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The role of Mn and Li promoters in supported rhodium catalysts in the formation of acetic acid and acetaldehyde

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Abstract

Rh–Mn–Li/SiO_2 catalysts consisting of 1 wt% Rh for the synthesis of C_2 oxygenates from syngas were studied by $CO + H_2$ reaction and characterized by TPR, H_2-TPD, ESR and IR techniques. The Rh–Mn–Li/SiO_2 catalysts, which showed a good selectivity for the formation of acetic acid and acetaldehyde, have been found to be quite different from the Rh–V/SiO_2 catalysts reported previously, which mainly promoted the formation of ethanol. Comparing with the Rh–V/SiO_2 catalysts, the Rh–Mn–Li/SiO_2 exhibited lower capacity of hydrogen adsorption, lower hydrogenation activity, more intense interaction of the manganese oxide with the Rh component, and more intense bands of twin-adsorbed CO (i.e. more Rh^{1+} ion). The good selectivity of the Rh–Mn–Li/SiO_2 catalysts towards acetaldehyde and acetic acid formation were correlated to these features. © 1997 Elsevier Science B.V.

Keywords: Rhodium; Manganese; Lithium; Acetic acid; Acetaldehyde

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1. Introduction

The catalytic conversion of syngas to C_{2+} oxygenated compounds is a topic of growing interest from both practical and mechanistic points of view. It was reported by Bhasin et al. that C_{2+} oxygenated compounds such as ethanol, acetaldehyde and acetic acid were selectively obtained from syngas over rhodium catalysts under high-pressure conditions [1]. Ichikawa found that a pyrolytic rhodium cluster catalyst supported on lanthanum oxide gave ethanol in 61% selectivity at sub-atmospheric synthesis gas reaction [2]. At present many studies have been devoted to seeking new catalysts with high activity and selectivity to C_{2+} oxygenated compounds from syngas [3–7]. As a consequence of these investigations a rhodium-based catalyst was suggested as a promising candidate for the direct production of C_{2+} oxygenated compounds from syngas. The effects of various supports and promoters on the catalytic activity and selectivity to the formation of C_{2+} oxygenated compounds have also been studied extensively.

In our laboratory, we have also investigated and developed two kinds of rhodium catalysts

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for the production of C_{2+} oxygenated compounds from syngas [8]. One is the Rh–V/SiO_2, and the other is the Rh–Mn/SiO_2. The former favored the formation of ethanol, and practically no acetic acid product was observed in the syngas reaction [9,10], the latter tended to produced acetic acid and acetaldehyde [11,12]. The cause of the difference in product distribution between these two catalyst systems is not clear so far. In this paper we report some interesting results of the syngas reaction and of characterization research of Rh–Mn/SiO_2 catalysts for the synthesis of C_2 oxygenates from syngas, and discuss the reasons for the difference in product distribution between the Rh–Mn/SiO_2 and the Rh–V/SiO_2 catalysts.

2. Experimental

Catalysts were prepared by impregnating SiO_2 (20–40 mesh, BET surface area 200 m^2/g, Haiyang Chemicals Plant, China) with an aqueous solution of $RhCl_3 \cdot xH_2O$ (Johnson Matthew Company, UK) and/or $Mn(NO_3)_2$ and/or $LiNO_3$, and drying at 393 K. pH values of the solutions were ca. 1.2. Rhodium loading in all of the catalysts was 1 wt%. The ratio of Rh/Mn for syngas reaction was 1:1, the others are stated in the context.

2.1. Syngas reaction

The catalyst was reduced by pure hydrogen in the reactor in-situ before the reaction. The temperature was raised at 2 K/min up to 623 K, and then held constant for at least 8 h. The H_2 flow rate was 4 l/h and the pressure was 0.5 MPa. The loading of catalyst is 0.3 g ($\sim$ 0.6 ml) for each test. The reaction system consisted of a small fixed bed tubular reactor with an external heating system, which was made of 316L stainless with 300 mm length, 6 mm internal diameter. The effluent passed through a condenser filled with 150 ml of cold water. The produced oxygenated compounds were dissolved into the water and analyzed by off-line gas chromatography. The gaseous effluents were analyzed by an on-line GC. In this work, the steady stage was achieved at about 200 h from the start of the reaction. Hence, sampling was carried out after 200 h of reaction. Liquid samples were analyzed by collecting the sample for 4 h, while the gas products were analyzed for each hour.

