

An Attempt to Selectively Oxidize Methane over Supported Gold Catalysts

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Abstract The potential of supported gold catalysts for the selective gas-phase oxidation of methane to methanol with molecular oxygen was investigated. A broad range of supported gold-based catalyst materials was synthesized using reducible and non-reducible support materials. Although the formation of small gold nanoparticles was established for all catalyst materials, only a very low activity for the total oxidation of methane was observed, at temperatures >250 °C. Since no traces of partial oxidation products, such as methanol, formaldehyde, formic acid, methyl formate, dimethyl ether and CO, were observed it was concluded that supported gold catalysts are not able to selectively oxidize methane to methanol under these experimental conditions.

Keywords Gold · Oxidation · Methane · Methanol · Alkanes · Heterogeneous catalysis

1 Introduction

The selective production of methanol from methane is generally considered as a ‘holy grail’ in heterogeneous catalysis and will be crucial for the exploitation of natural gas reserves [1]. Large natural gas reserves are still available and the proven world reserves are growing [2]. Unfortunately, many of the world’s gas reservoirs are

found at remote locations. This makes their exploitation not economically feasible due to the high transportation and storage costs. In addition, associated gas from oil fields often has a negative value to the producer and is re-injected or simply flared or vented [3]. The amount of flared and vented natural gas per year is estimated to account for 5% of the annual world production [4].

Liquefaction by efficient on-site oxy-functionalization of natural gas into methanol would offer a solution for the transportation and storage problems and provide a suitable feedstock for the production of high value hydrocarbons, as gasoline and light olefins, through MTG/MTO technology [5, 6]. Unfortunately, due to the high stability of methane, activation of the strong C–H bond (439 kJ/mol) requires high temperatures. One commercial way of utilizing methane as feedstock is by conversion into synthesis gas (H_2/CO mixture) by autothermal reforming, steam reforming or dry reforming with CO_2 . These reactions are highly endothermic and demand high temperatures, typically 800–950 °C, and pressure. Therefore, although modern syngas plants are highly efficient (80% of the thermodynamic efficiency is easily achieved) the production of synthesis gas from methane is capital intensive and only cost effective on large scale [7].

Direct methane valorisation, surpassing the costly syngas production, still attracts major attention in both academia and industry [8–19]. Although proof-of-principle studies have been successful, it has not led to any commercial application yet, mainly due to the low yields and high costs. The key factor in a direct conversion route is to protect the formed methanol from over-oxidation [1, 20]. Therefore, much of the research has focussed on conversion routes based on the formation of methyl esters as for example in the form of methylbisulphate [15, 21]. Such methods have been reported and are promising. However,

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it must be noted that large amounts of sulphuric acid or SO_3 are consumed (2 mol of SO_3 per mole of produced MeOH) which adds significant to the process costs. A highly active catalyst system for this reaction was reported by Periana et al. [22]. Using a homogeneous platinum–bipyrimidine complex, turn-over numbers of ~ 300 at 81% selectivity towards methanol were achieved [22]. In 2010, Palkovits et al. [16] were the first to report on a solid catalyst system reaching superior activity as compared to the Periana system. Although the catalyst stability was still a concern, the development of solid catalyst systems for the direct oxidation of methane to methanol thus seems feasible. Although the bisulphate route is a promising method, a direct catalytic oxidation route, using molecular oxygen as oxidant, would significantly reduce the process costs and waste production and would therefore be preferred.

Gold catalysts have shown remarkable activities and selectivities in selective oxidation of CO [23–26], alcohols [27–32], and olefins [33–35] already. These topics are covered by extensive reviews, published in the last decade [36–45]. Also in the field of selective alkane oxidation, gold catalysts have shown promising results. For instance Au/SiO₂ has been shown to be able to selectively oxidize methane to methanol in ionic liquids, using trifluoroacetic acid and trifluoroacetic anhydride as acidic reagents and K₂S₂O₈ as oxidant [46]. Also, a gas mixture of CH₄ and O₂ was reported to selectively convert into formaldehyde at temperatures below 250 K when Au₂⁺-clusters were introduced. A wide variety of supported gold catalysts have been reported to exhibit great performance in selective liquid phase cyclohexane oxidation [47–49]. Inspired by the promising results reported on selective oxidation of cyclohexane over gold-based catalyst materials [49], in this publication we have investigated the potential application of supported gold catalysts for the selective oxidation of methane into methanol. Unfortunately, no indication of selective C–H bond activation was observed. In line with several recent publications, these results cast doubts on the applicability of gold nanoparticles for selective alkane oxidation [50–56].

