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Unusual selectivity of oxygenate synthesis Formation of acetic acid from syngas over unpromoted Rh in NaY zeolite

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Abstract

Syngas conversion over Rh/zeolite-NaY catalysts at high-pressure lead to high yields of acetic acid. This unusual selectivity toward one oxygenate in the absence of any catalyst promoter is most pronounced at lower temperature; the apparent activation energy for overall CO-hydrogenation is 23.7 kcal/mol, but for the formation of acetic acid it is 11.9 kcal/mol. The selectivity is little affected by the protons formed during the reduction of Rh. In stiu FT-IR measurement reveals that changes in activity and selectivity during the start-up period are caused by thorough catalyst reconstruction, converting the original Rh^0 clusters to multinuclear $Rh_6(CO)_{16}$ and $CH_3Rh_y(CO)_x$ and/or mononuclear $CH_3Rh(CO)_x$ carbonyl complexes, and smaller Rh^0 clusters. Stable acetate groups, but not the surface bound acetyls, are formed and detected by FT-IR. Most of the cooperating Rh species survive when the pressure is lowered from 1.0 to 0.1 MPa, maintaining a high acetic acid selectivity that is vastly superior to that of the fresh catalyst. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Syngas; Zeolite; Oxygenate synthesis; RH catalyst; Acetic acid; Metal carbonyls

1. Introduction

Rhodium is the most versatile catalyst for syngas conversion reactions. The product selectivity depends significantly on the metal dispersion, the nature of the support and its impurities or additives acting as catalyst promoters [1–3]. The propensity of supported rhodium to catalyze the formation of valuable oxygen-containing compounds, aldehydes, alcohols, acetic acid and acetates, appears to be a consequence of its position in the center of Group VIII metals of the periodic table: CO dissociation and insertion of undissociated CO are both possible. In traditional Rh catalysts promoters are crucial for the formation of oxygenates, especially ethanol. Many kinds of metal oxide have been used to maximize the formation of oxygenates over Rh catalysts. The total selectivity to C_{2+} oxygenates can sometimes amount to 70% (on carbon base) of the products [4,5]. Ethanol, acetaldehyde, acetic acid and the acetates are always among the oxygenate products, no single product being dominant. The action of promoters to direct the Rh catalyzed conversion of syngas towards one particular group of products has been the object of many studies [1–10]. Recently, two of the present authors showed that it was possible to form acetic acid selectively from syngas at high pressure with a novel catalyst consisting of unpromoted rhodium in zeolite NaY [11,12]. At 1.0 MPa and 250°C the selectivity

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to acetic acid was 45–56% with a syngas of equal moles CO and H_2, but 67% with a CO-rich syngas ($CO/H_2 = 3$); other oxygenates never exceeded 10% of the acetic acid. Exposure of the Rh/NaY to high-pressure of syngas was found crucial to induce this selectivity, but subsequent release of the syngas to atmospheric pressure still retained a high selectivity to acetic acid [11].

In the present study, some variables of the catalyst treatment and the effect of reaction temperature have been examined. In situ FT-IR is used to monitor the working catalyst under different pressures of the syngas. Attention is directed to the detection of Rh-carbonyls and their functions to check the ideas mentioned previously [11].

2. Experimental

Rh/NaY catalysts without promoter were prepared by ion exchange of NaY with a 2×10^{-3} M solution of $[Rh(NH_3)_5Cl]Cl_2$ (Fluka) in double deionized water. The NaY zeolites was LZY-54 from UOP with the composition: $Na_{56}(AlO_2)_{56}(SiO_2)_{136}\cdot nH_2O$. After ion exchange, the sample was calcined in O_2 at 500°C and reduced in H_2 up to 450°C. Experimental detail for the catalyst preparation was described in the earlier reports [11,12]. The load of rhodium in the zeolite was 2.9%. The standard catalyst, Rh/NaY, was treated with aqueous NaOH solution at pH = 11 to neutralize the protons formed during the reduction of Rh ions. The Rh particle size after reduction was about 1.0 nm by TEM and the metal dispersion measured by H_2-TPD was $H/Rh = 0.91$, indicating that Rh particles are inside the cages of the zeolite [11]. This procedure of catalyst preparation was modified when it was desired to maintain the protons that are formed during the reduction of Rh ions. In this case the neutralization with aqueous NaOH was omitted; such samples will be called Rh/HNaY. A Rh/NH_4NaY sample was prepared following Treviño and Sachtler [13] by calcination in O_2 at 200°C of the precursor loaded with the Rh–ammine complex, followed by reduction in H_2 at the same temperature. The limitation of the temperature to 200°C should prevent complete decomposition of the ammine ligands; during the reduction the remaining NH_3 ligands are released when metallic Rh and protons are formed; they neutralize the protons [13,14].

