Evidence for the Formation of Hydrogen by Surface Reaction between Hydroxyl Groups and CO Molecule over Ga_2O_3–Al_2O_3

Masaaki Haneda,*[†,††,†††] Emmanuel Joubert,[†] Jean-Christophe Ménézo,[†] Daniel Duprez,[†] Jacques Barbier,[†] Nicolas Bion,[††]
Marco Daturi,[††] Jacques Saussey,[††] Jean-Claude Lavalley,[††] and Hideaki Hamada[†††]
[†]*Laboratoire de Catalyse en Chimie Organique, Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers, Cedex, France*
[††]*Laboratoire de Catalyse et Spectrochimie, UMR 6506, ISMRA, 6 Bd du Maréchal Juin, F-14050 Caen, Cedex, France*
[†††]*National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565*

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Surface reaction of CO with Al_2O_3-supported metal oxide catalysts was studied. Reversible reduction/oxidation was observed for In_2O_3–Al_2O_3. Although the exposure of Ga_2O_3–Al_2O_3 to CO caused the formation of CO_2, the successive reoxidation by O_2 was not observed. This was accounted for by the reaction of surface hydroxyl groups on Ga_2O_3–Al_2O_3 with CO, leading to CO_2 and H_2.

Al_2O_3-supported metal oxide catalysts have been studied extensively as the catalyst for removal of NOx emitted from lean-burn and diesel engine exhausts.[1] In general, the surface acidity[2] as well as the redox property[3] would be regarded as factors to determine the DeNOx activity. Accordingly, it is very important to characterize in detail the catalyst surface for understanding the relation between DeNOx activity and catalyst features. In the course of this study, it was found that the surface reactivity of Ga_2O_3–Al_2O_3 toward CO is quite different from that of Al_2O_3 and In_2O_3–Al_2O_3. We will report the unique catalytic behavior of Ga_2O_3–Al_2O_3 for the surface reaction with CO.

Al_2O_3, In_2O_3–Al_2O_3 and Ga_2O_3–Al_2O_3 were prepared by sol–gel method described in detail elsewhere.[4] The catalyst precursors were finally calcined at 873 K for 5 h in air. The loading of In_2O_3 and Ga_2O_3 was fixed at 5 and 30 wt%, respectively. BET surface area was found to be as follows: Al_2O_3 207 m^2g^{-1}, In_2O_3–Al_2O_3 227 m^2g^{-1}, and Ga_2O_3–Al_2O_3 191 m^2g^{-1}. The surface reactivity toward CO at 723 K was measured with a pulse method. After the sample (0.1 g) was oxidized at 673 K, ten pulses of CO (0.267 mL) were injected on the catalyst bed every 2 min, followed by five pulses of O_2. Unconverted CO and O_2 and produced CO_2 in CO pulses were analyzed with a gas chromatograph using a Porapak Q column. The surface species formed by the reaction of CO on the catalyst surface were studied using infrared spectroscopy in static conditions. Prior to the measurement, the self-supporting sample disk was oxidized at 873 K for 1 h and then evacuated at the same temperature. The activated sample was exposed to CO (1.33 kPa) at 373 K, followed by heating up to 773 K in the presence of CO. IR spectra were recorded at room temperature with a Nicolet 710 FT-IR spectrometer.

Table 1 shows the total amount of CO uptake and CO_2 formation in 10 pulses of CO and that of O_2 uptake in 5 pulses of O_2. The reduction of alumina by CO was not recognized. In_2O_3–Al_2O_3 led to CO uptake and CO_2 formation with similar values. Good recovery of oxygen was also observed, indicating reversible reduction/oxidation of indium oxide. On the other hand, Ga_2O_3–Al_2O_3 gave relatively large amounts of CO uptake and CO_2 formation (practically equal quantities), but the O_2 uptake was much lower than the CO uptake.

