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Spectroscopic and Kinetic Studies of the Reaction of $CO + H_2O$ and $CO + O_2$ and Decomposition of HCOOH on Au/H-Mordenite Catalysts

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The surface species formed from the reaction of $CO + H_2O$ and $CO + O_2$ and decomposition of HCOOH on Au incorporated into H-mordenite zeolite have been studied by means of *in situ* FTIR spectroscopy. On H-mordenite, a bidentate formate species (2912, 1536, and 1390 cm^{-1}) is produced upon exposure to the $CO + H_2O$ gas mixture at 323 K, as well as different carbonate-like species (1956, 1852, 1705, and 1360 cm^{-1}). The latter species was extensively formed in a short time and was responsible for hindering the CO_2 adsorbed species. However, Au/H-mordenite presented different vibration modes of formate species with a high emphasis on the monodentate ones (2950, 2916, 2896, 1690, and 1340 cm^{-1}). The HCOOH adsorption on Au/H-mordenite showed two bands at 1622 and 1590 cm^{-1} of the ν_{as}(OCO) species, suggesting the formation of two types of formate species. The decomposition rate of the formate species formed on Au moieties was faster than that formed on H-mordenite. This was consistent with the calculated activation energies of CO_2 formation that showed a lower value (40.1 kJ/mol) on the former sample than on the latter one (63.3 kJ/mol). A dehydrogenation mechanism is proposed ($HCOOH \rightarrow H_2 + CO_2$) for the decomposition of HCOOH on the Au/H-mordenite catalyst. On the other hand, the Au/H-mordenite catalyst activated the CO oxidation reaction. This reaction proceeded mainly through the formation of carboxylate species at first, which tended to obviate with time, preferring the formate species. The latter species resulted from the interaction of CO with OH stretching of the zeolite assisted by the presence of gas phase O_2. The formate species is further decomposed with time to carbonate species. © 2000 Academic Press

Key Words: **H-mordenite; gold; *in situ* FTIR; $CO + H_2O$ and $CO + O_2$ reactions; HCOOH decomposition.**

INTRODUCTION

It has been known for a long time that pure gold is inactive as a catalyst due to the filled *d*-band. However, recent work has clearly shown that gold is capable of catalyzing many reactions such as the oxidation of CO when Au is intensely dispersed on a specific group of oxide supports (1). The activities observed were very sensitive to the preparation conditions and the nature of the support, which has a decisive influence on the particle size of gold and its structure at the gold–metal oxide interface (2).

As a result of introducing gold ions inside the zeolite cages, e.g., NaY, a high catalytic activity for NO decomposition and NO reduction by CO in the presence and absence of hydrogen has been established with high performance (3, 4). Our recent work on zeolite-encapsulated gold catalysts explored high catalytic activities for the $CO + H_2O$ reaction (water–gas shift reaction, WGSR) at low temperatures (5). An unidentate formate species was identified on Au^+/zeolites as a surface intermediate when WGSR took place. In order to identify surface species produced in the course of a reaction, the species are usually confirmed by adsorption of the possible compounds by which the adsorbed species may be generated (6). Formic acid is one of the simplest molecules produced from the WGS and CO hydrogenation reactions. Therefore, study of the adsorption of this molecule on Au^{n+}/zeolites has been motivated by our recent results that suggested that Au^+ was the active site on which the formate species was formed (5). However, more emphasis on the role of Au^+ for catalyzing that reaction can be clarified by carrying out the reaction on the bare zeolite surface.

CO oxidation is another very important reaction established by Au/oxide catalysts. Haruta and colleagues (7) illustrated that gold is able to adsorb both oxygen atoms and CO at the same time when it is dispersed on ZnO support. They proposed that the oxidation of CO occurred on the gold side of the Au–ZnO interfacial perimeter and a carbonate-like species was formed as an intermediate. In view of the established dispersion of Au^+ inside zeolites, an improved CO chemisorption was reached (8). To elucidate the role of this adsorbed CO, the bound form, and the ability to contribute reactions, a low-temperature catalytic CO oxidation on Au/zeolites can be carried out. Besides, insight into the surface intermediates that might be formed upon using the H-mordenite zeolite as a substrate for Au ions in comparison with those of oxides is of interest.

Therefore, the major objective of the present work is to identify the adsorbed species derived from $CO + H_2O$ and $CO + O_2$ reactions on H-mordenite-encapsulated gold catalysts by means of *in situ* FTIR spectroscopy. The study of the reaction mechanisms has been supported by the formic acid decomposition

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at elevated temperatures as a reference to elucidate the surface species derived from the above-mentioned reactions. To the best of our knowledge, a similar study on Au/zeolites has not been reported.

EXPERIMENTAL

Sample Preparation

Five weight percent Au/H-mordenite was prepared at room temperature by careful mixing of $AuCl_3$ (Strem Chemicals, 99% purity) with partially dehydrated H-mordenite zeolite at 523 K under a nitrogen atmosphere. More details on the sample preparation can be found elsewhere (5, 9).