The CO hydrogenation reaction was performed with 300 mg calcined catalyst at 230–270°C with an equimolar mixture of H_2 and CO ($CO/H_2 = 1$) in a home made bronze fixed-bed flow reactor. The space velocity of reacting feed (GHSV) is 15 000 h^{-1} and the total syngas pressure is 1.0 MPa. The set up of the reaction system was basically the same as those described previously [11], except that all tubing from the syngas cylinder to the reactor are made of copper. Reduction of the catalyst was always done in situ under hydrogen at 400°C for Rh/NaY and Rh/HNaY samples. For Rh/NH_4NaY, the reduction temperature was 200°C.

In situ transmission FT-IR spectroscopy study was carried out with a high pressure IR cell designed by catalysis researchers at Xiamen University. The main body of the cell was made with a stainless steel tube (i.d. 16 mm) that is aligned inside with a quartz tube (i.d. 14 mm). The cell was connected at both ends to bronze jackets that are fitted with window material (CaF_2 crystal). Connected to each jacket is also a small copper tube for gas inlet and outlet, respectively. The jackets are also engineered for cooling with water. A self-supporting wafer of the catalyst (ca. 8–9 mg/cm^2) was placed in the middle of the cell, on both sides of the wafer were engineered bars of CaF_2 crystals to shorten the cell light path to ca. 4 mm. This design should prevent formation of iron carbonyls under high pressure of CO (syngas). A furnace mounted on the cell body allows heating the wafer up to 700°C. The catalyst wafer (Rh/NaY) was reduced in situ with H_2 at 400°C for 1 h, followed by monitoring the IR spectrum of the syngas reaction at 250°C under different pressure. The spectrometer was Perkin-Elmer FTIR-2000. All spectra were recorded with 16 scans at the reaction temperature with a resolution of 4 cm^{-1}.

3. Results

3.1. Reaction studies

Results of the reaction over the standard Rh/NaY catalyst at 250°C were described comprehensively in earlier publications [11,12]. The present reaction study focuses on effects of residual protons in the catalyst and the reaction temperature on the steady state selectivity of oxygenates, especially acetic acid.

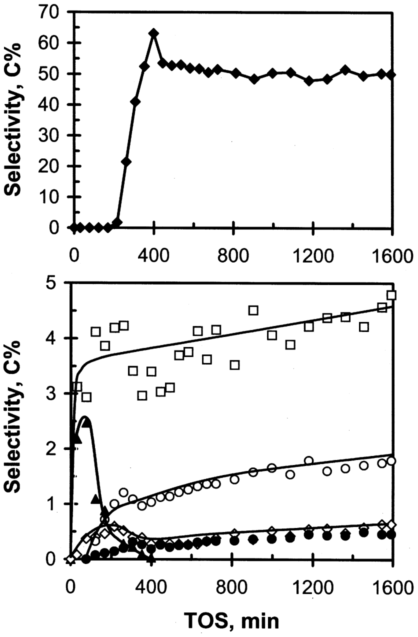

Fig. 1. Selectivity change of the oxygenate products during the syngas reaction. –◆–: acetic acid; –□–: acetaldehyde; –▲–: ethanol; –◇–: propionaldehyde; –○–: ethyl acetate; –●–: methyl acetate.

Syngas reaction over standard Rh/NaY produces 45–55% acetic acid (on the carbon base) in the steady state. Formation of the other oxygenates, acetaldehyde, propionaldehyde, methyl and ethyl acetates remains below 5% of the products. Ethanol, which was frequently reported to be the main oxygenate component over promoted rhodium catalysts [1,4,6,7], is undetectable under the steady state conditions [11,12]. A presentation of the reaction time course for the formation of the individual oxygenates is given in Fig. 1. Only during the first few hours a small amount of ethanol ($<3\%$) is detected. Evolution of the ethylacetate ($<2\%$) under steady state catalysis suggests that ethanol formed at this stage (ca. 1%) reacts quickly with the acid. The catalyst selectivity for acetic acid is quite stable; no change of the selectivity was observed in a run that lasted for longer than 50 h. Acetic acid remains to be more than 90% of the total C_{2+}-oxygenates.

