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Kinetics of the Methanation Reaction over Ru, Ru–Ni, Ru–Cu, and Ni Clusters in Zeolite Y

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Clusters of Ru, Ni, and a series of Ru–Ni and Ru–Cu bimetallics in a Y-type zeolite were investigated as catalysts for the reaction of CO with H_2 to form CH_4. Although the particle size of the Ru clusters indicates that they remained in the large cavities of the zeolite, the turnover numbers for several samples were in agreement with those observed for Ru/Al_2O_3. By contrast, the nickel clusters were located on the external surface of the zeolite, and the turnover number was more than an order of magnitude less than that observed for Ni/Al_2O_3. The presence of ruthenium in bimetallic clusters caused the average particle size to decrease significantly, relative to the values which were observed for pure nickel or pure copper. The turnover numbers for the Ru–Ni zeolites decreased linearly with respect to the addition of Ni, but the decrease in initial activity was much more severe upon addition of Cu to the RuY zeolite. The supported ruthenium catalysts exhibited a marked decline in activity during the reaction, but the addition of excess nickel (1:7 atomic ratio) brought about a stabilization in activity which even exceeded the stability of the supported Ni catalysts. The decrease in activity is attributed to the build-up of excess carbon which results from the dissociation of CO. The presence of Ni is believed to moderate the activity of ruthenium for this reaction, thus providing more sites for dissociative chemisorption of H_2.

INTRODUCTION

The catalytic formation of methane from carbon monoxide and hydrogen has been the subject of an increasing amount of research since the discovery of the reaction in 1902 by Sabatier and Senderens (*1*). Several extensive reviews have been published recently (*2*–*4*). The relative activity, expressed as turnover numbers, of the group VIII metals on a limited number of supports has now been reasonably well established and reliable kinetic data are available. The reaction mechanism, however, is still the subject of controversy (*2*, *5*, *6*).

Possible support effects have been noted by several investigators (*2*). Vannice (*7*) studied the activity for methanation by palladium supported on a zeolite catalyst and found that the turnover numbers fell between those for silica- and alumina-supported samples. In this study, the average particle size was 30 Å, which indicates that most of the metal was located on the external surface of the zeolite, rather than in the internal voids. For other hydrocarbon reactions, dramatic changes in catalytic activity have been observed for metals which are dispersed within zeolite catalysts. For example, Boudart and Dalla Betta (*8*) have observed an order of magnitude increase in turnover number for the isomerization and hydrogenolysis of neopentane over plati-

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num which was dispersed in a Y-type zeolite. The increased activity was attributed to an electronic effect where the zeolite served as an electron withdrawing group.

In the present study, it was of interest to determine the influence of the zeolite on the methanation activity of metal clusters that were small enough to fit into the large cavities. Ruthenium proved to be useful for this purpose. Studies demonstrating the exchange of ruthenium complexes into a Y-type zeolite, and the chemistry of these intrazeolytic complexes have recently been reported (*9–11*), and in a subsequent paper ESCA results will be presented which confirm that upon reduction to the metal the ruthenium remains within the zeolite cavities (*12*).

Because of the recent developments in the catalytic chemistry of bimetallic clusters, experiments were also carried out to determine the influence of nickel or copper on the activity of ruthenium in a zeolite. Since one is able to obtain a uniform distribution of metal ions in a zeolite, this catalyst appears to be an ideal system for the formation of uniform bimetallic clusters. Sinfelt (*13*) has demonstrated that ruthenium and copper form an integrated system when dispersed on a silica support, although they are immiscible in the bulk. The influence of copper on the methanation activity of supported ruthenium and unsupported nickel has been determined by Bond and Turnham (*14*) and by Araki and Ponec (*6*). In both cases the presence of the copper effected a decrease in turnover number, presumably due to the dilution of multicentered catalytic sites by the copper atoms. Except for a limited study by Bartholomew (*15*), there has been no previous report on the activity of ruthenium–nickel clusters.

Of the group VIII metals, ruthenium has been observed to be the most active metal for methanation at 275°C, when compared on the basis of turnover numbers (*16*). This high initial activity decreased substantially during the course of the methanation reaction, even when pure reactants were used (*17*). The loss in activity has been attributed to some form of carbonaceous deposit, i.e., elemental carbon, a surface carbide, or a partially hydrogenated material. In this respect, it is interesting to note that ruthenium has the greatest hydrogenolysis activity of the group VIII metals (*18*). Since the hydrogenolysis reaction normally leads to the formation of a carbonaceous residue, one would expect that a decrease in the hydrogenolysis activity, perhaps by the formation of bimetallic clusters, would result in a more stable catalyst for the methanation reaction.

EXPERIMENTAL

Apparatus. Kinetic studies were carried out mainly a Pyrex recirculating reactor, having a volume of 670 cm^3. The system included a glass pump of the type first described by Porter *et al.* (*19*) with a capacity of 250 to 300 cm^3 min^{-1}. To remove water formed by the reaction the gases were passed through a cold trap which was maintained at 77 K. Using an inline sampling valve, gases were analyzed for methane and carbon monoxide by gas chromatography.

Continuous flow experiments also were carried out using an aluminum tubular reactor with two equivalent beds. These could be arranged such that the second bed would receive the products of the first bed, and sampling of the gas phase between the beds was possible. Aluminum was chosen as the reactor material to prevent contamination of the catalyst by metal carbonyls and to eliminate any catalysis of the reaction by the vessel. The flow rate was measured using a Matheson mass flow meter. Samples were removed using a gas-tight syringe and were analyzed for CO, CO_2, H_2O, C_2H_4, C_2H_6,

C_3H_6, and C_3H_8 using a Carle 311 gas chromatograph.

Adsorption studies were performed using a Worden 4302 fused quartz vacuum microbalance. The microbalance was connected to a vacuum system which was capable of achieving 1×10^{-6} Torr (1 Torr = 133.33 N m^{-2}). Deuterium isotherms were determined at 100°C for all catalysts except for the NiY zeolite, for which the isotherms were measured at room temperature. Carbon monoxide isotherms were determined at room temperature for all catalysts.

For the reduction studies a glass system of the type described by Beyer *et al.* (*20*) was used to determine the uptake of hydrogen during the reduction of the sample over 16 hr at 400°C. Corrections were made for the small amount of adsorbed gas by exposure of the sample a second time to hydrogen for 2 hr. Here it is assumed that the second uptake of hydrogen was the result of chemisorption, rather than further reduction of the catalyst. The possible reduction of Ru^{3+} by NH_3 during the decomposition of the $Ru(NH_3)_6{}^{3+}$ complex was also considered. Helium was recirculated over a zeolite containing the complex, and a cold trap maintained at 77 K was located downstream from the catalyst. The presence of N_2 in the gas stream was followed by gas chromatography.