The in Situ FTIR Study

In situ infrared spectra of the sample were recorded with a Shimadzu double-beam FTIR-4100 spectrometer with 40 coadded scans at 2 cm^{-1} resolution. The sample was pressed into a self-supporting wafer and mounted in a quartz infrared cell with CaF_2 windows that connected to a vacuum (10^{-5} Torr) closed circulating Pyrex system with a dead volume of 270 cm^3. More information on the vacuum system and the infrared cell can be found elsewhere (5).

Kinetic Study

The formic acid decomposition and CO oxidation reactions were performed in a closed circulating manifold system made of Pyrex glass connected with a U-type reactor, in which the Au/H-mordenite sample was charged. The catalyst was treated by being heated under vacuum (10^{-4} Torr) at 323 K for 0.5 h prior to the admission of formic acid (3.0 Torr) or the reacting gas mixture of CO/H_2O of different ratios. The gas phase reactants and products were analyzed by on-line gas chromatography (Shimadzu 8A) using two columns packed with Porapak Q and Molecular Sieve-5A. The detector used was thermal conductivity operated at 333 K for the separation of CO, CO_2, H_2O, and H_2.

RESULTS AND DISSCUSSION

The Water–Gas Shift Reaction

Figure 1 shows the IR spectra in the region 3000–1300 cm^{-1} obtained when an Au/H-mordenite catalyst is exposed to a CO/H_2O (6 : 1) gas mixture at 323 K as a function of time. The obtained spectra were subtracted from the background for each spectrum. The initial spectrum, recorded after 10 -min of contact time, showed a strong band at 2192 cm^{-1} and a very small band at 2128 cm^{-1}. These bands are assigned to the chemisorbed CO onto Au^+/H-mordenite and Au^0/H-mordenite, respectively, as they coincide with those reported for CO-coordinated Au–NaY (9). Some other bands at 2950, 2916, and 2896 cm^{-1} in the C–H stretching region and at 1340 cm^{-1} in the C–H bending vibration appeared, together with a band at 2500 cm^{-1}. Besides, the appearance of the 1690 cm^{-1} band characteristic of the $\nu_{C=O}$ vibration is indicative of the formation of either carboxylate [C=O (OH)] or formate species [O(C=O)]. However, the presence of absorption bands in the C–H absorption region appears to rule out the possibility of the existence of carboxylate species. Furthermore, a band at 1936 cm^{-1} and a shoulder at 1850 cm^{-1} attributed to bridging or organic-like carbonates species (10) were detected together with the evolution of a band at 2354 cm^{-1} attributed to CO_2 adsorbed species. The intensities of all the bands were enhanced with time. However, a preferential decrease of CO_2 bands (2384 and 2354 cm^{-1}) was detected with increasing time from 133 to 220 min. This decrease was parallel to the increase in intensity of organic-like carbonate bands at 1936 and 1850 cm^{-1}. Furthermore, this decrease in CO_2 bands was associated with the decrease in the relative band intensity of Au^+–CO/Au^0–CO with time, pointing out the great participation of the Au^+–CO species in the reaction. It can be suggested that the observed absorption bands at 2950, 2916, 2896, 1690, and 1340 cm^{-1} represent different vibration modes of formate species adsorbed on Au as well as on the H-mordenite zeolite sample. The assignments of IR bands are listed in Table 1. The assignments are described hereinafter.

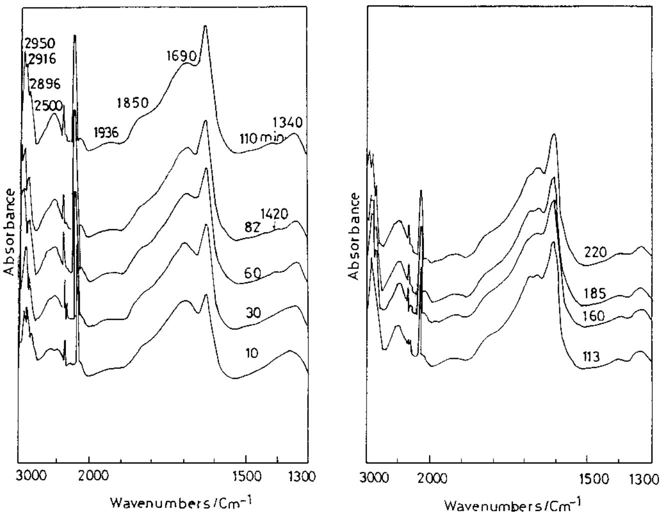


FIG. 1. *In situ* FTIR spectra of the CO + H_2O (6 : 1) gas mixture adsorbed on 5 wt% Au/H-mordenite at 323 K as a function of time.