The effect of protons on the specific catalysis for acetic acid formation is investigated with Rh/HNaY. The reaction at 250°C gives 38–44% acetic acid under steady state catalysis. A comparison is made in Table 1 of the syngas reaction over this Rh/HNaY and the standard Rh/NaY catalysts. The very similar product distribution over these two catalysts indicates that protons formed during the catalyst reduction ($H^+/Rh = 3$) do not affect the main feature of the catalysis. This is in contrast with the cases where a promoted Rh catalyst was used for selective ethanol synthesis [13].

Also included in Table 1 are the reaction results over Rh/NH_4NaY catalyst in which protons formed during the reduction of the Rh–ammine complex were neutralized with NH_3 molecules that are released in situ from the complex. After a stable CO-conversion level has been reached (TOS = 6–10 h) the selectivity to acetic acid over Rh/NH_4NaY is ca. 45%. This is close to those obtained over Rh/NaY and Rh/HNaY. The conversion levels of CO and the distribution of other products by carbon number over the three catalysts in Table 1 are also quite close to each other. Rh/NH_4NaY and the other two catalysts differ, however, in the formation of oxygenates other than acetic acid. Only traces of acetaldehyde and acetates are detected in the early stages with this Rh/NH_4NaY catalyst when the acetic acid constitutes as high as 98% of oxygenate products during this stage. With Rh/NaY and Rh/HNaY 3–4% acetaldehyde is always detected before the detection of acetic acid (see also Fig. 1 and Ref. [11]). In addition, the olefin/paraffin ratios in hydrocarbon products are several times higher with the Rh/NH_4NaY catalyst, as represented by the values of C_2H_4/C_2H_6 and C_3H_6/C_3H_8 ratios. The iso/normal ratios in butane and pentane decrease with the increase of TOS.

Effect of the reaction temperature was studied in the range of 230–270°C with Rh/NaY catalyst; the results are given in Table 2. The selectivity to acetic acid at 230°C is higher (61%) than that at 250°C (50%) and 270°C (24%). These changes are balanced mainly by increased formations of methane and C_2 hydrocarbons; While no significant changes in the composition of the oxygenate products is observed. Less olefins and branched hydrocarbons are formed at higher temperature.

The reactivity data for CO conversion in Table 2 permit a good measurement of the apparent activation energy for overall CO-hydrogenation over the Rh/NaY catalyst, which is 23.7 kcal/mol or 100 kJ/mol. This number is in good agreement with those of Ellgen et al. [15] for unpromoted (26 ± 7 kcal/mol) and

Table 1
Effect of catalyst neutralization on the syngas reaction (250°C; 1.0 MPa; $CO/H_2 = 1$; TOS = 13 h; GHSV = 15 000 h^{-1})

	Catalyst						
	Rh/NaY[a]	Rh/HNaY[a]	Rh/NH_4NaY				
TOS (h)	12.3	13.0	11.0	12.5	20.8	30.7	46.0
Conversion (%)	1.10	1.06	0.99	1.01	1.03	0.99	0.97
Selectivity, C (%)							
CH_4	20.29	26.56	27.16	26.71	25.10	24.80	25.00
C_2	9.18	9.31	6.76	6.02	7.08	9.34	10.26
C_3	7.02	6.46	7.37	7.23	7.91	7.73	7.79
C_{4+}	11.64	11.53	12.97	13.26	13.9	13.3	11.70
EtOH	0	0	0	0	0	0	0
AcH	4.33	3.07	0.17	0.39	5.00	6.30	6.19
AcOH	45.34	41.12	45.58	46.38	39.82	36.89	37.15
Other oxygenates	2.20	1.96	0	0	1.14	1.71	1.92
C_2H_4/C_2H_6	0.07	0.06	0.20	0.23	0.33	0.40	0.41
C_3H_6/C_3H_8	0.84	0.60	2.18	2.34	2.91	3.42	3.49
Iso-/*n*-C_4H_{10}	0.68	0.48	1.05	0.88	0.51	0.45	0.43
Iso-/*n*-C_5H_{12}	2.64	2.15	3.08	2.41	1.63	1.39	1.36

[a] Catalysis of Rh/NaY and Rh/HNaY does not change significantly with the reaction TOS under steady state.

