Catalysis Letters Vol. 103, Nos. 1–2, September 2005 (© 2005)
DOI: 10.1007/s10562-005-6497-3

Promoting effect of Mo on alcohol formation in hydroformylation of propylene and ethylene on Mo-Rh/SiO_2

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Received 4 April 2005; accepted 17 May 2005

It is found that the addition of Mo to Rh/SiO_2 (Mo-Rh/SiO_2) promoted alcohol formation in hydroformylation of propylene and ethylene, at the same time it drastically enhanced the activity of hydroformylation and hydrogenation. It is suggested that H_2 adsorption sites, which are not inhibited by CO adsorption, are present on Mo-Rh/SiO_2. The sites can cause high H_2 activation, and it can be related to the additive effect of Mo in hydroformylation reactions.

KEY WORDS: hydroformylation; propylene; ethylene; alcohol; molybdenum; rhodium.

1. Introduction

Hydroformylation is an important industrial process for producing oxygen containing compounds, especially aldehydes, from olefins. It has been known that rhodium is the most active catalyst for hydroformylation. Although the catalyst development for the gas-phase [1,2] and liquid-phase [3–6] hydroformylation has been performed, the additive effect of various components on heterogeneous Rh catalysts has been investigated [7–15]. It has been reported that the additives such as Fe, Zn promote the formation of alcohols in ethylene hydroformylation [1,8]. It has also been reported that Mo is an effective additive for alcohol formation in hydroformylation, and cluster-derived [11] and ZrO_2-supported catalysts [16] have been investigated.

In this letter, it is reported that Mo-promoted Rh/SiO_2 (Mo-Rh/SiO_2), which was prepared by the conventional impregnation method, exhibited higher activity in hydroformylation of ethylene and propylene in terms of alcohol formation than previous reports. In addition, the promoting effect of Mo on hydrogen activation under the presence of CO is discussed on the basis of the characterization results by means of FTIR, TPD, and H_2–D_2 exchange rate measurements.

2. Experimental

2.1. Catalyst preparation

All catalysts were prepared by impregnating an aqueous solution of metal salts on SiO_2 support (Q-100 or G-6; Fuji Silysia Chemical Ltd.). Before the impregnation, SiO_2 was calcined in air at 1173 K for 1 h to avoid the structural change during the catalyst preparation (BET surface area: Q-100: 38 m^2/g, G-6: 535 m^2/g). Rh/SiO_2 (Q-100 and G-6) catalysts were prepared by the incipient wetness method using $RhCl_3 \cdot 3H_2O$ (N.E. Chemcat Corporation >98%). Unless otherwise stated, the SiO_2 (Q-100) support was used. The preparation of Mo-added Rh catalysts (Mo-Rh/SiO_2) was as follows: after the impregnation with a $RhCl_3 \cdot 3H_2O$ aqueous solution and drying at 383 K for 12 h, the modification with additive component was carried out by subsequent impregnation using the aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, NH_4VO_3, $Fe(NO_3)_3 \cdot 9H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$ (WAKO Pure Chemical Industries Ltd., >99%). After drying modified catalysts at 383 K for 12 h, they were calcined in air at 773 K for 3 h. Rh/SiO_2 was also calcined at 773 K for 3 h. The loading amount of Rh was 4 wt%, and the amount of additive was represented by molar ratio of Mo/Rh in the range between 0.2 and 1.0. In the case of M-Rh/SiO_2 (M = V, Fe, Zn), the additive amount was adjusted to the molar ratio of M/Rh = 1. As a reference, a SiO_2-supported Mo catalyst (denoted as MoO_3/SiO_2) was prepared by a similar impregnation method to Mo-Rh/SiO_2, and treatment conditions were also the same. The loading amount of Mo was adjusted to the same amount of Mo-Rh/SiO_2 (Mo/Rh = 1).