For electron microscopy, samples of the catalysts were embedded in an Arldite–Epon epoxy mixture and sectioned with a glass knife. The thin sections were examined using a Hitachi HU-11E transmission electron microscope (TEM) operating at 100 kV and 20 μA.

Materials. The zeolite catalysts were prepared by standard ion exchange into an NaY material, obtained from Linde. The ruthenium was exchanged in the form of $Ru(NH_3)_6{}^{3+}$, which was prepared by the method of Ferguson and Love (*21*). Nitrate solutions of Ni^{2+} and Cu^{2+} were used for the exchange of these cations. The ruthenium complex was also exchanged into a CaY zeolite which was prepared by the method of Costenoble *et al.* (*22*). The bimetallic catalysts were prepared by sequential exchange; generally the most abundant ion was exchanged first, followed by the exchange of the second ion. After being rinsed in distilled water several times, the catalysts were dried at 80°C and stored in a hygrostat over saturated NH_4NO_3. The concentrations of the metals are reported as weight percent of the hydrated zeolite. The alumina samples containing 0.5% Ru and 2% Ni, or a combination of the two, were prepared by impregnating Catapal alumina with $Ru(NH_3)_6{}^{3+}$ or Ni^{2+}, followed by drying at 100°C.

The standard pretreatment for the catalysts (100 mg) used in the recirculating system consisted of evacuation for 1 hr at 25°C, 100°C, and in 100°C increments to 400°C. At this temperature the catalysts were reduced in recirculating H_2 for 16 hr with the cold trap in the system. In lieu of evacuation, the catalysts (100 mg) in the flow system were purged with He flowing at 30 cm^3 min^{-1} in 100°C increments up to 400°C, and reduced at 400°C with H_2 flowing at the same rate for 16 hr. Catalyst samples (500 mg) in the microbalance were evacuated overnight at room temperature to remove most of the water, subjected to the standard vacuum pretreatment at elevated temperatures, and reduced in flowing H_2 at 400°C for 2 hr, followed by reduction in static H_2 for 14 hr.

The carbon monoxide was obtained from Matheson and for the recirculating experiments the gas was ultra-high purity, (99.8%) whereas for the gravimetric experiments the carbon monoxide was of Matheson purity (99.99%). In one experiment the higher purity gas was used in the recirculating reactor and the same kinetic results were obtained. Both gases were further purified by passing through a trap at 77 K and an activated charcoal

TABLE 1

Ru, Ni, Cu Reduction Studies

Catalyst	Metal[a] (μmoles)	H_2 (μmoles)	H_2/metal
2% RuY	40.4	45.2	1 12
0.5% RuY	9.95	10.5	1.06
0.5% RuCaY	10.0	8.0	0.80
2% CuY	61.8	60.2	0.97
2% NiY	69.8	71.0	1.02
0.5% Ru, 0.07% NiY	12.35	13.6	1.11
0.5% Ru, 0.30% Ni	19.8	13.9	0.70
0.5% Ru, 1.12% Ni	49.8	34.9	0.70
0.5% Ru, 2% Ni	77.3	66.2	0.86
0.5% Ru, 0.06% CuY	14.1	17.9	1.24
0.5% Ru, 0.1% CuY	13.7	10.1	0.74
0.5% Ru, 0.3% CuY	19.7	16.1	0.82
0.5% Ru, 2% CuY	76.6	73.1	0.95

[a] 200-mg samples.

trap, respectively. Hydrogen used for the reduction reactions was also Matheson purity (99.999%) and was used as received. Deuterium which was C.P. grade from Matheson (99.5 mole%) was further purified by passing through an Engelhard Deoxo purifier followed by a dehydrated molecular sieve trap to remove water. Matheson purity helium (99.9999%) was used as received to pretreat the catalysts in the flow system. A mixture of 26.4% carbon monoxide in hydrogen from Air Products Co. was used to study the kinetics in the flow system. It was purified by passage through an activated charcoal trap to remove any metal carbonyls. Matheson ultra-high purity methane (99.99%) was used to calibrate the gas chromatograph.

RESULTS

Characterization of Metal Clusters

Reduction studies. The reduction of Cu^{2+} during the decomposition of $Cu(NH_3)_4^{2+}$ in zeolites has been reported to occur (*23*), and it appears that a similar reaction gives rise to molecular N_2 during the standard pretreatment of the RuY zeolites. Small amounts of N_2 were observed in the gas phase at temperatures up to 300°C and a relatively large amount was detected at 400°C. Subsequent hydrogen uptake at 400°C, as indicated in Table 1, suggests that the Ru^{2+} was further reduced to the zero valence state. Furthermore, the reduction of Cu^{2+} and Ni^{2+} was essentially complete in the zeolite samples.

Adsorption studies. Chemisorption of deuterium and carbon monoxide was used to determine the dispersions of the zeolite catalysts. The chemisorption of deuterium on ruthenium was determined at 100°C and the linear portion of the isotherm above 200 Torr was extrapolated to zero pressure to eliminate the effect due to physical adsorption. Isotherms for chemisorption of deuterium on nickel were plotted at 26°C and the quantity of deuterium was determined in a manner similar to that described for the ruthenium samples. Blanks on the zeolite and the alumina demonstrated that the supports did not chemisorb a significant amount of D_2. Carbon monoxide isotherms were determined up to a pressure of 150 Torr for both the catalyst and the support. Following the practice adopted by other investigators, monolayer coverage was assumed to occur at 100 Torr of CO. The quantity of carbon monoxide held by the support was subtracted from that held by the catalyst to determine the chemisorption by the metal.

Following the adsorption step, the catalysts were then aged by treatment in a static hydrogen–carbon monoxide mixture for 2 hr at 280°C. A second reduction was carried out at 400°C, and isotherms were determined for the used catalysts.