Mn-promoted Rh/SiO_2 (24 ± 2 kcal/mol) catalysts. Combining the CO reactivity data with the selectivity to acetic acid, we get also the activation energy for the synthesis of acetic acid: 11.9 kcal/mol or 50 kJ/mol. This number is just a half of that for the overall CO-hydrogenation reaction.

Table 2
Activity and selectivity of Rh/NaY catalyst different temperature (1.0 MPa; $CO/H_2 = 1$; TOS = 13 h; GHSV = 15 000 h^{-1})

	Reaction temperature (°C)		
	230	250	270
Conversion (%)	0.44	1.10	2.73
$TOF^{*}10^3$ (s^{-1})	1.10	2.50	6.30
Selectivity, C (%)			
CH_4	11.47	20.29	34.75
C_2	5.68	9.18	15.17
C_3	6.35	7.02	7.80
C_{4+}	8.32	11.64	10.53
EtOH	0.00	0.00	0.35
AcH	3.68	4.33	4.04
AcOH	61.50	45.34	23.81
Other oxygenates	2.99	2.20	2.35
C_2H_4/C_2H_6	0.201	0.07	0.03
C_3H_6/C_3H_8	2.17	0.84	0.41
Iso-/*n*-C_4H_{10}	1.13	0.68	0.36
Iso-/*n*-C_5H_{12}	3.15	2.64	1.55

3.2. FT-IR studies

The absence of iron carbonyls formation in the IR cell was confirmed in an experiment with self-supported NaY wafer that was exposed to flowing CO (0.5 MPa) and syngas (1.0 MPa) for more than 20 h. In stiu FT-IR spectra are shown in Fig. 2 of the "unpromoted" Rh/NaY catalyst at 250°C in flowing syngas reaction at different pressures. Upon exposing the in situ reduced Rh/NaY catalyst to the syngas flow at 0.1 MPa, absorptions appear for gem-dicarbonyl $Rh(CO)_2{}^+$ (2110, 2098, 2045 and 2022 cm^{-1}), bridged (1800–1900 cm^{-1}) and linear-CO (2000–2080 cm^{-1}) species on Rh metal [9,10,16,17]. The bands of linear-CO are superimposed to those of the dicarbonyl ions. Weak bands are also observed at 1760 and 1720 cm^{-1}. Increase of the syngas pressure to 1.0 MPa transforms the dicarbonyls and some of the bridged- and linear-CO species to $Rh_6(CO)_{16}$ which shows distinct strong absorptions at 2098 and 1760 cm^{-1} [19–22]. Besides, absorptions near 2060, 2040 and 2020 cm^{-1} were sometimes also assigned to $Rh_6(CO)_{16}$ [20,21]. The