2.2. Hydroformylation of propylene and ethylene

Hydroformylation of ethylene and propylene was carried out in a fix bed flow reactor system under atmospheric pressure. Catalysts were pretreated under a hydrogen flow (30 ml/min) at 573 K for 1 h. After the reactor was cooled down to room temperature, the reactant gases for hydroformylation of olefin ($P_{olefin} = P_{CO} = P_{H_2} = 33.8$ kPa) were fed to the catalyst bed, and then the reaction temperature increased step-by-step,

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1011-372X/05/0900–0015/0

and it was kept for about 1 h at each reaction temperature. Analysis of the efficient gas was carried out by gas chromatograph. Ethylene, propylene, ethane and propane were analyzed by FID gas chromatograph (Shimadzu GC-14B) using VZ-10 column (3 mm i.d., 2 m). Oxygenates (butanals, butanols, propanal and 1-propanol) were analyzed by FID gas chromatograph (Shimadzu GC-8A) using Stabilwax fused silica capillary column (RESTEK, 0.53 mm i.d., 60 m). Carbon monoxide was analyzed by TCD gas chromatograph (Shimadzu GC-8A) using Porapak Q column (3 mm i.d., 2 m). The stable activity was observed during the activity test. The catalyst amount was 0.1 g, and the total flow rate of the reactant gases was 6 ml/min, and this corresponds to GHSV = 3600 h.

2.3. *Catalyst characterization*

X-ray diffraction (XRD) was carried out using an X-ray diffractometer (Philips X'Pert MRD) equipped with a graphite monochromator for Cu$K\alpha$ (40 kV, 20 mA) radiation. The mean particle size was calculated from the XRD line broadening measurement using Scherrer equation [17,18]. H_2 and CO chemisorption measurements were carried out in a conventional volumetric adsorption apparatus; detailed procedures were described elsewhere [19,20]. The amounts of the total H_2 chemisorption (H/Rh) and the irreversible CO chemisorption (CO/Rh) were measured at room temperature after H_2 reduction at 573 K.

Fourier transform infrared spectra (FT-IR) of CO adsorption were recorded at room temperature by FT-IR spectrometer (Nicolet, Magna-IR 550 spectrometer) in transmission mode using quartz glass IR cell with CaF_2 windows connected to a vacuum-closed circulating system. The catalyst was well mixed with the same weight of SiO_2 (fine powder, AEROSIL SiO_2 380, BET 380 m^2/g), and it was pressed into a disk of 20 mm and a weight of about 0.03 g. CO (7 kPa) was exposed to the catalyst at room temperature after the reduction with H_2 (7 kPa) and evacuation at 573 K. After CO adsorption, the gas was evacuated. FT-IR spectra of adsorbed CO were obtained at room temperature under vacuum. Temperature-programmed desorption (TPD) of adsorbed CO on the catalyst was carried out in a closed circulation system equipped with quadrupole mass spectrometer (Balzers QMS 200F). CO (7 kPa) was exposed to the sample at room temperature after H_2 reduction and evacuation at 573 K. The amount of the catalyst was 0.10 g, and the temperature was increased from room temperature to 773 K with the rate of 10 K/min.

H_2–D_2 exchange was carried out under presence of CO in the closed circulation system equipped with the quadrupole mass spectrometer. The catalyst amount was 0.5 g, and the catalyst sample was reduced in 33.3 kPa of H_2 at 573 K for Rh-based catalysts and at 1023 K for MoO_3/SiO_2, subsequently evacuated at the same temperature. After the temperature reached the reaction temperature, reactant gases ($P_{H2} = P_{D2} = P_{CO} = 20$ kPa, P_{Ar} = 6 kPa as internal standard gas) were introduced, and they were continuously circulated during the reaction. The reaction was carried out in the range of room temperature to 353 K, and the gas phase was analyzed by QMS every 4.5 min.