In order to account for the role of Au toward the WGSR and to determine whether the formed intermediate (formate or carboxylate) is intimate to Au species or to the substrate, the same reaction was carried out on the parent H-mordenite zeolite (Fig. 2). Bands at 2448, 1705, 1625, and 1536 cm^{-1} were clearly observed after 5 min. After 1 h, the bands at 1705, 1625, and 1536 progressively increased in intensity with the evolution of other bands at 2912, 1956, 1852, and 1360 cm^{-1}. Besides, a tiny band at 2376 cm^{-1}, characteristic of CO_2 adsorbed species, was also developed. As time elapsed, the 1536-cm^{-1} band showed a marked decrease in intensity together with a subsequent increase in the band at 1360 cm^{-1}, confirming that they do not belong

TABLE 1
IR Absorption Bands of Adsorbed Species as a Result of the Reaction of CO + H_2O and CO + O_2 and Decomposition of HCOOH on Au/H-Mordenite and H-Mordenite Samples

	IR bands (cm^{-1})	
Species	On H-mordenite	On Au/H-mordenite
Bidentate formate	ν(CH), 2912; ν_{as}(OCO), 1536; ν_s(OCO), 1390	
Unidentate formate		ν(CH), 2950 (2960)[a], 2916 (2900)[a], 2896 (2700)[a] (2896 and 2800)[b]; δ(CH), 1340 (1390)[a] (1380)[b]; νC=O,1690 (1680)[b]; $\nu_{as}(COO^-)$, (1622 and 1590)[a] (1630)[b]; $\nu_s(COO^-)$, (1356)[a] (1330)[b]
CO coordinated gold		Au^+–CO, 2192; Au^0–CO, 2128
Organic-like carbonate	1956, 1852	1936, 1850
Monodentate carbonate and (bidentate)	νC=O, 1705(1590) (1660)[c]; $\nu_{as}(COO^-)$, 1425; $\nu_s(COO^-)$, 1360	
CO_2 ads. and (asym.str.ν_3)	2376 and (2448)	2354 , 2384, and (2500)
H bonded HCOOH		1730
Carboxylate		ν_{as}(OCO), 1500; ν_s(OCO), 1324

[a] The values in parentheses are those of formate species resulting from HCOOH ads.

[b] The values in parentheses are those of formate species resulting from the CO + O_2 reaction. The other values in parentheses represent the type of species mentioned between brackets. The values without parentheses are those species resulting from the CO + H_2O reaction.

[c] The value in parentheses is that of carbonate species resulting from the CO + O_2 reaction.

to the same species. The latter band was not shifted upon using D_2O instead of H_2O (not shown). The preservation of this band after isotope admission confirmed that it does not contain hydrogen atoms. Thus, this band is assigned to the carbonate species. On the contrary, the C–H stretching vibration at 2912 cm^{-1} was sensitive to the isotopic H/D exchange, confirming the presence of formate species. After 2 h of reaction time, two bands at 1390 and 1425 cm^{-1} were formed. One can assign the 1536 and 1705 cm^{-1} bands to carbonate or carboxylate species. However, after 5 h, the 1536 cm^{-1} band disappeared while the 1705 cm^{-1} band was preserved. The prominent appearance of the 1705 cm^{-1} band together with the band at 1360 cm^{-1} confirmed the existence of carbonate species on the surface. Accordingly, the 2912 cm^{-1} band of C–H stretching vibration together with the bands at 1536 and 1390 cm^{-1} are assigned to $\nu_{as}COO^-$ and ν_s COO^- of formate species, respectively. Similar asymmetric and symmetric formate vibrational bands were formed on the CuO–MgO catalyst, while performing WGSR, at 1540 and 1400 cm^{-1}, respectively (11). Further confirmation was achieved on an alumina support following formic acid adsorption to show bands at 2912, 1598, and 1395 cm^{-1} (12).

During the reaction at 348 K, the formate band at 2912 cm^{-1} declined in intensity to indicate the earlier decomposition of formate species. This is a consequence of the weak bond formed between the formate species and the zeolite that is manifested by the low $\Delta\nu = (\nu_{as} - \nu_a)$ value, i.e., 146 cm^{-1}. This could lead us to propose that the formate structure formed on the H-mordenite sample could be a bidentate formate species that used to show lower $\Delta\nu$ values than those of bridge and monodentate formate species. As a consequence of the formate decomposition, another type of carbonate species was observed at 1590_{sh} cm^{-1} and attributed to a bidentate carbonate ion (11). The earlier disappearance of the 2448 cm^{-1} band, assigned to asymmetric stretching vibration ν_3 (13) after 5 min, confirmed that the CO_2 lifetime is shortened to be converted instantaneously into carbonate species.

By comparison of the bands over Au/H-mordenite with those observed over H-mordenite, it can be noted that only a band at 2912 cm^{-1} in the C–H stretching region was revealed on the latter sample, like the 2916 cm^{-1} band in the former one. Thus, this band can be assigned to the C–H stretching vibration of formate formation on zeolite. The 1956 and 1852 cm^{-1} bands were distinctively formed and had higher frequencies over the H-mordenite sample compared with the Au/H-mordenite one. The shift of the 2500 cm^{-1} band to a higher frequency for the sample containing Au compared with the 2448 cm^{-1} band of the Au-free sample could be attributed to the polarizing strength of Au^+ species.