The results of the chemisorption measurements are given in Table 2, where the dispersions were determined from D_2 isotherms. In one case the gases were reacted in the recirculating reactor over a 500-mg sample of 0.5% RuY. The sample was subsequently transferred to the microbalance and reduced in H_2. The dispersion was 71%, which agrees well with that

TABLE 2

Deuterium Chemisorption Data

Catalyst	Fresh catalyst			Used catalyst		
	μmoles D_2/g	Dispersion	L(Å)	μmoles D_2/g	Dispersion	L(Å)
0.5% RuY	23	0.93	9.8	16	0.63	14.5
0.5% RuCaY	24	0.96	9.5	15	0.59	15.5
2% RuY	90	0.91	10	57	0.58	15.7
2% NiY	12	0.07	140	5	0.03	353
0.5% Ru, 0.06% CuY	17	0.68[a]		8.4	0.34[a]	
0.5% Ru, 0.1% CuY	13	0.54[a]		8.2	0.33[a]	
0.5% Ru, 0.3% CuY	15	0.60[a]		6.2	0.25[a]	
0.5% Ru, 2% CuY	11	0.43[a]		4.1	0.17[a]	
0.5% Ru, 0.07% NiY	13	0.43		10	0.33	
0.5% Ru, 0.3% NiY	19	0.39		13	0.27	
0.5% Ru, 1.2% NiY	31	0.26		16	0.13	
0.5% Ru, 2% Ni	40	0.21		39	0.20	
0.5% Ru/Al_2O_3[b]	11	0.46	20			
0.5% Ru Al_2O_3	5.2	0.21	43	5.0	0.20	45
2% Ni/Al_2O_3	4.6	0.03	360	2.5	0.02	680
0.5% Ru, 2% Ni/Al_2O_3	30	0.15		14	0.07	

[a] Dispersion defined as the fraction of Ru atoms on the surface.

[b] Commercial Englehard catalyst.

obtained following reaction in the static system. The dispersions for the ruthenium–nickel system are based on the *total* metal content of the system, as both ruthenium and nickel chemisorb deuterium strongly. The dispersions for the ruthenium–copper system are based upon only the ruthenium, since copper, in the form of the pure metal, does not chemisorb hydrogen strongly, and it is generally assumed that adsorption is also weak for copper in bimetallic clusters. Dispersions measured for the fresh catalysts were high for ruthenium (>90%), but they decreased to about 60% upon exposing the catalysts to reacting gases at 280°C. Dispersions measured for the ruthenium–nickel catalysts ranged from 43 to 21% for the fresh catalysts and from 33 to 13% for the used samples. The ruthenium–copper catalysts similarly ranged from 68 to 43% for the fresh samples and from 40 to 17% for the used catalysts. The dispersions for the pure 2% NiY and the 2% Ni/Al_2O_3 were both quite low. On the 0.5% Ru/Al_2O_3 the initial dispersion was lower than on the corresponding zeolite sample, but the dispersion did not decrease significantly when the alumina sample catalyzed the reaction. A decrease in dispersion of about 50%, however, was noted for the 0.5% Ru, 2% Ni/Al_2O_3 samples following the reaction. In both cases the final dispersion with alumina as a support was considerably less than with the zeolite as a support.

Because of the relatively large amount of CO adsorption by the zeolite lattice, there is a degree of uncertainty in the number of CO molecules per metal atom. Nevertheless, the CO/D ratios were generally greater than two and in the case of bimetallic systems the ratios were greater than four in several cases. With the exception of the 0.5% RuCaY sample

TABLE 3

Average Particle Size for Pure Metals

Sample	Sample size[a]	System	Average size (Å)	Dispersion
		Ruthenium		
0.5% RuY	254	Recirculating[b]	13	0.64
0.5% RuY	804	Flow[b]	15	0.46
0.5% RuCaY	939	Flow[b]	15	0.18
0.5% RuCay	1000	Flow[b]	14	0.60
0.5% RuCaY	586	Recirculating[b]	14	0.57
0.5% RuCaY	489	Recirculating[b]	14	0.58
0.5% RuCaY	163	Microbalance[c]	27	0.25
2% RuY	510	Recirculating[b]	14	0.60
2% RuY	677	Microbalance[c]	19	0.17
		Nickel		
2% NiY	138	Recirculating[b]	166	0.05
2% NiY	397	Flow[b]	65	0.09
2% NiY	545	Flow[b]	60	0.06
2% NiY	555	Microbalance[d]	43	0.17
2% NiY	250	Microbalance[c]	66	0.12
		Copper		
2% CuY	482	Microbalance[d]	65	0.10

[a] Number of particles measured.

[b] Treated in dynamic H_2–CO mixture at 280°C.

[c] Treated in static H_2–CO mixture at 280°C.

[d] Reduced only in H_2 in microbalance.

the CO/D ratio decreased upon subjecting the catalysts to reaction conditions. Detailed results of the CO chemisorption studies are reported elsewhere (*24*).

Particle sizes for ruthenium and nickel based on deuterium chemisorption data were calculated by assuming that the particles were spherical. The validity of 1:1 hydrogen atom to metal atom has been demonstrated in the literature (*25*). The surface area of the metals was calculated using 9.04 and 6.76 Å^2 as the areas of ruthenium and nickel atoms, respectively, and the atomic volumes were assumed to be 13.76 and 10.46 Å^3.

Electron microscopy results. Samples of the fresh and used catalysts were examined by electron microscopy, and the average particle sizes determined for the metallic phase are given in Table 3. Particles could barely be resolved for ruthenium–zeolite samples which had only been reduced, but not exposed to the reactants at elevated temperatures. Based on the resolving power of the microscope, for these samples an upper limit of 10 Å is reported. Dispersions were approximated by assuming spherical particles. The individual areas and volumes were summed and divided by the respective atomic area or volume to obtain N_s, the number of metal atoms on the surface, and N_t, the total number of metal atoms in the sample. The ratio N_s/N_t is the dispersion.

With the exception of the one TEM sample which was exposed to the reactants in the microbalance, the agreement between the particle sizes and dispersions as determined by the two techniques is excellent for the RuY samples. The adsorption data for the NiY zeolite, however, indicated a much lower dispersion than was determined from the TEM measurements. As will be shown in the section on kinetic data, nickel on the zeolite behaved in an unusual manner, and it is likely that either (a) the reduction of the Ni^{2+} was incomplete for the samples located in the bucket of the microbalance or (b) hydrogen chemisorption is inherently decreased, thus giving an apparent dispersion value which is too low.

The observed distribution of particle sizes is given by the graphs of Fig. 1.

