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Rh/NaY: A Selective Catalyst for Direct Synthesis of Acetic Acid from Syngas

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Marked differences in catalytic selectivity are observed for Rh catalysts on two different supports, NaY or SiO_2, for the conversion of synthesis gas to hydrocarbons or C_2-oxygenates. High selectivity towards acetic acid is specific for the zeolite-supported catalysts; acetaldehyde is formed over Rh/SiO_2. For Rh/NaY, the selectivity varies strongly during the first hours on-stream, indicating some reconstruction of the catalyst particles while the zeolite framework remains fully intact. Also the response to changes in pressure is unique: at 1 MPa the conversion is one order of magnitude lower than at 0.1 MPa, but the selectivity for acetic acid is two orders higher at 1 MPa. However, when the pressure is lowered, the catalyst still "remembers" its high pressure activity and selectivity. Adding water vapor to the feed lowers the activity of Rh/NaY and increases the selectivity for methane and acetaldehyde. A qualitative rationalization of these findings is proposed, based on the assumption that Rh carbonyl clusters are formed in the zeolite cavities at high pressure of CO. Rh clusters, providing the metal ensembles required for CO dissociation, operate in concert with carbonyl clusters, which are instrumental for the CO insertion into metal alkyl bonds and the formation of acetate groups. © 1998 Academic Press

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, its impurities, and the additives acting as catalyst promoters (1). Rh/SiO_2 is selective for methane at low dispersion, but produces higher hydrocarbons at high dispersion (2). Of greater industrial interest is the propensity of rhodium to catalyze the formation of valuable oxygen-containing compounds, alcohols, aldehydes, and acetic acid, if the metal is in contact with an appropriate oxide (3–11). Supports and promoters, including V_2O_3, La_2O_3, CeO_2, MnO, TiO_2, ZrO_2, and ThO_2 have been used, mainly to maximize the formation of ethanol. Selectivities ranging from 20–70% have been reported (12, 13). A high selectivity for methanol was found for magnesia-supported rhodium (13). Dissociative adsorption of CO is the crucial condition for the formation of alkyl groups from syngas (14), as it requires an ensemble of five contiguous Rh atoms. Insertion of undissociated CO has unambiguously been proven by Orita *et al.* (15) to be crucial for the formation of C_{2+} oxygenates such as acetaldehyde. The catalytic versatility of rhodium thus appears to be a consequence of its position in the center of Group VIII of the periodic table: CO dissociation and insertion of undissociated CO are both possible. The distribution of higher oxygenates, therefore, follows the Schulz–Flory law (16). 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 (17–22). In some cases, it appears that the promoted system acts as a bifunctional catalyst (23, 24).

The CO insertion concept predicts that acetyl groups $C_nH_{2n+1}CO$- are formed on the catalyst surface. Fukushima *et al.* (25) observed the simultaneous formation of acetyl and acetate groups. On the basis of studies with labeled molecules, these and other authors proposed that acetyl is the common intermediate for ethanol and acetaldehyde (26–28). Naito *et al.* (29) showed that the activity of supported rhodium catalysts for higher oxygenate synthesis correlates with the intensity of the IR bands for acetate groups. Acetate ions were also proposed by other researchers as intermediates in ethanol synthesis (30–33). However, it has also been argued that acetate groups on the support surface could be mere spectators (34–36); i.e., only acetyl groups would be reactive intermediates (5, 11–13).

Single crystal work of Bowker and Li provided evidence for stable acetate groups on Rh (110) and (111) surfaces holding co-adsorbed oxygen (37, 38). Bowker argues that under syngas conversion conditions surface acetyl should be very short lived, but acetates are more plausible intermediates for oxygenate synthesis (39). Stable acetate groups are also formed on alumina-supported Rh particles when oxygen is adsorbed on their surface (40). Treviño *et al.* recently reported that acetate groups are formed on MnO

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clusters in Rh/MnNaY catalysts, but only those at the interface of Rh and MnO are swiftly reduced to ethanol (24).

In the present work, Rh inside the cavities of NaY is compared with Rh on SiO_2 and remarkably different selectivities have been observed. Acetic acid formation is strongly preferred over Rh/NaY, but acetaldehyde is a major product with Rh/SiO_2. While catalysts with high selectivity for acetic acid might be of industrial interest, the present work is directed purely towards a better understanding of the cause for this support-controlled selectivity. As metal carbonyl clusters are known to readily form in zeolite cavities under high pressure of CO (41, 42), one wonders whether Rh carbonyl complexes might be involved in the specific catalysis of syngas conversion over zeolite encaged Rh. In this paper, a systematic comparison will be presented of the performance of Rh/NaY and Rh/SiO_2 catalysts probed both at elevated and atmospheric pressures. To eliminate promoter effects by other oxides, much effort was done to minimize the concentration of impurities. As water is a reaction product and the heat of adsorption of water is higher on zeolites than on amorphous supports, a special study of the effect of water on the selectivity has also been included in this work.

2. EXPERIMENTAL

2.1. Catalyst Preparation and Pretreatment

Rh/NaY catalysts were prepared by ion exchange by dropwise addition of a $2 \times 10^{-3} M$ solution of $[Rh(NH_3)_5Cl]Cl_2$ to a 5-g/L slurry of NaY zeolite in doubly deionized water. Stirring of the slurry was continued for another 70–80 h in order to obtain a homogeneous distribution of the Rh over the zeolite supercages (43). Four NaY samples with almost equal composition, $[Na_{56}(AlO_2)_{56}(SiO_2)_{136} \cdot nH_2O]$, were used; they were kindly provided by UOP. These are assigned LZY-54 (Lot No. 10027–45) and LZY-52 (Lot Nos. 5155–59; 968084061002-5; 968087061020-5–8). They were calcined in an air flow at 500°C for 3 h before use; they will further be called NaY-A, -B, -C, and -D. In some preparations, NaY-A was cleaned twice by ion exchange with a 12 *M* $NaNO_3$ solution at ca 60°C for 12 h; the number of Na^+ ions in this $NaNO_3$ solution exceeded that of the Al atoms in the zeolite 12–15 times. Such specially cleaned NaY-A is further called NaY-WA. $[Rh(NH_3)_5Cl]Cl_2$ (Fluka, Lot No. 01322JG) and $NaNO_3$ (Lot No. 07016MN) were used as purchased. Usually, 3–5 g NaY was used for the exchange with the $[Rh(NH_3)_5Cl]Cl_2$ solution (~0.002 *M*). After ion exchange, the samples were separated by filtration and thoroughly washed with doubly deionized water (300 ml/g; 2 times) to remove the Cl^- ions. All samples were calcined in O_2, reduced in H_2, and exchanged again with NaOH to neutralize the protons formed during the reduction of the rhodium ions. The rhodium loading was 2.8–3.0 wt% for all Rh/NaY samples. Elemental analysis confirmed the absence of chlorine in all reduced catalysts.

Calcination of the Rh loaded samples was carried out in flowing O_2 (UHP, Linde) with a flow rate of ≥700 mL/(min · g), while the temperature was ramped at 0.5 K/min to 500°C, then held at this temperature for 2 h. At this temperature, O_2 was then replaced by Ar (UHP, Linde; 120 ml/min). After holding under flowing Ar at 500°C for 20 min, the samples were cooled to room temperature. The gas flow was then switched from Ar to H_2 (UHP, Linde; 40 ml/min) and the catalyst was reduced up to 450°C with a temperature ramp of 8 K/min. The H_2 and Ar were purified by passing them over MnO/SiO_2 and a 4A molecular sieve.

The Rh dispersion, measured by H_2-TPD after the TPR treatment, was 0.91 which corresponds to a particle size of 11 Å in agreement with our previous TEM observations.

The protons formed during the reduction of rhodium ions were neutralized by slurrying the reduced samples overnight in a NaOH solution of $pH = 11$. The neutralized samples were filtered, washed, and dried in an air flow. Recalcination of the neutralized samples was carried out at 500°C in O_2 (120 ml/min) with a temperature ramp of 8 K/min.

