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An investigation of the activity of coprecipitated gold catalysts for methane oxidation

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Coprecipitated Au on transition metal oxide catalysts have been tested for their activity toward methane oxidation. Catalyst activities fall in the order Au/Co_3O_4 > Au/NiO > Au/MnO_x > Au/Fe_2O_3 ≫ Au/CeO. The Au/Co_3O_4 catalyst is active just below about 250°C. The catalysts are proposed to have more than one type of reactive site since the supports are also active at higher temperatures. Analysis of spent catalysts with X-ray photoelectron spectroscopy indicates that Au exists in at least two oxidation states on some of them, a reduced state and an oxidized state. The activity for methane oxidation increases with increasing oxidation of Au in the oxidized state.

Keywords: catalysis; methane oxidation; gold; metal oxides; X-ray photoelectron spectroscopy

1. Introduction

Catalytic oxidation is an important method to remove methane from systems where it appears as an undesired contaminant or waste product. Methane is one of the most difficult hydrocarbons to oxidize catalytically [1,2]. Conventional noble metal supported catalysts (Pt or Pd on Al_2O_3) have been previously reported to show reasonable activity only above 300°C [3,4]. A more recent study has reported that Pd/Al_2O_3 is active below 300°C [5]. Lower temperatures would be beneficial in applications such as trace contaminant control in spacecraft, where methane accumulates as a result of metabolic processes, and automotive emission control, where methane is being considered as an alternative fuel [6].

A study was undertaken to find a low temperature methane oxidation catalyst based on the above motivating factors. Investigations focused on a selection of catalysts consisting of Au on a transition metal oxide. These types of catalysts had been shown to be active for CO oxidation at temperatures as low as −70°C [7] and had been found to be better than traditional Pt or Pd supported catalysts for CO

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oxidation [8,9]. Previous studies had also shown that CO oxidation catalysts could be active for methane oxidation [6] and that methane oxidation occurred over some of the transition metal oxide supports being considered [3].

Results are reported for Au supported on MnO_x, Fe_2O_3, Co_3O_4, NiO, and CeO_x. Activities of the catalysts for methane oxidation are compared and are related to the oxidation states of Au determined using X-ray photoelectron spectroscopy (XPS). Further information about the XPS analysis and a detailed kinetic study will be published elsewhere [10,11].

2. Experimental

The catalysts were coprecipitated from a solution of tetrachloroauric acid ($HAuCl_4$) and a transition metal nitrate corresponding to the desired substrate metal using 1 M sodium carbonate as the precipitating agent following procedures previously reported to give catalysts with peak activity toward CO oxidation [12]. All reagents were ACS grade or better purity (Aldrich Chemical Co.). The precipitate was removed from solution by ultrafiltration and systematically washed using deionized water. After being dried at 100°C, each sample was ground and sieved to 100–170 mesh. Calcining was performed using oxygen at 200°C for 30 min. All of the solutions were prepared to produce end products containing 5 at% Au. A blank Co_3O_4 support (with no Au) was also prepared in a similar manner for comparative analysis.

A laboratory microreactor was used for catalyst characterization. The reactant gas was a certified mixture (Iweco, Inc.) containing 1.48% CH_4 and 21.0% O_2 balanced with He. The bed temperature was measured using thermocouples placed around the exterior of the reactant bed. Each test run used approximately 200 mg of catalyst, giving a corresponding reactor space-time of roughly 0.2 s. Outlet gas composition was measured using a Hewlett-Packard 5890 gas chromatograph with flame ionization detector. Methane reaction rates were calculated from the change in concentration between the inlet and outlet streams, the stream flow rate, and the total mass of catalyst loaded.

Reactor operating conditions were selected to minimize mass and heat-transfer effects. A relatively high flow rate was used to ensure turbulent flow conditions and corresponding high mass transfer rates. The conversion efficiency at the nominal flow velocity was twice that at half the nominal flow velocity, indicating that mass transfer limitations were negligible. Conversion efficiencies (fractional conversions) were nearly identical for a given catalyst using different methane inlet concentrations. Because this nearly doubled the adiabatic temperature rise expected in the bed in one case, the bed temperature was adequately controlled. The experiments were repeated again after cooling the catalyst, and virtually identical activities were obtained in each case.