Conditions for the temperature programmed reduction(TPR) of the catalysts were: catalyst sample 10 mg, $H_2/Ar = 5:95$ (volume ratio), flow rate 20 ml/min, heating rate 16 K/min.

Temperature programmed desorption of H_2 (H_2-TPD): ca. 50 mg of catalyst was reduced in flow hydrogen at 593 K for 1 h, and then cooled to room temperature. The desorption experiment was performed in temperature programmed rate of 32 K/min. Argon was used as the carrier gas.

ESR spectra of catalysts were recorded by TEJ-PE-2XG spectrometer at frequency of 9.426 GHz and RT. Treating conditions are shown in the text.

IR study of adsorbed CO: The IR spectroscopy studies were conducted in a quartz cell. The catalyst wafer (20 ± 1 mg, diameter 15 mm) was reduced in situ by flow hydrogen at 607 K for 1 h and evacuated to 1.3×10^{-3} Pa. IR spectra of adsorbed CO were recorded by a PE-580B IR spectrometer. Its resolution is 2.3 cm^{-1} in the range of 900–4000 cm^{-1}.

3. Results and discussion

3.1. Syngas reaction

3.1.1. Product distribution

It would be very interesting to know the product distribution of syngas conversion on the Rh–Mn/SiO_2 catalyst. The composition of oxygenated products is presented in Table 1. Fig. 1 shows the distribution of oxygenated compounds and gaseous hydrocarbons in the products of syngas conversion at reaction condi-

Table 1
Composition of C_2-oxygenated products in small-scale performances

CH_3CHO (wt%)	C_2H_5OH (wt%)	PrOH (wt%)	MeOAc (wt%)	EtOAc (wt%)	BuOH (wt%)	HOAc (wt%)
31.7	30.0	1.5	0.6	3.9	0.58	31.6

$T = 563$ K, $P = 3.0$ MPa, $H_2/CO = 2$, SV = 27000 ml/g · h, PrOH = C_3H_7OH, MeOAc = CH_3COOCH_3, EtOAc = $CH_3COOC2H_5$, BuOH = C_4H_9OH, HOAc = CH_3COOH.

tions: $T = 563$ K, $P = 3.0$ MPa, SV = 27000 ml/g · h. From Fig. 1 it can be found that the Rh–Mn/SiO_2 catalyst produced C_2 oxygenated compounds selectively. Methane was a major component in the gaseous products. Besides methane, hydrocarbons with carbon number up to 6 were found, but their amount decreased sharply with the carbon number. Fig. 2 presents the relationship between the logarithmic value of the concentration of oxygenated compounds and hydrocarbons with carbon number of these compounds. From Fig. 2, we can also find that the distribution of oxygenated compounds on the Rh–Mn/SiO_2 catalyst is quite different from the Anderson–Schulz–Flory (ASF) distribution of ordinary Fischer–Tropsch synthesis, but the distribution of hydrocarbons in the gaseous products followed the ASF distribution [13].

$$\mathrm{Ln}\, C_n = \mathrm{Ln}\frac{1-\alpha}{\alpha} + n\,\mathrm{Ln}\,\alpha$$

C_n: concentration of produced hydrocarbons and oxygenates with n carbon number, α: relative probability of chain growth.

According to the distribution of oxygenated and hydrocarbon products, it could be deduced that the reaction intermediate 'CH_x' was formed over the Rh–Mn/SiO_2 catalyst surface and that the rate of chain growth was lower than that of CO insertion into the 'CH_x' species on the Rh–Mn/SiO_2 catalyst surface.

3.1.2. *Influence of reaction conditions on activity and selectivity*

The experimental data of CO conversion, STY and selectivity to C_2 oxygenated compounds under different reaction conditions are presented in Tables 2–5. The experimental results indicate that, when the reaction temperature was elevated, the CO conversion, the production of C_2 oxygenated compounds and the formation of methane increased, but the selectivity to C_2 oxygenated compounds decreased. It can also be found that when the total reaction pressure was elevated, the conversion of CO and the STY of C_2 oxygenates and methane increased significantly, while the selectivity to C_2 oxygenates increased slowly. The STY of C_2 oxygenated compounds was 444 g/kg · h at 593 K of reaction temperature and 3.0 MPa of total reaction pressure. In the produced oxygenated compounds, ethanol, acetaldehyde and acetic acid were the most-abundant compounds.