Three percent Rh/SiO_2 catalysts were prepared by wet impregnation. The support was a kieselgel 60 (Fluka, Silica gel 60; EEC No. 2315454; 550 m^2/g) with a particle size of 0.063–0.2 mm (70–230 mesh ASTM). The vendor claimed that the iron impurity was below 20 ppm. The rhodium source was $RhCl_3 \cdot xH_2O$ (Johnson/Matthey). One Rh/SiO_2 sample was prepared with SiO_2 as purchased. Another sample, Rh/SiO_2-L, was prepared after leaching the support with a concentrated HCl solution to remove traces of iron. This procedure was previously used by Nonneman *et al.* (1). Leaching was done with 11 *M* HCl (Fisher Chemicals, Lot No. 945578; Fe impurity <0.05 ppm) in several stages; first, the 11 *M* HCl (50 ml/g-SiO_2) was used at room temperature for one week. In the following stages, the temperature was 100°C and the HCl was renewed twice after 12 h. The leached support was washed with doubly deionized water, first at 100°C, then at 20°C. Vessels of polypropylene were used to avoid contamination from glassware. The Rh/SiO_2 samples were reduced at 300°C in flowing H_2 (40 ml/min). The Rh dispersion in Rh/SiO_2 is $H/Rh = 0.45$.

2.2. CO Hydrogenation

The catalysts were tested in a stainless steel fixed-bed flow reactor manufactured by Xytel Corp. with automatic control of temperature, pressure, and feed flow rate. All gases were of ultrahigh purity grade. To prevent any intervention in the reaction of iron carbonyl, which could be formed in the steel cylinders conventionally used for syngas, we purchased the syngas ($CO/H_2 = 1$) in an aluminum cylinder. In addition, two Al_2O_3 traps were used to ensure complete removal of any carbonyl that might have formed in the ducts. One trap was placed next to a charcoal trap, which adsorbs hydrocarbon impurities, the other was located just prior to the reactor inlet. A 300-mg calcined catalyst sample was loaded into the reactor for each run. Reduction of the catalyst was always done *in situ*. After pressurizing the reactor under H_2, the catalyst was reduced from room temperature to 400°C in a H_2 flow (ca 80 ml/min) with a ramp of ca 4 K/min. Reduction of the catalyst was continued for 1 h at 400°C, followed by lowering the temperature to 250°C. At this temperature, the gas flow was switched from H_2 to syngas to start the reaction. Unless otherwise stated, a total pressure of 1 MPa, a CO/H_2 ratio of 1, and a space velocity of 15000 h^{-1}, were used as standard reaction conditions.

Product analysis was done using an HP 5890 gas chromatograph with a 50 m capillary column filled with cross-linked methyl silicone, and a FID detector. During analysis, the column temperature was programmed from −60 to 112°C in three steps. Catalyst activity was expressed in terms of CO conversion to organic products (i.e., excluding carbon dioxide and water). The selectivity to each product was given based on carbon efficiency; i.e., the selectivity to a product X is defined as 100 times the number of moles of carbon in product X divided by the total number of moles of carbon in all products other than CO_2.

3. RESULTS

3.1. Rh/NaY Catalysts

3.1.1. Rh/NaY Prepared with Commercial NaY

It has always been found in the present work that over Rh/NaY with $CO/H_2 = 1$, methane is initially, i.e., at reaction times <20 min, produced with a selectivity >95% (on a carbon basis). The methane selectivity decreases rapidly within the first 60 min. Figure 1 shows the activity of Rh/NaY-A catalyst for the reaction, as well as the overall product selectivity in relation to the time on-stream (TOS). Data at TOS > 1050 min are obtained after switching the feed from $CO/H_2 = 1.0$ to $CO/H_2 = 3.0$, continuing the reaction for 250 min, then switching back to $CO/H_2 = 1.0$. In the first 4–5 h, the catalyst favors the production of methane and other hydrocarbons; the selectivity for oxygenates with two and more carbon atoms (C_{2+} oxygenates) remains below 10%. After that period, the selectivity for the C_{2+} oxygenates increases rapidly at the expense of hydrocarbon products, stabilizing at 57–60% in another 2 h. Methanol is the only detectable C_1 oxygenate, never exceeding 0.5% in the products. Since the focus of the present work is on C_{2+} oxygenates, Fig. 2 shows the selectivities of all oxygenates

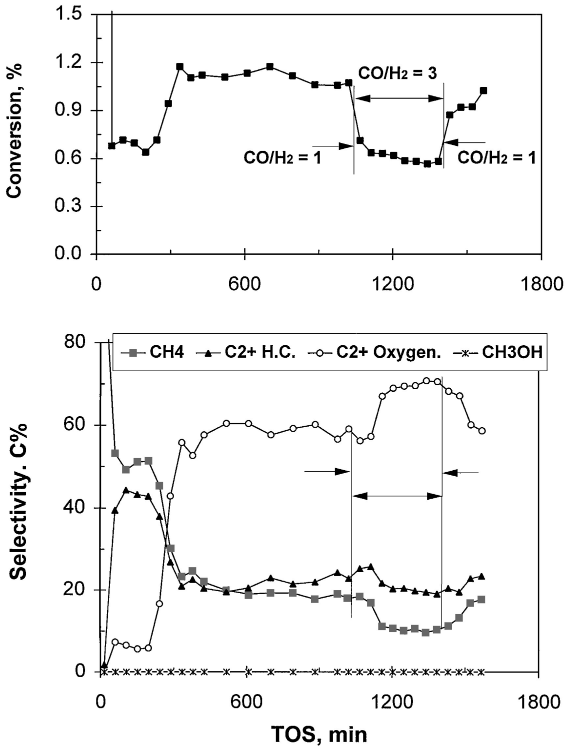

FIG. 1. Activity and selectivity of Rh/NaY-A catalyst. Note that the CO/H_2 ratio is switched between 1.0 and 3.0 during the reaction.

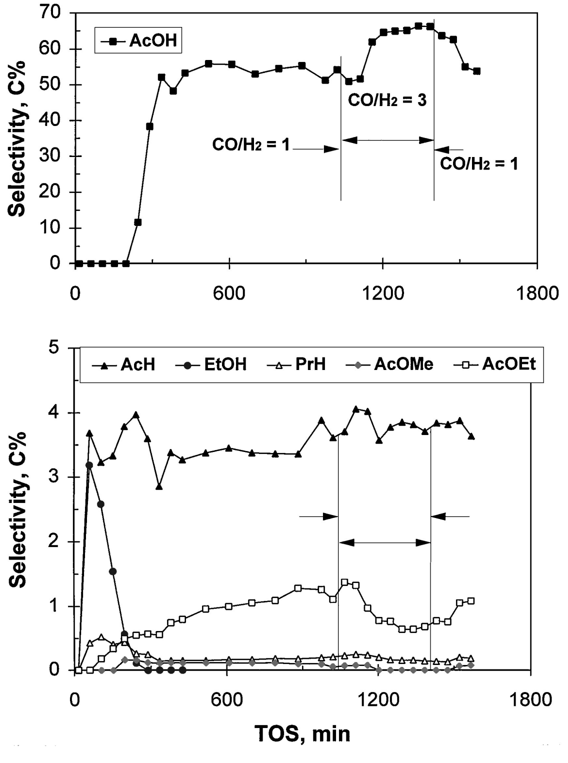

FIG. 2. Selectivity for oxygenates over Rh/NaY-A catalyst. Note that the CO/H_2 ratio is switched between 1.0 and 3.0 during the reaction.

