The promoter function of molybdenum in $Rh/Mo/SiO_2$ catalysts for CO hydrogenation

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A series of $Rh/Mo/SiO_2$ catalysts with fixed Rh and different Mo contents were studied by FT-IR, chemisorption and CO hydrogenation. The FT-IR results at room temperature under CO atmosphere indicate that the addition of Mo to Rh/SiO_2 suppresses the linear and bridged CO species and promotes the twin CO species, which is consistent with the chemisorption results. It is suggested that the Mo promoter works via stabilization of Rh^{1+} ions and the coverage of Rh sites. The molybdenum promotes the formation of oxygenates and shifts the selectivity from hydrocarbons to oxygenates.

Keywords: rhodium; molybdenum; oxygenates; hydrogenation; CO adsorption

1. Introduction

The CO hydrogenation over rhodium catalysts is of particular interest for the route of synthesis gas to oxygenates [1–3]. It was found that the addition of Mo to Rh/SiO_2 catalysts brings about a change in product distribution and increases the activity more than tenfold [4–7]. In spite of the large amount of experimental data, the role of the promoter on the reaction path to oxygenates and increase of reactivity is still controversial. Mills et al. [4] reported the unusually high activity of Rh–Mo catalysts for CO hydrogenation and high selectivity to oxygenates and consequently proposed a dual-site mechanism. It was suggested that hydrogen is activated on Mo^{5+}, where it is not inhibited by CO and then it migrates and reacts with CO on Rh. Sachtler et al. [6] suggested that molybdenum oxides partly cover the surface of rhodium crystallites, thereby forming mixed oxides containing Mo–O–Rh bonds. These mixed oxides decrease the heat of CO chemisorption and increase the surface concentration of hydrogen. The presence of positive rhodium ions under the reaction conditions is responsible for the formation of oxygen-containing products. However, Kip et al. [5] found that not only CO chemisorption but also hydrogen chemisorption was suppressed by the presence of molybdenum

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oxide. In the present paper, a series of $Rh/Mo/SiO_2$ catalysts were studied and some new evidences were found that will shed more light on the function of Mo promoter in the reaction of CO hydrogenation to oxygenates on Rh–Mo catalysts.

2. Experimental

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was obtained from Wako Pure Chemical Co. Ltd. and $Rh_4(CO)_{12}$ from N.E. Chemcat Corp. Silica gel (Davison grade 57, specific surface area about 300 m^2/g, 16–32 mesh) obtained from Fuji Davison Co. Ltd. was dried in vacuum at 200°C for 2 h just before impregnation. A series of $Rh/Mo/SiO_2$ catalysts were prepared by a two-step impregnation method. Mo/SiO_2 was prepared by an incipient wetness impregnation from an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ for 24 h. The Mo content was varied from 0 to 5 wt%. The sample was dried by slowly increasing the temperature from room temperature to 120°C in a rotary vacuum evaporator and then calcined in a quartz tube with flowing H_2 at 450°C for 4 h. 1 wt% of rhodium was deposited on the SiO_2 or on the Mo/SiO_2 by dipping them in a hexane solution of $Rh_4(CO)_{12}$ for ca. 24 h, followed by drying and hydrogen calcination in a similar way as in the case of Mo/SiO_2. The contents of Rh and Mo on the catalysts were estimated with a Seiko SEA-2010 X-ray fluorescence analyzer.

The CO hydrogenation was performed in the system as described elsewhere [8]. Typical reaction conditions were as follows: 3 ml of catalyst, syngas pressure of 2.1 MPa with a CO : H_2 : Ar mole ratio of 3 : 6 : 1, gas flow rate of 100 ml/min and GHSV of 2000 $\ell\,\ell^{-1}\,h^{-1}$. The products were analyzed directly by an on-line GC system as described previously [8]. Product selectivities were determined from the carbon efficiencies based on the amount of CO reacted.