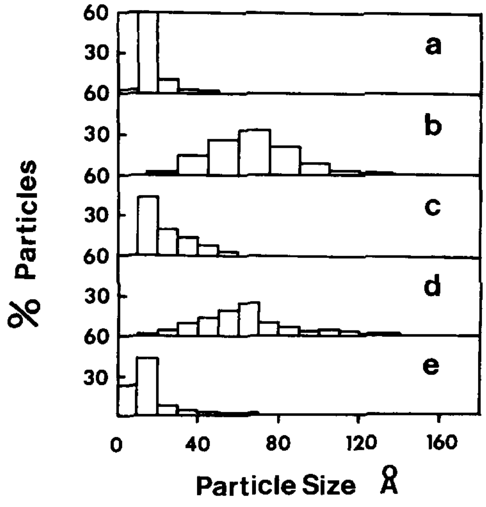

FIG. 1. Metal particle size distribution for (a) 0.5% RuY, (b) 2% NiY, (c) 0.5% Ru, 2% NiY, (d) 2% CuY, and (e) 0.5% Ru, 2% CuY.

TABLE 4

Initial Rates of Methanation

Catalyst	Ru:M	Rate (moles CH_4 sec^{-1} g^{-1}) $\times 10^9$	N[a]($\times 10^3$)sec^{-1}	
			Recirculating	Flow
2% NiY	—	50.9	5.0	5.8
0.5% RuY	—	274	9.4	10.8
0.5% RuCaY	—	460	15.9	14.0
2% RuY	—	3620	31.5	—
0.5% Ru, 0.06% CuY	5:1	93.2	5.5	—
0.5% Ru, 0.1% CuY	3:1	48.3	2.9	—
0.5% Ru, 0.3% CuY	1:1	15.2	1.2	—
0.5% Ru, 2% CuY	1:6.5	23.8	2.8	—
0.5% Ru, 0.07% NiY	4:1	215	8.1	—
0.5% Ru, 0.3% NiY	1:1	241	6.6	—
0.5% Ru, 1.16% NiY	1:4	251	5.8	—
0.5% Ru, 2% NiY	1:7	239	3.3	9.1
2% Ni/Al_2O_3	—	2120	230	140[b]
0.5% Ru/Al_2O_3	—	208	19.8	—
0.5% Ru, 2% Ni/Al_2O_3	1:7	2020	73	53[b]
0.5% Ru/Al_2O_3[c]	—	245	10.8	—

[a] At 280°C, $P_{CO} = 150$ Torr, $P_{H_2} = 450$ Torr.

[b] As conversions were rather high (~10%) flow reactor may not fit differential requirements.

[c] Englehard Ru/Al_2O_3 catalyst assumed stabilized.

For the reduced RuY zeolite, after the catalytic reaction, the particles exhibited a narrow size distribution which was centered around an average particle diameter of ca. 15 Å. As shown in Fig. 1b the particle size distribution for the NiY zeolite was much broader. Copper clusters exhibited a broad distribution, with some particles being as small as 15 Å and others were as large as 800 Å. This result is qualitatively in agreement with the location of copper metal both inside and outside of the zeolite crystallites, as previously deduced using other techniques (*26*). The presence of ruthenium in bimetallic clusters had a marked effect on shifting the distribution curve to lower particle sizes. Even for samples which were predominantly nickel (0.5% Ru, 2% Ni) the maximum in the distribution curve (Fig. 1c) was shifted to <20 Å.

X-Ray diffraction results. Examination of the zeolite structure by X-ray diffraction demonstrated that no loss occurred in crystallinity upon exchange, pretreatment, or reaction. No lines which could be attributed to metal crystals were observed for the ruthenium nor for any of the ruthenium–nickel clusters in the zeolite. The copper(111) line observed in the 2% CuY sample was broadened sufficiently to indicate a 300-Å particle size. For the 0.5% Ru, 2% CuY catalyst a diminished copper(111) line, relative to the zeolite lines, was observed. This line was broadened to nearly the same extent as in the pure CuY zeolite. For a badly sintered 2% NiY sample a (111) line was observed, and broadening indicated a particle size of 180 Å, but no metal lines were observed with other NiY samples. This is consistent with the distribution for NiY as given in Fig. 1. Since the particle size limit for detection by X-ray diffraction is nominally

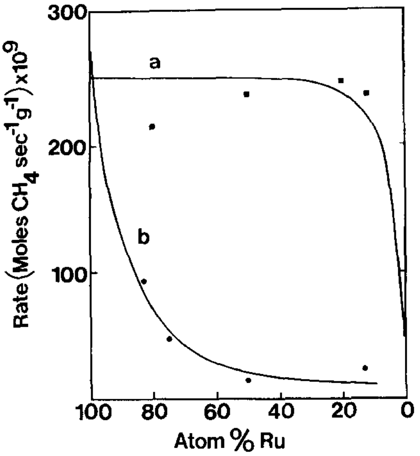

FIG. 2. Specific activity versus atom percent ruthenium in (a) ruthenium–nickel zeolites and (b) rutherium–copper zeolites.

50 Å, most of the nickel particles were not observed. Furthermore, the remaining nickel was of too low a concentration for detection.

Kinetic Data

Initial rates. After 100 mg of catalyst was given the standard pretreatment in the recirculating reactor, the reactor was cooled to 280°C in H_2 and the gas was removed by evacuation for 1 min. Except for the experiment in which the order of the reaction was being determined, a mixture of 450 Torr H_2 and 150 Torr CO was then admitted to the reactor. Methane formation was followed over a period of 1 hr. In general, the first one or two runs on a catalyst gave 10 to 50% lower activity than was subsequently measured for the catalyst. In the following discussion only the third and following runs will be reported. Although the initial rate of methane formation decreased, the maximum activity could be regenerated by reduction in recirculating H_2 at 400°C for 2 hr.

The initial rates of methane formation are presented in Table 4 where specific activity is based on the mass of catalyst (zeolite plus metal). The activity for the 2% NiY was only about one-fifth of that determined for the 0.5% RuY on the basis of specific activity. A 2% Ni/Al_2O_3 catalyst, however, had an activity more than a factor of 40 greater than the 2% NiY. The specific activity of the 0.5% RuY was about the same as that observed for the alumina-supported samples. The 0.5% RuCaY sample was nearly 50% more active than the sodium form and the 2% RuY displayed more than 10 times the activity of the 0.5% RuY on a weight basis.