TABLE 1

Normalized Composition of the C_{2+} Oxygenate Products over Rh/NaY-A Catalyst

TOS, min	60	243	334	700	1203	1475
Composition, C%						
AcH	50.49	23.82	5.12	5.85	5.17	5.66
EtOH	43.63	0.68	0	0	0	0
PrH	5.88	1.58	0.26	0.29	0.29	0.20
AcOMe	0	0.98	0.20	0.20	0	0
AcOEt	0	3.28	1.00	1.83	1.12	1.09
AcOH	0	69.66	93.42	91.83	93.42	93.05

including acetaldehyde (AcH), ethanol (EtOH), acetic acid (AcOH), methyl acetate (AcOMe), ethyl acetate (AcOEt), and propionaldehyde (PrH). Apparently, AcOH is the predominant product in the steady state of the reaction, constituting up to 93% of the total C_{2+} oxygenates (Table 1). Interestingly, EtOH, the main oxygenate component over promoted Rh catalysts, appears only as a very minor product (<3%) during the first few hours and is completely absent in the steady state (Figs. 2 and 3). The second significant oxygenate is AcH, which increases with TOS and reaches its steady state selectivity (ca 3–5%) in 2–3 h. AcOEt, apparently a secondary product of AcOH and EtOH, continues to increase with TOS. Only minute amounts of AcOMe and PrH are detected. At the conditions chosen here, the conversion remains in the range of 1.1–1.6% corresponding to a CO turnover frequency of $2 * 10^{-3}$–$3 * 10^{-3}$ s^{-1} (based on the Rh dispersion of the fresh catalyst).

While the selectivity for hydrocarbons decreases at longer TOS, the olefin/paraffin ratio increases steeply during the first 3–4 h and more slowly afterwards, as shown for the C_3 and C_2 hydrocarbons in Fig. 3. The same trend is observed for the *iso/normal* ratios of butane and pentane. Among the C_6 paraffin products, the ratio of the methylpentanes (2MP and 3MP) to *n*-hexane also increases with TOS (not shown in Fig. 3) The 2MP/3MP ratio remains near the equilibrium value of 2.

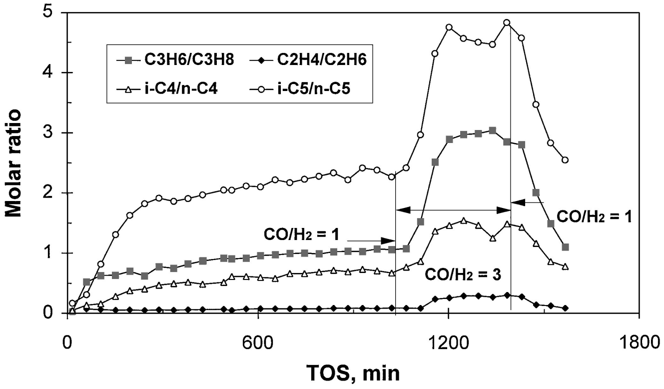

FIG. 3. Changes of olefin to paraffin and iso to normal ratios of selected hydrocarbons over Rh/NaY-A catalyst.

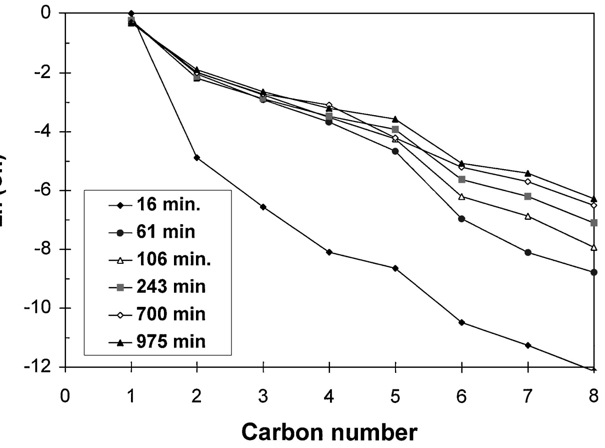

FIG. 4. Change of the Schulz–Flory plot of hydrocarbons over Rh/NaY-A catalyst.

The Schulz–Flory plots for the hydrocarbons are shown int Fig. 4 for different reaction times. At short TOS there is a large overshoot of methane, but at longer TOS, the plots approach linearity. The experimental error is relatively high with on-line analysis for the very low conversions used here. It appears that the slope of the Schulz–Flory plots decreases with TOS, indicating that the chain growth probability for the hydrocarbons increases during the first 3–4 h.

The significant selectivities for oxygenates found in the present work are at variance with previous data reported in this journal by Treviño *et al.*, which were obtained with the same reactor system; only negligible oxygenate formation was reported in that work for unpromoted catalysts (44). It is unclear whether this discrepancy is caused by the different zeolite batches used or by calibration errors in the earlier work that focused on manganese promoted catalysts. To test the effect of different zeolite histories, four Rh/NaY catalysts were prepared in the present work by the same procedure from four different NaY batches from the same vendor (UOP). Table 2 shows the results of the catalytic tests. Very similar conversions and selectivities were found for these catalysts. After 13 h on-stream the conversion at 250°C is between 1.1 and 1.6% and the TOF between 2 and $3 \cdot 10^{-3}$ s^{-1}. The selectivity to acetic acid, the main oxygenate product, is between 45 and 55%. It is, therefore, unlikely that different zeolite history is the cause of the discrepancy of the measured selectivities. The catalytic signature of Rh/NaY catalysts differs, however, quite significantly from that of Rh/SiO_2 tested under identical conditions. Note that the ratio acetic acid/acetaldehyde is consistently high over Rh/NaY, but one order of magnitude lower over Rh/SiO_2. Also, the proportionality between C_3 hydrocarbons and AcH reported by Burch *et al.* for Rh/SiO_2 (21) does not exist for Rh/NaY.

TABLE 2

Activity and Product Selectivity of Rh/NaY and Rh/SiO_2 Catalysts

Catalyst	Rh/NaY-A	Rh/NaY-B	Rh/NaY-C	Rh/NaY-D	Rh/NaY-WA	Rh/SiO_2	Rh/SiO_2-L[a]
Conv., %	1.12	1.15	1.15	1.64	1.49	1.48	2.40
TOF, 10^{-3} s^{-1}	2.5	2.6	2.6	3.7	3.3	6.7	10.8
Selectivity, C%							
CH_4	19.28	20.71	19.18	21.13	20.13	45.08	41.93
C_2	7.41	8.42	7.93	9.26	8.43	2.02	2.42
C_3	5.39	6.19	6.31	6.39	5.89	5.78	8.23
C_{4+}	8.71	9.93	10.43	11.92	10.32	4.81	10.05
EtOH	0.00	0.00	0.00	0.00	0.00	3.71	0.01
AcH	3.36	4.76	3.53	4.16	3.81	20.59	20.76
AcOH	54.45	46.87	50.37	43.28	49.11	15.02	15.19
Other oxyg.	1.41	3.12	2.26	3.85	2.68	2.99	1.42
C_2H_4/C_2H_6	0.08	0.09	0.10	0.07	0.06	0.08	0.04
C_3H_6/C_3H_8	0.94	0.93	1.14	0.76	0.88	1.47	1.21
Iso-/n-C_4H_{10}	0.73 (1.09)[b]	0.55	0.82	0.53	0.63	~0	0.02
Iso-/n-C_5H_{12}	2.38 (3.34)	1.86	2.44	1.73	2.11	0.08	0.05
2MP/n-C_6H_{14}	2.88 (2.07)	2.68	3.29	3.09	3.00	~0	0.12
3MP/n-C_6H_{12}	1.36 (0.99)	1.15	1.40	1.61	1.51	~0	0.15
2MP/3MP	2.12 (2.08)	2.34	2.35	1.92	1.99		0.79

Note. Reaction conditions: $CO/H_2 = 1$; $T = 250°C$; $P = 1.0$ MPa; $GHSV = 15000\ h^{-1}$; TOS = 13 h.

[a] Impurities have been leached with 11 *M* HCl at 100°C from this silica support.

[b] Values in parentheses are calculated based on thermodynamic equilibrium.

