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Remarkable enhancement of Fe–V–O_x composite metal oxide to gold catalyst for CO oxidation in the simulated atmosphere of CO₂ laser†

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A novel Au/Fe–V–O_x/Al₂O₃ catalyst displayed remarkable activity and good stability for CO oxidation in the simulated atmosphere of a CO₂ laser with high CO₂ levels up to 60 vol% and stoichiometric or even lower O₂/CO ratio. The improved surface labile lattice oxygen on the FeO_x and VO_x modified Al₂O₃ plays a crucial role in its outstanding performance for the CO oxidation reaction in an oxygen-poor atmosphere.

The carbon dioxide laser (CO₂ laser) which can be called the “invisible man”, emitting a laser with a wavelength of 10.6 μm in the infrared “body”, has become one of the most efficient and powerful lasers and has been widely used in laser cutting, welding, drilling and surface treatment. For CO₂ lasers, a persistent problem is the decomposition of CO₂ molecules in the discharge,^{1–3} accompanied by a host of gas products, such as CO, O₂, O, O₃, NO, and N₂O.⁴ With the increase of these species, especially CO as the main composition, the CO₂ laser will lose its output power or is even unable to work.^{5,6}

The catalytic oxidation of CO over the internal solid catalysts is a way to expand the life of sealed CO₂ laser *via* recombining CO and O₂. The main challenges for the catalyst are to work at the conditions with high CO₂ level and stoichiometric or even less O₂/CO ratio since some oxygen formed by CO₂ dissociation is probably consumed in other reactions. Some supported noble metal catalysts, such as Pt/SnO₂, Pt/MnO, Pd/SnO₂, Rh/SnO₂, Ru/MnO₂, have been investigated as promising catalysts for use in sealed CO₂ lasers. Among them, SnO₂ supported Pt and Pd catalysts showed the best performance. However, their deactivation with time was continuously observed in the process.⁷

Compared with supported Pt, Pd, Ru and Rh nanoparticles, supported gold nanoparticles, well-known for their excellent catalytic performance towards many heterogeneous catalytic reactions, have exhibited unexpectedly higher catalytic activity

for CO oxidation, especially at lower temperatures.⁸ This brings a possibility for the Au catalysts to serve in CO₂ laser and a number of works have shown some positive results. An increase in output power of a CO₂ laser was observed after gold was coated on the inside wall of a discharge tube in the presence of a discharge.⁹ Better activity and less deactivation of CO oxidation in CO₂ laser over Au/MnO₂ than Pt/SnO₂ were reported by Upchurch *et al.*¹⁰ A two-week constant output power of 10 W was observed in a transversely excited atmospheric pressure CO₂ laser (TEA CO₂ laser) when the Au/Fe₂O₃ catalyst was applied in its external body.¹¹ An even long-time life, 5 month's constant output power was obtained in a compact low-power (4 W) sealed CO₂ laser by incorporating a supported gold catalyst which was coated on outer jacket.¹²

Due to a large amount of CO₂ in the reaction feed gases, acidic supports are likely to be more durable, which could be helpful to maintain the activity of the catalysts during the reaction, for less carbonate species formatted on the surface of the support.¹³ Alumina is one of those kinds of suitable supports, owing to its neutral property, thermal stability, mechanical strength, *etc.*¹⁴ Our laboratory has prepared a series of very active and stable Au catalysts which are supported by metal oxides modified Al₂O₃ for the CO oxidation in oxygen-rich atmosphere.^{15–17} The output power of 160 W in a radio frequency excited CO₂ laser (RF CO₂ laser) can be maintained for more than two weeks *via* a continuous usage¹⁸ and for 4 months with a day-time operation mode by inputting one of our alumina-based Au catalysts. The output power (24 W) of a 600 mm long sealed CO₂ laser can be maintained for about 4.5 months when our coated Au catalysts working on the inside wall of a discharge tube with day-time operation model too (unpublished data). Au catalysts are so obviously to deserve an in-depth study in the atmosphere of CO₂ laser which features in high level of CO₂ and low O₂/CO ratio. An attempt has been made to clarify the working mechanism of Au catalysts in this specific

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situation and hope to finally meet the need from industries to provide a qualified catalyst for CO₂ laser with more than one year life.