To further confirm that formate species are the reaction intermediates of WGSR, the formic acid adsorption has taken place on the Au/H-mordenite sample. Figures 3A and 3B depict the IR spectra in two wavenumber regions obtained when Au/H-mordenite was treated with 3.0-Torr formic acid as a function of varying the evacuation temperatures. Bands appearing in the C–H stretching region after evacuation at 323 K (bottom spectrum in Fig. 3A) were at 2960, 2900, and 2700 cm^{-1} with a low-frequency tail containing another band at 2584 cm^{-1}. As the decomposition temperature increased to 373 K, the bands at 2960 and 2900 cm^{-1} showed an increase in intensity and were arranged as a doublet with the appearance of a small distinct

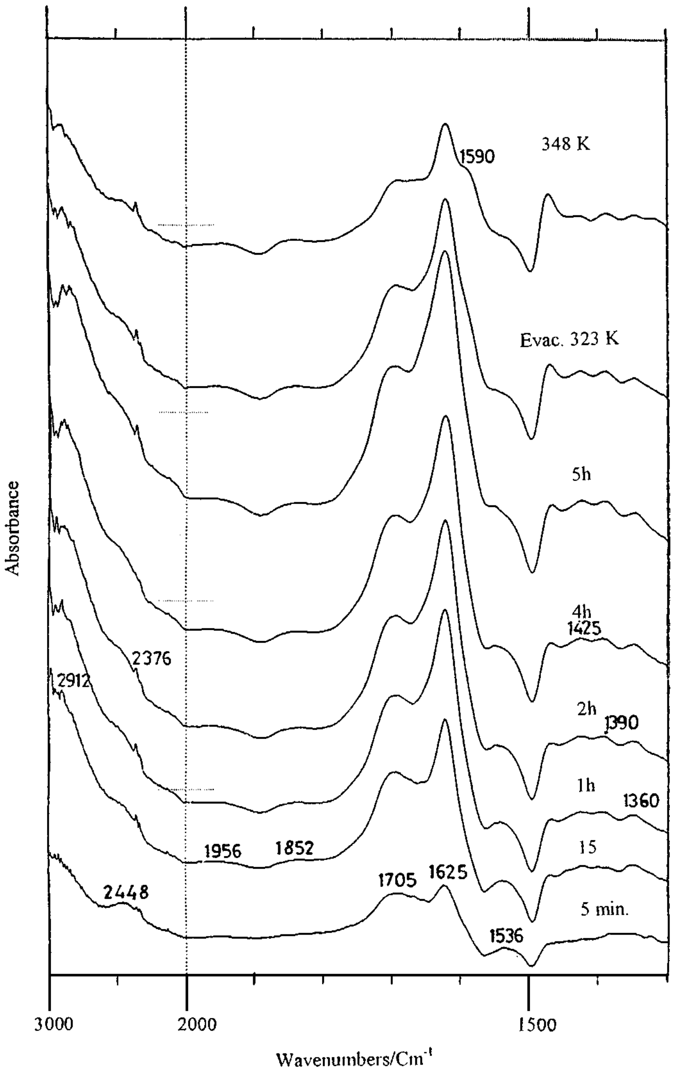


FIG. 2. *In situ* FTIR spectra of the $CO + H_2O$ (6 : 1) gas mixture adsorbed on H-mordenite at 323 K as a function of time and with increasing temperature.

band at 2368 cm^{-1}. The former band can not be attributed to physisorbed formic acid because prolonged evacuation at 373 K resulted in the prominent appearance of the band. The same band was also confirmed at 2950 cm^{-1} as a result of exposing the Au/H-mordenite sample to the $CO + H_2O$ gas mixture at 323 K (Fig. 1). Therefore, this band can be attributed to a combination band of δ (C–H) and $\nu(OCO)_{as}$, as has been evaluated as well for a band at 2933 cm^{-1} which arose when CeO_2 was exposed to HCOOH adsorption (14). The band at 2900 cm^{-1} represented a vibration mode of formate species adsorbed on Au/H-mordenite. Similar absorption bands at 2930 and 2850 cm^{-1} were revealed on Cu/SiO_2 when formic acid adsorption took place (15). These bands were attributed to the formation of a substantial concentration of unidentate copper formate species. One can attribute the 2900–2882 cm^{-1} band to the formate species formed on zeolite that resembled that seen at 2912 cm^{-1} upon exposing the H-mordenite sample to the $CO + H_2O$ gas mixture (Fig. 2). An increase in the CO_2 band at 2368 cm^{-1} was accompanied by the almost disappearance of the 2584 cm^{-1} band after being heated at 400 K. The 2700 cm^{-1} band decreased synchronously and less than the 2960 cm^{-1} one after being heated at 400 K. Thus, it can be attributed to an unidentate adsorbed species on Au similar to that reported for K/SiO_2 when formic acid adsorption took place to form $[HOOC^{-}K^{+}]$ at 2692 cm^{-1} (16). It can be seen that the decomposition rate of the formate species formed on the Au catalyst (2700 cm^{-1}) is faster than that on zeolite (2900 cm^{-1}) due to the observed decrease in intensity of the former and the perseverance of the latter during the rise in temperature.

