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Design of a Stable, Selective Catalyst for CO Hydrogenation: Osmium in Basic Y Zeolite

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Zeolite-entrapped osmium carbonyl clusters were prepared by converting adsorbed $[H_2Os(CO)_4]$ in the pores of Zeolite Y. The samples were characterized as CO hydrogenation catalysts at 1–30 atm, 300–365°C, and H_2/CO molar ratios of 0.3–9. X-ray fluorescence spectroscopy, infrared spectroscopy, X-ray powder diffraction, and transmission electron microscopy were used to characterize fresh and used catalysts. In a strongly basic zeolite (prepared by treatment of NaY with NaN_3), entrapped Os carbonyl clusters were formed, and the catalyst had a low activity for CO hydrogenation, at low conversions giving a non-Schulz–Flory distribution of C_1–C_5 hydrocarbons with high alkene to alkane ratios. The catalyst was stable, operating at 300°C and 19 atm with a H_2/CO molar ratio of 1 for more than 20 days with no significant loss in activity and only a moderate loss in selectivity. Infrared spectra of the used catalyst, which was yellow, indicate the presence of osmium carbonyl clusters. When an acidic zeolite, HY, was instead used in the preparation, the resulting catalyst was much less stable; during operation, the osmium migrated out of the cages, giving crystallites of metal and the common Schulz–Flory distribution of hydrocarbon products. These results suggest opportunities for synthesis of metal clusters in strongly basic zeolites and for preparation of shape-selective catalysts. © 1991 Academic Press, Inc.

INTRODUCTION

The practical value of hydrogenation of carbon monoxide catalyzed by metals is limited by the unfavorable Schulz–Flory distribution of hydrocarbon products. In attempts to increase the yields of C_{2+} hydrocarbons, particularly low molecular weight olefins (potentially valuable as feedstocks to replace petrochemicals), researchers have used zeolites as supports for the metals, attempting to impose a shape selectivity on the catalysis (*1*) or to control the performance through particle size effects (*2*). These attempts have been partially successful, giving unusual distributions of products (e.g., high yields of C_3 (*1*) or C_4 (*3*) hydrocarbons), but the catalysts have been unstable, because the zeolite pores have been plugged with products and/or because the metal has been oxidized or migrated out of the zeolite cages to form large aggregates (*4*), which give the Schulz–Flory product distribution.

The goal of this research was to design, synthesize, and test CO hydrogenation catalysts having the catalytically active species stably entrapped in zeolite cages. The strategy was to use organometallic chemistry to prepare metal clusters from small precursors in the cages, forming catalytically active metal clusters that would be too large to migrate through the zeolite apertures and therefore resistant to sintering outside the zeolite particles. A small, volatile organometallic precursor, $[H_2Os(CO)_4]$, was chosen, since it was expected to undergo reductive carbonylation to form metal carbonyl clusters that would be too large to migrate through the zeolite apertures. Precedent for the reductive carbonylation chemistry is found in the reaction of $[H_2Os(CO)_4]$ on the surface of MgO and in basic solution; condensation gives high yields of stable

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$[H_3Os_4(CO)_{12}]^-$ and $[Os_{10}C(CO)_{24}]^{2-}$ (*5*, *6*). Extension of this chemistry to a zeolite requires one with strongly basic character (*7*). For comparison, an acidic zeolite was also used as a support. The samples were tested as catalysts for CO hydrogenation and characterized by physical methods.

EXPERIMENTAL METHODS

All syntheses, including preparation of the organometallic precursor and of the zeolite-supported catalysts, and sample transfers were conducted with exclusion of air and moisture. The apparatus included Schlenk lines and N_2-filled glove boxes. The solvents were carefully purified, typically by distillation.

Catalyst Preparation

NaY crystalline zeolite powder (LZY-52) was supplied by Union Carbide; it had a unit cell size of 24.7 Å and a SiO_2/Al_2O_3 molar ratio of 4.74. The basic zeolite support was prepared from NaN_3 and NaY by the literature procedures (*8*, *9*), as follows: NaY powder was calcined in flowing O_2 (Matheson, extra-dry grade) at 400°C for 2 h, followed by evacuation (10^{-3}–10^{-4} Torr) for 12 h. NaN_3 (Fisher, reagent grade) was used as received. Methanol (Fisher) was dehydrated by distillation from magnesium and sublimed iodine. Crystalline, ground NaN_3, 0.25 g/g of NaY, was dissolved in the methanol. Calcined NaY was then mixed with this solution, with continuous stirring at room temperature for 2 h. The solvent was removed by evacuation and the solid dried under vacuum for 12 h. The sample was then transferred to a calcination tube in a N_2-filled glove box. Thermal decomposition of the NaN_3 thus introduced into the intracrystalline space of the zeolite was carried out as high-purity N_2 (99.999%, Matheson) flowed through the sample, with the temperature ramped from 300 to 400°C at a rate of 1°C/min. The sample was maintained at 400°C for 4 h, then cooled down. The resulting sample was characterized by infrared spectroscopy, having bands at 2186(m), 2076(s), 2036(vs), and 1973(m) cm^{-1}.

The acidic zeolite (HY) was prepared by ion exchange of NaY with aqueous 0.1 *N* NH_4Cl solution at 90 to 95°C. After ion exchange, the slurry was filtered, washed with sufficient deionized water to remove the remaining salt, and dried in an oven at 120°C for 12 h. The acidic form of the zeolite was prepared by decomposition of the ammonium cations at 350°C, releasing NH_3. The resulting HY zeolite, which still contained some Na^+, was calcined at 450°C in flowing O_2 (Matheson, extra-dry grade) for 4 h, followed by evacuation at 10^{-3}–10^{-4} Torr for 12 h.

$[H_2Os(CO)_4]$ was prepared by reduction of $[Os_3(CO)_{12}]$ with Na in liquid NH_3, followed by protonation of the resulting $[Na_2Os(CO)_4]$ with phosphoric acid (*11*). The resulting $[H_2Os(CO)_4]$ was vacuum transferred from the aqueous solution through a P_2O_5 trap to a Schlenk tube, which was immersed in a liquid-N_2 trap. The resulting compound in hexane had an infrared spectrum (ν_{CO} 2141 (w), 2067 (m), 2056 (s), and 2050 (vs) cm^{-1}) confirming its purity (*12*).

$[H_2Os(CO)_4]$ is volatile at room temperature, and vapor-phase transport was used to prepare the zeolite-supported Os catalysts, as follows: A 250-ml flask with 2–3 g of pretreated zeolite support was connected through a T-stopcock to a Schlenk tube containing the $[H_2Os(CO)_4]$. The flask and the Schlenk tube were immersed in liquid N_2. The flask and the connecting line were evacuated for 1–2 h, and then the liquid N_2 was removed from the Schlenk tube to allow $[H_2Os(CO)_4]$ to transfer under vacuum to the cold flask and condense. The liquid N_2 was then removed, and the flask was held at room temperature for 24 h and occasionally shaken. During this time the $[H_2Os(CO)_4]$ was partially adsorbed by the zeolite. Then the flask was evacuated for 1 h to remove excess $[H_2Os(CO)_4]$, and the resulting sample was removed and stored in the glove box.