Table 1. Surface reactivity estimated by CO-O_2 pulse method at 723 K

Catalysts	CO uptake	CO_2 formation	O_2 uptake
	μmol-CO g^{-1}	μmol-CO_2 g^{-1}	μmol-O g^{-1}
Al_2O_3	0.6	0	0.4
In_2O_3-Al_2O_3	70.4	55.2	57.6
Ga_2O_3-Al_2O_3	135.4	114.6	3.1

The following three possibilities for CO_2 formation arisen by the reaction of CO with the catalyst surface are considered: (1) reaction with lattice oxygen leading to oxygen vacancies,

$$CO + \text{“}O_{\text{-lattice}}\text{”} \rightarrow CO_2 + \text{“}\square\text{”} \qquad [1]$$

(2) reaction with surface hydroxyl groups leading to hydrogen,

$$CO + \text{“OH”} \rightarrow CO_2 + 1/2\, H_2 \qquad [2]$$

(3) disproportionation of CO leading to carbon deposits,

$$2CO \rightarrow CO_2 + C \qquad [3]$$

Apparently, CO_2 formation over In_2O_3–Al_2O_3 proceeds through the first possibility, because oxygen thus consumed is readily restored by O_2 addition. Over Ga_2O_3–Al_2O_3, the first and third possibilities would be excluded, because recovery of oxygen was not observed and the amounts of CO uptake and CO_2 formation were practically equal. At this point the second possibility, which is similar to water–gas shift reaction, could be plausible.

In order to verify the presence of hydrogen in the effluent gas from the catalyst exposed to CO pulses at 723 K, another set of experiments was carried out using a quadrupole mass spectrometer (Balzers) and an FT-IR spectrometer (Nicolet 550) fitted with a gas cell. The results are illustrated in Figure 1.

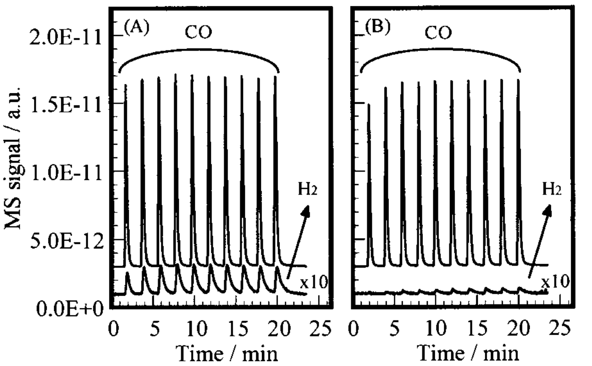

Figure 1. Analysis of the effluent gas after CO pulses were injected on (A) Ga_2O_3-Al_2O_3 and (B) In_2O_3-Al_2O_3 at 723 K.

Apparently, the formation of H_2 (M/e=2) by the injection of CO pulses was observed for Ga_2O_3–Al_2O_3 (Figure 1(A)), while little amount of H_2 was detected on In_2O_3–Al_2O_3 (Figure 1(B)). The formation of CO_2 was certainly recognized in the gas phase using FT-IR spectrometer (not shown). The amount of CO uptake and H_2 formation on Ga_2O_3–Al_2O_3 was evaluated to be 90.0 and 41.8 μmol g^{-1}, respectively. If the reaction [2] proceeds on the surface, the amount of H_2 formation should be one-half of the CO uptake. In fact, the value of H_2/CO is ca. 0.46, in good agreement with our hypothesis. It can be concluded that the surface hydroxyl groups of Ga_2O_3–Al_2O_3 are highly reactive toward CO, resulting in the formation of CO_2 and H_2.

Since water–gas shift reaction is known to proceed via the formation of formate intermediates,[5] identification of the surface species formed during the reaction was made using FT-IR spectroscopy. Figure 2 shows the IR spectra for Ga_2O_3–Al_2O_3. An intense IR band at 2227 cm^{-1} assignable to CO species interacting with Lewis acid sites was detected at all the temperatures. IR bands ascribed to hydrogen carbonate[6] were also detected at 1236, 1485 and 1637 cm^{-1} in the IR spectra above 473 K. It should be noted that new bands appeared at 1395, 1584 and 1997 cm^{-1} for reaction temperatures above 573 K. A gradual growth of these bands was also observed as the temperature increases.