TABLE 3

Effect of Syngas ($CO/H_2 = 1$) Pressure on the Activity and Selectivity of Rh/NaY Catalyst at 250°C under Steady Reaction State

Catalyst	Rh/NaY-A			Rh/NaY-WA
Pressure, MPa	0.10[a]	1.0[b]	0.1[c]	0.1[d]
Conv., %	31.48	1.49	1.09	1.71
Selectivity, C%				
CH_4	95.50	20.43	26.26	28.59
C_2	2.98	7.05	12.25	12.30
C_3	1.75	5.58	8.25	7.46
C_{4+}	1.10	8.54	9.65	11.21
EtOH	<0.01	0	0	0.00
AcH	0.07	4.94	6.1	4.59
AcOH	0.58	50.55	35.83	34.02
Other oxyg.	0.01	2.91	1.66	1.84
C_2H_4/C_2H_6	0	0.09	0.16	0.14
C_3H_6/C_3H_8	0.28	1.31	1.59	1.21
Iso-/n-C_4H_{10}	0.07	0.58	0.74	0.52
Iso-/n-C_5H_{12}	0.35	2.07	2.33	1.58
2MP/n-C_6H_{14}	0.52	2.74	3.19	2.27
3MP/n-C_6H_{12}	0.32	1.37	1.42	1.03
2MP/3MP	1.625	2.00	2.25	2.20

[a] The reaction began with 0.1 MPa syngas pressure (see Fig. 10).

[b] This reaction at 1.0 MPa was preceded by a 12 h reaction at 0.1 MPa (see Fig. 14).

[c] 7 h at 0.1 MPa after b.

[d] Before this reaction at 0.1 MPa, the catalyst was exposed to a reaction mixture at 1.0 MPa for 20 min.

3.1.2. *Effect of Impurities in Rh/NaY*

Work by Nonneman *et al.* (1) illustrates a significant effect of impurities in SiO_2 for the production of oxygenates from syngas over Rh catalysts deposited on this support. Therefore, much effort was done in the present work to minimize impurities in our supports. Exchangeable cations other than Na^+ were removed from the zeolites by extended ion exchange with an aqueous solution containing a large excess of $NaNO_3$. Catalysts prepared from NaY-A pretreated in this way will be denoted as Rh/NaY-WA, while Rh/NaY-A stands for catalysts prepared with untreated NaY, i.e. LZY-5 (Lot No. 10027-45). Another sample, Rh/NaY-D, was prepared from the $NaNO_3$ treated LZY-52 (Lot No. 968087061020-5-8). The catalytic test results are summarized in Table 2 and Figs. 5–8. They show that this secondary exchange procedure has only a minor effect on the catalytic signature.

Ion exchange does not remove impurities from the zeolite framework. It is conceivable that Fe, a rather ubiquitous impurity of zeolites, acts as a catalyst promoter. As ESR is an extremely sensitive technique for detecting Fe, we measured the ESR spectrum of NaY before and after the treatment with excess $NaNO_3$ (Fig. 9). Two ESR signals are observed before the treatment, which confirms the existence of an Fe(III) impurity in the zeolite framework ($g = 4.3$) and in the cationic positions ($g = 2.0$). After twofold ion exchange with the $NaNO_3$ solution the signal of the nonframework Fe ions has disappeared, while that of the framework Fe remains unchanged (Fig. 9b). Analysis

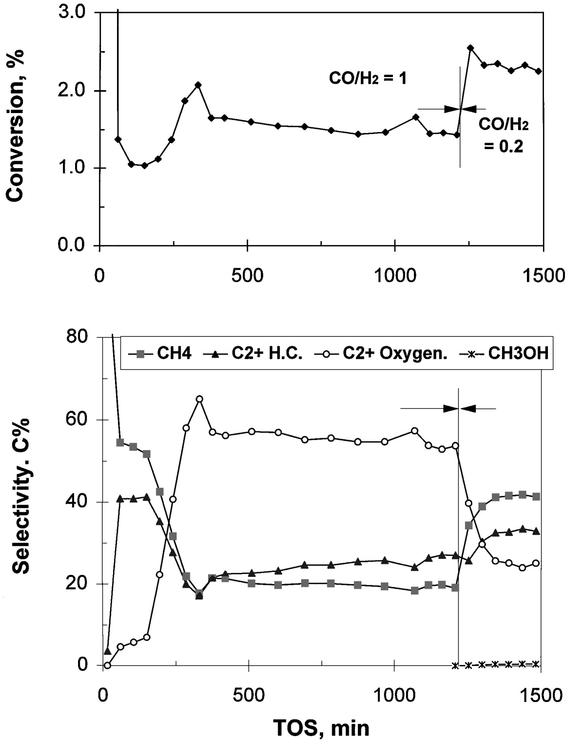

FIG. 5. Activity and selectivity of Rh/NaY-A catalyst. Note that the CO/H_2 ratio is switched from 1.0 to 0.2 after 12 h.

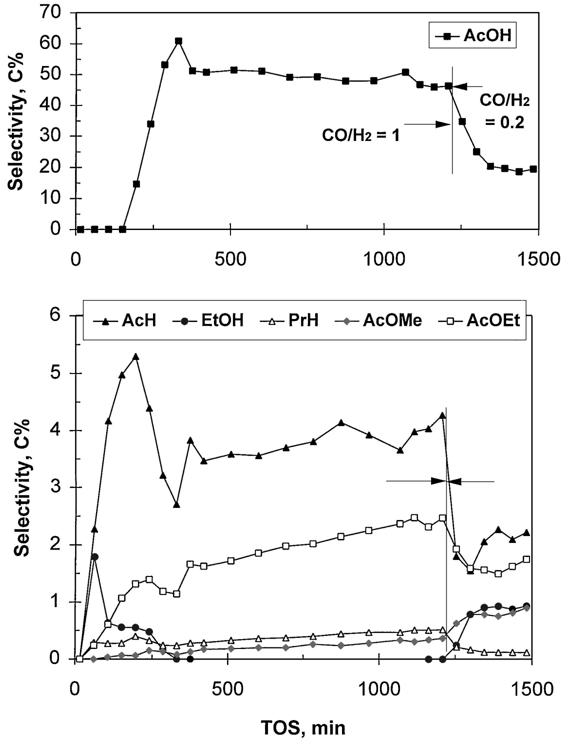

FIG. 6. Selectivity for oxygenates over Rh/NaY-WA catalyst. Note that the CO/H_2 ratio is switched from 1.0 to 0.2 after 12 h.

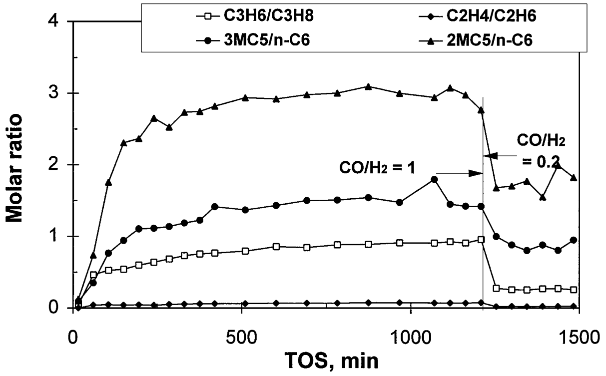

FIG. 7. Changes of olefin to paraffin and iso to normal ratios of selected hydrocarbons over Rh/NaY-WA catalyst.

by Galbraith Laboratories (Knoxville, TN) revealed that the Fe content of the washed sample (NaY-WA) is below 80 ppm. Combining this with the ESR signal intensities in Fig. 9, gives, as a rough estimate, a value of below 10 ppm for the nonframework Fe impurity of the original sample. The fact that removal of that Fe has little effect on the catalytic performance of Rh/NaY, suggests that the effect of any nonframework impurity is quite small.