Attempts were made to extract supported organometallics from the zeolites with solutions containing acetone (or other solvents) and [PPN][Cl]. Acetone (Fisher, certified ACS grade) was dried over activated 4A zeolite and stored under nitrogen. [PPN][Cl] (Strem) was used as received.

Catalyst Characterization

The Os and Na contents of the resulting samples (including those used in the catalysis experiments) were determined by X-ray fluorescence spectroscopy with a Philips PW 1410/80 automated X-ray spectrometer calibrated with similar standards.

Infrared spectroscopy was used to characterize the samples prepared from $H_2Os(CO)_4$ and the NaN_3-modified zeolite. Since the zeolite powder was difficult to press into a self-supporting wafer for transmission infrared spectroscopy, the diffuse reflectance mode was used. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was done with a Nicolet 7199 spectrometer with an *in situ* DRIFTS accessory (*13*). The DRIFTS apparatus allows experiments at high temperatures and gas treatments, but the cell was designed only for atmospheric pressure. The infrared experiments with the catalyst used at high pressures were done at low pressure after the catalyst had been removed from the reactor. Infrared spectra of liquid samples were measured in the transmission mode with samples in a 0.2-mm CaF_2 cell.

X-ray powder diffraction spectra to characterize zeolite crystal structures were measured with a Philips APD 3520 instrument operated at a voltage of 45 keV with a current of 40 mA. The samples were held in a sealed cell, protected from exposure to air.

Electron micrographs of fresh and used catalysts were recorded with a Philips 400T instrument operated in the transmission mode with a voltage of 80 keV. The powder samples were deposited on copper grids coated with light carbon films.

Catalyst Testing

CO hydrogenation kinetics measurements were made with a Cu-lined flow reactor having an inner diameter of $\frac{1}{4}$ in. Typically, 0.5–1.0 g of catalyst was loaded into the central (isothermal) zone of the reactor in the glove box; the upstream and downstream reactor sections were packed with glass wool. The gases used as feeds to the reactor were purified by passage through traps containing activated 5A zeolite; the H_2 also flowed through a Cu_2O trap. An activated carbon trap held at 275°C was used to decompose any metal carbonyl impurities in the CO feed. The CO hydrogenation reaction was investigated at various temperatures (300–365°C), pressures (1–30 atm), and feed compositions (molar ratio of H_2 to CO from 0.3 to 9). Each catalyst sample was brought on stream in a mixture of flowing equimolar CO and H_2 and brought to the desired reaction pressure. The catalyst was then heated to the desired temperature at a rate of 2°C/min. Time zero on stream was defined as the time when this temperature was reached. The effluent stream flowed through a heated line to prevent condensation of products, which were analyzed by an on-line Antek 300 gas chromatograph equipped with a Porapak Q column (4 ft in length and $\frac{1}{8}$ in. in inside diameter) and a flame ionization detector. Conversions ($<2\%$) were measured as a function of time on stream for periods as long as a few weeks to provide data characterizing catalyst deactivation. At the conclusion of each experiment, the catalyst was cooled to room temperature in flowing reactants, removed from the reactor in the glove box, and characterized by the physical methods mentioned above.

RESULTS AND DISCUSSION

Adsorption of $[H_2Os(CO)_4]$ *in Zeolite Y*

The zeolite prepared from NaN_3 has a strongly basic framework structure, as shown by its catalytic properties (*9*). The material has been characterized by a range of physical methods, including electron spin resonance and infrared spectroscopies, and suggested to incorporate Na_4^{3+} clusters in the sodalite cages (*7–9*). Being strongly basic, this zeolite was expected to provide within its solvent-like pores a medium for condensation of osmium carbonyls to form

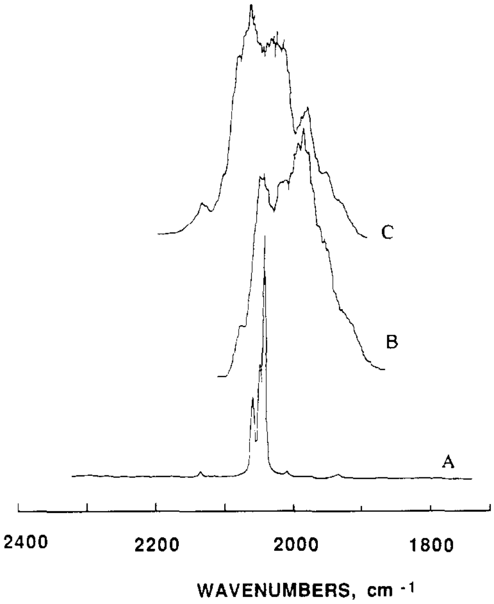

FIG. 1. Infrared spectra in ν_{CO} stretching region: (A) $[H_2Os(CO)_4]$ in hexane; (B) sample formed by adsorption of $[H_2Os(CO)_4]$ on the basic Zeolite Y; (C) sample formed by adsorption of $[H_2Os(CO)_4]$ on HY.

carbonyl clusters (*14*), as occurs on the basic MgO surface (*5, 6*).

Zeolite-supported Os catalysts were prepared by adsorption of $[H_2Os(CO)_4]$ vapor on the basic Zeolite Y and on HY. Samples with different Os loadings were made by variation of the time of contact. The highest Os loading measured with X-ray fluorescence was 10.6 wt% for the basic zeolite and 7.2 wt% for the HY. The initially gray basic Zeolite Y turned yellow after the adsorption of $[H_2Os(CO)_4]$, but the initially white HY did not change color after adsorption of $[H_2Os(CO)_4]$.

Infrared spectroscopy was used to characterize the metal carbonyl species in the zeolites. The spectra of the zeolite supports were subtracted from the spectra of the Os-containing samples. As illustrated in Fig. 1, the ν_{CO} spectra of both the fresh zeolite-supported samples are clearly different from the spectrum of the precursor $[H_2Os(CO)_4]$ in hexane and clearly different from each other. The ν_{CO} spectrum of the basic-zeolite-supported Os sample [2082 (w), 2056 (s), 2024 (s), 1993 (vs), and 1963 (m,sh) cm^{-1}; Fig. 1B], by comparison with the spectrum of $[H_2Os(CO)_4]$ (Fig. 1A), shows a broadening and a shift of the strongest CO band to lower frequency, suggesting that deprotonation of $[H_2Os(CO)_4]$ had taken place on the basic surface (*15*). These results and the yellow color of the newly made sample suggest the formation of anionic osmium carbonyl species on the basic zeolite surface. The bands at 2082 (w), 2024 (s), 1993 (vs), and 1963 (m) cm^{-1} are in good agreement with those of $[Me_4N][HOs_3(CO)_{11}]$ in CH_2Cl_2 [2083 (w), 2020 (s), 1996 (s), 1958 (m), and 1967 (w, br) cm^{-1}] (*16*). For comparison, the spectrum of $[H_3Os_4(CO)_{12}]^-/MgO$, which forms from various osmium carbonyl precursors on MgO (*17*), is 2085 (m), 2029 (s), 2008 (s), 1988 (s), 1967 (m,sh), and 1948 (m,sh) cm^{-1} (*17*).