On the other hand, the spectral changes in the region 2000–1300 cm^{-1} showed bands at 1730, 1680, 1622, 1590, 1390, and 1356 cm^{-1} after evacuation at 323 K. Upon evacuation at 373 K, the bands at 1730 and 1680 cm^{-1} are obviously decreased in intensity while a marked increase in intensity was shown for the bands at 1622, 1590, and 1356 cm^{-1}. Accordingly, the former bands can be ascribed to molecularly adsorbed HCOOH interacting via hydrogen bonding whereas the latter ones are attributed to surface formate species. The latter bands that were prominent even at 400 K suggested that these bands are of the same species. Thus, these bands can be clearly assigned to formate

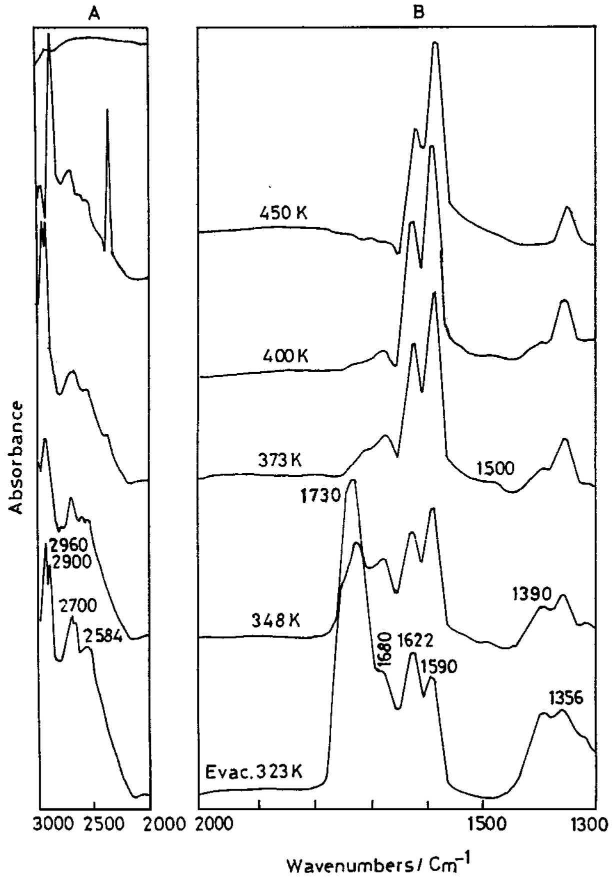


FIG. 3. *In situ* FTIR spectra of formic acid adsorbed on 5 wt% Au/H-mordenite at 323 K followed by evacuation at different temperatures.

species, i.e., $\nu(\mathrm{OCO})_{\mathrm{as}}$, 1622, 1590, δ(C–H), 1390; $\nu(\mathrm{OCO})_{\mathrm{s}}$, 1356 cm^{-1}. The bands at 1622, 1590, and 1356 cm^{-1} were stable until the sample was heated to 450 K. The presence of different bands at 1622 and 1590 cm^{-1} due to $(\mathrm{OCO})_{\mathrm{as}}$ suggested that more than one kind of formate species existed. In light of the frequency separation between $\nu(\mathrm{OCO})_{\mathrm{as}}$ and $\nu(\mathrm{OCO})_{\mathrm{s}}$ of formate ions, 266 cm^{-1}, a monodentate species is anticipated (17). The remaining band at 1590 cm^{-1} was indicative of the bidentate formate species that was similar to that obtained on the Cu/SiO_2 (1583 cm^{-1}) system during HCOOH adsorption (15). A band at 1500 cm^{-1} was produced after evacuation at 343 K and continued to appear due to the gradual decrease of formate species during evacuation till 450 K. This band is ascribed to carbonate species (11). Unlike the results of HCOOH decomposition on CeO_2, very intense bands due to carbonate species at 1516 and 1358 cm^{-1} appeared (14). This could be attributed to the evolution of stabilized CO_2 adsorbed species at 400 K. The higher Si/Al ratio in the mordenite sample was responsible for decreasing the amount of carbonate species formed since it lowered the average negative charge on the lattice oxygen (18).

On the basis of the foregoing results, the mechanism of this reaction proceeds through formic acid dehydrogenation over Au/H-mordenite. The mechanism of the reaction over Au/H-mordenite is shown in Scheme 1.