3.1.3. *Effect of Syngas Pressure*

Figure 10 shows the very strong effect of the syngas pressure at constant composition ($CO/H_2 = 1$) and temperature for Rh/NaY. The catalyst was initially tested at atmospheric pressure (0.1 MPa) for 12 h, during which time the CO conversion was above 30%. Hydrocarbons were the dominant products with a very high selectivity for methane (>93%). Oxygenates (AcH and AcOH) were present only in trace amounts (<0.5%). Upon increasing the pressure to 1.0 MPa, the conversion drops from 31% to 1.3% and the reaction pattern changes dramatically, becoming similar to that of Figs. 1 and 2 for the same syngas composition. The

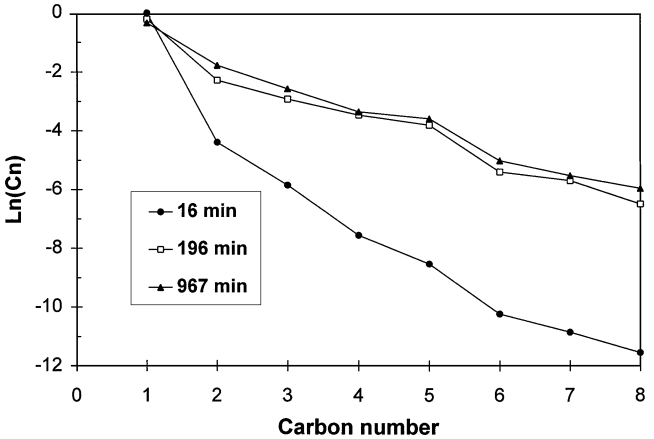

FIG. 8. Change of the Schulz–Flory plot of hydrocarbons over Rh/NaY-WA catalyst.

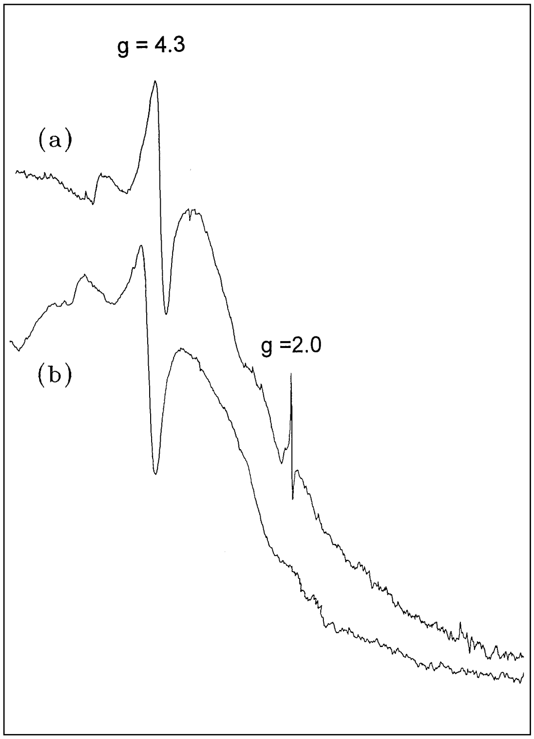

FIG. 9. ESR spectra of NaY-A (a) and its washed partner NaY-WA (b).

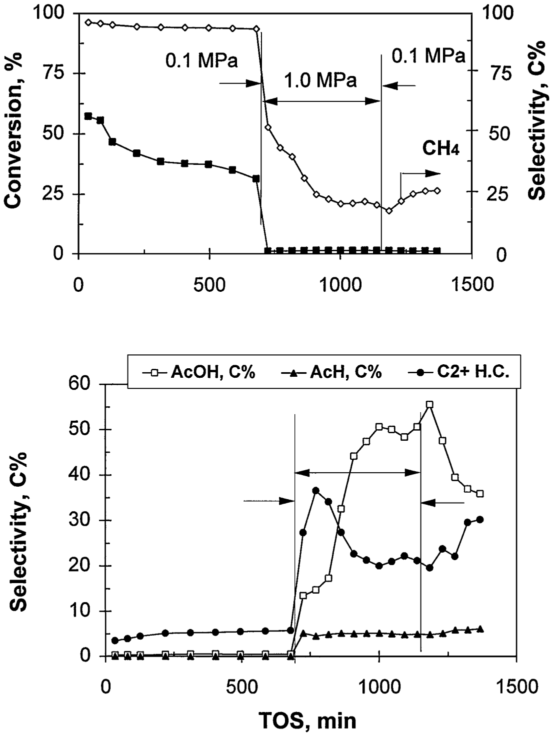

FIG. 10. Response of Rh/NaY-A catalyst to the syngas pressure. Note that the reaction at high pressure (1.0 MPa) changes both the catalyst activity and product selectivity.

selectivity to methane drops steeply, while the selectivity for acetic acid increases strongly, reaching a stable value of 50% in about 4 h. The selectivity for acetaldehyde reaches its ceiling of ca 5% in less than 1 h.

These changes are found to largely persist upon lowering the syngas pressure back to 0.1 MPa. The conversion remains low, as the selectivity to acetaldehyde does not return to its original low level, but the selectivity for acetic acid decreases from 51% to 36%.

To explore these irreversible effects further, a Rh/NaY-WA catalyst was initially exposed to reacting syngas at 1.0 MPa for only 20 min; then the pressure was lowered to 0.1 MPa and the reaction continued at 0.1 MPa for 12 h. The results are compared in Table 3 for this test and the one to which Fig. 10 refers. It is clear that even a rather brief exposure to syngas at 1.0 MPa lowers the conversion but induces a high selectivity towards acetic acid, e.g. 35% at 0.1 MPa under steady reaction. Temporary exposure to 1.0 MPa also affects the *olefin/paraffin* and *iso/normal* ratios at 0.1 MPa.

3.1.4. *Effect of CO/H_2 Ratio*

The CO/H_2 ratio has a pronounced effect on the product selectivity over Rh/NaY. This was examined with Rh/NaY-WA and Rh/NaY-A at 1.0 MPa by varying the CO/H_2 ratio between 0.2 and 3.0 (Table 4, and Figs. 1, 2, 5, and 6). The results indicate that a CO-rich syngas (CO/H_2 = 3) leads to a lower conversion but a higher selectivity for acetic acid,

TABLE 4

Effect of CO/H_2 Ratio on the Activity and Selectivity of Rh/NaY Catalysts

Catalyst	Rh/NaY-WA			Rh/NaY-A	
Pressure, MPa	1.0	1.0	1.0	1.0	1.0
CO/H_2	0.2	1.0	3.0	1.0	3.0
Conv., %	2.25	1.49	0.70	1.12	0.59
Selectivity, C%					
CH_4	41.38	20.13	10.96	19.48	10.41
C_2	18.03	8.43	4.36	7.41	5.45
C_3	6.93	5.89	4.75	5.39	5.23
C_{4+}	8.02	10.32	7.98	8.71	9.79
EtOH	0.83	0.00	0.00	0.00	0.00
AcH	2.22	3.81	3.26	3.76	3.37
AcOH	19.33	49.11	67.82	54.45	64.82
Other oxyg.	3.26	2.68	0.88	1.61	0.93
C_2H_4/C_2H_6	0.03	0.06	0.25	0.08	0.29
C_3H_6/C_3H_8	0.26	0.88	2.48	0.94	2.97
Iso-/n-C_4H_{10}	0.65	0.63	1.30	0.73	1.55
Iso-/n-C_5H_{12}	1.42	2.11	3.91	2.38	4.56
2MP/n-C_6H_{14}	1.83	3.00	5.29	2.88	4.68
3MP/n-C_6H_{12}	0.95	1.51	2.60	1.36	2.27
2MP/3MP	1.92	1.99	2.03	2.12	2.06

Note. Reaction conditions: $T = 250°C$; TOS = 13 h.