In contrast, the spectrum of the HY-supported sample has ν_{CO} bands at 2139 (w), 2108 (w,sh), 2076 (vs), 2036 (s), 1989 (m), and 1961 (w) cm^{-1}. The strongest band was shifted to a higher frequency than that characteristic of $[H_2Os(CO)_4]$. Different Os carbonyl species were formed from $[H_2Os(CO)_4]$ on the basic and the acidic zeolites.

In attempts to extract the Os species from the zeolite supports, the samples under N_2 were brought in contact with acetone and with an excess of [PPN][Cl] dissolved in acetone. The attempts failed with the sample prepared from the basic zeolite; the supernatant solutions were colorless, and no extracted species could be detected by infrared spectroscopy. After the attempted extractions, the solid samples remained yellow, and the infrared spectrum was unchanged. Since the infrared results suggest that adsorbed $[H_2Os(CO)_4]$ had been deprotonated by the basic zeolite support, the newly formed osmium carbonyl species are suggested to have been tightly ion-paired with the zeolite surface and/or to have formed structures large enough to be trapped in the zeolite cages.

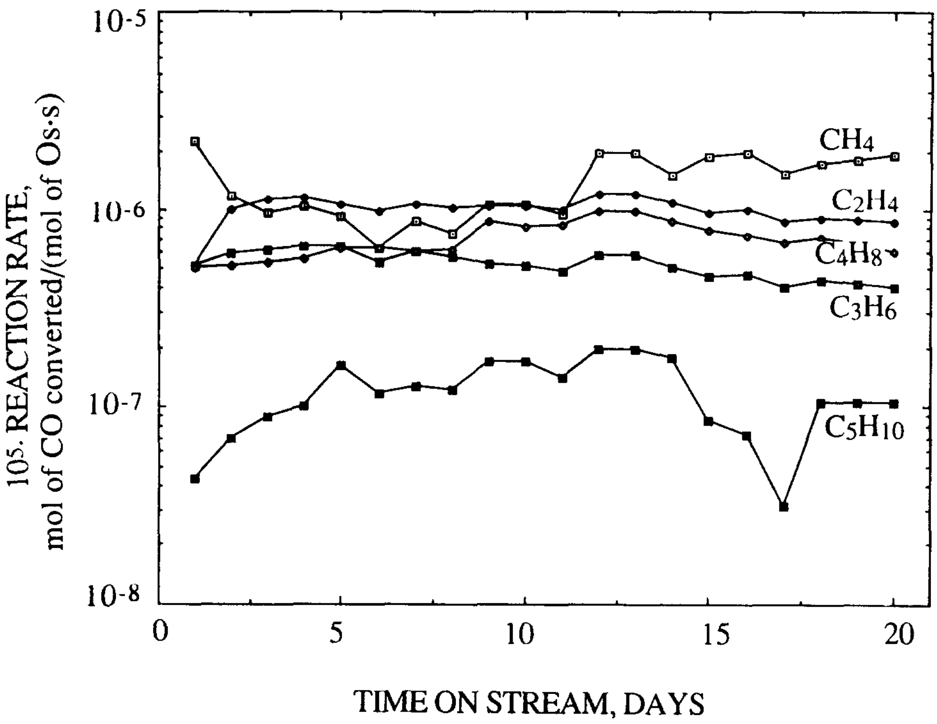

FIG. 2. Lack of deactivation of the basic-zeolite-supported catalyst (sample 2) in a flow reactor. Reaction conditions: 300°C, 19 atm, $H_2/CO = 1$ *M*.

In contrast, when the HY-supported sample (with an Os loading of 7.2 wt%) was extracted with acetone, the resulting supernatant solution was characterized by ν_{CO} bands at 2094 (m), 2067 (m,sh), 2054 (vs), 2048 (vs), and 2018 (m,sh) cm^{-1}, which are similar to those characteristic of $[H_2Os(CO)_4]$ in hexane (Fig. 1A), indicating that the $[H_2Os(CO)_4]$ had been physisorbed on HY.

Metal carbonyl hydrides exemplified by $[H_2Os(CO)_4]$ are weak Brønsted acids. Deprotonation of $[H_2Os(CO)_4]$ takes place in methanol, forming $[HOs(CO_4)]^-$ (*18*). The pK_a of $[H_2Os(CO)_4]$ in methanol is 15.2. The deprotonation of $[H_2Os(CO)_4]$ has also been observed to occur on the basic MgO surface (*5*). The anionic species $[HOs(CO)_4]^-$ in protic media undergoes condensation to form trinuclear anionic species (*18*):

$$[H_2Os(CO)_4] + B^- \rightarrow [HOs(CO)_4]^- + BH \quad (1)$$

$$2[H_2Os(CO)_4] + [HOs(CO)_4]^- \rightarrow [HOs_3(CO)_{11}]^- + CO + 2\,H_2, \quad (2)$$

where B^- is a Brønsted base. The known solution and surface chemistry of the osmium carbonyls is therefore inferred to be consistent with the suggestion that $[HOs_3(CO)_{11}]^-$ formed in the cages of the basic zeolite, consistent with the infrared spectra.

Catalyst Peformance in CO Hydrogenation

Both the Os-containing samples, one made from the basic zeolite and the other made from acidic zeolite, were found to catalyze CO hydrogenation at temperatures of 300°C or greater. Conversions were measured as a function of time on stream. Activities measured by the reaction rate calculated from low-conversion data are expressed in units of [mol of CO converted to hydrocarbons/mol of total Os · s]; the initial