It was expected that the decomposition of HCOOH proceeds through a dehydration mechanism because of the use of the zeolite as a substrate. However, the surface formate decomposed to CO_2 and H_2. This indicates that the activity of the formate decomposition is determined by gold species. In this mechanism the reduction of Au^{3+} is accomplished as a result of the trace amount of water in the zeolite channel into Au^{+}, as previously noted by Salama *et al.* (9). The evolution of CO_2 arises from the decomposition of formate ions, leaving behind atomic hydrogen on the surface. A gaseous hydrogen molecule appears when another formic acid molecule attacks the surface and thus produces formate ions once again on the surface.

The decomposition of surface formate species at various temperatures between 343 and 450 K and the reaction products using gas chromatography were measured. The decomposition rate of formate species to CO_2 on Au/H-mordenite and H-mordenite catalysts is shown in Fig. 4. The Au/H-mordenite showed higher activity toward formate decomposition than the H-mordenite sample. This was indicated by the higher activation energy for the latter sample (63.3 kJ mol^{-1}) compared with the former one (40.1 kJ mol^{-1}). This suggested that the reaction is more facile when Au is encapsulated in the H-mordenite zeolite. It was shown that the decomposition rate was independent of the pressure of formic acid. Hydrogen and carbon dioxide were produced at the same rate provided that formic acid was present in the gas phase.

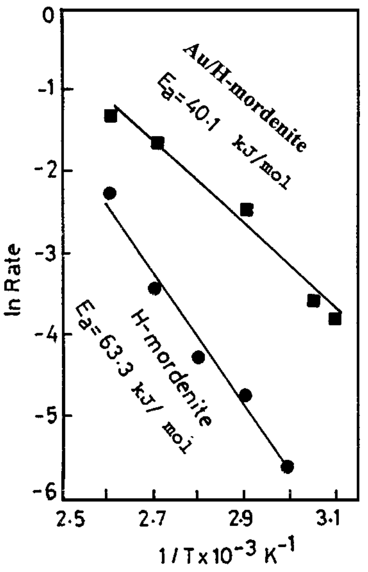
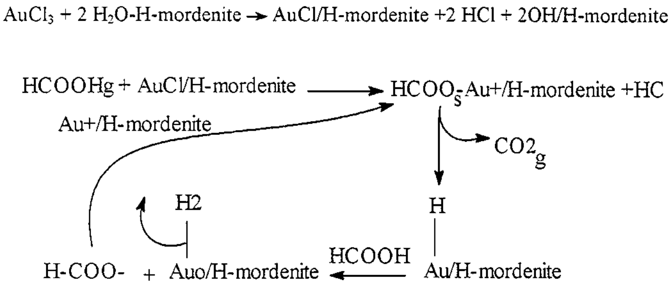


FIG. 4. Arrhenius plots for the decomposition rate of surface formate into CO_2 on H-mordenite and Au/H-mordenite samples.



SCHEME 1

The CO-Oxidation Reaction

Figure 5 shows spectra obtained for the Au/H-mordenite sample when a stoichiometric CO + O_2 mixture (100 Torr) was admitted at room temperature as a function of time. These spectra provide some insight into the possible reaction intermediates (carbonates or carboxylate compounds) formed on Au species during the catalytic oxidation of CO to CO_2. The *in situ* FTIR spectrum after 1.30 h showed bands at 2192, 2128, 1660, 1644, 1630, 1380, 1340, and 1324 cm^{-1}. By increasing the reaction time to 4.0 h, a broad band at 1950 cm^{-1} and a shoulder at 1856 cm^{-1} were built up in addition to a band at 2430 cm^{-1}. Meanwhile, the 1644 and 1660 cm^{-1} bands disappeared, giving another broad distinct band centered at 1680 cm^{-1}. As time elapsed (4–7 h), the 2192 cm^{-1} band gradually decreased in intensity, whereas the bands at 1950 and 1856 cm^{-1} remained constant. A shoulder at 1760 cm^{-1} is detected after 24 h of reaction time. The presence of C–H modes is confirmed by the bands in the νCH stretching region at 2896 and 2800 cm^{-1} and also at 1380 cm^{-1} in the νCH deformation region. It can be seen that this reaction proceeds very slowly to indicate carboxylate CO_2^- or carbonate species, after 1.30 h, characterized by bands at 1324–1380 cm^{-1} ($\nu_{\mathrm{s}}\mathrm{COO}^-$), 1630 cm^{-1} ($\nu_{\mathrm{as}}\mathrm{COO}^-$), and 1660 cm^{-1} (νC=O characteristic of carbonate compounds).

