RHODIUM SUPPORTED IN BASIC ZEOLITE Y: A SELECTIVE AND STABLE CATALYST FOR CO HYDROGENATION

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Catalysts prepared by a condensation reaction of $Rh(CO)_2(acac)$ within the supercages of zeolite Y made basic by treatment with NaN_3 are active for CO hydrogenation and selective for low-molecular-weight olefins and methanol. High partial pressures of CO (or $CO + H_2$) stabilize the catalyst. The predominant species in the catalyst are suggested to be rhodium carbonyl clusters trapped in the zeolite cages.

1. Introduction

Control of selectivity is a central challenge in the catalytic hydrogenation of carbon monoxide. Zeolites have been used as supports for metal catalysts in attempts to impose product shape selectivities and restrict the sizes of the metal aggregates, and some catalysts give high yields of lower-molecular-weight olefins [1,2]. However, the stabilities of almost all these catalysts are poor, since the metals easily migrate out of the zeolite cages to give metal particles, which act like conventional (unselective) catalysts. In contrast, a basic zeolite Y has been found to stabilize Os carbonyl clusters even at 300°C; in CO hydrogenation at low conversions, this catalyst has a low activity but is selective for low-molecular-weight olefins with only slow loss of catalytic activity and selectivity [3]. This result suggests opportunity for stabilizing zeolite-entrapped clusters of metals that are more active for CO hydrogenation than Os.

Rhodium on amorphous metal oxide supports is active for CO hydrogenation, and rhodium is of interest because its activity and selectivity depend markedly on the support properties [4]. The major products range from methanol when the support is rather strongly basic, to ethanol when the support is weakly basic, to hydrocarbons when the support is acidic. Rhodium carbonyl cluster anions in basic solutions, such as $[Rh_5(CO)_{15}]^-$ [5] and $[Rh_{12}(CO)_{30}]^{2-}$, [6] have been proposed to be catalytically active for the conversion of $CO + H_2$ into methanol and ethylene glycol, but pressures of hundreds of atmospheres are required. The high pressures of CO and basic solvents may stabilize the cluster anions at high temperatures.

The goals of this research were to prepare stable rhodium carbonyl clusters in a basic zeolite and to determine the catalytic properties for CO hydrogenation.

2. Experimental methods

The basic support was prepared from NaY zeolite powder (Union Carbide LZ-Y52) treated with NaN_3 dissolved in methanol [7,8]. Thermal decomposition of the NaN_3 took place as high-purity N_2 flowed through the sample, with the temperature being ramped from 250 to 400°C at a rate of 1°C/min. The sample was maintained at 400°C for 4 h, then cooled to room temperature.

The zeolite-supported Rh catalyst (0.5 wt% Rh) was prepared by vapor deposition of $Rh(CO)_2$(acac) in the basic zeolite. The organometallic precursor and the zeolite were mixed under dry N_2 and held under vacuum for 24 h at 90°C to allow the sublimation of the $Rh(CO)_2$(acac) into the zeolite pores. The resulting sample was handled in the absence of air and loaded into a copper-lined flow reactor and tested as a catalyst for CO hydrogenation at 225–325°C and 1–20 atm with feed molar ratios of H_2 to CO ranging from 0.5 to 3. 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 and a flame ionization detector. The analysis determined hydrocarbons and alcohols, but not CO_2.

Transmission infrared spectra (4 cm^{-1} resolution) of pressed wafers of catalyst were obtained with a Nicolet 7199 Fourier transform spectrometer.

3. Results

The infrared spectrum of $Rh(CO)_2$(acac) in hexane includes bands at 2084(s) and 2015(s) cm^{-1}. The spectrum of the basic zeolite includes bands at 2172(s), 2064(vs), 2036(m), 1985(w), and 1776(w) cm^{-1}. This gray material turned light yellow after the adsorption of $Rh(CO)_2$(acac). Unfortunately, any terminal carbonyl bands of the Rh-containing species in the basic zeolite were obscured by peaks characteristic of the zeolite. However, when the sample was treated in an equimolar $CO + H_2$ mixture at temperatures below 100°C, bridging carbonyl bands were observed at 1832 and 1766 cm^{-1}. These bands indicate that the mononuclear rhodium precursor was converted to rhodium carbonyl clusters in the basic zeolite.