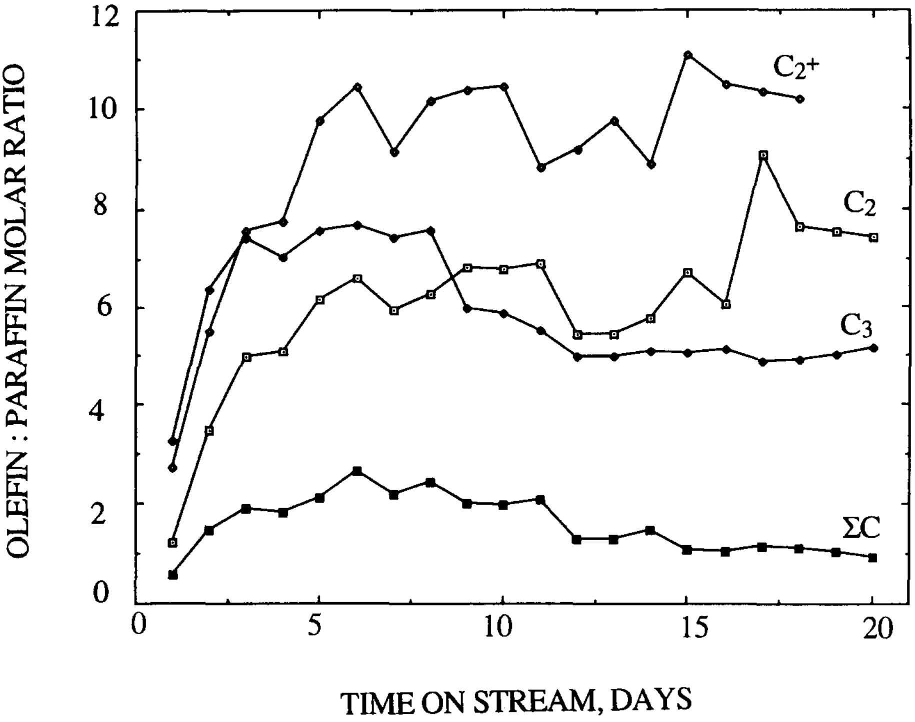

FIG. 3. Time dependence of olefin to paraffin ratio. Reaction conditions: 300°C, 19 atm, $H_2/CO = 1$ *M*.

Os loading of the catalyst was used in the calculations. The activity of the zeolite support, determined in blank experiments, was subtracted from the raw activity in the calculation of reaction rate; the correction was at most 30% and usually much less. Both catalysts were found to exhibit a cutoff at C_5 chain length at the low conversions observed, but otherwise the performance of the two was markedly different. The catalyst made from the basic zeolite, in contrast to that made from the acidic zeolite, had a relatively high selectivity for C_2–C_4 olefins and good stability.

A temperature of about 300°C or higher was required for observation of the activity of the catalyst made from the basic zeolite. The reaction rate averaged over a 20-day run at 300°C and 19 atm with a H_2/CO molar ratio of 1 was 8×10^{-6} [mol of CO/mol of Os · s]. Under these mild conditions, one of the catalysts was kept on stream for >20 days, and its activity (Fig. 2) and selectivity changed only moderately. The catalyst gave relatively high yields of C_2–C_4 hydrocarbons with high olefin/paraffin ratios. The C_2–C_4 products were as much as 60% (molar) of the hydrocarbon products, and the olefin/paraffin ratios for C_2 and C_3 were >4 (Fig. 3). No C_4 or C_5 paraffins were detected in the products. The product distribution deviates from the Schulz–Flory pattern (Fig. 4).

After 20 days on stream, the catalyst was removed from the reactor; it was still yellow, with no visible indication of metallic Os, suggesting the presence of Os carbonyl clusters. The total CO conversion to hydrocarbons during the 20 days of operation was 15.3 mol/mol of Os, confirming that the reaction was catalytic. The 20-day-old catalyst (sample 3) was extracted with dried hexane, but no hydrocarbon products (except for the solvent) were detected by gas chro-

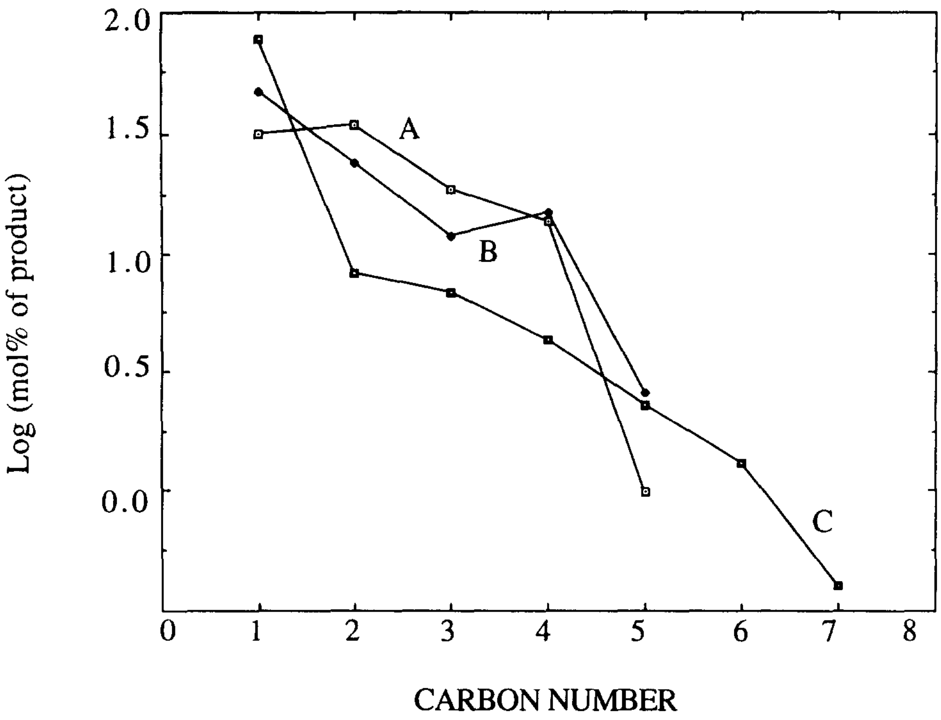

FIG. 4. Hydrocarbon product distributions in CO hydrogenation catalyzed by zeolite-supported osmium carbonyl. (A) Basic-zeolite-supported catalyst at 300°C, 19 atm, $H_2/CO = 1$ *M*, 2 days on stream. (B) As in (A), except 20 days on stream. (C) Al_2O_3-supported catalyst consisting of Os crystallites (5 wt% Os) at 275°C, 10 atm, $H_2/CO = 1$ *M*, 20 h on stream (*10*).

matography. This result is consistent with the inference that hydrocarbon product had not collected in the catalyst pores in any significant amount.

In summary, the results indicate that the Os supported in the basic zeolite catalyzes CO hydrogenation and, at least at low conversions, is selective for low molecular weight olefins and quite stable.

The HY-supported Os catalyst showed markedly different behavior. Upon heating to 200°C, a detectable conversion was observed, but it was too low to measure accurately. The initial reaction rate at 300°C and 19 atm with a H_2/CO molar ratio of 1 was 5×10^{-5} mol of CO/mol of Os · s, but it dropped quickly with time on stream. The product distribution also changed with time on stream, and at a near steady state at 347°C (with a reaction rate of 8×10^{-5} mol of CO/mol of Os · s), a typical Schulz–Flory product distribution was observed, with the yield of methane being as high as 90 mol%, which is about 30% higher than characteristic of the catalysts made from the basic zeolite (Table 1). No olefins were observed in the products; rather, hydrogenation of any olefins formed was evidently rapid, as evidenced by the observation that the trace amounts of olefins that were produced with the HY support alone were converted.