For the bimetallic systems specific activities are plotted versus atom percent ruthenium in Fig. 2. The effect of addition of copper to the 0.5% RuY catalyst was to cause the specific activity to drop by one order of magnitude at an atomic ratio of 1:1. The activity of the 0.5% Ru, 2% CuY catalyst increased slightly, but this was probably due to errors of measurement as the activity of the catalyst was low. The specific activity for the ruthenium–nickel system first decreased when small amounts of nickel were added and then increased with the addition of more nickel. The addition of a large amount of nickel to the alumina-supported ruthenium resulted in an activity near that observed for the pure nickel on alumina.

Using the specific activities in conjunction with the specific adsorption data, the turnover numbers listed in Table 4 were calculated for the catalysts. Turnover numbers for the 0.5% RuY and 0.5% RuCaY were 9.4×10^{-3} and 15.9×10^{-3} sec^{-1}, respectively. The 2% RuY had a turnover number of three times that which was observed for the 0.5% RuY. A possible cause of this effect will be discussed later. Turnover numbers for the 0.5% Ru/Al_2O_3 also fell within this range. A commercial catalyst (Englehard) had a turnover number of 11×10^{-3} sec^{-1}, while that determined for a sample impregnated in this laboratory had a turnover number of 20 × 10^{-3} sec^{-1}. The turnover number obtained for the commercial catalyst was based upon an initial dispersion measurement as it was assumed to be a stabilized catalyst. Turnover numbers varied most widely between the supported nickel catalyst. The 2% NiY had a turnover number of 5 × 10^{-3} sec^{-1} while the 2% Ni/Al_2O_3 yielded a value of 230 × 10^{-3} sec^{-1}. As the dispersion for this catalyst was very low, the error in the adsorption measurement may account in part for the excessively high value. Where the approximation of a differential reactor was valid there was good agreement between the turnover numbers obtained using the two types of reactors.

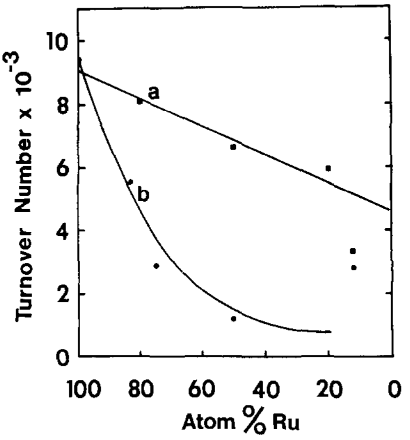

FIG. 3. Turnover number versus atom percent ruthenium in (a) ruthenium–nickel zeolites and (b) ruthenium–copper zeolites.

The turnover numbers for the bimetallic catalysts versus the atom percent ruthenium are plotted in Fig. 3. The ruthenium–nickel system demonstrated, in general, smoothly decreasing turnover numbers from 0.5% RuY to 2% NiY. The only exception was in the 0.5% Ru, 2% NiY which was 35% lower than that observed for the pure supported nickel. The ruthenium–copper system showed a more pronounced decrease in activity upon the addition of small amounts of copper to the RuY sample, but even at large Cu/Ru ratios the catalyst maintained considerable activity.

Kinetic parameters for methane formation are presented in Table 5. Activation energies obtained for 0.5% RuY and 2% NiY samples were 26.8 ± 0.8 and 23.0 ± 0.9 kcal $mole^{-1}$, respectively. The ruthenium–nickel alloys all displayed values which essentially fell within these bounds. An increase in the activation energy was observed for the ruthenium–copper system upon the addition of copper, as shown in Fig. 4.

TABLE 5

Kinetic Data[a]

Catalyst	$N \times 10^3$ (sec^{-1})	X	Y	Ea(kcal $mole^{-1}$)	A(sec^{-1})
0.5% RuY	9.4	1.38 (0.12)	−0.52 (0.07)	26.8 (0.8)	3.14×10^8
2% RuY	31.5	1.08 (0.42)	−0.63 (0.04)	26.5 (1.4)	5.73×10^8
2% NiY	5.0	0.66 (0.07)	−0.56 (0.07)	23.0 (0.9)	3.39×10^6
0.5% Ru, 0.07% CuY	5.5	1.35 (0.20)	−0.37 (0.07)	33.7 (2.8)	1.22×10^{11}
0.5% Ru, 0.1% CuY	2.96	1.58 (0.07)	−0.41 (0.08)	36.4 (4.3)	8.07×10^{11}
0.5% Ru, 0.3% CuY	1.23	—	—	29.7 (4.2)	—
0.5% Ru, 2% CuY	2.83	1.52 (0.10)	−0.59 (0.05)	28.3 (1.4)	3.55×10^{11}
0.5% Ru, 0.07% NiY	8.17	1.25 (0.05)	−0.58 (0.05)	23.1 (0.4)	8.02×10^6
0.5% Ru, 0.3% NiY	6.6	1.23 (0.15)	−0.42 (0.04)	22.9 (4.8)	6.93×10^6
0.5% Ru, 1.2% NiY	5.8	1.15 (0.06)	−0.31 (0.08)	24.2 (0.6)	2.28×10^7
0.5% Ru, 2% NiY	3.3	0.98 (0.12)	−0.43 (0.04)	27.3 (0.6)	9.95×10^7

[a] Assuming $N = A P_{H_2}{}^X P_{CO}{}^Y \exp[Ea/RT]$; numbers in parentheses represent standard deviations.

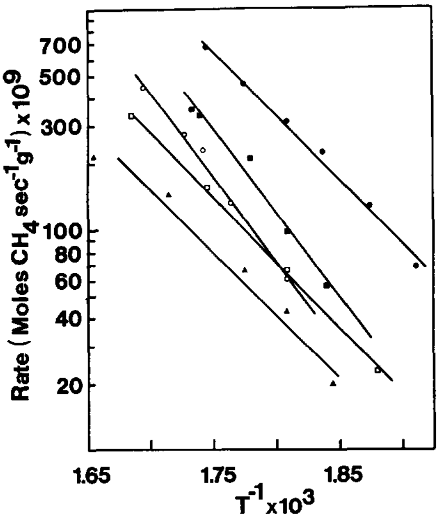

FIG. 4. Logarithm of the reaction rate versus reciprocal temperature for ruthenium–copper zeolites; ●, 0.5% RuY; ■, 0.5% Ru, 0.06% CuY; ○, 0.5% Ru, 0.1% CuY; ▲, 0.5% Ru, 0.3% CuY; □, 0.5% Ru, 2% CuY.

The pressure dependency with respect to CO showed no clear trends for the zeolite catalysts, but the presence of nickel caused the hydrogen pressure dependency to be somewhat lower than for pure 0.5% RuY. Furthermore, there was a fairly regular decrease in the hydrogen pressure dependency for the ruthenium–nickel catalysts as the nickel content was increased.