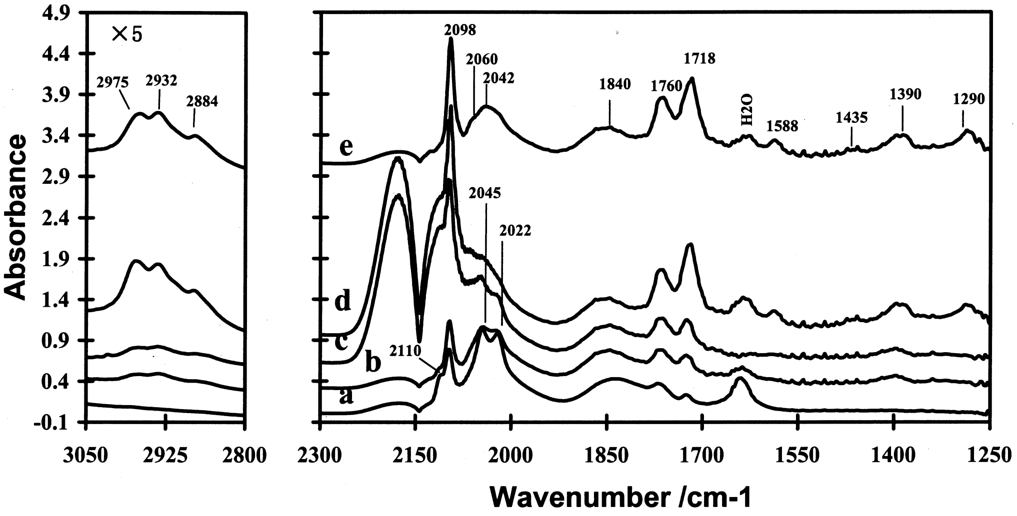

Fig. 2. In situ FT-IR spectra of the working Rh/NaY catalyst exposed in the syngas of different pressure at 250°C. **a**: → 0.1 MPa for 15 min; **b**: → 0.1 MPa for 300 min; **c**: → 1.0 MPa for 30 min; **d**: → 1.0 MPa for 300 min; **e**: → after releasing the pressure to 0.1 MPa for 180 min.

band at 1720 cm^{-1} increases with the syngas pressure up to a reaction time of 5 h, its intensity remains constant at longer time. Small growing features near 1585, 1390 and 1290 cm^{-1} accompany the growth of the 1720 cm^{-1} band. Remarkably, the features that have been stabilized during the reaction at 1.0 MPa of syngas does not change when the cell is decompressed to 0.1 MPa (Fig. 2**e**).

To verify the assignment of the bands at lower wave numbers (1720, 1585, 1390 and 1290 cm^{-1}), IR spectra of adsorbed acetic acid and acetaldehyde on Rh/NaY were taken and their behavior at elevated temperature examined. Adsorption of acetaldehyde on reduced Rh/NaY at room temperature gives sharp absorptions at 1725, 1400 and 1355 cm^{-1}. Desorption and decomposition to adsorbed CO (2015 and 1850 cm^{-1}) of the adsorbed aldehyde become prominent at above 100°C, all these absorptions disappear (Fig. 3**a** and **b**) when the temperature approaches the syngas reaction temperature (250°C). On the other hand, adsorption of acetic acid on the same catalyst gives a sharp adsorption at 1720 and a shoulder at 1760 cm^{-1} for the monodentate acetate group; weak absorptions at 1585 and 1440 cm^{-1} for bidentate acetate group are in agreement with numerous reports on silica-supported catalysts [23]. Absorption at 1290 and 1390 cm^{-1} are vibrations from the single C–O bond and CH_3 groups of the adsorbed acetates. At above 100°C a small part of the acetate groups are observed to decompose to chemisorbed linear (2016 cm^{-1}) and bridged-CO (1850 cm^{-1}), but the main feature of the adsorbed acetates remains unchanged at 250°C, as is shown by Fig. 3**c**. Thus, the spectra in Fig. 2 indicate formation of surface acetates in the syngas reaction.

4. Discussion

Our previous data [11,12] have shown that the high selectivity for acetic acid synthesis from syngas is unique for the unpromoted Rh/NaY catalyst. The present work with Rh/HNaY (Table 1) reveals that protons of concentration similar to that of Rh ($H^+/Rh = 3$) exert no significant effect on the formation of acetic acid. This is in contrast to Treviño et al. [9,13] who showed that neutralization of the zeolite protons with NaOH was essential for the formation of oxygenates over MnO promoted Rh/NaY catalysts. In their case ethanol was the main component of the oxygenate product, protons remaining in the zeolite functioned as Brönsted acid sites catalyzing secondary reactions of ethanol to hydrocarbons. This difference forms a strong support for the conclusion