3. Results and discussion

Results of the activity test of propylene hydroformylation over various catalysts are listed in table 1. In the case of two Rh/SiO_2 catalysts, *n*-butanal was produced as a main oxygenate product, although propane was formed by hydrogenation of propylene as a byproduct. In contrast, butanols were mainly obtained over the M-Rh/SiO_2 catalysts. Previously it has been reported that additives such as V, Fe, Zn are effective for the formation of alcohols in hydroformylation of olefins [1,8]. From the comparison of M-Rh/SiO_2 catalysts at M/Rh = 1, it was found that Mo-Rh/SiO_2 showed highest conversion of propylene and at the same time, the selectivity to butanols, especially *n*-butanol, was also high. The ratio of *i*-butanol to *n*-butanol over Mo-Rh/SiO_2 was higher than that of *i*-butanal to *n*-butanal over Rh/SiO_2. In terms of yield of oxygenates, it is found that Mo is more effective than other components.

Catalytic performance of Mo-Rh/SiO_2 was strongly dependent on the amount of Mo. At Mo/Rh = 2, the

Table 1

Results of propylene hydroformylation over Rh-based catalysts supported on SiO_2 at 418 K

Catalyst	Support	M/Rh (Molar ratio)	Conversion (%)	propylene-based selectivity (%)		
				butanols (*i*/*n*)	butanals (*i*/*n*)	propane
Rh/SiO_2	Q-100	0	0.03	0 (–)	37 (0.00)	63
	G-6	0	0.57	1 (0.29)	33 (0.40)	66
Mo-Rh/SiO_2	Q-100	0.2	0.19	27 (0.12)	6 (0.29)	67
		0.5	1.27	32 (0.12)	< 1 (0.00)	68
		1	0.65	39 (0.20)	< 1 (0.00)	61
V-Rh/SiO_2	Q-100	1	0.11	68 (0.30)	2 (0.00)	30
Fe-Rh/SiO_2	Q-100	1	0.17	57 (0.12)	7 (0.63)	36
Zn-Rh/SiO_2	Q-100	1	0.07	68 (0.38)	15 (0.54)	17

Table 2

Characterization results and TOF of propylene hydroformylation over Rh/SiO$_2$ and Mo-Rh/SiO$_2$

Catalyst	Support	Mo/Rh (molar ratio)	XRD		Adsorption		(H/Rh) /(CO/Rh)	(CO/Rh)/*D*	ToF[c] (10^{-2}/min)			Activation energy[d] (kJ/mol)		
			Praticle size d[a]/nm	*D*[b]	H/Rh	CO/Rh			butanols	butanals	propane	butanols	butanals	propane
Rh/SiO$_2$	Q-100	0	14	0.08	0.041	0.036	1.1	0.45	0.0	0.6	0.6	–	74	72
	G-6	0	2.9	0.38	0.498	0.445	1.1	1.17	0.0	1.0	1.9	–	–	–
Mo-Rh/SiO$_2$	Q-100	0.2	4.2	0.26	0.042	0.029	1.4	0.11	4.1	0.9	10	–	–	–
	Q-100	0.5	3.3	0.33	0.058	0.020	2.9	0.06	47	0.3	99	20	–	36
	Q-100	1	1.9	0.58	0.014	0.004	3.5	0.01	146	0.9	228	–	–	–

All samples were reduced at 573 K before the characterization.

[a] Calculated from XRD line broadening measurement using Scherrer equation [17,18].

[b] Dispersion of Rh metal is calculated on the basis of 1.1/*d* (particle size (nm)) [19].

[c] Calculated from CO uptake and formation rate of each product in propylene hydroformylation at 418 K.