In order to improve and maintain the catalytic activities for CO oxidation under lean or rich conditions, lots of studies have done on oxygen storage materials (OSM), *e.g.*, Prof. M. S. Hegde developed the CeO₂ or SnO₂ based OSM supported catalysts^{19,20} using their own creative solution combustion method.²¹ They found that the high rates of CO oxidation by O₂ over Pd ion substituted OSM are shown to be due to highly labile lattice oxygen and the oxide ion vacancies. Similarly, the main point for supported gold nanoparticles to be more efficient relies in the adsorption, activation rate of O₂ and its reaction rate with CO during the reaction. For iron and vanadium oxides possess a very rich redox behavior associated with its various oxidation states (Fe³⁺, Fe²⁺, and V⁵⁺, V⁴⁺, V³⁺, V²⁺), the employment of these oxides to Al₂O₃ could highly increase the surface oxygen species of the catalyst. In this communication, we successfully developed for the first time FeO_x and VO_x modified γ -Al₂O₃ (denoted as Fe-V-O_x/Al₂O₃) supported Au catalysts, which were not only much more active in the simulated atmosphere of CO₂ laser than Au/Al₂O₃ but also stable. Moreover, further studies revealed that compared with Au/Al₂O₃, the higher dispersion of Au nanoparticles and the increased concentration of surface oxygen on the support caused by the modification of FeO_x and VO_x accounted for their good performance. A comparison with the performance of Au/Al₂O₃ was made simultaneously in order to shed a light on the catalyst design for the application in CO₂ laser.

The Fe-V-O_x/Al₂O₃ support was prepared by a two step of incipient wetness impregnation of γ -Al₂O₃ with Fe(NO₃)₃ and NH₄VO₃ solution, respectively, and followed by calcination at 600 °C for 4 h. Au targeted at 1 wt% was deposited on both γ -Al₂O₃ and Fe-V-O_x/Al₂O₃ supports using the deposition precipitation method as reported previously¹⁶ (details see ESI†). The resultant Au/ γ -Al₂O₃ and Au/Fe-V-O_x/Al₂O₃ catalysts have actual Au loading of 0.77 wt% and 0.23 wt% (Table S1†), respectively, which were both lower than the target value due to gold loss in adsorption process.

Fig. 1a illustrates the profiles of CO conversions as a function of reaction temperature over Au/Al₂O₃ and Au/Fe-V-O_x/Al₂O₃ catalysts at a high space velocity (60 000 mL g_{cat}⁻¹ h⁻¹). Considering the obvious difference of the two curves, a significant support effect is observed. The Au/Al₂O₃ catalyst, with 0.77 wt% gold loading, gave a CO conversion of 52% at 60 °C and the CO conversion increased slowly with elevating the reaction temperature. Even though the temperature was elevated at 240 °C and reached 300 °C, the CO conversion over Au/Al₂O₃ catalyst was still lower than 75%, increased only *c.a.* 20%. However, for Au/Fe-V-O_x/Al₂O₃ catalyst, although its gold loading was only 0.23 wt%, the CO conversion was another story, unexpectedly, it was maintained at 100% from 60 °C to 300 °C in the simulated atmosphere of CO₂ laser.

In order to further explore the intrinsic catalytic activity, the specific rates at different temperatures of the investigated catalysts were also evaluated (Fig. 1b). The reaction rates over Au/Fe-V-O_x/Al₂O₃ catalysts were calculated to be 6.2 and