Kinetics of CO Hydrogenation Catalyzed by the Samples Made from the Basic Zeolite

The good stability and reproducibility of the supported catalysts made from the basic zeolite provided an opportunity for an investigation of the kinetics of CO hydrogenation. The effects of space velocity, pressure, temperature, and feed composition on catalyst

TABLE 1

Activities and Selectivites of Catalysts

Catalyst support	Os content, (wt%)	Time on stream (h)	Reaction conditions				$10^5 \times$ Reaction rate[c]	CO conversion, (%)	Selectivity (mol%)					Olefin/paraffin molar ratio		
			T(°C)	P(atm)	SV[a]	H_2/CO[b]			C_1	C_2	C_3	C_4	C_5	C_2	C_3	C_{2+}
HY	7.2	57	347	19	20	1	8.3	0.92	93.1	3.8	2.1	1.0	0.3	0	0	0
Basic NaY	10.6	173	340	19	20	1	10.3	1.0	61.6	20.7	9.3	6.7	1.7	4.1	4.5	5.7
Basic NaY	10.6	195	355	19	20	1	18.7	1.8	67.4	18.5	7.3	5.3	1.4	4.0	4.8	5.6

[a] Space velocity, ml/g of catalyst · min.

[b] Molar ratio.

[c] Reaction rate, mol of CO/mol of total Os · s, based on initial Os content.

performance were investigated under steady-state conditions. All the experiments reported here were conducted for CO conversions between 0.1 and 2.0%. The standard conditions were chosen to be 300°C, 19 atm, space velocity = 20 (or 10) ml/g of catalyst · min, and H_2/CO feed molar ratio = 1. Following each change in one of these variables, the catalyst was tested again under standard conditions. The results confirmed the stability of the catalyst and the reproducibility of the results.

The conversion to hydrocarbons was observed to be proportional to the inverse space velocity, demonstrating that the conversions were differential and that the rates reported above had been calculated appropriately.

The dependence of catalytic activity on reaction temperature is shown in Fig. 5. The apparent activation energies (calculated from the temperature dependence of the rates) are approximately 55, 36, 52, 30, 45, 30, and 41 kcal/mol for formation of methane, ethylene, ethane, propylene, propane, C_4 olefin, and C_5 olefin, respectively. As shown in Table 2, even after the catalyst had been used continuously at 365°C for 200 h, no significant change in activity or selectivity was measured. Evidently the catalytically active Os species in the basic zeolite were stable and tolerant of frequent changes in the process variables. This conclusion was confirmed by the characterization of the used catalysts, as described below.

Pressure was found to be crucial for stable performance of this catalyst. The results show that a pressure of at least about 11 atm was essential for stable catalytic performance. When one of the catalysts made from the basic zeolite was operated at atmospheric pressure, there was marked deactivation observed at each reaction temperature; but when the pressure was increased to 11 atm, the deactivation became very slow. There was no measurable loss of catalytic activity and no measurable change in selectivity in 30 h of continuous operation at 11 atm. These results suggest that high partial pressures of $CO + H_2$ stabilize the zeolite-entrapped Os carbonyl clusters, which may be precursors of the catalytically active species or catalytically active themselves.

As expected, increasing pressures of $CO + H_2$ led to increasing CO conversions and decreasing product olefin/paraffin ratios, corresponding to higher rates of olefin hydrogenation. The olefin/paraffin ratio for C_2 dropped more sharply than that for C_3 as the pressure was increased. The reaction rate is approximately proportional to the H_2/CO molar ratio in the range 0.3–3.0. The selectivity to paraffins increased with increasing H_2/CO ratio. Nonetheless, the high selectivities to olefins characteristic of the catalyst made from the basic zeolite were evident even at high H_2/CO ratios.

One of the catalysts (sample 2B) was treated twice at 320°C and 19 atm with a H_2/CO molar ratio of 9 for 24 h, the goal

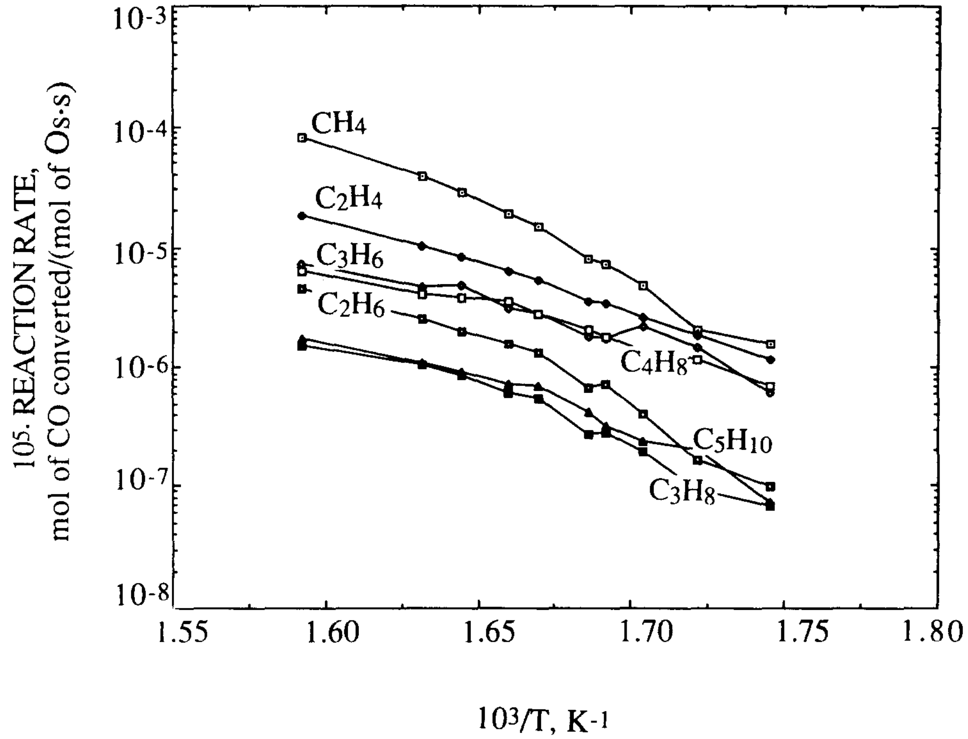

FIG. 5. Temperature dependence of rate of CO hydrogenation at 19 atm with a H_2/CO molar ratio of 1. The catalyst was Os carbonyl in the basic zeolite.

being to determine the effect of high H_2 partial pressures. After each treatment, the catalyst was brought back to the standard conditions (with a H_2/CO molar ratio of 1) and retested. The activity under standard conditions immediately following the change was 10 times higher than that observed before the change. Further, the activity declined rapidly during the 48 h of continuous operation following the change (Fig. 6). The used catalyst removed from the reactor was black at the upstream end of the catalyst bed, suggesting that Os metal particles had formed on the zeolite outer surface after treatment at the high H_2 partial pressure.