The XPS analysis was performed on the spent catalysts using a Perkin-Elmer

540 system. Samples were mounted on double-sided tape and high resolution scans were taken of the Na 1s, metal d (or f for Ce), O 1s, C 1s, and Au 4f regions at a pass energy of 8.95 eV. Atomic concentrations were calculated based on the areas under the respective peaks and tabulated element sensitivity factors for the instrument. The raw data were processed off-line to determine peak positions more accurately. Component peaks were deconvoluted where necessary. Details of the curve fitting procedures are given elsewhere [10].

3. Results and discussion

Catalyst activity was measured as the specific rate of methane conversion per gram of total catalyst (mmol/g min) at a given temperature. Results are shown in fig. 1 as a function of temperature for the four Au supported catalysts and a Co_3O_4 support. Points show the measured data and solid lines are fits using exponential functions that include activation energies and preexponentials [13]. Based on light off temperatures, the trend in activities for the Au catalysts was as follows: $Au/Co_3O_4 > Au/NiO > Au/MnO_x > Au/Fe_2O_3$. The Au on CeO_x catalyst was

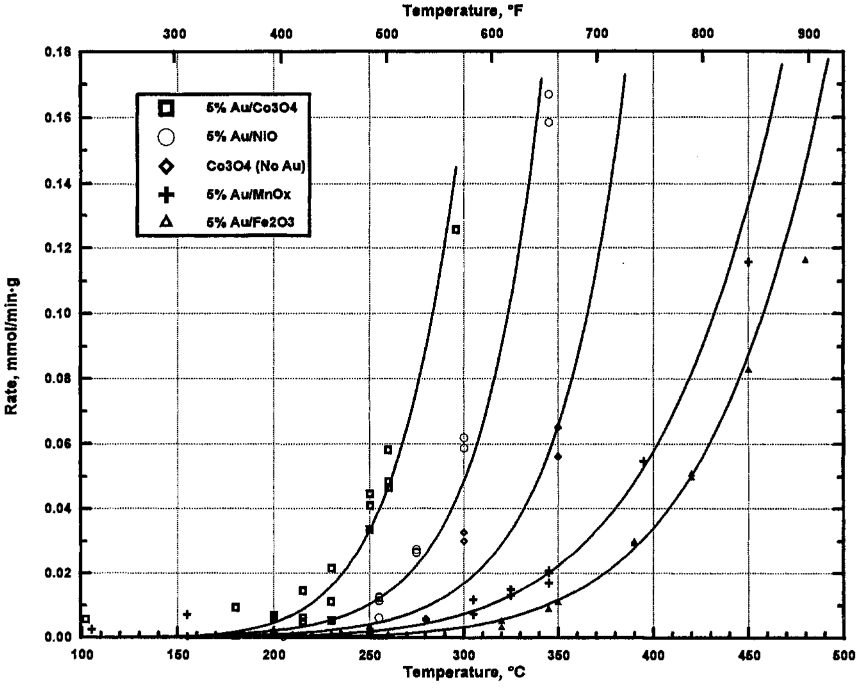

Fig. 1. Light-off curves for methane oxidation over catalysts consisting of 5% Au on MnO_x, Co_3O_4, NiO, Fe_2O_3, and CeO_x supports. Activity on a Co_3O_4 support is included for comparison. The feedstream composition was 1.48% CH_4 and 21% O_2 in He, and the reactor space-time was 0.2 s at a flowrate of ~ 65 ml/min. Points show the data and the solid lines are fits using exponential functions to activation energies and preexponentials [13].

inactive at the temperature range tested. The trend for the Au supported catalysts is the same as that previously reported for the blank supports [3]. The enhancement in activity due to addition of Au is apparent from a comparison of the curves for 5% Au/Co_3O_4 and Co_3O_4 (with no Au); the formed catalyst is active at a temperature roughly 50°C below the latter.