The major products observed in CO hydrogenation catalyzed by the zeolite-supported sample were C_1–C_5 hydrocarbons, CH_3OH, and C_2H_5OH. CH_3OCH_3

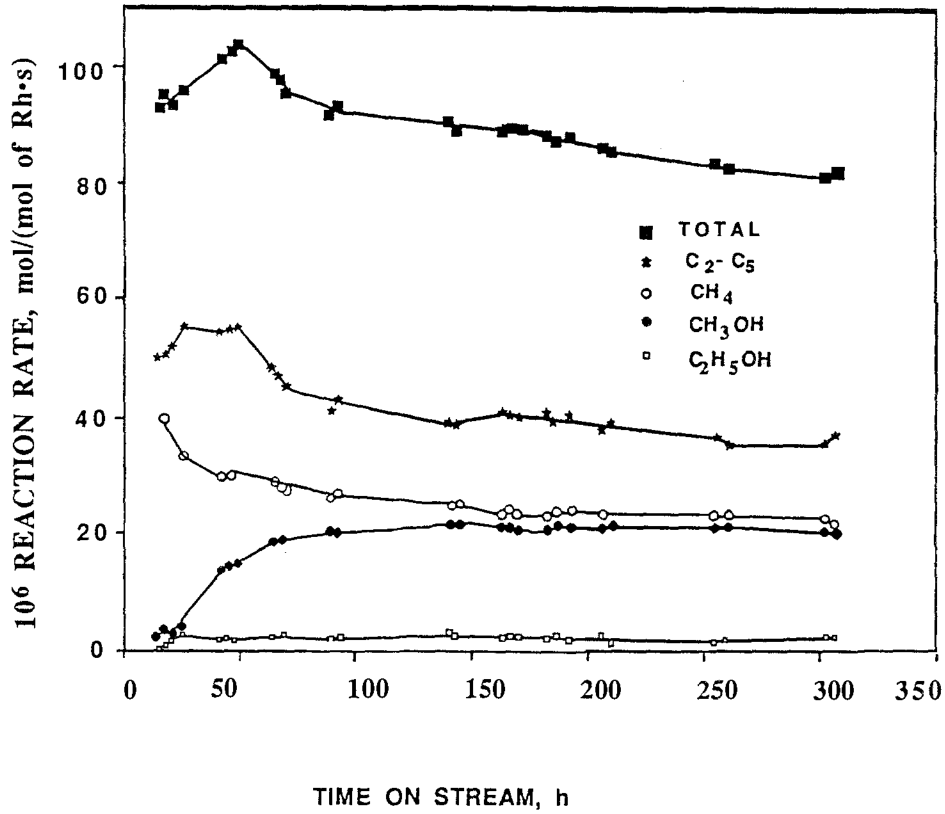

Fig. 1. CO hydrogenation catalyzed by zeolite-supported rhodium clusters: dependence of product distribution on time on stream in a flow reactor. Reaction conditions: 300°C, 20 atm, $H_2/CO = 1$ (molar).

and CH_3CHO were observed in trace amounts. The change in the product distribution at 300°C and 20 atm with time on stream in the flow reactor is shown in fig. 1. Activity maintenance was good, with the product distribution remaining nearly constant after about 100 h; the activities for methane, methanol and ethane formation were virtually constant for 200 h, but the activity for formation of C_2–C_5 hydrocarbons declined a few percent. There was a marked induction period for alcohol formation, with the initial formation rate being nearly zero. This result suggests the gradual formation inside the zeolite of the species that are catalytically active for alcohol formation. After 300 h on stream, the catalyst, removed from the reactor in the absence of air, was still light yellow, with no visible indication of metallic Rh, suggesting the presence of Rh carbonyl clusters. In contrast, catalysts prepared similarly on a γ-Al_2O_3 support are unstable, forming Rh metal particles and becoming black in a short time of operation.