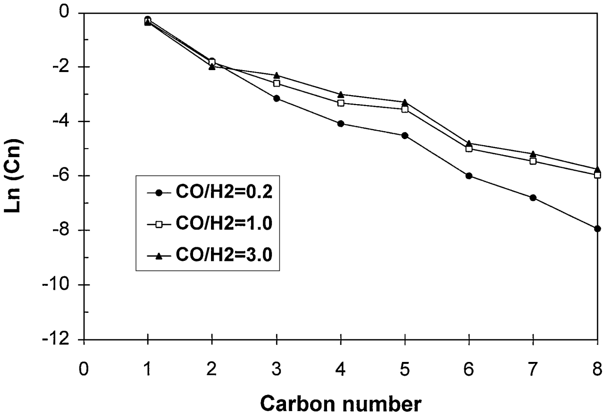

FIG. 11. Effect of CO/H_2 ratio on the Schulz–Flory plot of hydrocarbons over Rh/NaY-WA catalyst.

which reaches a value of 67% for CO/$H_2 = 3.0$. Conversely, a hydrogen-rich syngas (CO/$H_2 = 0.2$) displays higher conversion but produces mainly hydrocarbons. Clearly, the reaction order of the overall rate is negative in CO, but positive in H_2. The yield ($=$ conv $*$ sel) for acetic acid at this pressure is highest for the syngas with CO/H_2 ratio $= 1.0$. Again, data obtained over Rh/NaY-WA and Rh/NaY-A are indistinguishable.

In contrast to the change in the overall pressure, the effects of changing the syngas *composition* at a given pressure are reversible over Rh/NaY-A (see Figs. 1–3) at 1.0 MPa. The same holds for Rh/NaY-WA and the other Rh/NaY batches. Neither EtOH nor MeOH is formed under steady state conditions when the CO/H_2 ratio is ≥ 1.0 (Figs. 1, 2, 5, and 6). At a CO/H_2 ratio $= 0.2$, both EtOH and MeOH become detectable, with EtOH being larger.

As always observed in Fischer–Tropsch catalysis, a higher H_2/CO ratio lowers the *olefin/paraffin* ratio and gives a steeper Schulz–Flory plot, because H_2 is instrumental in chain termination and olefin hydrogenation. Figure 11 confirms that this general relation also holds for the present zeolite supported catalysts.

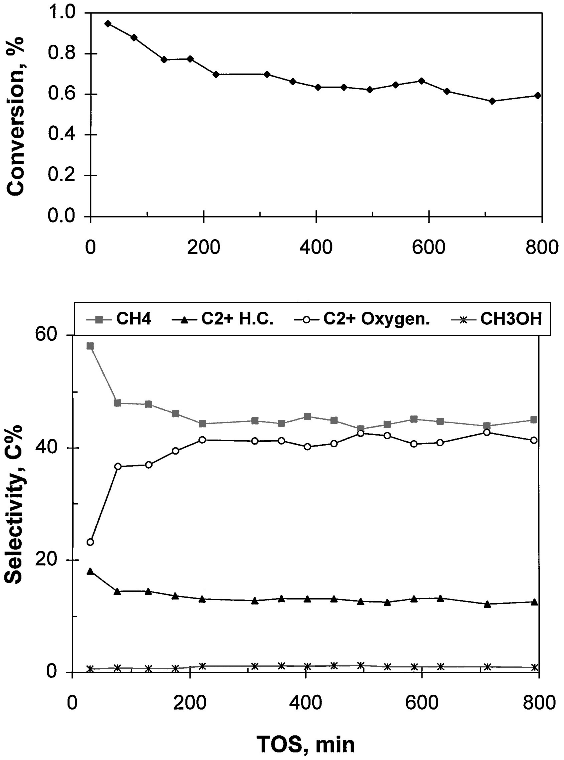

FIG. 12. Activity and selectivity of Rh/SiO_2 catalyst.

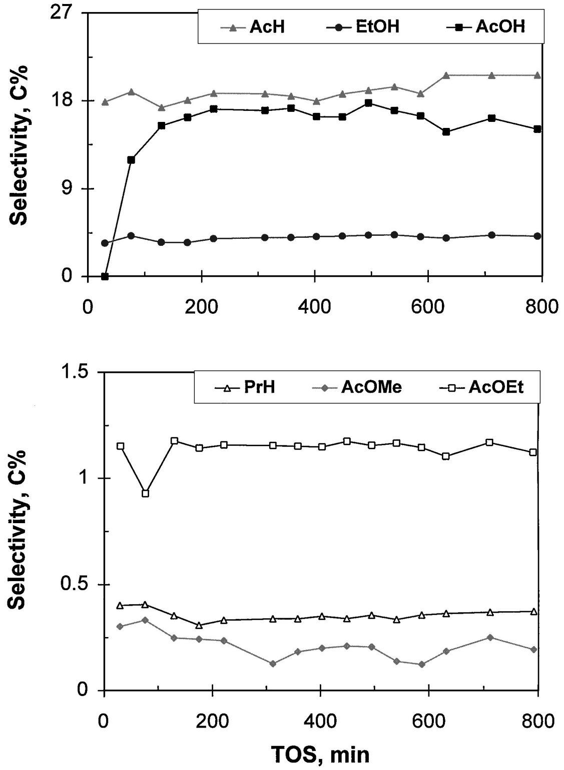

FIG. 13. Selectivity for oxygenates over Rh/SiO_2 catalyst.

3.2. Rh/SiO_2 Catalysts

Figures 12 and 13 show the activity and selectivities over a Rh/SiO_2 catalyst prepared from commercial silica. While the conversion is comparable to that over Rh/NaY, the selectivity for methane (>45%) is much higher, and that for oxygenates much lower, than those observed over Rh/NaY (Figs. 1 and 2). Among the oxygenates, the selectivity for the aldehydes is higher than over Rh/NaY but that for acetic acid is distinctly lower. The steady state for acetic acid is reached in 1–2 h, while it takes 4–5 h over the Rh/NaY. Over Rh/NaY, the formation of AcOH is accompanied by a simultaneous increase in CO conversion; no such parallelism is apparent over Rh/SiO_2. Also noticeable is

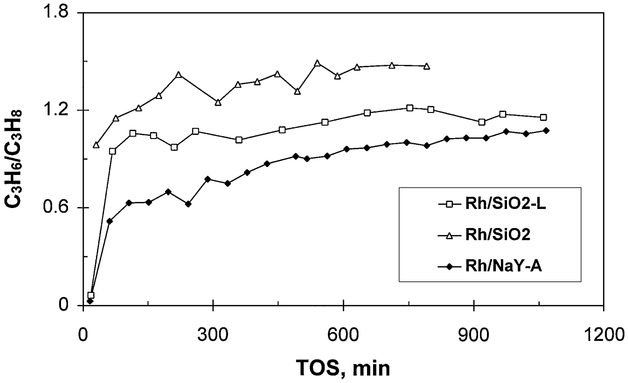

FIG. 14. Change of propene/propane ratio over Rh/SiO_2 and Rh/SiO_2-L catalysts.

the formation of 4–5% EtOH over Rh/SiO_2 (Fig. 13 and Table 2).

Leaching of the impurities from SiO_2 with an 11 *M* HCl solution, prior to the impregnation of rhodium, leads to the Rh/SiO_2-L catalyst. Conversion and selectivity over this catalyst are similar to those of Rh/SiO_2, except that no EtOH is formed over Rh/SiO_2-L (Table 2).

Under high pressure, both Rh/SiO_2 catalysts favor the formation of acetaldehyde, in agreement with earlier studies of Nonnemann *et al.* (1) and Burch and Petch (21). The absence of EtOH over Rh/SiO_2-L confirms the claim that EtOH formation is promoted by impurities in the silica (1). This is further supported by our observation that the reduction of Rh/SiO_2 at very high temperature (800°C) increases the formation of EtOH, indicating that a larger fraction of the impurities is reduced to their promoting state. As Nonnemann *et al.* worked at atmospheric pressure, they did not observe the formation of acetic acid demonstrated in the present study.

The *olefin/paraffin* ratio is found to be higher over Rh/SiO_2 than over Rh/NaY, while this ratio increases with TOS over both catalysts, as shown in Fig. 14 for the C_3 components. The *iso/normal* ratio of the C_4 - C_6 paraffins is much higher over Rh/NaY (Table 2). The Schulz–Flory plots, shown in Fig. 15 for Rh/SiO_2, do not change appreciably with reaction time.