[d] Temperature range: 403–448 K.

formation of aldehyde was also observed, however, at Mo/Rh = 0.5 and 1.0, the formation of aldehyde was negligible, i.e. the ratio of butanols to butanals was very high. Especially, the selectivity of butanols in hydroformylation increased with increasing Mo content, on the other hand, the activity of hydroformylation and hydrogenation decreased in the range of Mo/Rh > 0.5. Therefore, the optimum content of Mo was determined to be Mo/Rh = 0.5. The additive effect of Mo on hydroformylation reaction has also been reported over the Rh-Mo cluster-derived catalysts [11], and similar behavior has been observed. From the comparison, the selectivity of hydroformylation on this work was much higher than that on the previous report [11]. This means that the effective Rh-Mo interaction is formed even by the impregnation preparation methods. Here we used SiO$_2$ (Q-100) support with low surface area (38 m^2/g). On the other hand, it is possible to prepare Rh/SiO$_2$ catalyst with much higher BET surface area to obtain more highly dispersed Rh metal particles. Therefore, we also tested Rh/SiO$_2$ (G-6). As listed in table 1, the conversion over Rh/SiO$_2$ (G-6) was much higher than that over Rh/SiO$_2$ (Q-100). However, the activity of Rh/SiO$_2$ (G-6) did not reach the level of Mo-Rh/SiO$_2$, and the main oxygenate was also aldehyde.

The results of adsorption and XRD measurements are listed in table 2. From the XRD analysis, the particle size of Rh and the dispersion of Rh/SiO$_2$ (Q-100) are determined to be about 14 nm and 0.08, respectively. On the other hand, the dispersion of Rh/SiO$_2$ (G-6) was much higher as expected. The results of Mo-Rh/SiO$_2$ are also listed in table 2. Although the adsorbed amount of CO was comparable to that of hydrogen over two Rh/SiO$_2$ catalysts, H/Rh was much higher than CO/Rh in the case of Mo-Rh/SiO$_2$. For comparison, the ratio (H/Rh)/(CO/Rh) on Mo-Rh/SiO$_2$ is also listed in table 2. The ratio increased with increasing Mo content, which is characteristic of Mo-Rh/SiO$_2$. The particle size (*d*) of Rh metal from XRD is much dependent on the additive amount of Mo. As shown in table 2, the dispersion (*D*) from XRD was much higher than that from the adsorption amount, which indicates that the surface of Rh metal particles was covered with Mo species. The coverage of Mo species on Rh metal surface can be expected from (CO/Rh)/*D* as shown in table 2. The turnover frequency (TOF) in hydroformylation of propylene over Mo-Rh/SiO$_2$ was much higher than other catalysts, and this indicates that the Mo addition drastically promoted hydroformylation reaction over the Rh catalysts.

Figure 1 shows the reaction temperature dependence of Mo-Rh/SiO$_2$ (Mo/Rh = 0.5) in propylene hydroformylation. The selectivity of oxygenate formation was almost constant at 343–358 K, however, it decreased gradually with increasing reaction temperature. The selectivity toward butanols was almost the same as that to oxygenates, which means very low selectivity to

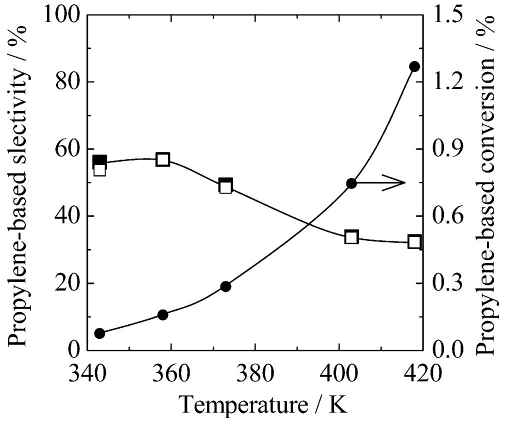

Figure 1. Reaction temperature dependence of propylene hydroformylation over Mo-Rh/SiO$_2$ (Mo/Rh = 0.5) catalyst. ●: propylene-based conversion, ■: propylene-based selectivity of oxygenates (butanols + propanals), □: selectivity of butanols. Reaction conditions: catalyst weight 0.1 g, $P_{C_3H_6} = P_{CO} = P_{H_2} = 33.8$ kPa, total flow rate = 6 ml/min, total pressure = 0.1 MPa, reduction temperature = 573 K.

butanals in all the temperature range. Activation energies in hydroformylation of propylene are also listed in table 2. On Rh/SiO$_2$, the activation energy of propane formation was comparable to that of aldehyde formation. The activation energies of the formation of propane and butanols on Mo-Rh/SiO$_2$ were rather low compared to those on Rh/SiO$_2$.