Selectivities were determined for several of the catalysts and the results are presented in Table 6. The addition of nickel to the ruthenium–zeolite catalyst increased the selectivity for the formation of CH$_4$ relative to that of the ruthenium zeolite, whereas, the addition of copper to the ruthenium up to 1:1 atomic ratio, decreased the selectivity. Initially the alkane to alkene ratios were large, but these ratios decreased dramatically upon exposure of the catalyst to the reactants for longer periods of time.

Decrease in activity. The decrease in activity for the supported ruthenium catalysts is shown in Fig. 5. When compared on the basis of percentage activity loss, the zeolite-supported catalysts lost activity by a factor of 3–4, whereas the alumina catalysts lost activity by a factor of 8–10 after 24 hr. The nickel catalysts could not be compared in this manner in the recirculating system as the rate of methanation for the alumina-supported sample was much higher and 100% conversion was realized too quickly. The effect of alloying the ruthenium with the nickel was observed in the recirculating system and is shown in Fig. 6. A remarkable stabilization in activity was obtained at an atomic ratio of nickel to ruthenium of ca. 7:1.

In the recirculating system it was necessary to periodically evacuate the gases and replace them with more H$_2$ and CO. To establish the possible effect of this evacuation on the activity of the catalyst, a flow system was employed and the decrease in activity was compared to that in the recirculating system. The decreases

TABLE 6

Selectivities for Hydrocarbon Formation

Catalyst	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$
0.5% RuY	85	8.0 (4.1[a], 0.7[b])	4.0 (1.9[a], 0.4[b])	3.0	0.3
2% NiY	92	4.1 (34, 22)	2.1 (3.6, 2.7)	1.4	0.1
0.5% Ru, 2% NiY	91	4.2 (84, 15)	3.1 (45, 4.5)	1.5	0.1
0.5% Ru, 0.3% CuY	76.5	10.8	7.8	3.6	1.2

[a] Initial alkane/alkene ratio.

[b] Alkane/alkene ratio after catalyst was exposed to reactants for 30 hr in flow system.

in percentage activity for several of the catalysts are given in Table 7. Agreement was good between the results from the two reactors.

In order to gain insight into the effect of possible poisons, a series of experiments was performed in which the catalyst was heated under an argon atmosphere or treated with water, methane, ethane, or carbon monoxide prior to reaction. To determine the volatility of the poisoning substance, following the deactivation of the 0.5% RuY catalyst, 200 Torr of argon was circulated over the catalyst at 400°C with the cold trap in place. The activity of the catalyst was not regenerated after 24 hr of this treatment. Therefore, it was concluded that the poison was not a volatile substance.

The addition of water (ca. 20 Torr) to the reactivated ruthenium catalyst for 10 min resulted in a slight increase in activity. Water also had no effect upon the activity of the nickel catalyst, and the 0.5% Ru, 2% NiY catalyst lost activity by only 10%.

Bosquet *et al.* (*6*) reported that methane had an adverse effect upon the reaction over supported nickel catalysts through product inhibition. Methane (25 Torr) was circulated over the reactivated catalyst for specified periods of time and the activity was compared to standard runs. A decrease in activity of about 10 to 15% was noted after 24 hr of exposure; therefore it is concluded that methane did not have any severe adverse effects upon the activity of the catalyst.

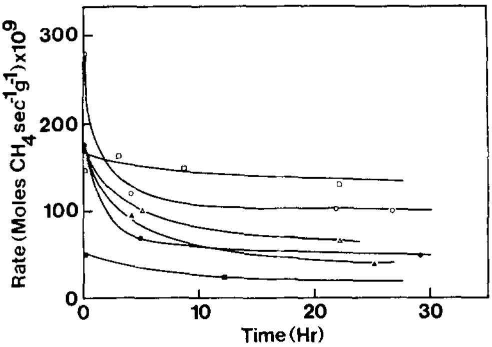

FIG. 6. Methanation activity versus time of exposure to reactants: ○, 0.5% RuY; ●, 0.5% Ru, 0.06% NiY; ▲, 0.5% Ru, 0.3% NiY; △, 0.5% Ru, 1.1% NiY; □, 0.5% Ru, 2% NiY; ■, 2% NiY.

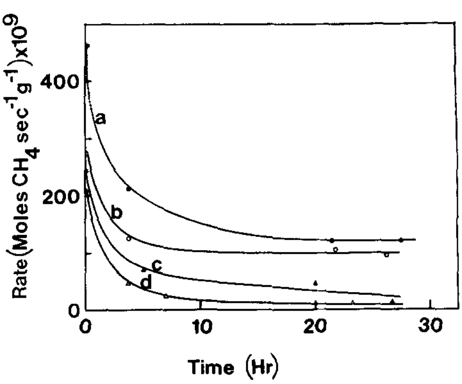

FIG. 5. Methanation activity versus time of exposure to reactants for 0.5% ruthenium catalysts; (a) 0.5% RuCaY, (b) 0.5% RuY, (c) 0.5% Ru/Al_2O_3, and (d) 0.5% Ru/Al_2O_3 (Engelhard).

The effect of ethane as a poison through the likely deposition of the products of hydrogenolysis was investigated. After reduction in hydrogen, 25 to 50 Torr of ethane was circulated over the catalyst for periods of 10 to 60 min at 280°C.

TABLE 7

Activity Loss (%) in 24 hr

Catalyst	Flow system	Recirculating system
0.5% RuY	62	64
0.5% RuCaY	68	77
0.5% Ru/Al_2O_3		94
0.5% Ru/Al_2O_3[a]		89
0.5% Ru, 0.06% NiY		73
0.5% Ru, 0.3% NiY		77
0.5% Ru, 1.1% NiY		63
0.5% Ru, 2% NiY	25	19
0.5% Ru, 2% Ni/Al_2O_3	24	
2% NiY	36	56
2% Ni/Al_2O_3	34	

[a] Commercial Englehard catalyst.

The activity of the catalyst decreased by less than 10%. Since the hydrogenolysis reaction is nearly first order in ethane and of a negative order in hydrogen, the rate of hydrogenolysis should be dependent upon the coverage of the surface by ethane. Therefore, short exposures of the catalyst to pure ethane would be expected to have a stronger effect on the deactivation than under methanation reaction conditions in which the surface would be covered by carbon monoxide.