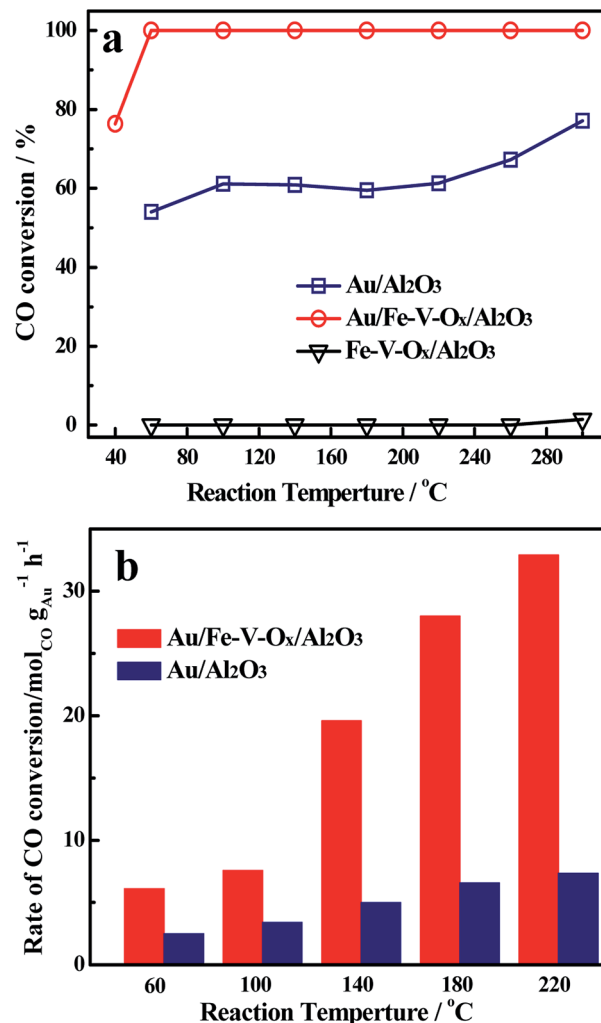


Fig. 1 (a) CO conversions as a function of the reaction temperatures over Au/Al₂O₃ and Au/Fe-V-O_x/Al₂O₃ catalyst in the simulated atmospheres of CO₂ laser and (b) their specific rates at different temperatures. Reaction conditions of (a): 60 vol% CO₂ + 1 vol% CO + 0.5 vol% O₂ + 0.5 vol% H₂O and balance N₂. Weight hourly space velocity (WHSV): 60 000 mL g_{cat}⁻¹ h⁻¹.

7.4 mol_{CO} g_{Au}⁻¹ h⁻¹ at 60 °C and 100 °C, respectively: *c.a.* 2.5 times higher than the results of Au/Al₂O₃ (2.5 and 3.1 mol_{CO} g_{Au}⁻¹ h⁻¹). When the temperatures were elevated to 140, 180, and 220 °C, the more striking observation is that the reaction rate of Au/Fe-V-O_x/Al₂O₃ catalyst reached 19.8, 27.9, and 32.9 mol_{CO} g_{Au}⁻¹ h⁻¹, respectively, which were nearly four times as high as those of Au/Al₂O₃ (5.1, 6.8, and 7.2 mol_{CO} g_{Au}⁻¹ h⁻¹).

It is interesting that in the feed of 1% CO in air, 0.1 g of Au/Al₂O₃ can completely convert 1% CO at -11 °C with a space velocity of 60,000 mL g_{cat}⁻¹ h⁻¹, at where only the conversion of CO over same amount of Au/Fe-V-O_x/Al₂O₃ is 27% (Fig. S1†). The reaction rates at this temperature for Au/Al₂O₃ and Au/Fe-V-O_x/Al₂O₃ are 3.41 and 3.96 mol_{CO} g_{Au}⁻¹ h⁻¹, respectively. This means that the modified catalyst is slightly active than unmodified one in oxygen-rich atmosphere, but much more active in CO₂-rich (or oxygen-poor) atmosphere.



In addition, the Au/Fe-V-O_x/Al₂O₃ catalyst presented similar stability to Au/Al₂O₃ with time on stream of the simulated atmosphere of CO₂ laser at space velocity of 154, 200 mL g_{cat}⁻¹ h⁻¹, only minor activity loss was observed at the beginning of the test and then the CO conversion reached a plateau (Fig. S2†). Furthermore, we chose a well-known active and stable gold catalyst 1 wt% Au/Fe₂O₃-HGI and 1 wt% Au/MnO₂-HGI provided by Haruta Gold Incorporation and prepared by M. Haruta's laboratory to benchmark and compare with our catalysts. As shown in Fig. S2 (ESI†), even at a high space velocity of 154, 200 mL g_{cat}⁻¹ h⁻¹, the CO conversion at 220 °C over our Au/Al₂O₃ and Au/Fe-V-O_x/Al₂O₃ was higher than that of 1 wt% Au/Fe₂O₃-HGI and 1 wt% Au/MnO₂-HGI tested at a low space velocity of 120, 000 mL g_{cat}⁻¹ h⁻¹, and the Au/Fe-V-O_x/Al₂O₃ catalyst performed much more active during the 750 min's long time test.