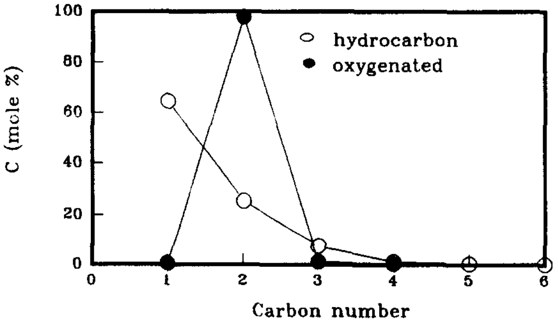

Fig. 1. Distribution of products on the bench-scale experiment.

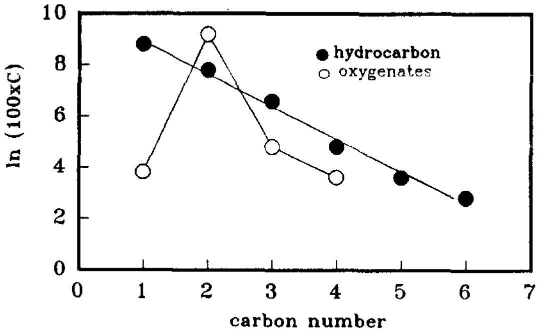

Fig. 2. Relation of logarithm of concentration versus carbon number.

Table 2
Effect of reaction temperature on the activity and selectivity to C_2-oxygenated compounds

Temp. (K)	CO conv. (%)	$STY_{C_2\text{-oxy}}$ (g/kg · h)	STY_{CH_4} (g/kg · h)	$S_{C_2\text{-oxy}}$ (%)
563	3.6	205.8	46.1	56.8
573	4.8	260.7	53.4	67.0
583	7.4	314	127.6	49.5
593	9.5	427	189	44.9

$P = 3.0$ MPa, SV = 27000 ml/g · h.

Table 3
Effect of reaction pressure on the activity and selectivity to C_2-oxygenated compounds

P (MPa)	Conv. (CO%)	$STY_{C_2\text{-oxy}}$ (g/kg · h)	STY_{CH_4} (g/kg · h)	$S_{C_2\text{-oxy}}$ (%)
3.0	9.5	427	189	44.9
4.5	11.9	586	220	49
6.0	14.6	736	279	50.6
7.0	16.4	869	311	53.4

$T = 593$ K, SV = 27000 ml/g · h.

The increase of reaction pressure was favorable to the STY and selectivity to C_2 oxygenates.

3.1.3. Test of durability of the Rh–Mn/SiO$_2$ catalyst with reaction time

The change in catalyst performance with the lapse of reaction time was measured with the small-scale apparatus. The measurement was carried out continuously for near 400 h. After the first 200 h, the steady state of reaction was achieved. The activity and selectivity to C_2-oxygenated compounds were found to be quite stable throughout the whole durability test. The results of the catalyst durability test are shown

Table 4
Effect of reaction temperature on the distribution of produced oxygenated products

T (K)	C_1-oxy (mol%)	C_2-oxy (mol%)	C_3-oxy (mol%)	C_4-oxy (mol%)
563	0.43	97.9	1.24	0.38
573	1.08	96.5	1.25	0.5
583	1.46	95.7	1.71	1.13
593	2.55	94.4	1.80	1.2

$P = 3.0$ MPa, SV = 27000 ml/g · h.

Table 5
Effect of reaction pressure on the distribution of oxygenated products

P (MPa)	C_1-oxy (mol%)	C_2-oxy (mol%)	C_3-oxy (mol%)	C_4-oxy (mol%)
3.0	2.55	94.4	1.8	1.2
4.5	5.7	90.0	2.3	2.0
6.0	7.3	88.0	2.4	2.4
7.0	10.3	84.8	2.4	2.5

$T = 578$ K.

Table 6
Durability of Rh–Mn/SiO_2 catalysts

Time on stream (h)	Temp. (K)	Pressure (MPa)	Feed rate (l/h)	STY (g/kg · h)	S_{C_2-oxy} (%)
208	593	3.0	8.5	454	42.9
298	593	3.0	8.5	444	44.7
398	593	3.0	8.5	484	47.8

in Table 6, no deterioration of the catalyst activity was observed during the life test for near 400 h.