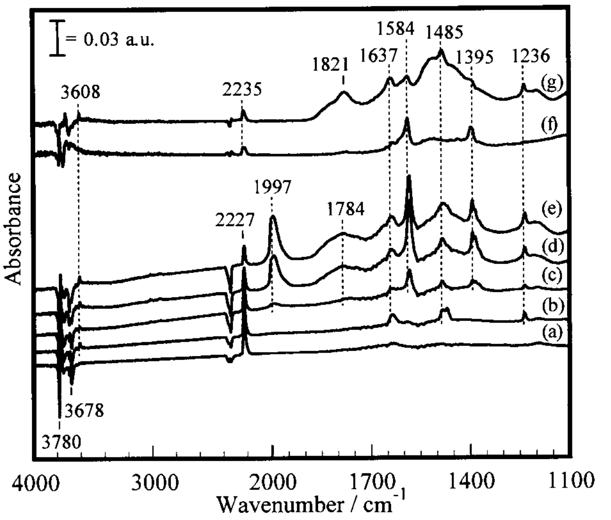

Figure 2. FT-IR spectra of adsorbed species formed after the exposure of Ga_2O_3-Al_2O_3 (a-e), Al_2O_3 (f) and In_2O_3-Al_2O_3 (g) to 1.33 kPa of CO at elevated temperatures. (a) 373 K, (b) 473 K, (c) 573 K, (d), (f), (g) 673 K, and (e) 773 K.

The bands at 1395 and 1584 cm^{-1} are assignable to the ν_s(COO) + δ(CH) and ν_{as}(COO) of adsorbed formate species, respectively. The frequency of the band at 1997 cm^{-1} is in good agreement with that of hydrogen species adsorbed on α-Ga_2O_3 reported by Meriaudeau and Primet.[7] As shown in Figure 3, an intense band at 1987 cm^{-1} appeared along with some shoulder bands when Ga_2O_3–Al_2O_3 was exposed to 13.3 kPa of H_2 at 573 K in static conditions. An isotopic shift from 1987 cm^{-1} to 1432 cm^{-1} was also observed when deuterium instead of hydrogen was adsorbed on Ga_2O_3–Al_2O_3. Since adsorption of H_2 on Al_2O_3 gave quite different IR spectrum, the 1987 cm^{-1} band can be assigned to hydrogen species adsorbed on Ga^{3+} sites, represented by Ga^{+y}–H species. From these results, it is the most plausible that the band at 1997 cm^{-1} detected in the presence of CO at elevated temperatures is assigned to Ga^{+y}–H species formed by the reaction of CO and the surface hydroxyl groups.

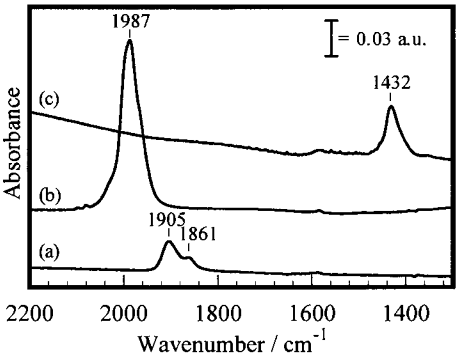

Figure 3. FT-IR spectra of adsorbed hydrogen species after introduction of 13.3 kPa of H_2 at 573 K. (a) Al_2O_3 and (b) Ga_2O_3-Al_2O_3. (c) Isotopic effect of deuterium (9.3 kPa) adsorption on Ga_2O_3-Al_2O_3 at 473 K.

Shido et al.[8] reported that OH groups on MgO and ZnO can react with CO to form surface formates. In the present work, the same reaction is presumed to take place on the surface of Ga_2O_3–Al_2O_3, as confirmed by the appearance of negative bands at around 3680–3780 cm^{-1} (Figure 2). Although the need of water for the decomposition of formate to hydrogen has been reported,[8] the formation of hydrogen species was observed above 573 K even though H_2O was not added in the feed gas. Hydrogen might be formed through the reaction of formate with the neighboring OH groups. Carbon dioxide would be formed by the decomposition of hydrogen carbonates, leading to the regeneration of OH groups. We also think that H_2O would play the role of regeneration agent if it is present. The remarkable catalytic behavior about hydrogen formation seems to be a unique feature of Ga_2O_3–Al_2O_3, because the formation of hydrogen species was not observed for Al_2O_3 and In_2O_3–Al_2O_3 (Figure 2). Ga_2O_3 dispersed on alumina might play an important role for hydrogen storage.

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