To reveal the unique properties of Au/Fe-V-O_x/Al₂O₃ catalyst for CO oxidation in the simulated atmosphere of CO₂ laser, further studies were performed to discuss the influence of the modification of FeO_x and VO_x on the structure of the Au active sites. The Au L₃-edge X-ray absorption near-edge structure spectra (Fig. S3†) indicated that the chemical state of gold nanoparticles in Au/Fe-V-O_x/Al₂O₃ was mainly metallic Au, which is the same as the chemical state of Au/Al₂O₃ prepared by a same manner as reported previously,¹⁴ so we could know that the increased activity was not ascribed to the change of the chemical state of Au.

There was no Au diffraction peaks observed in the XRD patterns of both Au/Al₂O₃ and Au/Fe-V-O_x/Al₂O₃ presented in Fig. S4,† implying the presence of Au nanoparticles smaller than 2 nm in a diameter as major species. This point can be verified from the typical images HAADF-STEM images (Fig. 2a and b, S5 and S6†) and their Au nanoparticle size distributions (Fig. 2c and d). For Au/Al₂O₃ catalysts, most of the Au nanoparticles were dispersed well on the surface of Al₂O₃ (Fig. 2a),

but severely sintered Au nanoparticles larger than 10 nm were observed (Fig. S5a and b†). But we could not find any visible large Au nanoparticles for Au/Fe-V-O_x/Al₂O₃ catalyst despite our careful observations (Fig. 2b, S6a and b†), indicating that the Au nanoparticles deposited on the surface of Fe-V-O_x/Al₂O₃ support were fairly uniform than those of the Au/Al₂O₃ catalysts. Fig. 2c and d also clearly showed that the particle size distributions of Au/Fe-V-O_x/Al₂O₃ catalysts was much more uniform with a mean particle size of 2.0 ± 0.7 nm. These results demonstrated that the modification of FeO_x and VO_x on the surface of Al₂O₃ supports could stabilize small Au nanoparticles during the preparation process. The FeVO₄ identities formed on alumina surface due to the modification of FeO_x and VO_x, which is evidenced by the Raman peak at 804 cm⁻¹ in Fig. S7,† probably play certain role in hindering aggregation of small Au nanoparticles.

To ascertain the influence of the chemical properties of the supports on their catalytic activity, we further focused on the concentration of surface oxygen species, which has pronounced effect for CO oxidation, through the temperature-programmed desorption of oxygen (O₂-TPD) over Au/Al₂O₃ and Au/Fe-V-O_x/Al₂O₃ catalysts. Generally, the desorption of the adsorbed oxygen was activated *via* the following procedures: O₂ (adsorbed) → O₂⁻ (adsorbed) → O⁻ (adsorbed) → O²⁻ (lattice).²² During the characterization of O₂-TPD, if the more adsorbed oxygen species be desorbed from surface of the catalyst at low temperatures, it indicates the more labile lattice oxygen could be attend the CO oxidation in the range of reaction temperatures we tested. By means of the O₂-TPD analysis of the Au/Al₂O₃ and Au/Fe-V-O_x/Al₂O₃ catalysts, two different desorption peaks of oxygen species were observed in Fig. 3 and could be distinguished by their desorption temperatures as reported in the literature.²³ For both of Au/Al₂O₃ and Au/Fe-V-O_x/Al₂O₃ catalysts, the peaks at low temperatures are ascribed to the desorbed oxygen species, which are weakly chemisorbed surface oxygen, and the peaks at the temperatures higher than the 400 °C are attributed to the release of oxygen in the lattice of the supports,

