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Potassium Titanate: An Alternative Support for Gold Catalyzed Carbon Monoxide Oxidation?

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Abstract It has been found that gold supported on potassium titanate, $KTiO_2(OH)$ can, under some circumstances, exhibit a superior performance for the oxidation of carbon monoxide, relative to that obtained with titania as a support. It appears that the dispersions of gold on the two types of support are sufficiently similar that other factors are responsible for the improved activity noted. It may be that the higher basic character and/or detailed structural features of the titanate surface plays a role.

Keywords Gold · Potassium titanate · CO · Oxidation

1 Introduction

Recently simple procedures have become available to synthesize tubular TiO_x material [1, 2]. There is still controversy as the precise nature of these materials and their formation with their properties being dependent on the synthetic route used [1, 3–11] While these materials hold promise in the areas of photovoltaics and nanoelectronics [12, 13], a few reports have recently appeared where they have been exploited as catalyst supports [1, 3, 14].

Au supported on titania has been widely used in CO oxidation reactions [15–17], and numerous factors have been shown to enhance the activity of the Au/TiO_2 catalyst [15, 18] including Au particle size [19, 20]. Haruta et al. have demonstrated that the existence of strong interactions between Au particles and the support is imperative for high activity in CO oxidation [18]. Moreover, moisture is also known to positively enhance the activity at controlled concentrations [20]. Although the Au/TiO_2 catalyst is known to be very active for CO oxidation a major setback is that the catalyst is active over a short period of time due to deactivation at low temperatures. It is clear that the majority of studies on gold/titania by far have involved the use of commercial Degussa P25 titania, essentially a mixture of anatase and rutile, though some work with titania from other sources has been reported [13, 21–27]. Systematic investigations of titania polymorphs are much rarer and the role of support morphology has been the subject of few studies. In the current study, the have used a titanate obtained from KOH/TiO_2 as a support for the Au catalyzed CO oxidation reaction. We also report on some effects of morphological and structural modification of titania on the activity and stability of Au supported catalysts for CO oxidation.

2 Experimental

2.1 Synthesis of Titanate $KTiO_2(OH)$ Sheets

The synthesis procedure used to generate the titanate has been described elsewhere [12]. Commercial TiO_2 (P25) powder (25 g) was added to a 200 mL solution of 2.8×10^{-1} M KOH in a 1 L stainless steel autoclave. The mixture was heated for 24 h at 120 °C (stirring at 500 rpm). The resulting material was cooled, then allowed to age for 2 days in the base solution. It was then repeatedly centrifuged and washed with deionized water until the conductivity was below 100 μS cm^{-1}. The material was finally dried in air at 120 °C for at least 12 h. From here onwards the resultant material shall be referred to simply as the titanate, $KTiO_2(OH)$.

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2.2 Preparation of Gold-Supported Catalysts

Deposition-precipitation was the method used to load gold onto the TiO_2 (P25) and $KTiO_2(OH)$ [28]. In each case the support was slurried in distilled water (600 mL) and stirred vigorously. Required amounts of diluted $HAuCl_4$ solution (10^{-2} were added slowly to the supports with continuous stirring. The pH was maintained at 8.5 by adding 15% NH_4OH drop wise in the case of TiO_2 (P25) while in the case of $KTiO_2(OH)$ the pH was already at ~9; so the addition of NH_4OH was not necessary. The precipitated solutions were aged for 2 h. A solution of $NaBH_4$ was prepared in ice water and added in the required amount as a reductive treatment [29] The resulting catalyst powders of Au–TiO_2 (P25) and Au–$KTiO_2(OH)$ were dark purple and light pink and contained a maximum of 1.1 wt% and 0.8 wt% Au loading respectively.

2.3 Sample Characterization

The X-ray diffraction patterns were obtained on a Philips PW 1820 diffractometer with Cu Kα (1.54178 Å) radiation. High-resolution TEM images were obtained using a JEOL 2010 electron microscope with a LaB_6-cathode operated at a voltage of 200 kV. Raman measurements were made using the micro-Raman attachment of a Jobin-Yvon T64000 Raman spectrometer, configured in triple subtractive mode.

FTIR spectra were recorded using a Bruker Tensor 27 IR-spectrometer equipped with KBr detector and CaF_2 windows at a spectrum resolution of 4 cm^{-1}. The sample powder was pressed (~10 MPa) into a self-supporting disc that was placed in a sample holder fitted with an internal heating coil.