2 Experimental

2.1 Catalyst Preparation

The supports SiO₂ (Engelhard), Al₂O₃ (Engelhard), ZSM-5 (Zeolyst), TiO₂ Degussa, P25), ZrO₂ (Degussa), CeO₂ and Nb₂O₅ (ABCR) were used as received. The SBA-15 support was prepared according to the procedure as described by Zhao et al. [57] A 1 wt% gold loading on the supports was obtained by deposition precipitation of HAuCl₄ in dilute HCl (Sigma Aldrich, 99.99%) with diluted NH₄OH

(aq) (Merck, 25%). The support was dispersed in 50 mL water and the pH was adjusted to 9.5 with NH₄OH. The slurry was let to equilibrate by stirring for 30 min. The gold precursor was diluted in 30 mL demi-water and added drop wise to the support slurry, while maintaining a constant pH by addition of NH₄OH (aq). After addition, the slurry was stirred for an additional 30 min, filtered and washed until no chloride was detected anymore with a AgNO₃ (aq) solution. The catalysts were dried at 60 °C overnight and calcined at 400 °C for 4 h.

2.2 Catalyst Characterization

UV–Vis–NIR diffuse reflectance (DR) spectroscopy was performed on a Varian Cary 500 spectrometer with a DR setup using a white Halon standard for background subtraction. N₂-physisorption isotherms were measured using a Micromeritics Tristar 3000. Samples were dried prior to analysis at 250 °C for at least 12 h. Transmission electron microscopy (TEM) micrographs were taken on a Tecnai 20 microscope operating at 200 kV, equipped with an energy dispersive X-ray (EDX) detector and high-angle annular dark field (HAADF) detector. X-ray Fluorescence (XRF) analysis was performed on a Spectro X-Lab 2000.

2.3 Catalytic Performance

The catalytic performance of the gold-based catalysts was evaluated in temperature programmed reaction studies in a

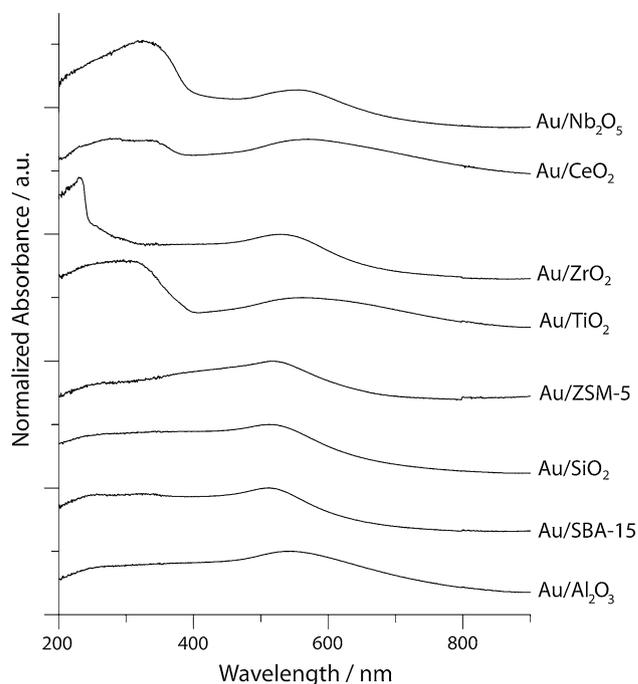


Fig. 1 UV–Vis–NIR DR spectra of the different supported gold catalysts under study

