO_2, TiO_2 and ZrO_2 [20]. Increased catalytic activity of Au/MnO_x/TOS compared to Au/TOS and Au/MnO_x was observed, suggesting strong synergism between the Au and Mn.

The oxidation of propene was examined by Gluhoi et al. over Au/γ-Al_2O_3, and the effects of various added metal oxides in multicomponent catalysts of the type $Au/MO_x/\gamma$-Al_2O_3, where M = Ce, Mn, Fe and Co were also studied [21]. The catalysts were prepared by deposition-precipitation with urea. The most active catalyst was found to be M = Ce, followed by Fe > Mn > Co. However, again there were variations in the gold particle size. Delannoy et al. studied the oxidation of propene over TiO_2, δ-Al_2O_3 and CeO_2, with the gold nanoparticles added by deposition-precipitation using urea [22]. Both TiO_2 and δ-Al_2O_3 were inactive, but were active in the presence of gold, with $Au/TiO_2 > Au/\delta$-Al_2O_3. CeO_2 was catalytically active in its own right, and Au/CeO_2 was found to be the most active catalyst.

Recently, we reported the effects of gold nanoparticles on the catalytically active metal oxides β-MnO_2, α-Fe_2O_3, Co_3O_4 and NiO as supports and for multicomponent catalysts of the type $Au/MO_x/\gamma$-Al_2O_3 (M = Mn, Fe, Co, Ni) for the complete oxidation of isobutane [37,41]. Isobutane was chosen as it is the smallest saturated alkane that contains a tertiary C—H bond, which leads to high reactivity and thus to a low temperature for complete hydrocarbon oxidation unlike, for example, methane. This in turn leads to smaller thermal effects on the aggregation of gold nanoparticles. The sizes of the gold nanoparticles were measured both before and following catalysis, and only small changes were observed. Notably, the gold nanoparticles were introduced by adsorption of preformed *n*-C_6SAu nanoparticles and subsequent calcination. Some effects were observed from residual sulfate for β-MnO_2 and Co_3O_4, but not for the $Au/MO_x/\gamma$-Al_2O_3 catalysts. The current study extends investigations of the effects of gold nanoparticles on the complete oxidation of isobutane over CeO_2 and the supported metal oxides, MO_x (M = Mn, Fe, Co, Ni), using CeO_2 with different surface areas as the support, which potentially allows a direct comparison of the effects of different metal oxides. Also, this is the first report of isobutane oxidation over CeO_2-based oxide catalysts. Cerium dioxide has several advantages as a support. It is potentially reducible, and has oxygen storage/release capacity [22,42]. Thus this approach allows an investigation of the different effects and activities of the transition metal oxides MO_x, where M = Mn, Fe, Co and Ni, as part of supported multicomponent MO_x/CeO_2 catalysts for the complete oxidation of isobutane.

2. Experimental

2.1. General

Chloroauric acid ($HAuCl_4.3H_2O$, Sigma–Aldrich, ≥49.0% Au), tetra-*n*-octylammonium bromide ($C_{32}H_{68}NBr$, Sigma–Aldrich,