Nitrogen adsorption-desorption isotherms were measured on a Micromeritics TRISTAR 3000 analyzer. The samples were degassed under vacuum for several hours before nitrogen adsorption measurements. The specific surface area was determined by the Brunauer–Emmet–Teller (BET) method.

2.4 Catalytic Activity Measurement

All catalyst samples were treated at 300 °C in either 20% O_2 (balance He) or 5% H_2 (balance He) for 2 h prior to testing. The two catalysts were tested for CO oxidation activity in a continuous flow fixed-bed glass reactor (6 mm i.d). Between 50 mg and 100 mg of solid catalyst (powder particle size about 150 μm) samples were loaded into the reactor. The gas mixtures consisted of 1% CO and 5% O_2 balanced in He and the total flow was generally 47 sccm. The course of the reaction was monitored quantitatively by GC analysis, using a Carbosieve SII packed column (2 m × 2 mm).

3 Results and Discussion

3.1 Textural Characterization of the Samples

In Table 1 the textural data for the samples are summarized. The specific surface area of the titanate material $KTiO_2(OH)$ was three times more than that of the commercial TiO_2 (P25). The deposition of gold on both materials did not significantly alter the features of the support.

3.2 Structural Properties

3.2.1 Raman Spectroscopy

The structural differences between TiO_2 (P25) and the titanate $KTiO_2(OH)$ is revealed by the Raman results (Fig. 1). The TiO_2 (P25) profile showed more intense and sharper peaks than those of $KTiO_2(OH)$ and this can be attributed to the fact that the former is more crystalline while the latter is amorphous. Some of the peaks might have shifted due to a particle size effect [30]. New peaks were observed for the $KTiO_2(OH)$ and are mainly due to the structural changes in the TiO_2, e.g. from three-dimensional crystallites to two-dimensional sheets [10]. Gold did not have any influence on the characteristic Raman profiles of the two supports.

3.2.2 X-ray Diffraction Analysis

Figure 2 shows the typical experimental powder XRD profiles taken from the titanate samples. The diffraction peaks are much broader for the $KTiO_2(OH)$ sample than those obtained from TiO_2 (P25) (not shown) crystals, and a thorough literature search shows that the profile cannot be attributed to any of the known crystal structures of TiO_2 [30]. Gold was not readily detected on Au–TiO_2 (P25). e.g., the Au (111) diffraction line at $2\theta = 38.4°$ overlaps with a line due to the TiO_2 support.

Table 1 Physical properties of the studied samples

Sample	Gold loading (wt%)	S_{BET} $m^2\ g^{-1}$	Pore volume $cm^3\ g^{-1}$	Particle size of Au (nm)*
TiO_2(P25)	–	49.4	0.16	–
$KTiO_2$(OH)	–	182	0.49	–
Au–TiO_2(P25)	1.1	49.0	0.30	5.1
Au–$KTiO_2$(OH)	0.8	162	0.43	4.7

* Determined by TEM

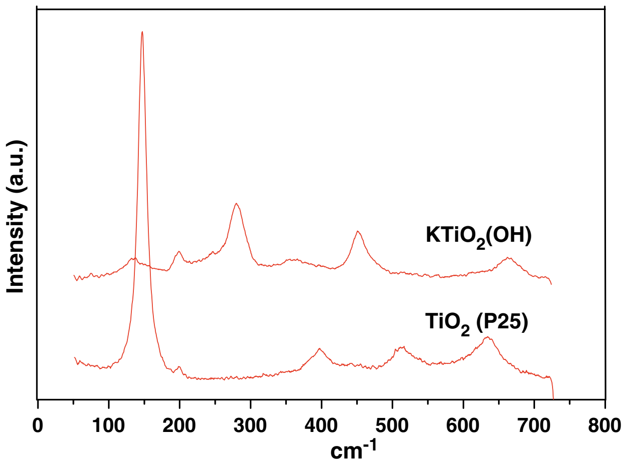

Fig. 1 Raman spectra of as prepared titanate $KTiO_2(OH)$ and commercial TiO2 (P25)