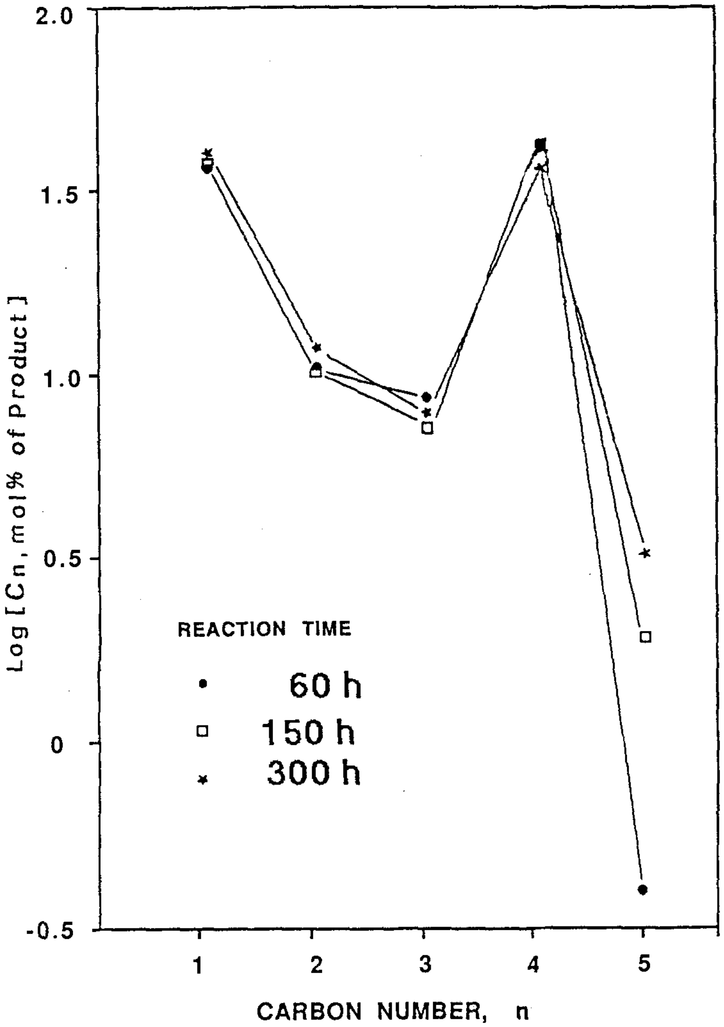

Fig. 2. Hydrocarbon product distribution in CO hydrogenation catalyzed by zeolite-supported rhodium clusters. Reaction conditions as stated in caption of fig. 1.

The hydrocarbon product distribution is shown in the Schulz-Flory plot of fig. 2. Products with chain lengths > 5 were formed in only very low yields at the low conversions observed (0.13%). A substantial deviation om a linear Schulz-Flory plot is evident, with a maximum at C_4. This molecular weight distribution did not change substantially with time on stream in the flow reactor.

Product distribution data are summarized in table 1. At low conversion the catalyst is selective for C_2–C_5 hydrocarbons with high olefin/paraffin ratios. The catalyst gave appreciable yields of methanol (20%), as much as 50% C_2–C_5 hydrocarbons, and only relatively small yields of CH_4 (30%); these yields are percentages of the hydrocarbon + alcohol products.

Table 1
Catalytic performance of supported rhodium catalysts for CO hydrogenation

Catalyst	Reaction conditions	CO conversion (%)	Activity and selectivity					Olefin/paraffin ratio			Ref.
				CH_4	C_2–C_5	MeOH	EtOH	C_2/C_2	C_3/C_3	C_4/C_4	
Rh/Y [a]	300 °C, 20 atm		A [g]	1.01	1.69	0.67	0.08				
	$CO/H_2=1$	0.13						1.6	4.5	16.7	This work
	60 h on stream		S [h]	28.8	48.5	19.2	2.4				
	300 °C, 20 atm		A [g]	0.79	1.48	0.73	0.09				
	$CO/H_2=1$	0.12						2.3	3.9	18.9	This work
	300 h on stream		S [h]	25.5	47.6	23.6	2.8				
	325 °C, 20 atm		A [g]	2.29	3.76	1.16	0.12				
	$CO/H_2=1$	0.28						1.0	4.2	16.4	This work
	100 h on stream		S [h]	30.6	50.3	15.6	1.5				
Rh/Al_2O_3 [b]	300 °C, 20 atm		A [g]	27.2	8.64	1.86	3.74				
	$CO/H_2=1$	1.56						0.3	3.2	2.1	This work
	100 h on stream		S [h]	64.7	20.6	4.4	8.9				
$Rh_6(CO)_{16}$ [c] in Y	250 °C, 30 atm		A [g]	1.00	0.40	0.50	0.10	–	–	–	
	$CO/H_2=0.5$	–	S [h]	46.6	24.7	24.2	4.3				[11]
Rh/Y [d] 10 Å	250 °C, 30 atm		A [g]	10.80	3.50	0.10	0.90	–	–	–	
	$CO/H_2=0.5$	–	S [h]	70.5	22.7	0.60	6.0				[11]
Rh/Y [e] 30 Å	250 °C, 30 atm		A [g]	105	15.0	0.40	2.50	–	–	–	
	$CO/H_2=0.5$	–	S [h]	85.5	12.1	0.30	2.10				[11]
Rh/Y [f]	250 °C, 1 atm		A [g]	1.40	1.20	0	0	–		–	
	$CO/H_2=1$	5.30							1.5	[14]	
	40 h on stream		S [h]	52.7	46.3	0	0				