X-ray diffraction (XRD) analyses of the catalysts were carried out under normal atmospheric conditions using a MAC Science MXP18 model diffractometer. X-ray photoelectron spectra (XPS) were measured by a Shimazu ESCA 850. Just prior to the measurements of XPS, the samples had been treated in situ at 450°C for 2 h in flowing hydrogen.

FT-IR spectra were recorded using a Perkin-Elmer 1720X FT-IR spectrometer which is equipped with a high temperature/pressure diffuse reflectance chamber made by Spectra-Tech Inc. Catalyst in powder form was reduced in situ in this cell at 300°C for 2 h and then cooled down to room temperature in flowing H_2. Carbon monoxide was introduced to the cell at 25°C for 1–120 min and gaseous CO was flushed out by He before spectrum recording. Spectra were recorded by using 100 scans and 2 cm^{-1} resolution. No procedure was adopted to remove chemisorbed hydrogen before CO adsorption.

The amounts of hydrogen or carbon monoxide chemisorbed were measured by using a conventional glass apparatus at room temperature. The CO chemisorption

followed the hydrogen chemisorption. Chemisorbed H_2 has not been removed before exposure of CO.

3. Results

3.1. XRD AND XPS MEASUREMENTS OF CATALYSTS

No XRD peaks are detected related to Rh and Mo species for Rh/SiO_2, Mo/SiO_2 and $Rh/Mo/SiO_2$. The particles of Rh species are considered to be highly dispersed (particle size is smaller than ca. 2 nm) and Mo species may be amorphous. The XPS profiles for Rh are not clear probably because of low Rh contents. No XPS peaks are found around 228 eV which correspond to Mo metal, and many complicated peaks appear between 228 and 239 eV [9]. These results indicate the presence of mixtures of Mo oxides and no Mo metal on the catalysts even after the treatment in flowing hydrogen at 450°C.

3.2. FT-IR SPECTRA OF CO ADSORPTION

The FT-IR spectra of CO adsorption on the $Rh/Mo/SiO_2$ catalysts are shown in fig. 1. Spectrum A shows the CO adsorption on the Rh/SiO_2 sample. Three bands are observed at about 2067.8, 1910 and 1829 cm^{-1}. According to the literature, the band at 2067.8 cm^{-1} is assigned to *linear* CO on Rh metal [10,11]. The two bands below 2000 cm^{-1} come from *bridged* CO surface species; the band at about 1829 cm^{-1} was assigned to a 1 : 2 CO–Rh species and the band at 1910 cm^{-1} was assigned to a 3 : 2 stoichiometry [12]. Addition of 0.5 wt% molybdenum to Rh/SiO_2 causes a sharp decrease of the intensities of the *linear* CO band and the two *bridged* CO as spectrum B indicates. The spectrum C shows the CO adsorption on the $Rh/Mo/SiO_2$ with 1 wt% of Mo content. The intensity of the *linear* CO band at 2067.8 cm^{-1} is decreased about 90% and the two bands corresponding to bridged CO have almost disappeared. Two new bands at about 2101 and 2034.6 cm^{-1} are developed by the modification with Mo. The intensities of these bands increase, while that of the *linear* CO decreases with the increase of Mo content as spectra C to F indicate. The intensities of the *linear* CO and the new bands are not affected with the CO exposure time varied from 1 min to 120 min, and the shifts of wavenumbers are negligible with the change of Mo contents and the time. The decrease of the *linear* CO band does not quantitatively correspond to the increase of the new bands, and the ratio of the intensities between the two bands is not so clear because of the interference of the *linear* CO band. However, the new two bands can be assigned to anti-symmetric and symmetric vibrations for *twin* CO species on highly dispersed Rh^{1+} site by referring from many literatures [10,11]. No IR bands are detected in the case of Mo/SiO_2 sample (5 wt%).