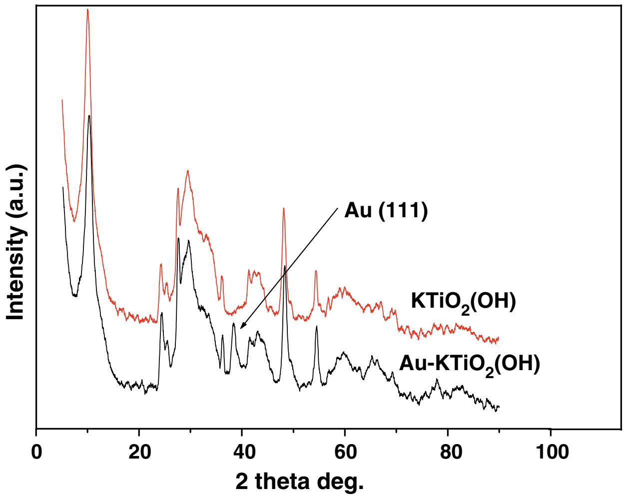

Fig. 2 X-ray diffraction patterns of as prepared $KTiO_2(OH)$ and Au–$KTiO_2(OH)$ samples

3.2.3 *Electron Microscopy*

The morphology of the titanate $KTiO_2(OH)$ revealed by the use of TEM, suggested that the titanate was in the form of very thin sheets which could roll up into layered sheets of titanium oxide [30]. TEM images of the as prepared Au–$KTiO_2(OH)$ and Au–TiO_2 (P25) catalysts showed that the Au average particle sizes were 4.7 and 5.1 nm respectively. The particle size distributions are shown in Fig. 3. The chemical composition of the Au–$KTiO_2(OH)$ and $KTiO_2(OH)$ samples was examined by EDS and the presence of potassium was confirmed in both samples.

3.2.4 *Infrared Spectroscopy*

FTIR was used to characterize the titanate $KTiO_2(OH)$ sheet material and the IR data demonstrated the existence of large amounts of water and hydroxyl groups in the spectrum (H_2O at 1,624 cm^{-1} and a strong O-H stretching vibration between 3,600 and 2,500 cm^{-1}) [31]. Two OH stretch vibrations at around 3,645 cm^{-1} and 3,707 cm^{-1} were still visible even after the sample had been heated up to 220 °C where the dehydration of the sample was complete (as evidenced by DSC studies). This suggested that the absorption bands could be considered to be due to entities contained in the crystal structure. The fact that there are two OH stretch vibrations suggests the presence of different chemical environments (bridging modes) of the hydroxyl groups in the titanate structure.

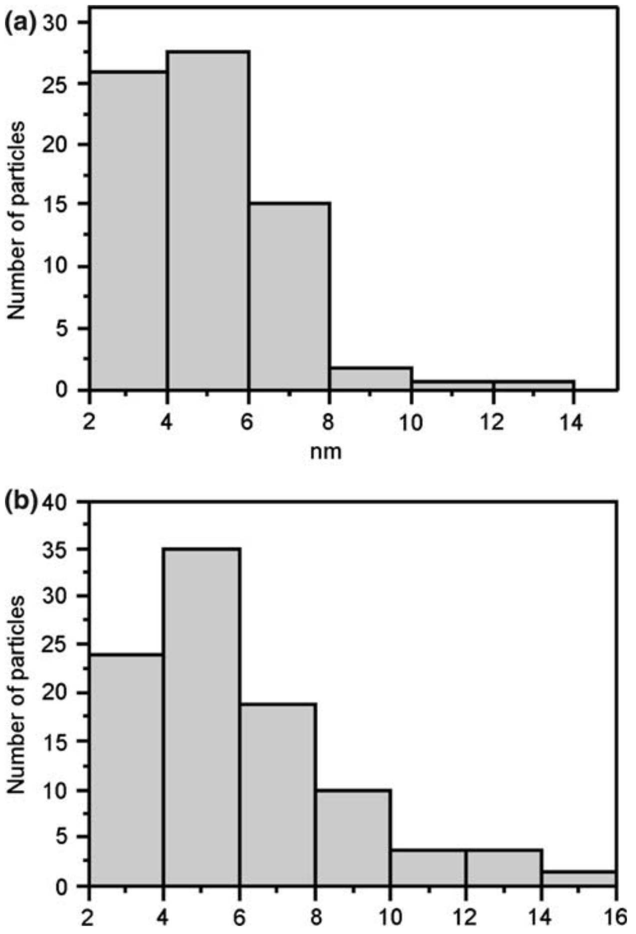

Fig. 3 Size distributions of Au metallic particles in as prepared (**a**) Au–TiO2 (P25) and (**b**) Au–KTiO2(OH) as revealed by TEM