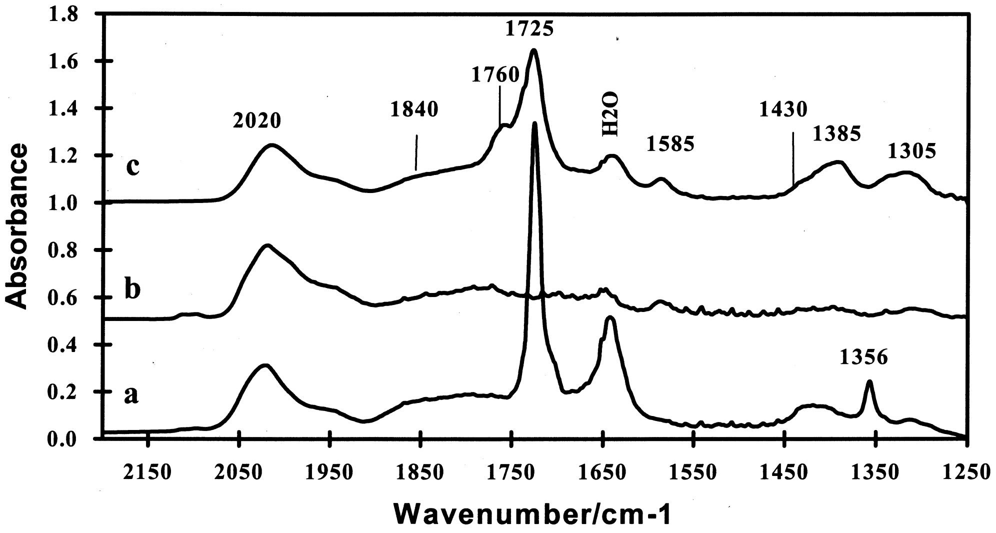

Fig. 3. FT-IR spectra of Rh/NaY catalyst with adsorbed acetaldehyde and acetic acid at elevated temperature. **a** and **b**: acetaldehyde at 110 and 250°C, respectively; **c**: acetic acid at 250°C.

that the selective formation of acetic acid is a distinct feature of the unpromoted Rh in the zeolite.

Likewise, neutralization of the protons with NH_3 has also little effect on the formation of acetic acid. It does, however, affect formation of acetaldehyde; initially Rh/NH_4NaY produces very little acetaldehyde, but production of this molecule increases slowly at extended reaction times (Table 1), when ammonium ions may decompose and protons may be formed. Also noticeable in Table 1 is the dependence on the reaction TOS of the olefin/paraffin ratios in C_2 and C_3 paraffin and the iso/normal ratios in butane and pentane; the former ratios increase while the latter decrease with TOS during the first 20 h of the reaction. Previously we reported that both ratios increase with TOS over Rh/NaY, with the iso/normal ratios increase more steeply than the olefin/paraffin ratios [11]. These differences may have implication on the reaction mechanism of NH_4^+ ions in the catalyst, which requires further study.

The FT-IR data reveal the formation of $Rh_6(CO)_{16}$ from isolated gem-dicarbonyls of $Rh^+$and larger Rh-clusters. Whereas in conventional promoted and unpromoted silica-supported Rh catalysts acetyl groups are prominent [22], the present data show acetate groups in Rh/NaY (Figs. 2 and 3). This suggests that the unusual selectivity of the present Rh/NaY catalysts for the synthesis of acetic acid is related to its ability to form acetate intermediate. Conversely, the acetyl intermediate, which is observed on conventional Rh catalysts, is unstable under the condition of syngas conversion at 250°C.

A unique response of Rh/NaY to the syngas pressure was described in our earlier report: at 1.0 MPa the activity for CO hydrogenation is one order of magnitude lower, but the selectivity for acetic acid is two order of magnitude higher than at 0.1 MPa [11]. As is known that metal carbonyl clusters in zeolite cavities form preferentially at high CO pressure [25,26], this observation led to the suggestion that some Rh carbonyl clusters will be instrumental in the formation of acetic acid from syngas over these catalysts. Over conventional silica supported Rh catalysts no formation of $Rh_6(CO)_{16}$ was detected even under high pressure of syngas [7,22,24,27,28]. With zeolite supported catalysts absorptions of $Rh_6(CO)_{16}$ are observed under conditions of the selective synthesis of acetic acid (1.0 MPa), but they do not change with the reaction time (Fig. 2). This confirms earlier data of Rode et al. [20] and Takahashi et al. [29] that $Rh_6(CO)_{16}$ itself is not active for olefin hydroformylation. However, these authors showed that exposure to olefin or H_2 molecules of the $Rh_6(CO)_{16}$-supported zeolites could induce catalysis for CO-insertion in the hydroformylation reaction. The rather weak bands at 2060, 2040, and 2025 cm^{-1} (Fig. 2**c** and **d**) are sometimes assigned also to $Rh_6(CO)_{16}$; they were absent when this complex was adsorbed on silica or alumina surface [18,19]. It is possible that these bands are due to other Rh-carbonyls like $CH_3Rh(CO)_x$. Rode et al. [20] assigned a band at 2040 cm^{-1} to an asymmetric CO-vibration of $Rh(C_3H_7)(CO)_2$ attached to the zeolite framework. Also, carbonyls of a $Rh(C_2H_5)(CO)_4$ complex in homogeneous system showed absorptions at 2115 (symmetric), 2037 (asymmetric), and 2019 cm^{-1} (asymmetric) [30,31]. This symmetric stretch band near 2115 cm^{-1} in our spectra (Fig. 2) is probably obscured by the strong absorption at 2098 cm^{-1} of the $Rh_6(CO)_{16}$.