3.2. Characterization results

TPR results are shown in Fig. 3. The Rh/SiO_2 catalyst without promoter gave a reduction peak of lower temperature at ca. 433 K (profile a), while the Mn/SiO_2 sample exhibited a higher one at ca. 603 K (profile b). Addition of Mn to the Rh/SiO_2 catalyst led to a shift of the reduction peak of rhodium to a higher temperature, but a shift of the reduction peak of the manganese component itself to a lower temperature. These results indicated that manganese had a suppression effect for the reduction of the rhodium precursor. On the other hand, rhodium can promote the reduction of the manganese component.

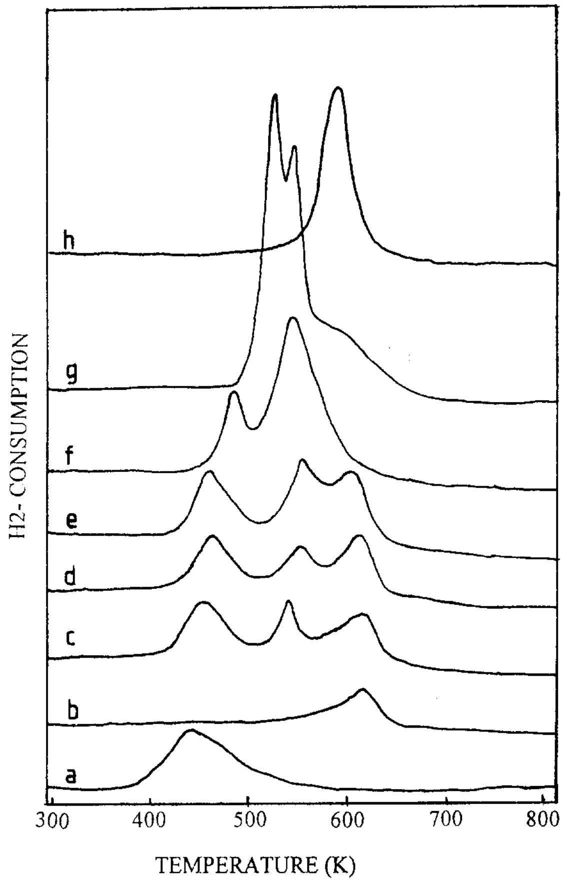

Fig. 3. TPR profiles of various catalysts: a, 2%Mn/SiO_2; b, 1%Rh/SiO_2; c, 1%Rh–2%Mn/SiO_2; d, 1%Rh–2%Mn–0.05%Li/SiO_2; e, 1%Rh–2%Mn–0.15%Li/SiO_2; f, 1%Rh–2%Mn–0.3%Li/SiO_2; g, 1%Rh–2%Mn–0.5%Li/SiO_2; h, 1%Rh–0.15%Li/SiO_2.

The introduction of Li to the Rh–Mn/SiO_2 catalysts further retarded the reduction of rhodium as well as promoted the process of manganese oxide reduction (profile d, f, e). The profile peak at ca. 503 K in Fig. 1 seemed related to the reduction of the NO_3^- radical. The addition of Li to Rh/SiO_2 played a suppressing role to the reduction of rhodium, as shown by profile h. The larger area of reduction peak in profile h than that in profile a (Rh/SiO_2) seemed related to reduction of $LiNO_3$, presumably to $LiNO_2$.

The H_2-TPD profiles of both 1%Rh/SiO_2 and 1%Rh–2%Mn/SiO_2, as shown in Fig. 4 had 2 peaks, which were ascribed to desorbed hydrogen from two kinds of sites. The addition of manganese to Rh/SiO_2 led to shifts of two desorption peak towards higher temperature and an increase of peak area. The increase of hydrogen desorption amount due to the addition of Mn appeared to be related to hydrogen spilling over on the surface of the catalyst.

ESR spectra of the 2%Mn/SiO_2 sample before and after reduction are shown in Fig. 5. The spectrum before reduction (spectrum a) exhibited a sextet of Mn^{2+} ion, and indicated that