The results in fig. 1 show that the most efficient 5% Au/Co_3O_4 catalyst becomes active in the 200–250°C temperature range. This is lower than had been reported for traditional noble metal catalysts at the time of the investigations [3,6]. A more recent study has since shown that Pd on Al_2O_3 catalyst can be active at about this temperature range [5]. Given the costs of the respective noble metals and the fact that the Au catalysts were not optimized for the results in fig. 1, Au/Co_3O_4 is a viable competitor as a low temperature methane oxidation catalyst. Results from a recent study appear to support this conclusion [14]. The inactivity of the 5% Au/CeO_x catalyst is not completely understood, as unsupported CeO_2 has been reported as moderately active toward methane oxidation [3]. The CeO_x sample had markedly different physical properties (color, density, and granularity) than the other samples. These physical differences may contribute directly to the observed inactivity or be a sign of underlying chemical differences in the catalyst that effect the activity.

Gold supported on transition metal oxides has been previously investigated as a catalyst primarily for CO oxidation. Coprecipitated Au on Co_3O_4, Fe_2O_3, and NiO were reported to be active for CO oxidation at temperatures as low as −70°C [7], and coprecipitated Au on CuO, CeO_x, and MnO_x were found to be better than traditional Pt or Pd supported catalysts for CO oxidation [8,9]. Activity for CO oxidation was also reported for Au on Fe_2O_3 [12,15] and Au on MnO_x [15]. More recent studies have shown that CO oxidation activities for some of these catalysts and their supports are effected by water [14,16]. One study has been made of the H_2 oxidation activity of Au supported on transition metal oxides [9], and methane oxidation has also been reported over a Au on Co_3O_4 catalyst in the time since the results shown in fig. 1 were obtained [14].

Because the CO, H_2, and CH_4 oxidation reactions may proceed by distinctly different mechanisms that may even change from one catalyst to the next, a basis for understanding the differences in activities of the Au on transition metal oxides for methane oxidation is still lacking. Detailed kinetic studies are being undertaken to try to rectify this problem [11]. Because the supports show a measurable level of activity without Au [3], a dual site mechanism may explain the enhanced activity when Au is added. The two sites would be the Au and the support. This would mean that rates should be compared per gram of catalyst as in fig. 1 rather than per gram of Au. Speculation that the Au and the support function as different reaction sites for CO oxidation has been made earlier [9].

Catalyst compositions determined from XPS are given in table 1. All samples showed residual amounts of Na. Concentrations of Na above about 5% were accompanied by the appearance of a carbonate peak in the C 1s region, suggesting

Table 1
Atomic concentrations of elements on catalyst samples determined using XPS. Numbers after the metal represent catalyst allotments prepared at different times. Concentrations may not sum to 100% due to rounding

Sample	Atomic concentrations (%)				
	Na	metal	O	C	Au
Co-1	5.1	16.8	51.4	25	1.6
Co-2	3.6	20.8	64.2	10.2	1.2
Co-3	1.8	18.6	47.8	31.3	0.49
Ni-1	trace	22.6	62.7	14.4	trace[a]
Ni-2	0.64	34.6	47.4	17.4	trace[a]
Mn-1	6.5	16.7	57.0	17.5	2.3
Mn-2	4.5	24.7	42.3	28.0	0.65
Fe-1	26.3	7.6	46.0	20.0	0.08
Fe-2	5.4	12.1	45.0	36.5	0.02
Ce	2.9	4.7	34.7	57.7	0.01

[a] Reliable analysis was not possible due to interference from the shape of the background for the oxide support.

that Na was in the form of a carbonate. No significant amount of Cl was visible on any of the samples, showing that the washing steps were successful in removing unprecipitated $HAuCl_4$. The Au concentrations measured by XPS were all much lower than expected from the amount of Au used during coprecipitation. This discrepancy is attributed to several factors. The $HAuCl_4$ may not have precipitated completely, and the subsequent rinsing steps removed any excess Au (as unprecipitated $HAuCl_4$). The Au may have been incorporated in the matrix of the catalysts and thereby have been partially hidden from analysis. This factor is probably important for the Ce supported catalyst due to the expanded (and therefore porous) nature of the support. Finally, the catalyst surface may have been covered by a carbonaceous overlayer (note the carbon concentrations in table 1) that hid the underlying Au, especially if it was very highly dispersed across the support surface. The relative importance of these factors is the subject of further investigations.