3.3 CO Oxidation

The catalytic activities of differently conditioned catalysts for CO oxidation are plotted in Figs. 4 and 5. Treating the two catalysts Au–TiO_2 (P25) and Au–$KTiO_2(OH)$ under an oxidizing atmosphere, generally results in the latter being significantly more active than the former. Reductively conditioned Au–$KTiO_2(OH)$ catalyst also showed a higher activity than the Au–TiO_2 (P25) catalyst treated under the

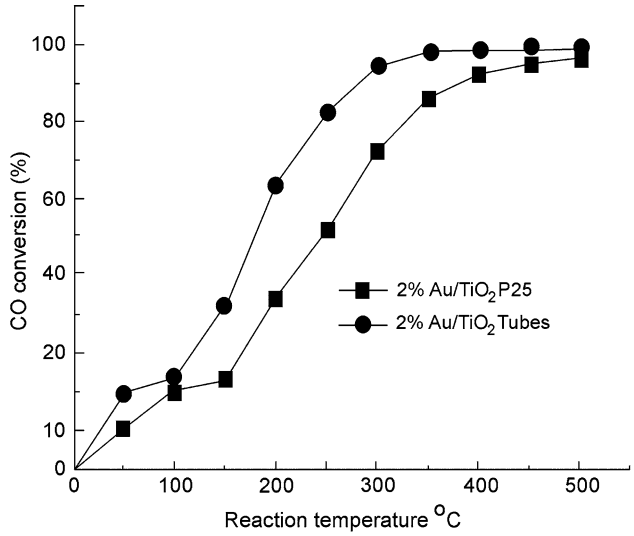

Fig. 4 CO conversion over Au–TiO$_2$ (P25) and Au–KTiO$_2$(OH) catalysts that were calcined in 20% O$_2$ (balance He) for 2 h prior to testing

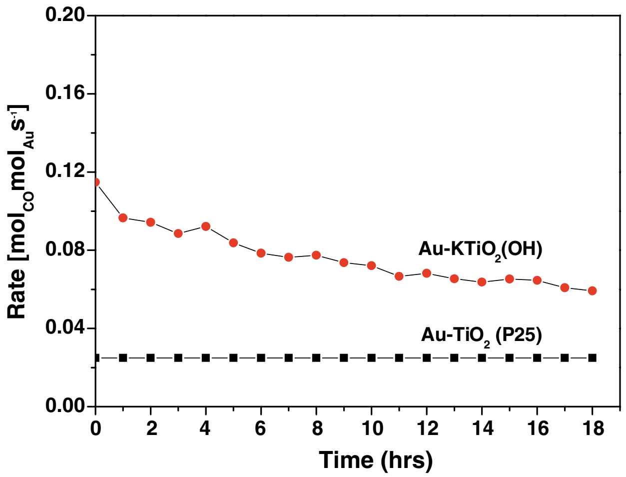

Fig. 5 CO conversion over Au–TiO$_2$ (P25) and Au–KTiO$_2$(OH) catalysts that were calcined in 5% H$_2$ (balance He) for 2 h prior to testing. Reaction ran at 355 K

same reductive conditions, but it was noted that deactivation of the former was more rapid. The treatment conditions applied ultimately affect the composition of any catalyst and in this case the contribution of ionic Au species may have played a significant role. XPS and HRTEM work needs to be done to establish whether enhancement in activity with the titanate support is due to a particle size effect or chemical effects. However, in view of the similar particle size distributions obtained for both Au–TiO$_2$ and Au–KTiO$_2$(OH) it seems likely that chemical effects may well be largely responsible for the observed differences in activity. In general terms, it may be assumed that the KTiO$_2$(OH) is a more basic support than TiO$_2$ and this factor also has to be considered. Basic oxides such as magnesia have been shown to be particularly active for supported gold [32–34], and more acidic oxides such as zeolites, for example, are in general less active [35]. Very little systematic work has however been reported to date and so the precise role of support acidity-basicity is not yet clear. The addition of Group 1 metal ions to TiO$_2$ has been observed to *increase or decrease* the activity of Au–TiO$_2$ catalysts subsequently prepared from the treated support, depending on the concentration level to which the Group 1 metal ions are added [36], an effect which appears to be related to the electronic environment of the gold in the solids [36]. A further factor may well be the detailed stricture of the support at the nanoscale. Nanosized ceria, for example appears to lead to higher activity when used to support gold [37], than other forms of ceria. Nevertheless, the current work adequately demonstrates that titanate materials may well be useful in offering a further support system for gold mediated catalysis, even if the precise reasons for the higher activity remain obscure. Further work will demonstrate whether the effect is a general one for gold-based catalysis.

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