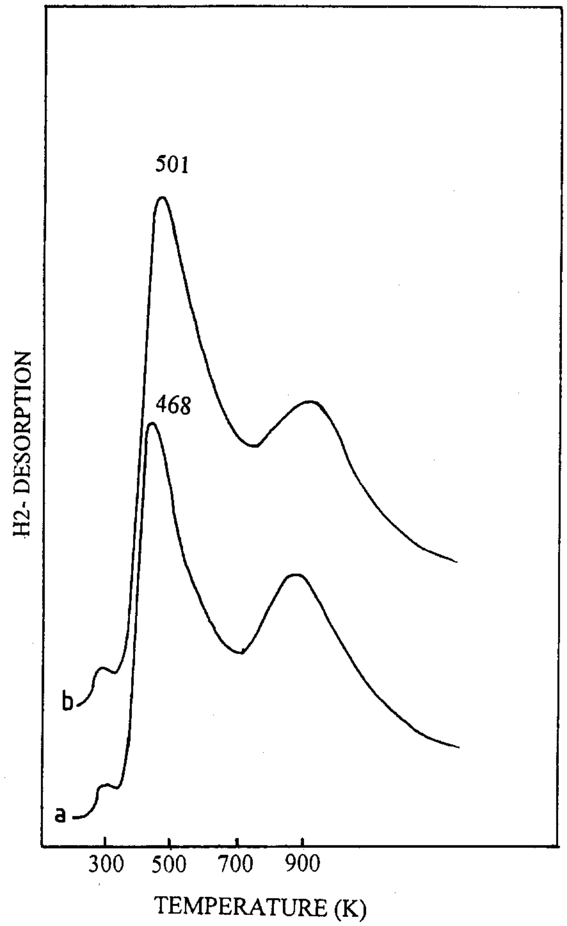

Fig. 4. H_2-TPD profiles of catalysts: a, 1%Rh/SiO_2; b, 1%Rh–2%Mn/SiO_2.

the sample contained very few Mn^{2+} ion. During the drying process of the sample after impregnation, its color first changed from colorless to pink, and finally changed to black. This implied that the Mn^{2+} ion impregnated onto silica was oxidized to ions of higher valence by oxygen in air, possibly to Mn^{4+}. This change of the sample color supported the ESR results. In the spectrum of the sample after reduction at 613 K for 1 h, no fine structure of Mn^{2+} sextet were observed, and ESR signal intensity of the sample increased sharply, suggesting large amount of manganese ions of higher valence was reduced to Mn^{2+}. This observation was consistent with the above conclusion.

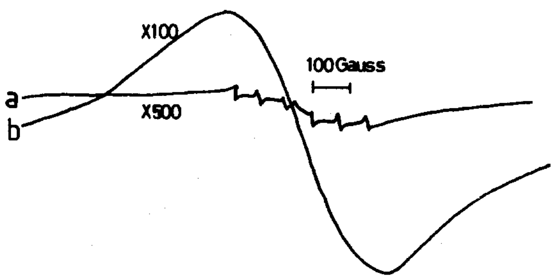

Fig. 5. ESR spectra of 2%Mn/SiO_2. a, evacuated at RT for 0.5 h before reduction; b, after reduction at 603 K for 1 h.

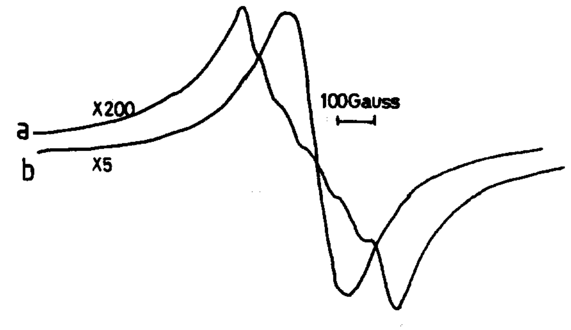

Fig. 6. ESR spectra of 1%Rh–2%Mn/SiO_2. a, evacuated at RT for 0.5 h before reduction; b, after reduction at 603 K for 1 h.

As shown in Fig. 6, the ESR signal of a 1%Rh–2%Mn/SiO_2 catalyst was obviously higher than that of the 2%Mn/SiO_2 sample, and the hyperfine structure of the spectrum was not so clear as that of the latter. This may be due to more amount of Mn^{2+} ion existing in this catalyst, and revealed that the rhodium component in the 1%Rh–2%Mn/SiO_2 sample had a tendency of stabilizing the Mn^{2+} ions. Wilson et al. [11] have suggested that this would lead to the formation of composite oxides of rhodium and manganese. The hyperfine structure in the ESR spectrum of the 1%Rh–2%Mn/SiO_2 catalyst after reduction at 603 K disappeared completely, the peak width became narrower, whilst the intensity was increased. This implied that a large amount of Mn^{2+} ions was produced during the reduction of this catalyst, and the coupling interaction between the Mn^{2+} ion formed during reduction increased. This resulted in the disappearance of the Mn^{2+} hyperfine structure. Simultaneously, the obvious difference between the ESR spectra of the

$2\%Mn/SiO_2$ and the $1\%Rh–2\%Mn/SiO_2$ after reduction by hydrogen at similar conditions was observed, i.e., the Mn^{2+} signal intensity of the latter is about 20 times greater than that of the former. Occurrence of rhodium promoted the reduction of manganese ion of higher valence to Mn^{2+}. The spectrum peak of the reduced $1\%Rh–Mn/SiO_2$ catalyst became narrower, which suggested a change of the magnetism environment at the surrounding of the Mn^{2+} ion. Possibly, certain substance of weaker magnetism such as a composite of Rh^{1+} and manganese oxide was formed, and the magnetism interaction within the catalyst was weakened.