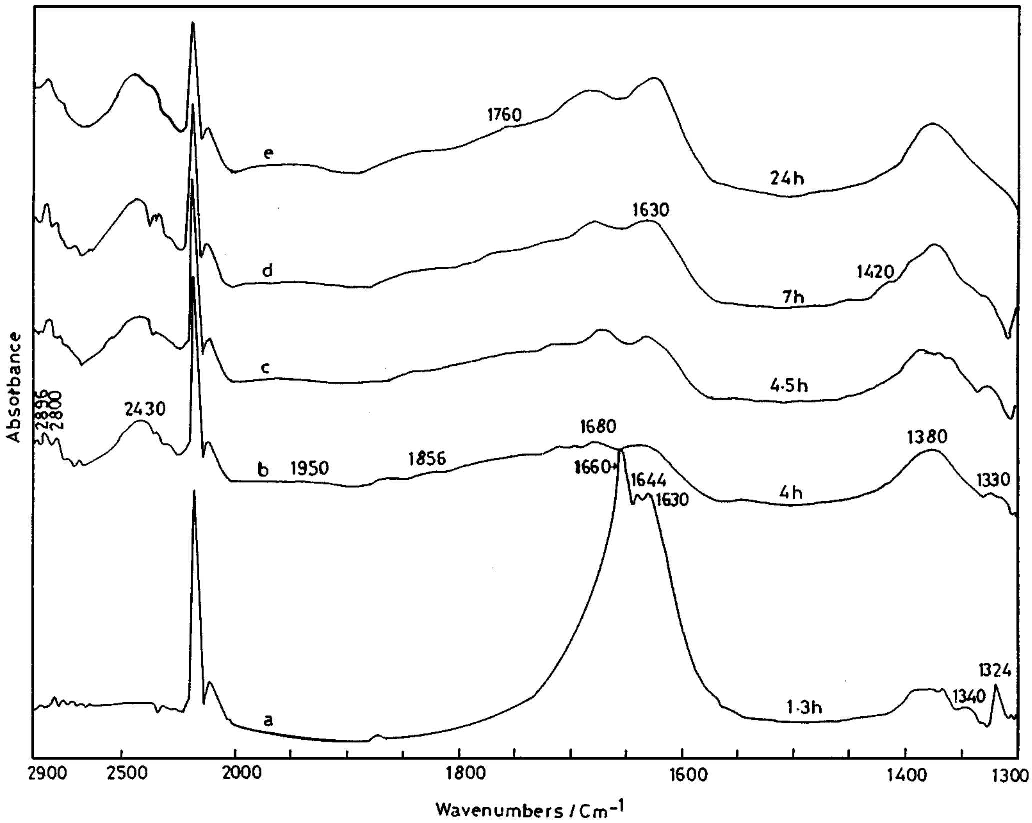


FIG. 5. *In situ* FTIR spectra of the $CO + O_2$ (1 : 1) gas mixture (50 Torr each) adsorbed on 5 wt% Au/H-mordenite at 323 K as a function of time.

These bands are similar to those observed on NiO (1380, 1630, and 1670 cm^{-1}) when carbon monoxide oxidation took place at room temperature and they were attributed to carbonate species (19). The absorption band at 1644 cm^{-1} could be attributed to O_2^- adsorbed on Au/zeolite as were those observed on many oxides at low temperatures (20). It is evident that the appearance of spectrum 5a changed to indicate invariable bands shaped independent of time in the spectra from 5b to 5e. This is a consequence of changing the intermediate to formate species characterized by maxima at 1330 ($\nu_s COO^-$), 1630 ($\nu_{as} COO^-$), 1680 ($\nu C{=}O$), 2800 (νC–H), and 1380 cm^{-1} (δCH). This contribution from formate that is emphasized in the spectra from 5b to 5d was also seen by Vannice and co-workers (21) during CO oxidation carried out on Au supported on anatase. The structure of the formate is monodentate type as a result of the high frequency separation between the bands at 1630 and 1330 cm^{-1} (300 cm^{-1}) similar to those in $C(HgOCOH)_4$ and $Cd(HCOO)_2$ ($\nu C{=}O$ 1677–1700, νO–C 1337–1360 cm^{-1}) (22). The evolution of carbonate species was reflected by a band at 1420 cm^{-1} as well as a shoulder at 1760 cm^{-1}, in spectrum 5e, that can be assigned to the C=O stretching of carbonate species, as has been determined by Little (19). The disappearance of the 1330 cm^{-1} band as well as the significant reduction in the C–H stretching bands at 2896 and 2800 cm^{-1} and the appearance of the bands at 1420 and 1760 cm^{-1} with time confirmed the gradual decomposition of the formate species in favor of carbonate formation. The surprising low concentration of carbonate species with time confirmed that the gas phase O_2 activates the reactivity of CO toward Au ions. The activation of adsorbed CO in the reaction with the surface lattice oxygens in the presence of molecular oxygen in the gas phase can be related to an electron-withdrawing effect of the adsorbed oxygen that facilitates the nucleophilic attack of surface oxygens on CO. The effect of oxygen destroyed selectively the organic-like carbonate species that can be enhanced in the presence of reduced species. As can be seen in Fig. 1, an enhancement of the above-mentioned species in the presence of H_2O molecules has been attained because of the lowered oxidizing power of water molecules compared with those of oxygen ones. On the other hand, the sharp band of CO coordinated Au^+ sites at 2192 cm^{-1} showed a decrease in intensity to its half after 24 h of reaction, whereas the 2128 cm^{-1} band attributed to CO adsorbed on Au^0 did not show significant change with time.