Results of ethylene hydroformylation over two Rh/SiO$_2$ and Mo-Rh/SiO$_2$ (Mo/Rh = 0.5) catalysts are listed in table 3. An effect of Mo added is also observed similarly to hydroformylation of propylene. The conversion over the Mo-Rh/SiO$_2$ catalyst was much higher than that over Rh/SiO$_2$ (Q-100) and comparable to that over Rh/SiO$_2$ (G-6). By adding Mo, the main oxygenate product changed from propanal to 1-propanol. It follows from the results of hydroformylation of ethylene and propylene that addition of Mo sharply enhanced the activity and selectivity to alcohol and to olefin hydrogenation.

For the characterization of the reduced catalysts, we measured FT-IR spectra of CO adsorption on Rh/SiO$_2$ and Mo-Rh/SiO$_2$ (Mo/Rh = 0.2 – 1) catalysts as shown in figure 2. On Rh/SiO$_2$, twin CO (2094 and 2026/cm), linear CO (2053/cm), and bridge CO (1872/cm) were observed [21], and main adsorbed species was the bridge CO judging from their peak intensities. On Mo-Rh/SiO$_2$ (Mo/Rh = 0.2), linear CO (2044/cm) was mainly observed. In contrast, on Mo-Rh/SiO$_2$ (Mo/Rh = 0.5 and 1), twin CO (2096 and 2034/cm) was mainly observed, and this behavior agrees with the previous report [22]. Although the interaction between Rh and Mo are not clear at present, it is interpreted that Rh surface was modified with Mo species, and this is supported by the (CO/Rh)/*D* values in table 2.

As described above, the addition of Mo enhanced the formation activity of alcohols and alkanes in hydroformylation; this can be related to the effect of Mo on

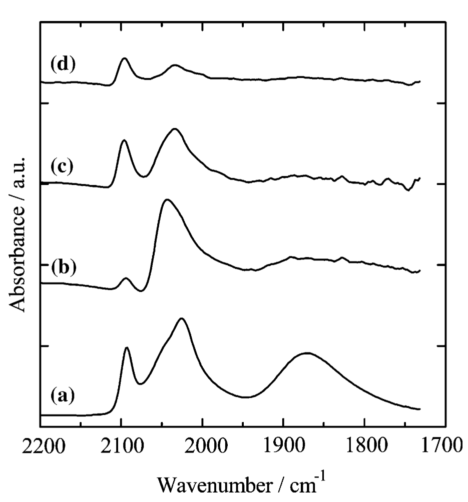

Figure 2. FT-IR spectra of CO adsorbed on Rh-based catalysts. (a) Rh/SiO$_2$, (b) Mo-Rh/SiO$_2$ (Mo/Rh = 0.2), (c) Mo-Rh/SiO$_2$ (Mo/Rh = 0.5), (d) Mo-Rh/SiO$_2$ (Mo/Rh = 1).

Table 3

Results of ethylene hydroformylation over Rh/SiO_2 and Mo-Rh/SiO_2 at 388 K

Catalyst	Support	Mo/Rh (Molar ratio)	Conversion (%)	Yield (10^{-2}%)			Selectivity (%)			TOF[a] (10^{-2}/min)			Activation energy [b] (kJ/mol)		
				1-propanol	propanal	ethane	1-propanol	propanal	ethane	1-propanol	propanal	ethane	1-propanol	propanal	ethane
Rh/SiO_2	Q-100	0	0.21	0	8	13	0	38	62	0.0	4.8	7.1	–	60	65
	G-6	0	1.88	1	123	64	< 1	65	34	< 0.1	5.5	3.4	–	–	–
Mo-Rh/SiO_2	Q-100	0.5	1.96	92	6	98	47	3	50	105.6	6.9	112.6	\31	–	50

[a] Calculated from CO uptake and formation rate of each product in ethylene hydroformylation at 388 K.