The XPS peaks on all of the samples were shifted substantially due to charging effects. Corrections for this problem have been described elsewhere [17,18]. For the results in this and a subsequent study [10], the binding energy of the main C 1s peak for each sample was shifted to 284.8 eV to represent adventitious carbon [17] and the shift applied to all peaks for each respective catalyst. This correction procedure was considered valid because the C 1s peak shapes were similar on the catalysts, with components that could be assigned to aliphatic, carbonyl, and carbonate carbon. Binding energies representing other states of carbon that might be found as a primary component on the catalysts range from 284.5 eV for a pure graphitic carbon to 285.2 eV for an aromatic carbon. This represents a spread in peak positions of about ±0.3 eV from the carbon reference state chosen. The arrangement of peak positions for one sample relative to another would not change if this shift were applied uniformly to all peaks on all samples. The following discussion has taken this into consideration.

Oxidation states of Au on the catalysts are best represented by the position of the Au $4f_{7/2}$ peak relative to that for bulk Au at 84.0 eV [17,18]. Offsets were therefore determined for the Au $4f_{7/2}$ peak on each catalyst. The Au peaks on the MnO_x, Co_3O_4 and Fe_2O_3 supports had clearly visible shoulders at higher binding energies from the main peak. These shoulders were resolved into an additional component peak by deconvolution [10]. Shoulders were not deconvoluted in peaks for Au on NiO or CeO_x supports because the Au peak intensities were low (see table 1) and the shape of the background interfered with deconvoluting the peaks, especially for peaks from the Au on NiO. Additional states of Au may however have been present on these catalysts.

Specific reaction rates for methane oxidation at 300°C are compared with offsets for the Au $4f_{7/2}$ peaks in fig. 2. The offset scale is plotted from positive to negative binding energy going from left to right following the tradition of showing XPS spectra as a function of decreasing binding energy. Energies to the left of the dotted line at zero offset represent Au in an oxidized state. Error in the positions of the peaks are shown in the plot. The errors were larger when the Au intensity was

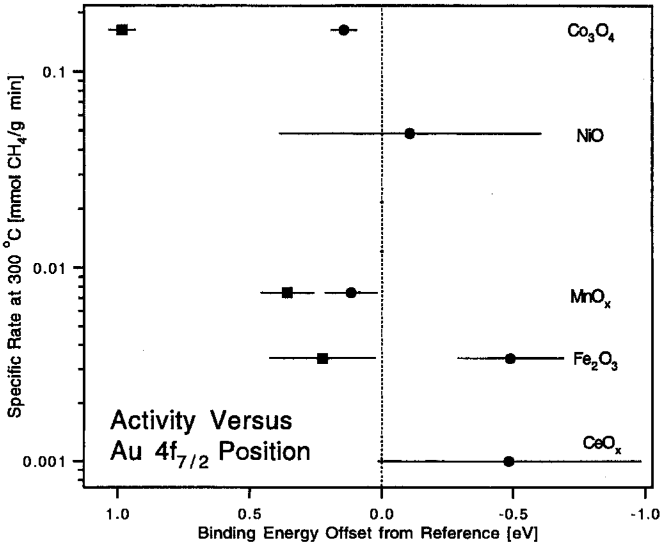

Fig. 2. Specific activity of metal oxide supported Au catalysts determined at 300°C from light-off curves versus the binding energy for the Au $4f_{7/2}$ peak determined from X-ray photoelectron spectroscopy for Au on Co_3O_4, NiO, MnO_x, Fe_2O_3, and CeO_x supports. Binding energies are plotted as offset from the bulk Au peak position (84.0 eV) after correcting for sample charging. The main peaks are shown as solid circles. The positions of peaks associated with shoulder states visible on the Co_3O_4, MnO_x, and Fe_2O_3 supported catalysts are shown as solid boxes. Error bars are based on estimated inaccuracies in determining the respective peak positions.