TABLE 2

Activity and Selectivity of Catalyst Supported in Basic Zeolite Y, Sample 2B[a]

Time on stream (h)	10^4 × Reaction rate[b]	CO conversion (%)	Selectivity (mol%)					Olefin/paraffin molar ratio		
			C_1	C_2	C_3	C_4	C_5	C_2	C_3	C_{2+}
363	1.56	2.2	72.2	18.8	4.9	2.9	1.2	7.9	22.9	11.1
563	1.75	2.4	71.7	18.6	5.6	2.8	1.3	13.2	—	20.0

[a] Reaction conditions: 365°C, 19 atm, H_2/CO = 1 (*M*), SV = 20 ml/g of catalyst · min.

[b] Rate in units of mol of CO/mol of total Os · s, based on initial Os content.

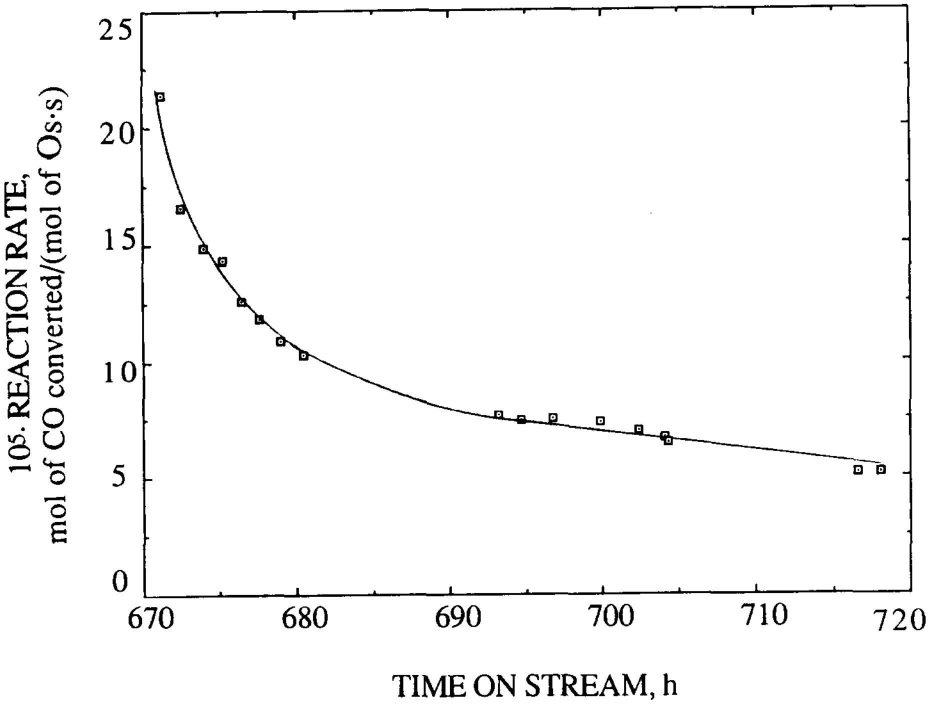

FIG. 6. Time dependence of activity of the basic-zeolite-supported catalyst treated with a high H_2 partial pressure. Reaction conditions: 320°C, 19 atm, $H_2/CO = 1$ *M*.

Characterization of Used Catalysts

All the used catalysts prepared from the basic zeolite (except sample 2B, the one treated at the high H_2/CO ratio) were still yellow when removed from the reactor; there was no visible indication of metallic Os particles on the supports. In contrast, the used catalyst prepared from the HY zeolite was light gray, suggesting the presence of Os particles.

Fresh and used catalysts were characterized by transmission electron microscopy. The fresh catalyst prepared from $[H_2Os(CO)_4]$ on the basic zeolite had uniformly dispersed scattering centers smaller than 10 Å (Fig. 7). The used catalyst which was on stream at 300°C and 19 atm with a H_2/CO ratio of 1 (*M*) for 20 days gave evidence of a few Os aggregates, ranging in diameter from about 60 to 100 Å on the outer surfaces of the zeolite crystallites (Fig. 7B). A sample (2A) that had been used at 300–355°C for 200 h appeared to be virtually identical to the fresh catalyst (sample 1). This result suggests that the Os carbonyl species in the basic zeolite are stable at high temperature and resistant to sintering when maintained in the equimolar CO + H_2 mixture. In contrast, many large particles, presumably Os, were observed on the outer surfaces of zeolite crystallites of the used catalyst sample 2B, which had been treated twice with high H_2 partial pressures. The average particle size was about 600 Å, but the particles were not detected by X-ray diffraction. This result indicates that the microscopically observed particles consisted of aggregates of much smaller particles.

We infer, therefore, that under the high H_2 partial pressure, the zeolite-supported Os carbonyl species fragmented and migrated out through the apertures of the zeolite. These fragments evidently formed Os aggregates on the outer surfaces of the zeolite. The product distribution data show that these behave as a conventional supported