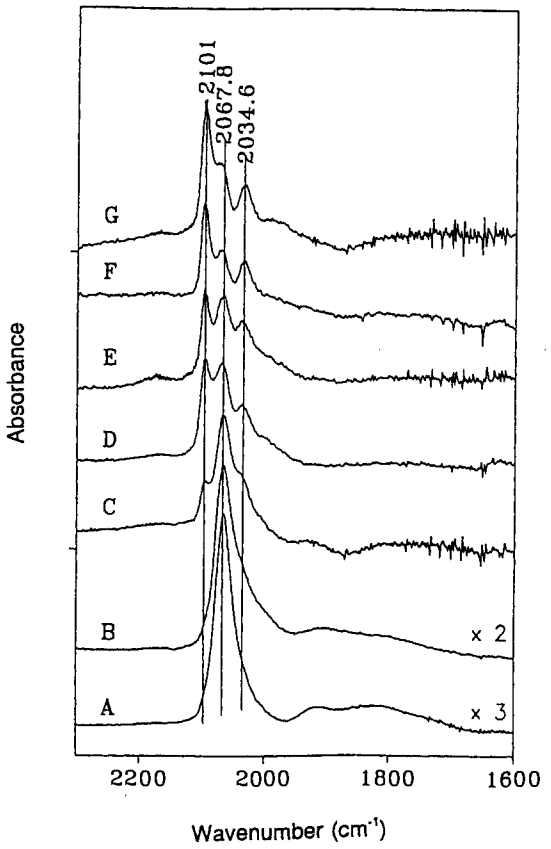

Fig. 1. FT-IR spectra of CO adsorption on $Rh/Mo/SiO_2$ catalysts with Mo content (wt%) of (A) 0, (B) 0.5, (C) 1, (D) 2, (E) 3, (F) 4, (G) 5.

3.3. CHEMISORPTION

Fig. 2 shows the H_2 and CO chemisorption measured by the volumetric method. The H_2 chemisorption on the Rh/SiO_2 catalyst indicates that the Rh is highly dispersed on SiO_2. The dispersion and average particle size of Rh are estimated as ca. 95% and smaller than 1 nm from the adsorption volume of H_2. However, the capability of H_2 chemisorption is decreased dramatically by modification with Mo, although the change of Rh dispersion is considered to be not so large from the result of XRD measurement. The higher the Mo content, the less the hydrogen chemisorbed. The CO chemisorption on $Rh/Mo/SiO_2$ shows different change as compared with H_2 chemisorption. The dispersion of Rh calculated from the chemisorption volume of CO is ca. 57%. A sharp decrease of CO chemisorption is observed when Rh/SiO_2 is promoted by low Mo content (<1 wt%). However, a slight increase of CO chemisorption is observed when the Mo content is continu-

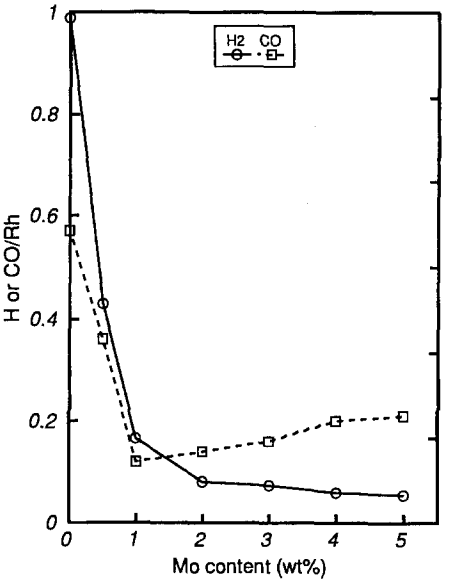

Fig. 2. Relation of chemisorption with Mo current.

ously increased. This slight increase of CO chemisorption is in full accordance with the appearance and increase of the twin CO species in FT-IR spectra (CO/Rh = 1 for linear CO, and 2 for twin CO). The amounts of H_2 or CO chemisorbed on Mo/SiO_2 are very small and can be neglected.