The effect of the Boudouard reaction, i.e., the disproportionation of carbon monoxide, and the dissociation of CO were investigated as a possible source of the poison. Carbon monoxide (150 Torr) was circulated over the reactivated catalyst for specified periods followed by brief evacuation and introduction of reactants. The activity of the catalyst decreased by almost 50% after 28 hr. It is likely that the reaction or the dissociation of CO contributes to the formation of excess surface carbon.

In an attempt to determine the effect of other gas phase products upon the deactivation of the catalyst, two equivalent beds of the reactor were placed in series such that the second catalyst bed would see the products of the first. The gas stream was sampled both before and after the second bed. The activity for the second bed did not decrease more rapidly than the first bed, thus gaseous products of the reaction did not appear to contribute significantly to the deactivation of the catalyst.

DISCUSSION

Size and Location of Metal Particles

Both the deuterium chemisorption data and the results from the electron microscopy study indicate that the dispersion of ruthenium in the 0.5% RuY, the 0.5% RuCaY and the 2% RuY zeolites was very high, and the evidence from electron microscopy indicates that the average particle size was less than 10 Å. These dispersions agree favorably with those obtained by Boudart and Dalla Betta (*8*) for Pt in a zeolite; however, they are considerably greater than the values obtained for comparable loadings of ruthenium on alumina. The size of the particles, together with the ESCA data given in a subsequent paper (*12*), suggest that most of the metal remains within the zeolite crystallites. Furthermore, it may be concluded that the particles are not located in the sodalite units of the zeolite since the CO/D ratio was rather large, and it is generally believed that CO does not enter the small cavities at room temperature.

The reaction brings about a growth in particle size to an average of ca. 15 Å. This estimated value may be somewhat high since a substantial fraction of the ruthenium atoms would not be available for hydrogen adsorption if the large cavities of zeolite were filled with a metal cluster. Moreover, using the TEM technique the particles which are smaller than 10 Å are not counted. Thus, it appears likely that even after the reaction the ruthenium clusters remain in the large cavities which have a diameter of 13 Å. The ESCA data also substantiate this conclusion. The dispersions obtained here agree favorably with those reported by Coughlan *et al.* (*11*) following the reduction of ruthenium in a 4.4% RuY sample in which the metal was exchanged as the $[Ru(H_2O)_6]^{3+}$ ion.

As has been previously noted from chemisorption and ESCA studies (*27*), elemental nickel tends to form large crystallites which are located on the external surface of the zeolite. The low dispersions were characteristic of the Ni on both the zeolite and the alumina samples.

It is interesting to note in Table 2 and Fig. 1 that 0.5% Ru had a significant effect on the formation of smaller nickel particles. In contrast the addition of a modest amount of Ni to the Ru resulted in the growth of the Ru–Ni clusters, relative to the ruthenium clusters formed in the RuY zeolite. The presence of copper likewise brought about a significant decrease in the dispersion of the ruthenium. In all cases most of the bimetallic clusters are probably located on the external surfaces of the zeolite particles, especially after the reaction has occurred over the catalyst.

Since the silica-supported ruthenium–copper clusters have been studied by two groups, it is interesting to compare their results with those reported here. Both Sinfelt (*13*) and Bond and Turnham (*14*) have observed that the ruthenium dispersion did not vary by more than a factor of two as the Cu:Ru ratio was changed from zero to unity. The values of the dispersion for the metal clusters on the zeolite, determined after the reaction, were similar to those reported previously, and as indicated in Table 2 the addition of copper brought about a modest decrease in dispersion as determined by deuterium chemisorption. When CO was chemisorbed on the bimetallic clusters in the zeolite, a CO/D ratio of ca. 4 was obtained before the catalytic reaction and a more common value of 1.3 was obtained after the reaction, which may be compared with a value of 1.2, determined from the data of Sinfelt. Bond and Turnham (*14*) used only CO to determine the dispersion in their samples. The larger CO/H ratios have been reported by Dalla Betta (*28*) for more highly dispersed ruthenium, and the results were attributed to multiple adsorption of CO on Ru located at edge and corner sites. An alternate possibility is that CO dissociatively chemisorbs and then dissolves in the particles in a manner similar to that reported for rhodium at somewhat higher temperatures (*29*).

Kinetics

The initial turnover numbers reported in Table 4 for the three RuY catalysts compare favorably with the values reported for the two 0.5% Ru/Al_2O_3 samples (Table 4) and with the value of 18 sec^{-1} obtained by Dalla Betta *et al.* (*17*) for 1.5% Ru/Al_2O_3, corrected to the same conditions. Vannice (*16*) reported a much greater value of 181 sec^{-1} for 5% Ru/Al_2O_3. If one takes the lower turnover numbers as being representative of the activity of supported ruthenium then one may conclude that the zeolite does not have a large effect on the activity of the metal, even though the particles are located in the large cavities.

The initial turnover numbers for the 2% NiY catalyst, however, were dramatically lower than the values obtained in this study for 2% Ni/Al_2O_3 and by others for various loadings of nickel on alumina, where turnover numbers of 100×10^{-3} sec^{-1} are typical (*2*). If the dispersion was actually greater, as indicated by the TEM data, the turnover numbers for the NiY zeolite would be even less than the value reported here. Since most of the nickel particles are believed to have been on the external surface of the zeolite crystallites, the decrease in activity cannot be attributed to an effect of the zeolite cages. One possible reason for the lower activity may be found in the nature of other cations within the zeolite. Schoubye (*30*) has observed that the presence of basic oxides such as K_2O had a severe deactivating effect upon nickel. It was proposed that the basic oxide donates electron density to the nickel, thus causing its behavior to simulate that of copper, which is inactive for the reaction. Recently Huang and Richardson (*31*) have studied the methanation reaction over nickel supported on amorphous silica–alumina and silica–alumina treated with sodium ions. The reaction over nickel on the pure silica–alumina gave turnover numbers of 50×10^{-3} sec^{-1}. The turnover numbers increased to ca. 300×10^{-3} sec^{-1} upon addition of 0.3% by weight Na^+ but decreased to less than 100×10^{-3} sec^{-1} upon the addition of 2.5% Na^+. The zeolite has 6% Na^+, but quantitative comparison of the two types of aluminosilicates may not be valid since the sodium is uniformly distributed throughout the zeolite, but is restricted to the external surface of the amorphous silica–alumina. The sodium effect, though of lesser magnitude, may have occurred for the ruthenium Y zeolites where the turnover number for the 0.5% RuCaY was 60% greater than that observed for the 0.5% RuY which contained sodium as the other cation. The influence of the sodium ion could also account for the greater turnover number of the 2% RuY sample, since the exchange level of ruthenium was higher and the level of sodium was lower.