3.3. Effect of Water Vapor Addition on Syngas Reaction

Figures 16 and 17 show the results over Rh/NaY-A and Rh/SiO_2-L caused by adding water vapor at 1.0 MPa. In these runs, H_2O was released at 150°C from a molecular sieve 4A previously loaded with water (45). This sieve was located inside a copper tube. After a reaction time of 12 h, the syngas flow was directed over this sieve. The pressure of the water vapor was controlled by heating down line of the copper tube to 84–87°C, thus increasing the H_2O vapor pressure in the feed to about 5% at 1.0 MPa.

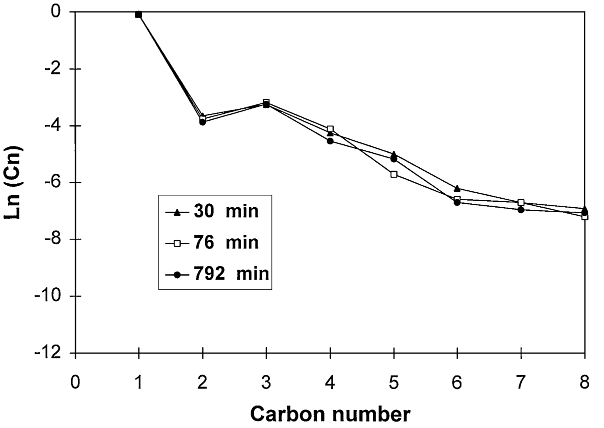

FIG. 15. Change of the Schulz–Flory plot of hydrocarbons over Rh/SiO_2 catalyst.

Water vapor addition induces a sharp drop in CO conversion over the Rh/NaY-A catalyst (Fig. 16). This is followed by a slower decrease. In contrast, the conversion over Rh/SiO_2-L decreases only slowly upon H_2O vapor addition (Fig. 17). The product selectivity is affected by the water vapor over both catalysts. Formation of AcOH is reduced five to sixfold over Rh/NaY-A, while it is totally eliminated over Rh/SiO_2-L.

The addition of H_2O vapor increases the selectivity for acetaldehyde and methane. This effect is more pronounced

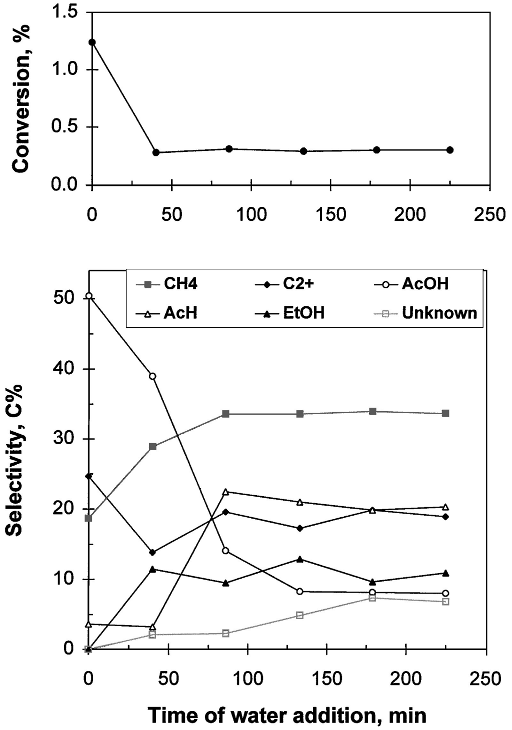

FIG. 16. Effect of water vapor addition on the syngas reaction over Rh/NaY-A catalyst.

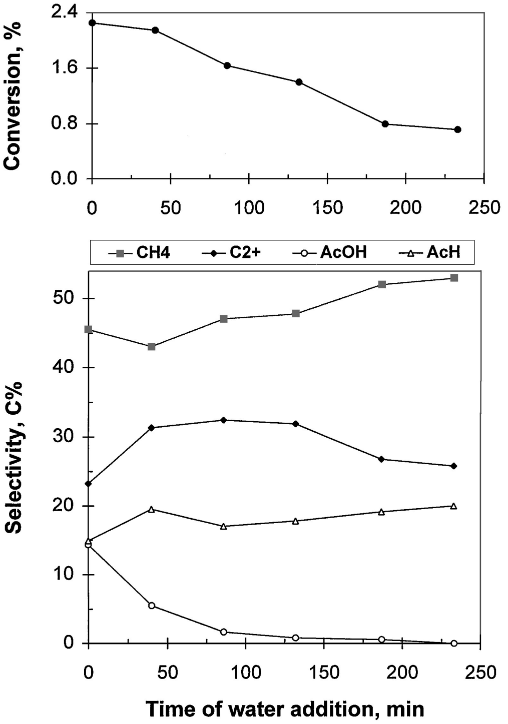

FIG. 17. Effect of water vapor addition on the syngas reaction over Rh/SiO_2-L catalyst.

over Rh/Na-A, where the AcH selectivity increases more than fivefold, than over Rh/SiO_2-L, where it increases by only 40%. Another significant difference is that the selectivity for ethanol increases from zero to ∼10% over Rh/NaY-A, but no ethanol is detected over Rh/SiO_2. In addition, new peaks with longer GC retention time appear in the effluent from Rh/NaY-A. Apparently, these unknown products are oxygenates but are different from the C_3 and C_4 alcohols and aldehydes for which the column was calibrated.

The effects caused by water vapor addition are not reversible when the feed is replaced by dry syngas. However, upon heating the catalysts to 400°C and reducing it for 30 min, the original activity and selectivity, found prior to exposure to the wet feed, are restored.

4. DISCUSSION

This study seems to be the first one where the catalytic performance in syngas conversion is systematically compared for zeolite supported and SiO_2 supported Rh, in the absence of an added promoter. To our knowledge, there is also no prior literature on the effect on syngas catalysis of varying the water pressure. The following points are of particular interest:

(1) Considerable amounts of oxygenates are formed in the absence of promoters, in particular at elevated pressure. A previous statement indicating the absence of oxygenates in the product over Rh/NaY (44) can no longer be maintained.

(2) The reaction order is positive in hydrogen and negative in CO.

(3) The slope of the Schulz–Flory curves is steeper and the olefin/paraffin ratio lower, at lower CO/H_2 ratios.

(4) The apparent activity and selectivities over Rh/NaY change strongly within the first hours on stream.

(5) Under identical conditions, the selectivity and the yield for acetic acid are significantly higher over Rh/NaY than over Rh/SiO_2, but more acetaldehyde is produced over Rh/SiO_2.

(6) Within the group of alkanes, the ratio of branched to linear molecules is significantly higher in the product over Rh/NaY than over Rh/SiO_2.

(7) Over Rh/NaY, the conversion is lower by more than an order of magnitude at 1 MPa, than at 0.1 MPa, but the selectivity for acetic acid is two orders higher at 1 MPa than at 0.1 MPa.

(8) Even temporary use at high pressure changes the catalytic activity and selectivity at low pressure towards the values that are characteristic for operation at high pressure.

(9) Water vapor in the feed strongly decreases the conversion over Rh/NaY and, simultaneously, the selectivities to methane and acetaldehyde increase.

The above points, (2) and (3), and the selectivity to acetic acid are considered normal for Fischer–Tropsch catalysts and shall not be discussed further. A brief discussion of the other points is given below.

Point (4) may, in part, be an artefact caused by the adsorption of products on the support. Such a chromatographic effect has been reported earlier by Kip *et al.* for Rh/Al_2O_3 who found the adsorption of acetic acid on the alumina (18). Copying their method, we have studied the effect of an NaY (300 mg) bed, downstream of the Rh/NaY-B catalyst, on the appearance of acetic acid. We found that this delayed the time for AcOH detection from 200 min to 340 min (Fig. 18). This indicates that the product pattern at low conversion is

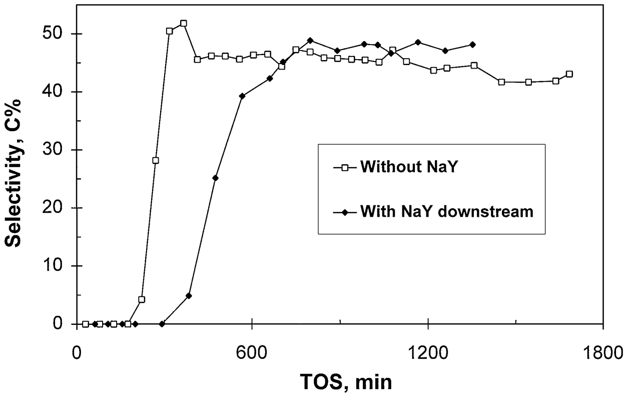

FIG. 18. Formation of acetic acid in the presence of a NaY bed downstream of the Rh/NaY-B catalyst.

indeed affected by the chromatographic effect for low times on-stream.