[b] Temperature range: 373–433 K.

H_2 activation. In order to evaluate the ability of H_2 activation under the presence of CO, the H_2–D_2 exchange rate under the presence of CO was measured. Figure 3 shows Arrhenius plots of the reaction over Rh/SiO_2, Mo-Rh/SiO_2 (Mo/Rh = 0.5) and reduced MoO_3/SiO_2. In the case of MoO_3/SiO_2, the state of reduced MoO_3/SiO_2 was adjusted to that of Mo-Rh/SiO_2 on the basis of temperature programmed reduction results, although the details are not shown here, and the average valence state of Mo after the reduction treatment was Mo^{2+}. On the MoO_3/SiO_2, the exchange activity was too low to measure accurately. Mo-Rh/SiO_2 was more active than Rh/SiO_2, and the activation energy on Rh/SiO_2 (69 kJ/mol) was much higher than that on the Mo-Rh/SiO_2 (29 kJ/mol). The difference in the exchange activity under the presence of CO can be related to the strength of CO adsorption. When adsorption of CO on the catalyst is weak, the catalyst will expose more vacant sites and exhibit high exchange activity. Therefore, we investigated the strength of CO adsorption by tem perature-programmed desorption (TPD).

Figure 4 shows TPD profiles of CO adsorption on Rh/SiO_2 and Mo-Rh/SiO_2 (Mo/Rh = 0.5). In the case of Rh/SiO_2, the CO desorption was observed at 360 and 475 K, and almost no CO_2 was observed. In contrast, in the TPD profile of Mo-Rh/SiO_2, the CO desorption was observed in the similar temperature range (370 K), and CO_2 desorption was clearly observed above 360 K. The CO_2 formation is due to CO disproportionation reaction ($2CO \rightarrow C + CO_2$) over Mo-Rh/SiO_2, which can proceed much more easily compared to Rh/SiO_2. This suggests an interaction between Mo and CO adsorbed on the surface of Rh, and especially between Mo^{δ} and the oxygen atom in CO, although this kind of interaction can not be observed in FT-IR spectra. Since Mo addition did not promote the selectivity to oxygenates (i.e. the CO insertion), the contribution of this kind of CO species seems to be small. It should be noted that the CO desorption profile on Mo-Rh/SiO_2 was similar to that on Rh/SiO_2, especially, in the temperature range (299–353 K), where H_2–D_2 exchange reaction was tested. This can not explain the performance of high H_2–D_2 exchange activity on Mo-Rh/SiO_2.

The high activation energy of H_2–D_2 exchange reaction on Rh/SiO_2 suggests that H_2 is activated on the vacant Rh sites under high CO coverage; the activation energy can include the energy of CO desorption [23]. On the other hand, the low activation energy on Mo-Rh/SiO_2 suggests the presence of H_2 activation sites, which are not inhibited by CO adsorption. This can be related to the adsorption property of (H/Rh)/(CO/Rh) > > 1 on Mo-Rh/SiO_2 (table 2). As shown in tables 2 and 3, the activation energy of alkane formation was similar to that of aldehyde formation on Rh/SiO_2, while those on Mo-Rh/SiO_2 were rather low compared to those on Rh/SiO_2. The tendency in the activation