The decrease in methanation activity upon the addition of copper to ruthenium was similar, though not as severe as that observed by Bond and Turnham (*14*) for the addition of copper to 1% Ru/SiO_2 catalysts. Turnover numbers for our catalysts at a 1:1 ratio of Cu:Ru decreased by a factor of 10 while they observed that the activity decreased by a factor of 100. We also observed an increase in activation energy while they found no change in this parameter upon the addition of copper. The hydrogen pressure dependency remained constant for our catalysts as a function of copper content, contrary to the decrease which they observed. Some of these differences may be attributed to the fact that the supports were not the same in the two studies. Our results indicate that the presence of the copper influences not only the number, but also the nature of the active sites; i.e., both a geometric effect and a ligand effect are operative.

Similar to Bond, we observed a decrease in the selectivity for methanation upon the addition of copper. Data of Blakely and Somorjai (*32*) indicate that C–C bond breaking occurs for platinum on stepped surfaces which have kinks, i.e., sites of low metal coordination number. The theory of Burton *et al.* (*33*) would place copper atoms preferentially at low coordination sites within bimetallic clusters. Furthermore, Sinfelt (*13*) has noted that copper strongly inhibits the activity of ruthenium for hydrogenolysis. If during the methanation reaction higher hydrocarbons were simultaneously removed by hydrogenolysis, then one would expect that the addition of copper would favor the formation of higher hydrocarbons.

The addition of nickel to the ruthenium had a much more subtle effect upon the initial activity. The turnover numbers displayed a modest, linear decrease with respect to the addition of nickel, with an exception being the turnover number determined for the 0.5% Ru, 2% NiY sample which was 30% lower than that obtained for the pure nickel. This linear decrease in activity is expected for two metals which are both active for the methanation reaction. Contrary to expectations the specific activity of the Ru, NiY zeolites did not increase with nickel loading, even though ruthenium brought about a decrease in nickel particle size (Fig. 1c). Nevertheless, the influence of the nickel is seen in the kinetic parameters (Table 5), the selectivities (Table 6), and the stability of the catalysts (Table 7). These factors are evidence for alloy formation in the zeolites. On alumina the influence of ruthenium on the more active nickel component was small based on specific activity, but was much greater based on turnover numbers. Bartholomew (*15*) has noted that the specific activity of a Ni/Al_2O_3 catalyst was considerably greater than was observed for a Ru, Ni/Al_2O_3 catalyst under a high pressure test reaction.

The decrease in activity upon exposure of the methanation catalyst to the reactants and products is in agreement with the observations of other investigators (*17*). The greater loss in activity for the ruthenium supported on alumina relative to ruthenium in the zeolite indicates that the effect cannot be attributed to the plugging of the rather narrow pores in the zeolite. Furthermore, it should be noted that the decrease in activity was not the result of a decrease in dispersion since the activity could be regenerated by heating the sample in hydrogen.

The loss in activity of the supported nickel samples was significantly less than with supported ruthenium, and the 0.5% Ru, 2% Ni, both on the zeolite and the alumina, exhibited the highest stability of any of the catalyst studied. As indicated in Table 7, the greater stability for the ruthenium–nickel zeolites was only realized for the sample which contained the largest amount of nickel.

Of the various gases used to purposely poison the catalyst, CO had the most pronounced influence on initial activity. Restrup-Nielsen (*34*) investigated the deposition of carbon from CO and CH_4 over supported nickel catalysts and on a supported nickel–copper alloy. It was observed that the carbon deposition followed an inverse relationship with particle size. On a sample having an average particle size of 400 Å, carbon deposition began at 280°C for CO and at 230°C for CH_4. Although the support had no effect on the rate of deposition of carbon from either gas, alloying the nickel with copper decreased the deposition of carbon from the CH_4 but not from the CO.

On clean ruthenium single crystals it has been demonstrated that CO adsorbs molecularly, rather than dissociatively (*35*); however, at 550°C the decomposition of CO to form graphite has been observed (*36*). The deposition of graphite was most rapid on the low index planes. Dalla Betta and Shelef (*37*) observed that exposure of Ru/Al_2O_3 to CO at temperatures of 300°C and greater resulted in a reduction in amplitude of the CO infrared band and a shift in band position to lower wave numbers. It was suggested that the formation of a surface carbide may be responsible for these effects. Sexton and Somerjai (*29*) have reported that CO dissociates on rhodium films at moderate temperatures and that the dissociation is favored by contamination of the surface with oxygen or carbon. Furthermore, there is increasing evidence which indicates that the mechanism for the methanation reaction involves the dissociation of CO, followed by hydrogenation of the surface carbon. If this is correct, then it follows that a good methanation catalyst must be able to dissociate CO under reacting conditions.

The evidence reported here seems to indicate further that the decrease in activity is the result of the accumulation of excess carbon on the surface, and that the carbon is mainly produced by the dissociation of CO. If as Araki and Ponec (*5*) postulate, CO can be dissociated only on sites where carbon atoms can be bound to several metal atoms simultaneously, then the formation of carbon would be self-poisoning. The ultimate effect of carbon on the methanation rate would be determined by the relative rates of carbon deposition and the hydrogenation of the carbon. If the hydrogenation of surface carbon is rate determining, it follows that the catalyst could be poisoned by the build-up of excess carbon.

The enhanced stability of the 0.5% Ru, 2% Ni catalysts can be understood if it is assumed that rapid dissociation of CO occurs on sites containing several Ru atoms, although the dissociation of H_2 requires only two Ru or two Ni atoms. Nickel itself would, of course, dissociate CO at a modest rate. Incorporation of both Ru and Ni in the clusters would then decrease the activity for dissociation of CO, but would not significantly affect the hydrogenation activity. Thus, excess surface coverage by carbon would not occur.

CONCLUSIONS

Viewed from the perspective of catalyst utilization the following conclusions may be drawn from this work:

(i) The zeolite does not significantly affect the turnover number for Ru, but it does enable one to maintain a highly dispersed state of the metal.

(ii) Ruthenium and nickel, as well as ruthenium and copper, appear to form bimetallic clusters, for which the dispersion is less than that of pure Ru, but greater than that of pure Ni or pure Cu.

(iii) At high Ni/Ru ratios (7:1) the metal is in a state of moderate dispersion and the catalytic activity is stable with respect to time.

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