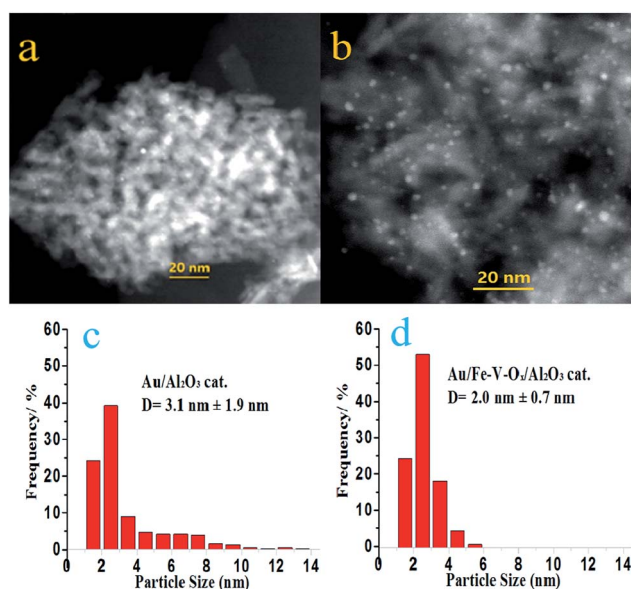


Fig. 2 HAADF-STEM images of Au/Al₂O₃ (a) and Au/Fe-V-O_x/Al₂O₃ (b) and their Au particle size distributions (c and d).

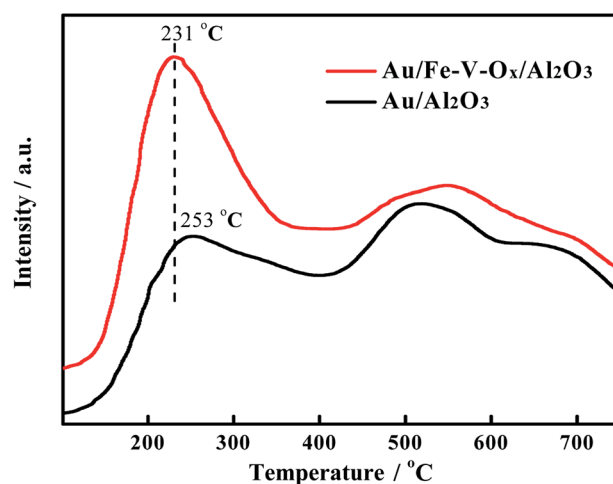


Fig. 3 O₂-TPD profiles of the Au/Fe-V-O_x/Al₂O₃ and Au/Al₂O₃ catalysts.



which is hard to be reacted and the difference in the peaks at higher temperature for two catalysts is somehow weak. In contrast, we can obviously see that the weakly chemisorbed surface oxygen species of Au/Fe–V–O_x/Al₂O₃ catalyst desorbed at the temperature of 231 °C, which was 22 °C lower than that of Au/Al₂O₃ catalyst (253 °C). Its peak area which represents the amount of the chemisorbed surface oxygen species is much larger. It suggests that the modification of FeO_x and VO_x on the surface of Al₂O₃ support truly increases the concentration of the chemisorbed surface oxygen (labile lattice oxygen), which could highly promote the oxidation of CO to CO₂ with the labile lattice oxygen on the support similar as reported in the literature before.^{24,25} This point was further confirmed by the higher formation rate of CO₂ on Au/Fe–V–O_x/Al₂O₃ than that of Au/Al₂O₃ at 200 °C in the atmosphere of 97%CO in N₂ (Fig. S8†). The oxidation of CO could only happen with the chemisorbed oxygen of the supports because of no or very little O₂ in the feed gas. Based on the above analysis, we can conclude that after modified by FeO_x and VO_x, even though its total content is only 2 wt%, the concentration of the labile lattice oxygen increase and thereby its catalytic activity can be markedly improved for the oxidation of CO in the simulated atmosphere of CO₂ laser.

In conclusion, we reported a highly active and stable Au/Fe–V–O_x/Al₂O₃ catalyst for CO oxidation in the simulated atmosphere of CO₂ laser. The improved labile lattice oxygen caused by the modification of FeO_x and VO_x on the surface of Al₂O₃ is of great importance for the CO oxidation at the conditions with low O₂/CO ratio.

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