Fig. 2 TEM micrographs of Au/ZrO₂ (a), Au/SBA-15 (b) Au/SiO₂ (c) Au/TiO₂ (d), and Au/ZSM-5 (e). Some Au particles and corresponding diameters are indicated by arrows

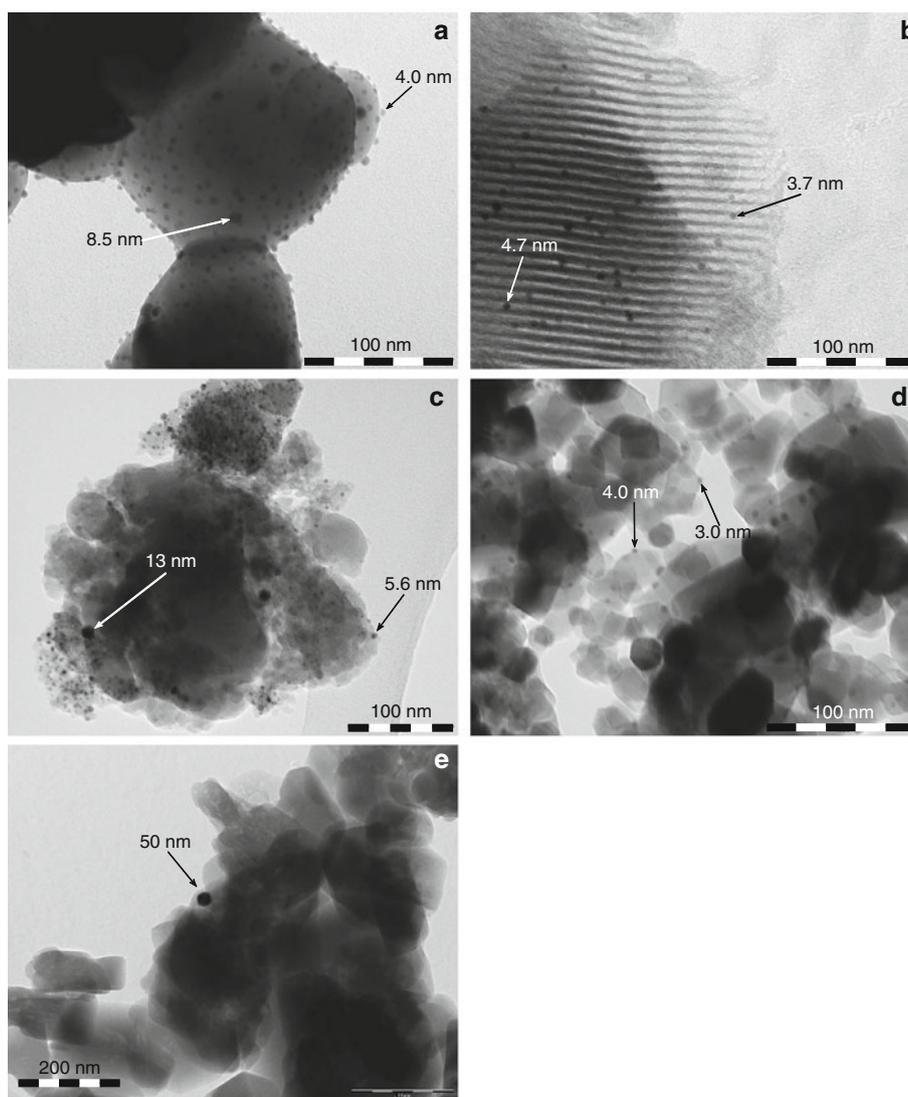


Table 1 Catalyst characterization and performance in methane oxidation at 400 °C of different supported gold catalysts