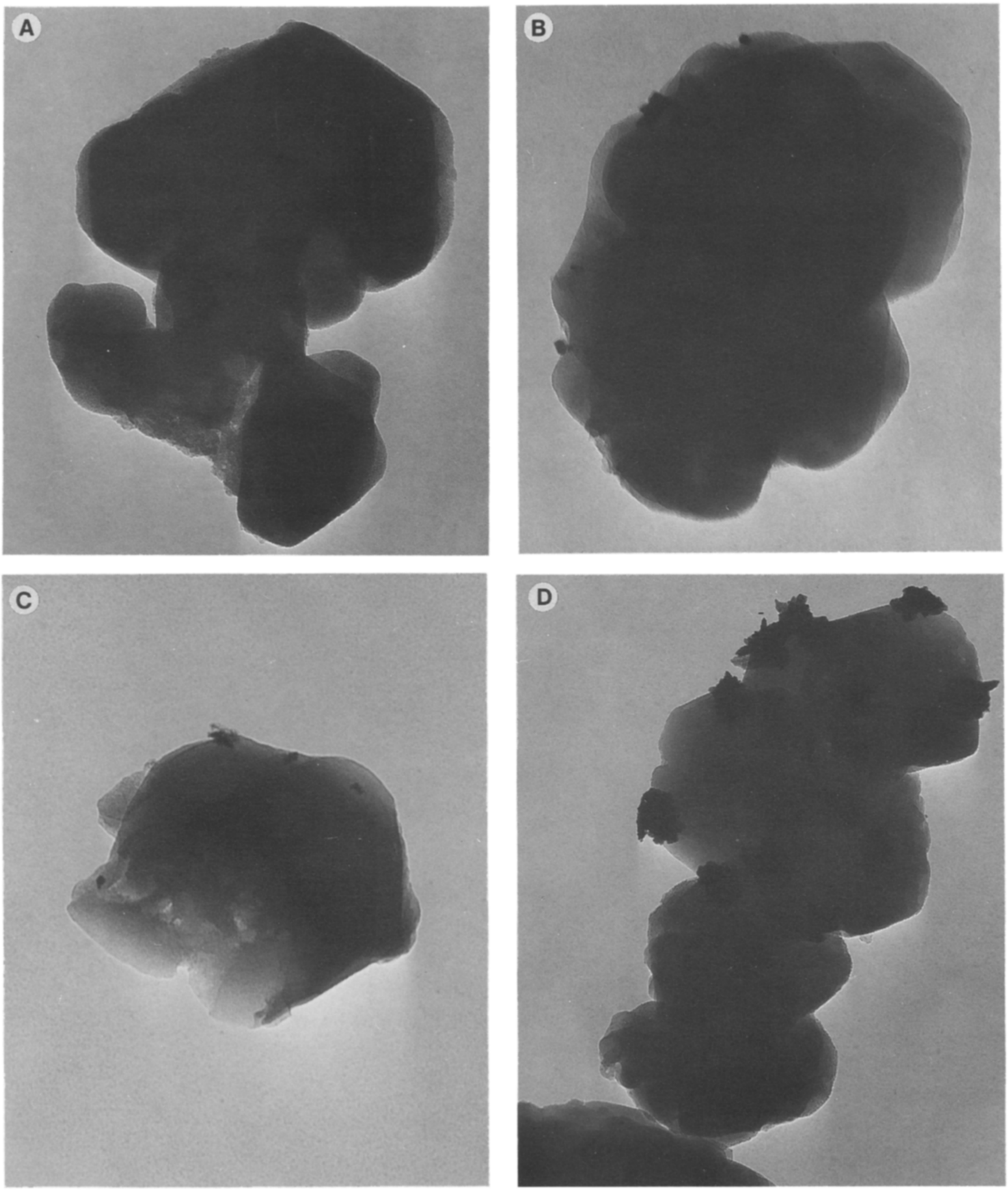

FIG. 7. (A) Electron micrograph of fresh catalyst derived from adsorption of $[H_2Os(CO)_4]$ on the basic zeolite; (B) micrograph of catalyst 1, used at 300°C, 19 atm, $H_2/CO = 1$ *M* for 480 h; (C) micrograph of catalyst 2A, used at 300–355°C, 19 atm, $H_2/CO = 1$ *M* for 200 h; (D) micrograph of used catalyst 2B, after exposure to $H_2/CO = 9$ *M*.

metal catalyst, giving the Schulz–Flory distribution of hydrocarbon products. These results are consistent with the inference that the catalytically active species in the more selective catalysts (those not exposed to high H_2/CO ratios) were trapped in the zeolite cages.

The X-ray diffraction data gave evidence of the zeolite framework structure; the results for the used catalysts were indistin-

TABLE 3

Metal Contents of Fresh and Used Catalysts

Catalyst	Support	Os content (wt%)		Os loss (%)	Na content (wt%)		Na loss (%)	Total time on stream (h)	Reaction temperature (°C)	Pressure (atm)	
		Fresh	Used		Fresh	Used				Initial	Operating
1	Basic NaY	8.9	8.4	6.5	7.5	6.6	11.7	480	300	19	19
2A	Basic NaY	10.6	10.1	5.8	7.0	4.6	34.6	200	300–355	19	19
2B	Basic NaY	10.6	8.6	14.5	7.0	5.3	24.3	440	300–365	19	19
3	Basic NaY	10.6	9.3	12.8	—	—	—	173	300–344	1	1,19
4	HY	7.2	6.2	13.3	2.8	3.1	—	56	300–344	19	19

guishable from those of the fresh catalyst. The X-ray data provided no evidence of the Os in any form.

The Os and Na contents of the used catalysts were measured with X-ray fluorescence spectroscopy (Table 3). The catalysts listed in this table (except sample 3) were brought on stream by the procedure described above; they were first pressurized in flowing CO + H_2 then heated to reaction temperature. Sample 3, instead, was first used at atmospheric pressure for 123 h before the pressure was increased.

The X-ray fluorescence analyses show that the catalyst brought on stream at atmospheric pressure lost 12.8% of its Os within a period of 173 h, which is almost twice as much as the loss from catalyst 2A. It is inferred that the greater Os loss was responsible for the rapid activity loss observed during operation of this sample. We suggest that the greater resistance to Os loss from the samples used at the higher CO partial pressures may be a result of stabilization of entrapped Os carbonyl clusters by CO (and possibly H) ligands. The high stabilities of some of these clusters are well established (*5*, *6*).

Some of the most stable known metal carbonyl clusters are Os carbonyl anions, and these are expected to have formed in the basic zeolite, much as they form on MgO and in basic solutions (*6*). They are not expected to form in the acidic zeolite, and, consistent with this expectation, the catalysts prepared from HY zeolite were found not be to stable. Rather than forming stable, entrapped Os cluster anions, $[H_2Os(CO)_4]$ in HY zeolite was apparently simply physisorbed, as inferred from the observation that it could be extracted intact from the zeolite. The physisorbed $[H_2Os(CO)_4]$ was easily desorbed; there was a 13% loss of Os within 56 h of continuous operation in flowing equimolar CO + H_2 at 19 atm, even before the sample was heated. We infer that the initial rapid deactivation of the HY-supported catalyst is an indication of rapid Os loss.

Lamb *et al.* (*5*, *6*) reported that MgO-supported Os carbonyl clusters are catalysts for CO hydrogenation at 275°C, giving a Schulz–Flory distribution of hydrocarbon products at 275°C and 10.5 atm with a H_2/CO molar ratio of 3. Their catalyst prepared from $[H_2Os(CO)_4]$ lost 36% of its Os in 2 days of operation, presumably as volatile Os carbonyls, e.g., $[H_2Os(CO)_4]$ itself or $[H_4Os_4(CO)_{12}]$ (*5*). The operating conditions for our basic-zeolite-supported catalysts (samples 1, 2A, and 2B) were similar, but the Os losses were much less (Table 3). We suggest that the relatively low losses of Os from the zeolite are associated with the entrapment of stable Os carbonyl cluster anions in the zeolite cages during the catalytic reaction.

The Na content of the parent NaY zeolite was 2.4 wt%. The basic zeolites prepared from NaN_3 initially contained about 7 wt% Na (Table 3). The data shown in the table indicate that some of the sodium was lost during the CO hydrogenation catalysis. We suggest that the sodium clusters that were presumably present in the sodalite cages broke up and that the Na migrated out of the intracrystalline regions.

Two of the stable used catalysts (removed from the reactor in the glove box after operating under CO hydrogenation conditions) were examined with infrared spectroscopy. The catalysts were used at a CO/H_2 ratio of 1 (*M*) at a pressure of 19 atm; one had been on stream for 480 h at 300°C, and the other had been on stream for 440 h, for 200 h at 365°C. The two used catalysts had very similar infrared spectra, as shown in Fig. 8.

These spectra agree very well with each other while being significantly different from that of the fresh catalyst. The spectrum of the used catalyst [ν_{CO} 2171 (w), 2086 (w), 2024 (w,sh), 1974 (m,sh), and 1947 (vs) cm^{-1}] shows a substantial shift to lower wavenumbers in comparison with the spectrum of the fresh catalyst.