It has been therefore demonstrated by the behavior of the reacting mixture, under the reaction conditions, that the mechanism of the reaction proceeds through carboxylate formation with no CO_2 band formation at the very beginning. Surface formate was then formed as a result of the possible interaction of CO with OH stretching of the H-mordenite zeolite. This is emphasized by the results of Basset *et al.* (23), who probed the

TABLE 2

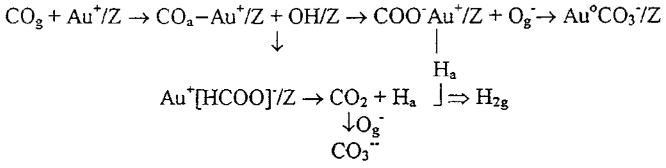
CO Oxidation Kinetics for the Au Encapsulated Inside H-Mordenite Zeolite

Catalyst	Temp (K)	CO : O_2[b]	Activity TOF[a] (10^{-3} s^{-1})	Activation energy, Ea 323–475 K (kJ/mol of CO_2)
5 wt% Au/H-mordenite	323	50 : 50	0.8	45.6
	373	50 : 50	1.2	
	425	50 : 50	1.75	
	475	50 : 50	1.95	
	523	50 : 50	2.1	
	573	50 : 50	1.7	
H-mordenite	373	50 : 50	0.08	

[a] TOF (turnover frequency) is defined as the number of reacted CO molecules divided by the total number of Au included in the catalyst.

[b] PCO = 50 Torr, PO_2 = 50 Torr.

possible hydrogen bonding of CO with OH, in view of the nucleophilic character of surface OH groups of zeolite toward CO, to form formate species. From the foregoing results, the following mechanism has been suggested.



In several investigations (24) carbon monoxide oxidation was activated on reduced surfaces more than oxidized ones. In conformity, the Au/H-mordenite catalyst showed high CO oxidation activities in the temperature range 323–523 K, as depicted in Table 2. The same result was also seen on Cu active sites formed upon reduction rather than that formed under redox conditions (25). The activity derived from the H-mordenite sample at 373 K was lowered by 15 times that of Au/H-mordenite at the same temperature. The noted decrease in the activity for the latter sample beyond heating at 523 K could be attributed to the segregation of gold particles. Thus, a marked decrease in the active sites can be anticipated. It can be seen that the influence of Au crystallite size on activity was primarily noted beyond heating at 425 K because of the interruption of the monotonous increase in the activity that used to be 0.4 and 0.45 s^{-1} for the temperature ranges 323–373 and 373–425 K, respectively (Table 2). This same result was also confirmed from XRD analysis (not shown) which indicated the gradual increase of the metallic Au phase at $2\theta = 38.18$ and 44.40° beyond raising the temperature to 373 K. As also shown in Table 2, the activation energy is estimated to be 45.6 kJ/mol over the 5 wt% Au/H-mordenite catalyst. This value is relatively low compared with those of Cu/Na-mordenite (91.1 kJ/mol) and Cu/H-mordenite (64.9 kJ/mol) catalysts used to activate the CO oxidation reaction (24).

CONCLUSIONS

(1) Water–gas shift reaction on H-mordenite proceeded through the formation of the bidentate formate species (ν_{CH}2912, ν_{as}COO$^-$1536, and ν_sCOO$^-$1390 cm^{-1}) that tended to decompose into carbonate species (1705, 1425, and 1360 cm^{-1}), besides the coexistence of organic-like carbonate species (1956 and 1852 cm^{-1}). The monodentate formate species was evident upon performing WGSR on an Au/H-mordenite sample through the well-developed absorption bands in the 3000- to 2800-cm^{-1} range along with bands at 1690 and 1340 cm^{-1} of asymmetric and symmetric stretching vibrations of the COO$^-$ group, respectively.

(2) Interaction of an Au/H-mordenite with HCOOH at temperatures in the range of 323 to 450 K results in the formation of different formate species. The dehydrogenation mechanism was proposed to be responsible for the formation of monodentate formate species that has been indicated by two asymmtric stretching vibrations at 1622 and 1590 cm^{-1}. The decomposition rate of HCOOH on Au/H-mordenite was higher than that on H-mordenite. This was emphasized by the activation energy that showed a lower value for the former (40.1 kJ/mol) than for the latter (63.3 kJ/mol).

(3) The catalytic CO-oxidation reaction on Au/H-mordenite proceeded initially through carboxylate formation followed by formate species. These species were formed by the reaction of CO with OH groups of zeolite that were assisted by the gas phase oxygen. These species were eventually dissociated to carbonate species.

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