low as on NiO and CeO_x or when the C 1s peak was broad as on Fe_2O_3. The specific rate for the Au/CeO_x catalyst was essentially zero at 300°C but was taken as 1×10^{-3} mmol/g min in order to show a point for this catalyst on the graph.

The points given as solid circles in fig. 2 show the oxidation state for the main Au constituent on each catalyst. This Au is in the lowest oxidation state on each catalyst and is considered to represent a reduced (nearly metallic) state. The exact oxidation state of this Au component with respect to metallic Au appears to depend on the support. It appears to be slightly oxidized on MnO_x and Co_3O_4 supports, definitely reduced on Fe_2O_3 and CeO_x supports, and reduced or nearly neutral on NiO. No correlation appears to exist between the oxidation state of Au in the reduced state and the catalytic activity of the catalyst for methane oxidation, although the two catalysts where the Au in this state is clearly reduced have the lowest methane oxidation activity.

Offsets for the Au $4f_{7/2}$ peak under the shoulder on some of the catalysts are shown by solid boxes in fig. 2. The Au in these states is oxidized, though it is not necessarily strongly oxidized. The Au $4f_{7/2}$ peak for Au_2O_3 would appear at an offset of 1.9 eV in fig. 2 by comparison [18]. The Au/Co_3O_4 and the Au/MnO_x catalysts may contain relatively minor amounts of such highly oxidized Au [10]. With the exception of the Au/NiO catalyst, the catalytic activity for methane oxidation appears to correlate directly with the degree of oxidation of Au in the oxidized state. The higher the oxidation of the Au in this state, the greater the activity toward methane oxidation. An underlying assumption in this proposal is that the Au states determined by XPS under ultrahigh vacuum conditions are also present during reaction conditions. The validity of this assumption at the given reaction conditions remains to be established.

A recent proposal has been made that oxidized states of Au on transition metal supports act synergistically to provide sites for oxygen adsorption during CO oxidation [19]. Based on this hypothesis, a possible explanation for the trend in fig. 2 is that the degree of oxidation of Au in the oxidized state effects the ability of this site to bind oxygen, and this alters the catalytic activity for CO or methane oxidation. Changes in metal loading and dispersion have been shown to change the oxidation state of the Au on MnO_x [20] and to influence overall conversion for CO oxidation [9,12]. Therefore, a clearer understanding of how the degree of oxidation of Au on transition metal oxide supports effects the reaction mechanism for methane oxidation will only be possible after metal loadings are verified and Au particle sizes determined. Further investigations of the Au electronic structure and methane oxidation activity after different catalyst pretreatments and at different Au loadings are also needed, in particular for the most active Au/Co_3O_4 catalyst. This work is ongoing.

4. Conclusions

Activities of coprecipitated Au on transition metal oxides for methane oxidation were studied using a microreactor technique. The observed trend in activities was $Au/Co_3O_4 > Au/NiO > Au/MnO_x > Au/Fe_2O_3 >> Au/CeO_x$. The Au/Co_3O_4 catalyst was active between 200 and 250°C, and the Au/CeO_x catalyst was inactive at the temperatures tested. A dual-site mechanism may explain the results since the catalyst supports are also active at higher temperatures. Analysis using X-ray photoelectron spectroscopy found that Au was present in a reduced and an oxidized state on some of the catalysts. Methane oxidation activities increased with increasing oxidation of Au in the oxidized state. The role of the reduced and oxidized Au states on the catalytic mechanisms for methane oxidation remains to be clarified.

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