Support	S_{BET} (m ² g ⁻¹)	Au loading ^a (wt%)	$D_{\text{av}}/\sigma^{\text{b}}$ (nm)	$T_{\text{light-off}}$ (°C)	$C_{400 \text{ °C}}$ (%)
Non-reducible					
γ -Al ₂ O ₃	235	0.8	4.1/1.2	280	0.25
SiO ₂	306	1.3	4.2/3.7	225	0.58
SBA-15	470	na	4.6/1.1	225	0.48
ZSM-5	134	1	>30	360	0.067
Reducible					
TiO ₂	47	1.2	3.6/1.4	225	0.78
ZrO ₂	5	0.8	3.9/1.4	270	0.37
CeO ₂	Low	0.8	1/0.2	280	0.37
Nb ₂ O ₅	8	1	na	>400	0

na Not available

^a Determined from XRF

^b Average particle diameter determined from TEM micrographs

quartz tubular fixed bed reactor in the range of 25–400 °C with a heating rate of 3 °C min⁻¹. A 50 mL min⁻¹ flow containing 20% CH₄ and 5% O₂ balanced with He was fed

to the reactor. The effluent gas stream was analyzed with a dual channel Interscience CompactGC equipped with Porabond Q and Molsieve 5MS columns and TC detectors.

3 Results and Discussion

After calcination all catalyst materials exhibited an intensive pink to purple colour caused by light absorption due to the surface plasmon resonance of colloidal gold particles [58]. In Fig. 1, the UV–Vis–NIR DR spectra of the gold catalysts under study are presented, clearly showing the typical absorption band at 500–550 nm. Figure 2 displays representative TEM micrographs of some of the catalyst materials. In the TEM images the gold particles are observed as dark gray dots. In Table 1, the average particle diameters and standard deviations as obtained from the TEM images are listed. It was observed that in the case of Au/SiO₂ besides small particles (~4 nm in diameter), also larger agglomerates and particles (~20 nm) were formed, which is the result of the poor interaction between gold and SiO₂. Also in the case of the Au/ZSM-5 catalyst only very large gold particles (30–200 nm) were observed as evidenced by the corresponding TEM micrographs.

The results of the temperature programmed reaction experiments are presented in Fig. 3. The light-off temperature for methane oxidation over a Au/TiO₂ catalyst material lay around 250 °C. Only the total combustion products CO₂ and water were observed in very small amounts and the methane conversion reached 0.8% at 400 °C. When comparing the performance of different catalyst materials on both reducible and non-reducible supports, only slight shifts in light-off temperature were found, but in all cases only very low conversions (<1%) were obtained at 400 °C, yielding CO₂ as the only carbon containing product. This temperature has been reported before by Gluhoi et al. [59] as the onset temperature for the total catalytic combustion of methane over supported gold catalysts. In 2006, Solsona et al. [60] reported on the use of gold catalysts for the total oxidation of low concentrations (0.5 mol%) of hydrocarbons in air. An onset for methane combustion of around 150 °C was found for their most active Au/CoO_x catalyst. In the light of these results, it must be noted that methanol oxidizes over gold catalysts already at ~80 °C [31]. Therefore, if small amounts of methanol would be formed, its survival under the conditions needed for methane activation is questionable. In Table 1 the numerical results for the different catalyst materials under study are summarized. No clear influence of the support material on the activity, other than that low BET surface area materials generally yielded larger particles and a lower activity, was found. This suggests that the activity is mainly a function of the gold particle size and the related number of Au surface atoms. However, due to the very low catalytic activity, there is no solid foundation for any conclusions on a structure activity relationship.

The results reported here are in complete agreement with recently published results on low temperature partial