Attempts were made to extract the surface species from these zeolites with [PPN][Cl] in acetone. The yellow used catalyst remained yellow after the extraction attempt, and the solvent remained colorless. No carbonyls were detected in the solvent by infrared spectroscopy, indicating that the extraction attempt failed. The infrared spectrum of the used catalyst, its yellow color, and the failure to extract any osmium carbonyl species all suggest that osmium clusters had been trapped in the zeolite after reaction, confirming the conclusions from the catalyst performance data.

Comparison of the infrared spectrum of the used catalyst with spectra reported for known (in particular, trinuclear and tetranuclear) osmium carbonyls did not lead to an identification of the supported species. Identification of entrapped Os carbonyls in the used catalyst evidently requires more information. EXAFS spectroscopy has been used to obtain structural information, and the results indicate the presence of very small osmium clusters, possibly triosmium, in both the fresh and used catalysts (*18*).

The basic-zeolite-supported catalyst is unique in that the catalytically active species appear to be trapped and stabilized in the zeolite cages by the atmosphere of CO + H_2. Catalysts of this type may offer prospects of application in shape-selective conversions of reactants including CO, but the activity of the catalyst supported by the basic zeolite is as much as several orders of magnitude less than the activities of more conventional catalysts [e.g., Os crystallites supported on alumina (5 wt% Os) have an activity of 5.1×10^{-3} mol/(mol of Os · s) at 300°C (*10*)]. One of the novel characteristics of the basic-zeolite-supported catalyst for CO hydrogenation is the high olefin to paraffin ratios in the products. Such ratios have been observed before for catalysts inferred to be metals in zeolites such as NaY with weakly basic properties (*19–21*). The zeolite basicity may be associated with a low activity for hydrogenation of primary olefin products. A possible advantage of the metal–carbonyl-derived catalysts over those prepared by ion exchange is that they do not require activation by reduction in H_2, which produces hydrogen ions in a zeolite.

The results presented here raise questions about the nature of the catalytically active species. There is no reason to doubt that the catalytically active species supported by the acidic zeolite are particles of Os metal, but plausible candidates for the basic-zeolite-supported catalyst include both osmium carbonyl clusters and Os particles. The evidence is as follows.

Results suggesting that osmium carbonyl clusters trapped in the zeolite cages may be the catalytically active species are the following: the present results, including the yellow color, the infrared spectra, and the stability of the catalyst, combined with EXAFS spectra of the used catalyst (*18*), suggest that the predominant osmium species are carbonyl clusters trapped in the zeolite supercages. The chemistry of osmium carbonyls in basic solutions and on the basic MgO surface demonstrates the stability of the cluster anions in basic media resembling

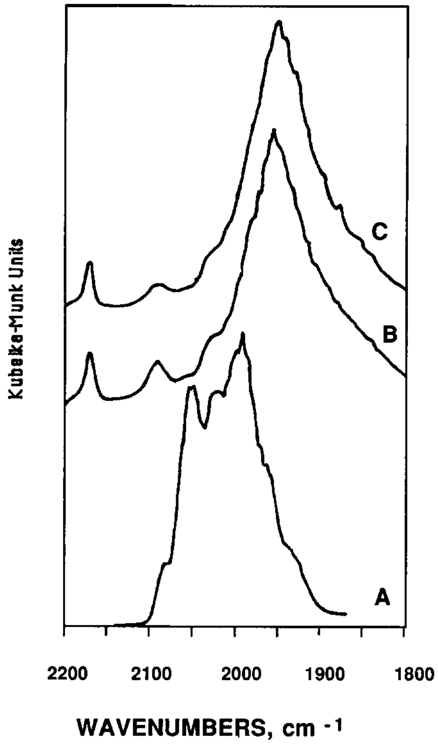

FIG. 8. Infrared spectra in ν_{CO} stretching region of (A) fresh catalyst prepared by adsorption of $[H_2Os(CO)_4]$ on the basic zeolite; (B) used catalyst after exposure to 1 : 1 H_2/CO (molar) at 19 atm and 300°C; (C) used catalyst, after exposure to 1 : 1 H_2/CO (molar) at 19 atm and 355°C.

that of the zeolite cages. The product distribution in CO hydrogenation catalysis (a non-Schulz–Flory distribution with a high olefin : paraffin ratio) is different from that of conventional alumina-supported Os crystallites (a Schulz–Flory distribution of hydrocarbons with little olefin) (*10*), consistent with the suggestion that the catalytically active species are different. The product distribution is also different from that of a MgO-supported catalyst inferred to consist of osmium carbonyl anions on the surface (a Schulz–Flory distribution of hydrocarbons) (*5*), consistent with the suggestion that the zeolite imposed a constraint on the product distribution. Further, the low activity of the catalyst supported by the basic zeolite is comparable to that of the catalyst inferred to consist of osmium carbonyl anions on MgO and markedly less than that of the conventional alumina-supported Os crystallites. All these results are consistent with the suggestion that the catalytically active species in the basic zeolite are osmium cluster anions and that the selectivity is characteristic of the clusters in the zeolite rather than simply osmium carbonyl clusters.

On the other hand, the results do not exclude the possibility of catalysis by undetected small Os crystallites present with the osmium carbonyl clusters in the catalyst. Since the activity of the catalyst is low, and the activity of Os metal relatively high, the observed activity would be explained by only a small amount of Os metal. The non-Schulz–Flory distribution of products might be explained as an artifact of the low conversions and an indication of reincorporation giving high yields of C_2 and C_3 products, and the high olefin : paraffin yields might be a consequence of the basicity of the support.

CONCLUSIONS

Adsorption of $[H_2Os(CO)_4]$ in Y zeolites results in the formation of supported species, with the structure depending on the acid–base properties of the zeolite. On basic Zeolite Y prepared by treatment with NaN_3, the adsorbed $[H_2Os(CO)_4]$ is deprotonated to form anionic species that undergo condensation to form Os carbonyl cluster anions so tightly anchored to the zeolite that they are not removed by cation metathesis with [PPN][Cl] in acetone. Under conditions of catalytic conversion of CO + H_2, new Os carbonyl clusters form inside the cages of the zeolite. In operation at low conversions, the catalyst is active for CO hydrogenation and selective for low molecular weight hydrocarbons with high olefin to paraffin ratios. The catalytic test results and infrared spectra indicate that the Os carbonyl clusters formed during catalytic hydrogenation of CO at 300°C are stable. The catalyst in the presence of CO + H_2 is tolerant of high temperatures for hundreds of hours with only small changes in structure and catalyst performance. The yellow color and infrared spectra of the used catalysts suggest the presence of Os carbonyl clusters. The product distribution data raise question of whether Os carbonyl clusters, rather than undetected particles of Os metal, may be the catalytically active species. The catalyst synthesis chemistry can be extended to other transition metals, exemplified by Rh (*19*).

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