The IR spectra of the Rh/SiO_2 catalysts with and without Mn and Li promoters were shown in Fig. 7. The band at 1875 cm^{-1} was ascribed to bridge-adsorbed CO, the band at 2067 cm^{-1} to linearly adsorbed CO, while the bands at 2092 cm^{-1} and 2022 cm^{-1} were ascribed to twin-adsorbed CO. It can be seen from Fig. 7 that the introduction of Mn and Li weakened the bridged CO and enhanced twin-adsorbed CO. This is easy to be understood from the demonstrated fact that during reduction, transition metal and alkali metal oxides in the catalysts can move onto the metal surface and partly cover it, and this would result in a being divided of bigger metal ensembles into smaller ones. As a result, a band of weakened bridged CO could be observed. Generally, it is considered that twin-adsorbed CO takes place on isolated Rh^{1+} sites [14,15]. Since the addition of Mn and Li to the Rh/SiO_2 catalysts suppressed the rhodium reduction, more Rh^{1+} ions would exist on the catalyst surface, so that more intense twin-adsorbed CO bands were recorded. Also, the above-mentioned TPR and ESR results supported this conclusion.

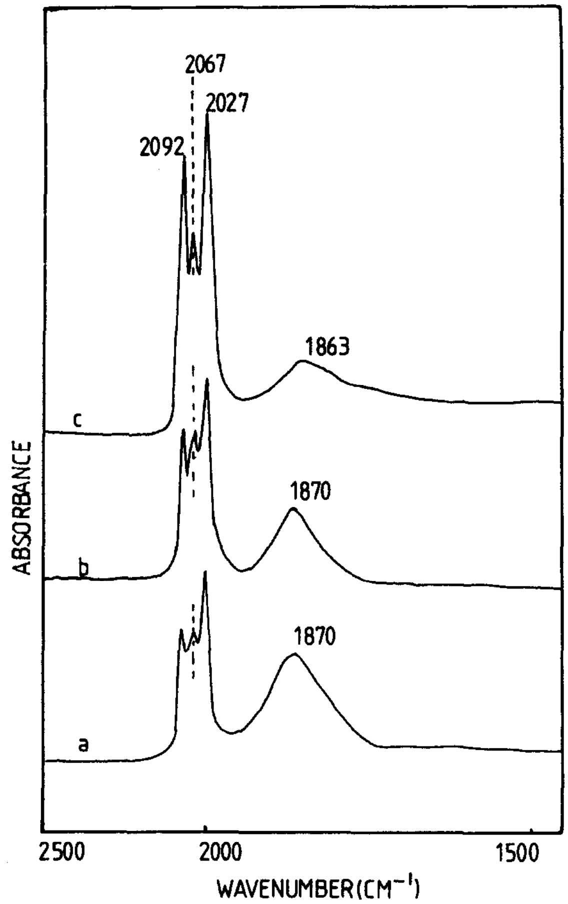

Fig. 7. IR spectra of CO adsorbed at RT on various catalysts: a, $1\%Rh/SiO_2$; b, $1\%Rh–2\%Mn/SiO_2$; c, $1\%Rh–2\%Mn–0.5\%Li/SiO_2$.

In the study of adsorbed CO on a $1\%Rh–2\%Mn–1\%Li/SiO_2$ catalyst at various temperatures, it has been found that the intensity of twin-adsorbed CO bands increased with higher temperature of adsorption, as shown by Fig. 8. The results indicated that more Rh^{+1} ions exist on the catalyst surface and favors the formation of acetic acid and acetaldehyde.