The most exciting finding of this study is remarkably high selectivity of Rh/NaY for acetic acid at 1.0 MPa. With an equimolar CO/H_2 feed a selectivity of 45–55% has been observed and with $CO/H_2 = 3.0$, the selectivity to acetic acid even reaches a value of 65–68%. These values are higher than those reported by Nakajo *et al.* for a multiply promoted catalyst Rh-Mn-Ir-Li/SiO_2 at 10 MPa and $CO/H_2 = 9$ (46). As the selectivity is virtually the same for the catalyst, based on the commercial support, and that in which virtually all exchangeable cations are Na^+, it is difficult to imagine that the last traces of Fe in the zeolite framework should be responsible for this spectacular selectivity. Iron ions in the zeolite framework can act as chemical anchors, thus increasing the metal dispersion (47), but they are not acting as catalytic sites comparable to the extra-framework transition metal ions and their oxides (48). Also, the absence of ethanol in the reaction product indicates the absence of a true promoter effect, as ethanol is typical for promoted Rh catalysts. There is prior evidence that acetic acid is formed at high pressure over nonpromoted Rh/SiO_2 (3, 5, 9, 18, 19, 21) and Rh/Al_2O_3 (18). The turnover frequencies measured here are similar to those reported by Schünemann *et al.* (49).

The data obtained with a wet feed (Figs. 16 and 17) show that water does not increase this selectivity; this eliminates a higher concentration of adsorbed water in the zeolite as the potential cause of the enhanced selectivity for acetic acid over zeolite-supported rhodium.

To rationalize the high selectivity of Rh/NaY toward acetic acid, two hypotheses still remain. First, work by Bowker *et al.* (37–40) shows that adsorbed acetate groups on Rh are stabilized by co-adsorbed oxygen. It is not impossible that, in a similar way, the acetate groups are better stabilized on Rh clusters inside zeolite cavities than in the mesopores of SiO_2. A higher stabilization of acetate groups could lead to higher selectivity for acetic acid.

There are, however, even stronger arguments for a different hypothesis, based on the well documented fact that in zeolites, Rh *carbonyl clusters* and carbonyl ions are formed at appreciable pressures of CO. All observed data are consistent with the model that Rh carbonyl clusters in contact with Rh clusters are responsible for the formation of oxygenates in zeolites. Previous IR work has identified a variety of Rh carbonyl complexes in the cages of zeolite Y (50–52). Among these, the carbonyl clusters $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ and the carbonyl cation $Rh^+(CO)_2$ are most prominent. The latter ion can coordinate with cage oxygen and hydroxyl groups (43). The work of Rode *et al.* suggests that $Rh_6(CO)_{16}$ in cages of Y and X zeolites is a catalyst precursor for propylene hydroformylation (50). No study of such carbonyl complexes in Y zeolite at a CO pressure >0.1 MPa and high temperature is known to us, but it appears probable that the relative concentration of various carbonyl complexes at a CO partial pressure $P_{CO} = 0.5$ MPa will be different from that at $P_{CO} = 0.05$ MPa. It also seems reasonable that adsorbed H_2O will interfere with these complexes. We agree with Stakheev *et al.* (41) that at $P_{CO} \geq 0.05$ MPa, metal clusters inside zeolite cages tend to be converted to carbonyl clusters, whereas at low P_{CO} CO is simply chemisorbed on metal particles. For instance, with Pd in NaY we identified $Pd_{13}(CO)_x$ clusters inside the cages of NaY (42), while such carbonyl clusters have never been reported on other supports or *in vitro*.

Metal clusters are beneficial for the dissociation of CO, because this process requires large ensembles. Metal atoms are also needed for the hydrogenation of surface carbon atoms towards methyl groups. It is difficult to visualize these processes on carbonyl clusters. This explains why, at high P_{CO}, when the metal ensembles required for CO dissociation become scarce, the CO conversion rate is one order of magnitude lower over Rh/NaY than at low P_{CO}. However, if metal clusters are in close contact with carbonyl clusters or carbonyl ions, it is easy to visualize that CO insertion, the key step for the formation of oxygenates, will be facilitated. This concept explains the most remarkable finding of the present study; the selectivity towards acetic acid is *higher*, two orders of magnitude, at $P_{CO} = 0.5$ MPa, than at $P_{CO} = 0.05$ MPa.

On the basis of this concept other findings can be rationalized which are difficult to explain in any other way. Water is known to destroy carbonyl complexes. It thus is easy to understand the present finding that H_2O lowers the selectivity for acetic acid, but increases that for methane, since carbonyl clusters will be destroyed and metal clusters are formed which provide the Rh ensembles required for CO dissociation. Besides destroying carbonyl clusters, adsorbed water will also reduce the effective width of the pores in the zeolite. This could explain the rapid decrease of the reaction rate upon switching from a dry to a wet feed.

The carbonyl clusters that are formed at high P_{CO}, will become metastable at lower P_{CO}, but their conversion to metal clusters may be slow. The spectacular observation in the present study that a Rh/NaY catalyst which has been "taught" at high P_{CO}, how to produce acetic acid, retains that propensity also when the pressure is lowered from $P_{CO} = 0.5$ to $P_{CO} = 0.05$ MPa, is easily understood, while it is difficult to find another explanation for this "*memory effect*." Note that after reduction at 400°C, the catalyst is brought back to its original state, which proves that no permanent change in the zeolite framework was imposed during the exposure to syngas at 1.0 MPa.

Another indication for the transformation of Rh clusters into carbonyl complexes is the olefin/paraffin ratio. Rh clusters are, of course, a more efficient hydrogenation catalyst than carbonyl complexes; olefins formed by dissociative *desorption* of alkylgroups from Rh particles will have a higher chance of surviving as olefins when the concentrations of metal clusters is low.

The two hypotheses discussed here—stabilization of acetate groups in zeolite cages and carbonyl cluster promotion of CO insertion into Rh-alkyl bonds—are not mutually exclusive. Figure 18 shows that the time before the oxygenates become detectable significantly exceeds the chromatographic retention time observed upon adding a NaY bed behind the catalyst. This fact is in conformity with a stabilization of the acetate groups in zeolite cages.

The higher *iso/normal* ratio of alkanes over Rh/NaY than over Rh/SiO_2 also deserves some discussion. Although great care was taken in the present work to minimize the concentration of acid protons during the preparation of Rh/NaY, it is possible that some Lewis sites are present in the zeolite. Once CO hydrogenation starts, the water formed in this reaction will transform these Lewis acid sites into Brønsted acid sites which will catalyze the transformation of linear alkanes into branched molecules. Moreover, the low conversion rate, in comparison to Rh/SiO_2, clearly indicates the transport limitation and, thus, the longer residence time for the hydrocarbons before they can escape. If acetic acid is formed inside the zeolite cages, this will further increase the residence time for the hydrocarbons and, thus, improve the extent of their isomerization to isoparaffins. SiO_2 has much wider pores; therefore, the formation of secondary products will be negligible at low conversion.

In conclusion, Rh/NaY is a novel and rather unusual catalyst for the conversion of syngas to oxygenates, in particular acetic acid. Selectivity to acetic acid is much higher at 1 MPa than at 0.1 MPa. This behavior can be rationalized qualitatively by assuming that rhodium metal acts in conjunction with carbonyl complexes; the relative concentration of metal cluster and carbonyl complexes changes strongly by increasing the partial pressure of CO from 0.05 to 0.5 MPa.

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