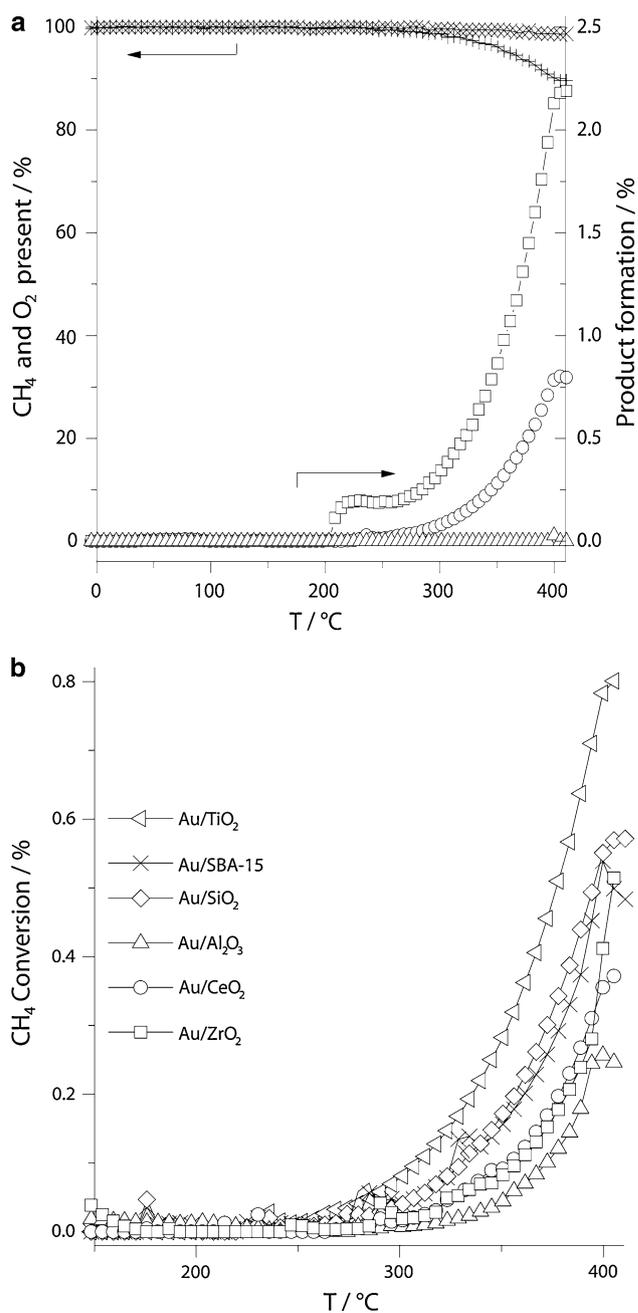


Fig. 3 Results for temperature programmed methane oxidation over supported gold catalysts. **a** Performance of Au/TiO₂: methane (*times*), O₂ (*plus*), MeOH (*open triangles*), CO₂ (*open circles*) and water (*open squares*). **b** Methane conversion versus temperature over different supported gold catalysts. Reactant flow composition: 5% O₂ and 20% CH₄ in He, total flow 50 mL min⁻¹

methane oxidation to synthesis gas over reference Au/TiO₂, Au/Al₂O₃ and Au/ZnO catalyst materials from the World Gold Council and AUROLite™, obtained in another laboratory [51–53]. In a recent publication by Lokesh et al. carbon and TiO₂ supported AuPd bimetallic nanoparticles have been successfully employed to selectively oxidize

toluene [54]. However, the monometallic gold catalysts did not show any activity in this reaction. Very recently the use of AuPd and AuPdCu based catalysts for the liquid phase oxidation of methane with aqueous hydrogen peroxide was disclosed. However, also in this case, the monometallic gold catalyst exhibited only very low activity and selectivity [56]. In high temperature (750 °C) methane oxidation, gold was found to poison the methane coupling activity of MgO when present in a low concentration of 0.04 wt%. At higher loadings the selectivity towards the formation of CO and CO₂ increased [50]. In the liquid phase selective oxidation of cyclohexane, gold catalysts have been reported to maintain high selectivities even at conversion <10% [47, 49]. However, by a thorough investigation of the reaction mechanism, we delivered proof for the occurrence of a radical-chain autoxidation mechanism. In fact, the gold catalysts caused an even higher loss of selectivity with increasing conversion as compared to the commercial autoxidation process [55]. These results confirm the doubts on the potential of supported gold nanoparticles for selective alkane oxidation, which is the main reason why we felt these results should be available in the open literature.

4 Conclusions

Based on our systematic investigation it is concluded that selective methane oxidation over supported gold catalysts is not possible under the applied experimental conditions. This finding was recently independently concluded in another laboratory as well, and in line with several recent publications, confirms that thus far, there is unfortunately no experimental proof of C–H activation of hydrocarbons with oxygen on supported gold catalyst materials.

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