3.4. ACTIVITY AND SELECTIVITY FOR CO HYDROGENATION

The catalytic activities of the $Rh/Mo/SiO_2$ are examined in the CO hydrogenation. The catalysts were re-activated in the reactor at 450°C for 2 h just before the reaction. CO conversion decreases at an initial stage of the reaction and reached constant at ca. 6 h after reaching the reaction temperature operated. The change of product distribution at the initial stage is small. Fig. 3 exhibits CO conversion versus Mo content of the catalysts at the stationary states at 220 and 234°C. The CO conversion is increased about five times by increasing the Mo content from 0 to 5 wt% at two different reaction temperatures. Both the Rh/SiO_2 (1 wt%) and Mo/SiO_2 (5 wt%) catalysts exhibit poor activity for CO hydrogenation. Fig. 4 shows the relation of selectivity with Mo content at 5% of CO conversion. The Rh/SiO_2 catalyst produces about 50% of light hydrocarbons less than C_4 and 36% of oxygenates in which methanol and ethanol are the main products and their selectivities are almost equal (ca. 14%). The main products produced by the Mo/SiO_2 catalyst are CO_2, methane and very little amount of oxygenates. The selectivity to oxygenates is increased and the product distribution is altered when the Rh/SiO_2 is promoted by molybdenum. The methanol is increased significantly while the ethanol is slightly decreased with the increase of Mo content. The increase of molybdenum results in the

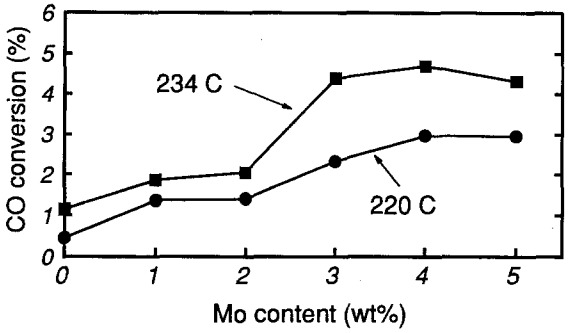

Fig. 3. Relation of Mo content with CO conversion.

increase of the selectivity for oxygenates but a slight decrease of the selectivity for C_2-oxygenates. The selectivities to methane and total hydrocarbons are decreased with the increase of Mo content.

4. Discussion and conclusion

The FT-IR observation indicates that the *linearly* bonded and *bridged* CO on Rh/SiO_2 catalyst are suppressed by the addition of molybdenum, while the amount of the *twin* CO species is increased by the increase of Mo content. These results are consistent with the CO chemisorption data that the capacity of CO adsorption decreases sharply and then slightly increases with the increase of Mo content.

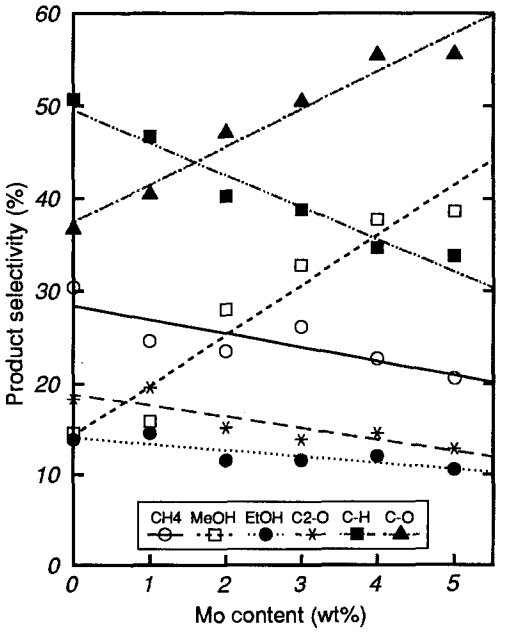

Fig. 4. Relation of selectivity with Mo content at CO conversion of 5%.