A major problem in the synthesis of C_2 oxygenates is how to select suitable promoters and preparation procedure to improve the activity and selectivity for the formation of C_2 oxygenates. Mn and Li as promoters of supported rhodium catalysts exhibited a good promoting effect, and have a pertinent feature that it promoted the formation of acetic acid and acetaldehyde. On the other hand, vanadium promoted the formation of ethanol. The good activity and selectivity of $Rh–Mn–Li/SiO_2$ and $Rh–V/SiO_2$ catalysts seemed related to the formation of composite sites of Mn or V promoter and Rh, which commonly catalyzed the formation of C_2 oxygenates. The tendency of Mn to

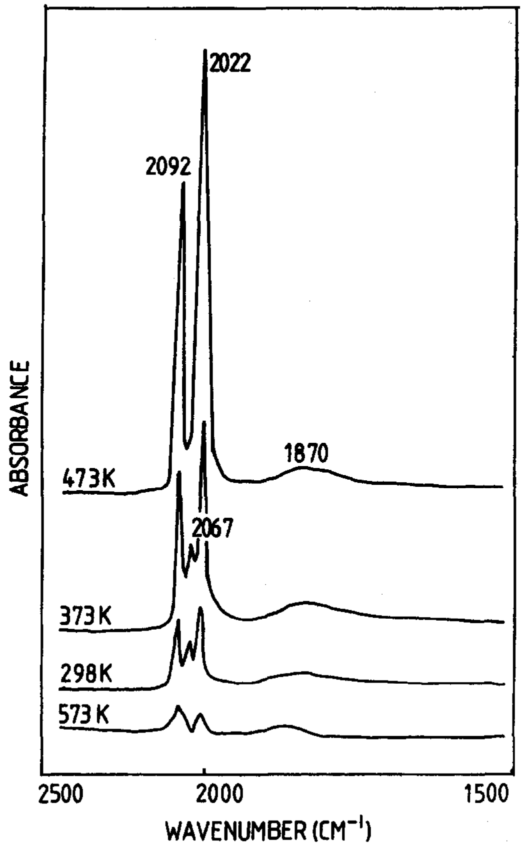

Fig. 8. IR spectra of CO adsorbed at various temperatures on 1%Rh–2%Mn–1%Li/SiO_2 catalysts.

promoting the formation of acetic acid and acetaldehyde seemed due to its lower capacity of hydrogen storage and lower ability of hydrogenation relative to V as well as due to its more intensive suppression of the reduction of rhodium in the Rh–Mn based catalysts, thus keeping more Rh^{1+} ions after H_2 reduction. The favoring effect of vanadium promoted catalysts to form ethanol can be attributed to its large capability of hydrogen storage as well as to the existence of fewer Rh^{1+} ions after reduction, as shown by a weakened twin-bands in the IR spectra of adsorbed CO [10].

In the previous paper [10] concerning the promoting effect of vanadium, it has been reported that the amount of hydrogen desorption from Rh–V/SiO_2 catalysts was much larger than that from the Rh/SiO_2 catalysts, and was found to be nearly proportional to the added amount of vanadium. The amount of hydrogen desorption from the 2%Rh–2%V/SiO_2 catalyst was 3–4 times of that from the 2%Rh/SiO_2. Comparing with the Rh–V/SiO_2 catalysts, the amount of hydrogen desorption from the 1%Rh–2%Mn/SiO_2 catalyst was about 1.3 times of that from the Rh/SiO_2 with the same rhodium loading.

In IR studies of adsorbed CO, a large shift of 60–70 cm^{-1} for the bridged CO was observed on the Rh–V/SiO2 catalysts, when the catalysts were cooled to room temperature in hydrogen after reduction and before CO was absorbed. On the other hand, no band shifts were recorded when these catalysts were evacuated to remove hydrogen after reduction, irrespective of that CO was adsorbed alone or coadsorbed with H_2. These results suggested that the spilled-over hydrogen possibly took part in the activation of adsorbed CO. In comparison to the Rh–Mn/SiO_2 or Rh–Mn–Li/SiO_2 catalysts, bands of the twin-adsorbed CO on the Rh–V/SiO_2 catalysts were much weaker and easier to be removed by heating in $H_2 + CO$ atmosphere. Up to now, a variety of adsorbed CO species, namely, linear, bridged, dicarbonyl, and tilted were recorded and a large shift of bridged CO band to a lower wave number on transition metal promoted rhodium catalysts. Ichikawa et al. [3] considered that the bridged CO was the active species for CO hydrogenation to C_2 oxygenates, based on a large shift of bridged CO band. Knozinger et al. [7] found that bridged, linear and tilted CO can all be hydrogenated in the studies of hydrogenating ability of various species of adsorbed CO, and they reached the conclusion that it is difficult to establish which species is responsible for the formation of C_2 oxygenates in the $CO + H_2$ reaction. Apparently, these different conclusions were due to the fact that the catalysts of different authors had different activity and selectivity towards C_2 oxygenates, and also different conditions were used in the characterization of the catalysts, although they had similar compositions. For example, some catalysts are active and selective for the synthesis of C_2 oxygenates, the others are not so good. Some catalysts for IR measurement of adsorbed CO experienced a treatment of high vacuum, and others reserved more hydrogen after reduction.