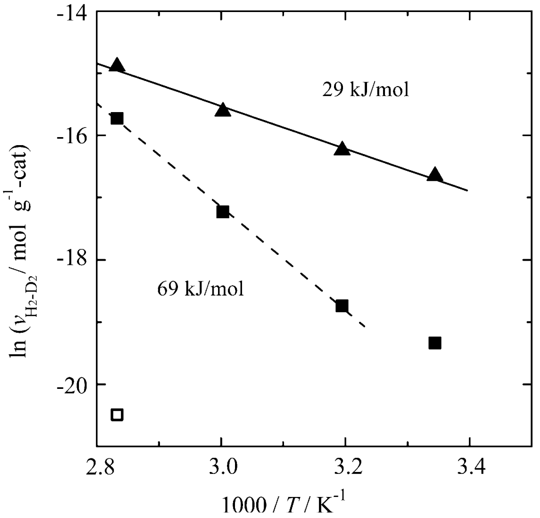

Figure 3. Arrhenius plots of H_2–D_2 exchange reaction under the presence of CO. ■: Rh/SiO$_2$, ▲: Mo-Rh/SiO$_2$(Mo/Rh = 0.5), □: MoO$_3$/SiO$_2$ Reaction temperature range: 299–353 K. $P_{H_2} = P_{D_2} = P_{CO} = 20.0$ kPa. Rh-based catalysts were reduced by H_2 at 573 K before reaction. MoO$_3$/SiO$_2$ was reduced by H_2 at 1023 K before reaction.

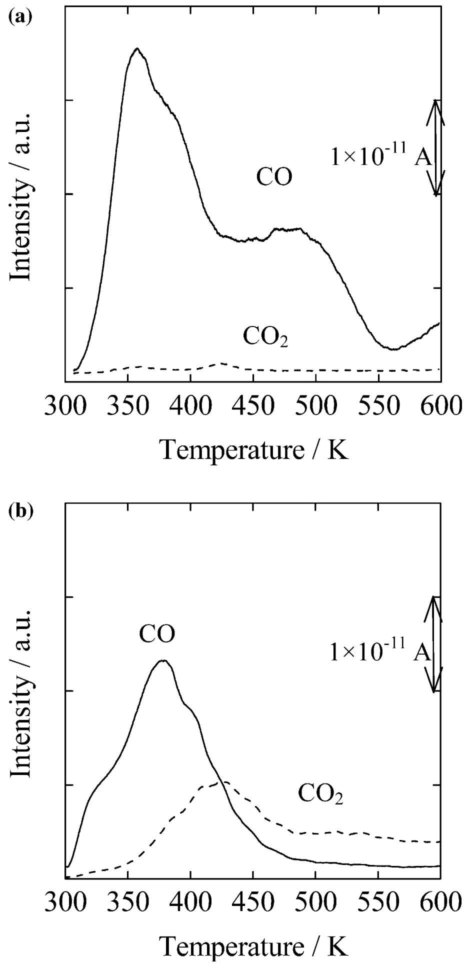

Figure 4. Temperature-programmed desorption (TPD) profiles of CO adsorbed on Rh-based catalysts. (a) Rh/SiO$_2$, (b) Mo-Rh/SiO$_2$ (Mo/Rh = 0.5).

energy of hydroformylation agrees well with that of H_2–D_2 reaction. This suggests that the addition of Mo promotes H_2 activation, and increases the activities of both hydroformylation and hydrogenation reactions. The formation route of alcohols in hydroformylation of olefins can be the hydrogenation of aldehyde. Considering from the reaction scheme of hydroformylation [8,11], hydrogenation of olefin to alkyl group, that of acyl group to aldehyde, and that of aldehyde to alcohol can be promoted.

4. Conclusions

Modification of Rh/SiO$_2$ with Mo (Mo-Rh/SiO$_2$) enhances the TOF and enables formation of butanols and 1-propanol in hydroformylation of propylene and ethylene. The optimum composition is Mo/Rh = 0.5. The surface of Rh metal particles in Mo-Rh/SiO$_2$ is covered with Mo species; more H_2 is adsorbed than CO. In the presence of CO, H_2–D_2 exchange is faster over Mo-Rh/SiO$_2$ than over Rh/SiO$_2$. This suggests the presence of H_2 activation sites, which are not inhibited by CO adsorption. Activation energies for the formation of alcohols and paraffins on Mo-Rh/SiO$_2$ are lower than those over Rh/SiO$_2$ in hydroformylation reactions.

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