XPS and XRD measurements of Rh/Mo/SiO_2 have indicated that Mo species are not metallic but a mixture of oxides after the hydrogenation treatment at 450°C. Since the *twin* CO species is considered to be formed on Rh^{1+} sites [10,11], it seems that the poorly reducible Mo oxides promote to oxidize Rh and stabilize the Rh^{1+} ions. The higher the molybdenum content, the more Rh ions, and therefore the stronger the twin bands. Sachtler et al. also suggested the formation of mixed oxides containing Mo–O–Rh bonds [6].

A mechanism called oxidative disruption induced by CO adsorption was adopted by several authors to explain the formation of Rh^+ sites on freshly reduced Rh/SiO_2 or Rh/Al_2O_3 [10,11]. This mechanism, however, must be dynamic and time consuming. In the present case, Rh^{1+} sites may have been formed before the contact to CO, because the adsorbed twin CO bands appear instantly by exposure of catalysts to CO gas and no time effect.

From the results of chemisorption measurements, Rh/SiO_2 shows a big loss of chemisorption capacity for both hydrogen and CO by the modification with Mo. These results are confirmed by FT-IR measurement of adsorbed CO species. By considering the fact that no big growth of Rh particles is observed, these results suggest the coverage of Rh sites by Mo oxides. The suppression of CO and H_2 chemisorption on Rh catalysts promoted by molybdenum was observed by a number of researchers [4–6,13]. Storm et al. found that addition of Mo to Rh/Al_2O_3 catalysts suppresses the chemisorption capacity of Rh for both H_2 and CO, and they attributed this suppression to a reduction of the surface available for the chemisorption of CO and H_2 [13]. Similar results were obtained by Kip et al. on Rh/SiO_2 catalysts promoted with Mo oxide [5]. The authors suggested the coverage of the Rh particles by the oxide promoter.

It is concluded that the Mo promoter works in two ways: (1) the oxidation of Rh and consequent stabilization of Rh^{1+} ions, and (2) the coverage of Rh sites by Mo oxides. These two effects actually depend on the interaction between Rh and Mo promoter. If Rh is contacted by Mo promoter but the interaction is very weak, the phenomenon of coverage of Rh sites should be observed. On the other hand, when the contact between Rh and Mo promoter becomes so intimate that Rh is oxidized, the Rh^{1+} ions should be observed. The electronic state of Rh in the Rh/Mo/SiO_2 is believed to be in a continuous distribution between Rh^0 and Rh^{1+}. The electronic densities depend on the pretreatment conditions and the content of promoter.

The results of the CO hydrogenation on the Rh/Mo/SiO_2 indicate that Mo promotes the formation of oxygenates and shifts the selectivity from hydrocarbons to oxygenates. However, it does not promote the formation of ethanol and actually shift the selectivity from ethanol to methanol. Similar results were reported by Kip et al. [5] on Rh/MoO_2/SiO_2 catalysts and by Guglielminotti et al. [7] on Rh/ZrO_2 promoted by Mo oxide. It has been assumed that Rh^{1+} ion sites provide the active centres in methanol synthesis [14]. Present results seem to support this assumption.

In the study of Mo catalysts for the synthesis of mixed alcohols from synthesis gas, Tatsumi et al. found that Mo supported on SiO_2 exhibits high activity for synthesis of mixed alcohols at high reduction temperature (>500°C) and suggested that the presence of both metallic Mo and MoO_2 species on the catalyst surface is necessary for the production of alcohols [15]. Their observation stimulates us to check Mo/SiO_2 again at high reduction temperature. Results show that activity for CO conversion is increased about tenfold and the selectivity to alcohols is also increased from less than 1% to about 10% when reduction temperature is raised from 450 to 550°C. This confirms the importance of reduction temperature towards the Mo/SiO_2 catalyst and also the $Rh/Mo/SiO_2$ catalysts. In the present study, all the catalysts were reduced at 450°C and Mo oxides are stable under this condition. Therefore, it is believed that Mo in the $Rh/Mo/SiO_2$ catalysts works as a promoter and not as active phase.

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