In the previous paper, R^{1+} ions were considered to be the sites for promoting the formation of C_{2+} oxygenates [5]. However, Ponec et al. [16] studied the relation between the R^{1+} ion concentration and selectivity of the formation of C_2 oxygenates in Rh/V_2O_3 catalysts by solvent extraction, and found that the most active and selective Rh/V_2O_3 catalysts contained no detectable amount of rhodium ions. This implied that the existence of rhodium ions was not necessary for the formation of C_2 oxygenates. In this study, both $Rh-Mn/SiO_2$ and $Rh-V/SiO_2$ were active and selective catalysts for the formation of C_2 oxygenates, but only the $Rh-Mn/SiO_2$ catalyst exhibited strong IR bands of twin adsorbed CO. These results do not support the opinion that rhodium ions are the sites of the formation of C_2 oxygenates. However, the high concentration of rhodium ions shown by strong IR bands of twin adsorbed CO had a good correlation with the selectivity towards the formation of acetic acid and acetaldehyde. A lower capacity of hydrogen storage and a lower ability of hydrogenation seemed to be the reason of leading to high selectivity for the formation of acetic acid and acetaldehyde. It deserves to mention that the $Rh-Mn/SiO_2$ catalysts which had a lower ability of hydrogen storage exhibited a somewhat lower activity than the $Rh-V/SiO_2$ catalysts. These results also supported our previous opinion that the spilled-over hydrogen on the catalyst surface takes part in the activation of adsorbed CO.

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References

[1] M.M. Bhasin, N.J. Bartley, P.C. Ellegen and T.P. Wilson, J. Catal. 54 (1978) 120.

[2] M. Ichkawa, Bull. Chem. Soc. Jap. 51 (1978) 2273.

[3] M. Ichikawa, A. Fukuoku and T. Kimura, in: Proc. 9th Int. Congr. Catal., M.J. Phillips and M. Ternan (Editors), Vol. 2, Calgary (1988) p. 569.

[4] H. Arakawa, T.A. Hanaoka, K. Takeuchi, T. Matsuzaki and Y. Sugi., Proc. 9th. Intern. Congr. Catal., Calgary, Vol. 2 (1988) p. 602.

[5] F.G.A. Van den berg, J.H.E. Glezer and W.M.H. Satchler, J. Catal. 93 (1985) 340.

[6] A.C. Stevenson, A. Listsyn and H. Knozinger, J. Phys. Chem. 94 (1990) 1576.

[7] A.S. Lisitsyn, S.A. Stevenson and H. Knozinger, J. Mol. Catal. 63 (1990) 201.

[8] P-Z. Lin, D-B. Liang, H-Y. Luo, C-H. Xu, H-W. Zhou and S-Y. Huang, Appl. Catal. 131(2) (1995) 207.

[9] H-Y. Luo, A.G.T.M. Bastein, A.A.T.P. Mulder and V. Ponec, Appl. Catal. 38 (1988) 241.

[10] H-Y. Luo, H-W. Zhou, L-W. Lin, D-B. Liang, C. Li, D. Fu and Q. Xin, J. Catal. 145 (1994) 232.

[11] T.P. Wilson, P.H. Kasai and P.C. Ellgen, J. Catal. 69 (1981) 193.

[12] H-Y. Luo, S-B. Xie, H-w. Zhou, L-W. Lin and D-B. Liang, China J. Catal. 16(2) (1995) 126.

[13] S.T. Sie, M.M.G. Senden and H.M.H. Van Wechem, Catal. Today 8 (1991) 371.

[14] C.W. Garland and J.R. Wilt, J.M. Chem. Phys. 36 (1962) 1049.

[15] A.C. Yang and C.W. Garland, J. Phys. Chem. 61 (1957) 1504.

[16] G. v.d. Lee, B. Schuller, Post, T.L.F. Favre and V. Ponec, J. Catal. 98 (1986) 522.