The formations of $Rh_6(CO)_{16}$ and $CH_3Rh(CO)_x$ species not only consume the isolated gem-dicarbonyls $Rh^I(CO)_2$ but also metallic Rh-clusters. This indicates reconstruction of Rh catalyst to smaller Rh-clusters inside the zeolite. Thus, the pressure effect on syngas conversion over Rh/NaY catalyst [11] can reasonably be explained based on the present data: the fresh catalyst showing high activity but low selectivity to acetic acid at low pressure contains mainly larger Rh^0 clusters that are required for CO-dissociation and hydrogenation; at high CO pressures these clusters reconstruct to smaller metallic Rh-clusters and carbonyl clusters, in particular $Rh_6(CO)_{16}$ and $CH_3Rh(CO)_x$, possibly also some $CH_3Rh_y(CO)_x$ complexes. Since smaller Rh^0 clusters are less active for olefin hydrogenation [28], the reconstruction of Rh catalyst inside NaY results in a rapid increase of the olefin/paraffin ratios in C_2 and C_3 hydrocarbons during the first few hours of the reaction when the catalyst reconstructs to develop the selectivity for acetic acid synthesis [11].

It is likely that the mononuclear $CH_3Rh(CO)_x$ complexes are active catalyst for the CO-insertion step of the acetic acid synthesis. This seems in agreement with Chuang and Pien [28] who showed that smaller metallic Rh-clusters or even mono-atomic Rh sites are active for the CO-insertion in the hydroformylation reaction. CO-insertion into the CH_3–Rh bond of a $CH_3Rh(CO)_x$ complex leads to acetyl. If the acetyl reacts quickly with surface oxygen atoms or hydroxyl groups to form surface acetate groups and/or acetic acid, its lack of IR-visibility would be understandable [2].

In the formation of acetic acid from syngas CO dissociation is required in order to create the methyl group and this dissociation is impossible on the mononuclear Rh complexes, as it requires at least five contiguous Rh^0 atoms. The CO dissociation and formation of methyl groups must proceed over the reconstructed Rh^0clusters. This is a clarification of the cooperative mechanism proposed in our earlier paper [11]. In the same work, we found that the high selectivity to acetic acid was maintained also upon lowering the pressure; we proposed that the carbonyl clusters, responsible for this selectivity, remain intact [11]. In accordance with this general view, the present IR spectra confirm that the spectrum stabilized at 1.0 MPa syngas does not change when the pressure is released to 0.1 MPa.

The measured activation energy of overall CO conversion with Rh/NaY catalyst (23.7 kcal/mol or 100 kJ/mol) is in good agreement with the activation barrier for CO dissociation (ca. 100 kJ/mol) estimated by Bowker [2]. Theoretical calculations by Koster and van Santen [32] gave similar number for the dissociation of CO on Rh-metal surface. This value is also close to the activation energy (21–25 kcal/mol) of F-T synthesis with Cobalt and Iron catalysts [33]. Thus, the unusual selectivity of Rh/NaY catalysts does not revise the general chemistry that CO dissociation is the rate-limiting step of CO hydrogenation reaction [1,2,34]. The decrease in acetic acid at the higher temperature seems not to be caused by secondary reactions of the acetic acid. Accordingly, acetaldehyde and ethanol, which are the possible hydrogenation products of acetic acid, are not significant products even at 270°C (Table 2). Higher selectivity for acetic acid at lower temperature is determined by the lower activation energy (11.9 kcal/mol) of its formation than for CO-hydrogenation (23.7 kcal/mol).

In conclusion, neutralization of the zeolite protons with NaOH or NH_3 has little effect on the selectivity of acetic acid with Rh catalyst inside the cages of zeolite NaY. The unique catalysis of Rh/NaY for the acetic acid synthesis seems related with the stabilization of multiunclear carbonyl clusters and/or monounclear Rh-carbonyls, that coexist and cooperate with Rh^0 clusters.

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