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[a] Rhodium in zeolite Y containing Na clusters prepared from NaN_3.

[b] Rhodium crystallites prepared from $RhCl_3$.

[c] $Rh_6(CO)_{16}$ entrapped in zeolite Y.

[d] 10 Å metal particles supported on zeolite Y.

[e] 30 Å particles supported on zeolite Y.

[f] Cation exchange of $RhCl_3$ with zeolite Y, $CO+H_2O$ at 100 °C, O_2 at 200 °C, and then H_2 reduction at 200–400 °C; sample suggested to be Rh_6Y.

[g] Activity, measured as reaction rate in mmol/g of metal/h.

[h] Selectivity, mol% of hydrocarbon and alcohol products; measurements of CO_2 were not made.

4. Discussion

The basic zeolite-supported Rh catalyst, like the Os catalyst prepared similarly [3], is active for CO hydrogenation, being selective for low-molecular-weight olefins, with good maintenance of both activity and selectivity. In contrast to the Os catalyst, the zeolite-supported Rh also catalyzes alcohol production. In this respect, it is comparable to the soluble rhodium carbonyls (presumably clusters) that catalyze CO hydrogenation to give methanol and ethylene glycol; these catalysts are also formed from the $Rh(CO)_2(acac)$ precursor [9,10]. According to LeFebvre et al. [11], small Rh metal particles give more C_2–C_5 hydrocarbons and also more methanol than large Rh particles (table 1), suggesting that their catalytic properties may approach those of the molecular rhodium clusters. The zeolite-supported catalyst appears to be intermediate in character between the molecular clusters and the supported Rh particles; its activity is an order of magnitude less than that of the supported Rh particles. Similarly, a basic zeolite incorporating Os carbonyl clusters has a lower activity than supported Os crystallites [3,12,13].

In summary, the zeolite-supported rhodium catalyst is characterized by low activity, low yields of methane, high olefin/paraffin ratios, and significant yields of CH_3OH. These results, combined with the catalyst color, lack of substantial deactivation, and lack of evidence of metallic Rh, suggest that the catalyst may consist of Rh clusters trapped in the zeolite cages. Numerous known Rh carbonyl clusters, e.g., $Rh_6(CO)_{16}$, are small enough to fit in the zeolite supercages [14]. Since the zeolite is basic, we might expect rhodium carbonyl anions to have formed; hence we speculate that the predominant species and possibly the catalyst precursors might be similar to those in solutions that catalyze CO hydrogenation to give ethylene glycol. However, the presence of some metallic rhodium particles cannot be ruled out; these form from the solutions of rhodium carbonyl clusters used for ethylene glycol synthesis as the H_2/CO ratio is increased [6].

The unique selectivity of the new catalyst may be associated with the narrow pore structure and the formation of clusters inside the zeolite cages, and the stability (indicated by the lack of changes in activity and color) may be attributed to the stabilization of Rh clusters by CO, the basic zeolite cages, and the geometry of the zeolite pores, with large cages (diameter = 1.2 nm) and small apertures (diameter = 0.8 nm) which may entrap the clusters and hinder their sintering into large, unselective Rh crystallites.

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