

Characterization and Catalysis of Pt-Cu Clusters in NaY

GIULIANO MORETTI¹ AND WOLFGANG M. H. SACHTLER²

Ipatieff Laboratory, Center for Catalysis and Surface Science, Department of Chemistry, Northwestern University, Evanston, Illinois 60208

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The metal clusters in Pt/NaY, Cu/NaY, Cu/NaHY, and Pt-Cu/NaY have been characterized by TPR, TPD, XRD, XPS, H₂ chemisorption, and methylcyclopentane (MCP) conversion as a catalytic probe. For Cu/NaY samples which had been calcined at 300°C the reduction proceeds by a two-step mechanism: Formation of Cu⁺ is followed by its reduction to Cu particles located in supercages and on the external surface of the zeolite. For acidic samples, Cu/NaHY, a high local concentration of protons prevents complete reduction to Cu⁰. Reduction of Pt/NaY calcined at 300°C results in small Pt particles in the supercages. Pt strongly catalyzes the reduction of Cu; the Cu TPR peaks merge with the Pt TPR peaks. This is even the case if initially all Pt ions are located in supercages and all Cu ions in hexagonal prisms. The reduced bimetal particles do not show memory of the original location of the ions prior to reduction. The surface of the particles is enriched in Cu, and the turnover frequency for MCP ring opening is low. The selectivity toward *n*-hexane, 2-methylpentane, and 3-methylpentane shows characteristic changes with composition and size of the bimetal particles. These results are rationalized in terms of a tentative model based on the geometry of particles and cages. © 1989 Academic Press, Inc.

A. INTRODUCTION

During the last decade considerable research effort has been directed toward the characterization of metallic particles entrapped in zeolite supports (1). There are strong incentives for work in this field. First, the geometrical constraints imposed by zeolite geometry can impose a peculiar selectivity to reactions catalyzed by the metal particles. Second, the chemical nature of the zeolite can be varied from being essentially inert to acidic. Bifunctional catalysts, containing a metal and an acidic function, are of potential use as reforming catalysts in the petroleum and petrochemical industries. The metal function can further be modified by using bimetallic catalysts, as is now done on a world-wide industrial scale with alumina-supported reforming catalysts. In comparison to their

monometallic counterparts bimetal catalysts often have superior activity, selectivity, and/or activity maintenance (2), and third, due to the presence of pores of dimensions comparable to the molecular dimensions, the metal particles produced by reduction of the exchanged metal ions can be very small. These particles, due to the unique physical and chemical properties of small aggregates of atoms (3), could present unusual catalytic activity and selectivity.

Elliott and Lunsford studied Ru-Ni and Ru-Cu bimetallic clusters entrapped in NaY (4). Naccache and co-workers characterized Pt-Cu, Ir-Cu, Ru-Cu, and Rh-Cu in NaY zeolites (5) and Pt-Cu in an ultrastable Y zeolite (6). Pt-Mo in Y zeolites has been studied by Tri *et al.* (7). Pt-Re in NaHY has been studied in our lab (8). Maskos and van Hooff reported for Ni-Cu in NaY that after reduction large alloy particles were formed at the outer surface of the zeolite crystal (9).

Previous results on the Pt-Cu/NaY cata-

¹ On leave from Centro di Studio del CNR "SACSO," Chemistry Department, University "La Sapienza," Rome, Italy.

² To whom correspondence should be addressed.

lyst have shown that after reduction at 500°C bimetallic clusters are formed in the supercages. The addition of copper decreased the specific activity of Pt for *n*-hexane hydrogenolysis and benzene hydrogenation (5). The overall activity and the selectivity toward isomerization of *n*-octane is enhanced by the addition of Cu to Pt in an ultrastable Y zeolite. It was proposed that increases in the acidic function and the number of metallic particles were responsible for this behavior (6). In the present paper we primarily intend to address two problems inherent to bimetal/zeolite systems, which should be clarified. First, it is known for amorphous supports such as alumina that the reduction of bimetal systems is not simply additive. For Pt + Re, e.g., it has been shown in our lab by TPR that the rhenium precursor can be reduced at much lower temperatures in the presence of Pt than in its absence (10). However, it has also been demonstrated that this effect is dependent on the surface mobility of the Re precursor: if it is immobilized by forming a surface compound with the support, its reduction is not catalyzed by Pt and very little formation of bimetallic clusters is observed (10).

For zeolite-supported systems no published work is known on the mutual effect of the reducibility of two metal precursors in the same zeolite, but our recent results with Ni + Pt show that the catalytic effect of Pt on the reduction of the second metal can be quite dramatic (11). One question which motivates the present research, therefore, concerns the possible catalysis of Cu reduction by the presence of Pt and the concomitant formation of bimetallic PtCu particles.

The second problem, motivating the present research, concerns the catalytic selectivity of the bimetallic catalysts. It is well known that alloying changes selectivity by changing the size of the relevant ensembles. If such bimetal particles are formed in zeolites, an additional effect on the selectivity which is basically of geomet-

ric origin is conceivable. Previous results with supported platinum as the catalyst show that the product pattern in the hydrogenolytic opening of the five-membered ring in methylcyclopentane depends in a characteristic way on the support (12). For Pt particles located inside Y zeolites it has been suggested that each particle fills its supercage incompletely (13); molecules can therefore be adsorbed in the narrow space between metal particle and cage wall. The geometric constraints of this peculiar situation prevent the adsorbed molecule from rolling over (14). Other work in our lab on the genesis of the reduced platinum particles suggests that a different geometry would be predicted for bimetallic/zeolite combinations (15, 16). The metal which is reduced first will act as a nucleation site for atoms of the second metal. As a result, particles will completely fill their cages or even bulge into adjacent cages. This should result in a different stereoselectivity of reactions catalyzed by such particles. In the present work we, therefore, address the question of changes in catalytic activity and selectivity that are caused by adding Cu to Pt, and we decided to use the conversion of methylcyclopentane as a test reaction which not only registers changes due to the by now familiar ensemble effect (17) but also probes for changes in the size and shape of the catalyzing metal particle.

B. EXPERIMENTAL

B.1. Sample Preparation

The catalysts were prepared starting with NaY zeolite, Linde (LZ-Y52) from Union Carbide. The monometallic Pt/NaY and Cu/NaY and the bimetallic Pt-Cu/NaY samples were obtained by the ion-exchange method. Two procedures were employed in the preparation of bimetallic samples. In the first the Pt ions were exchanged from an aqueous solution of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ (from Matheson) containing about 200 ppm of Pt. The exchange was done at 80°C for 12 hr adding dropwise the necessary amount of solution to the NaY slurry, under vigorous

TABLE 1
Chemical Composition of the Pt-Cu/NaY Catalysts

| Catalyst | wt% Pt (atoms/uc) | wt% Cu (atoms/uc) | Cu/Pt (atomic) | Pt% (atomic) |
|-----------------------|----------------------|----------------------|-------------------|-----------------|
| Pt/NaY | 2.4 (2.1) | — | — | 100 |
| Pt-Cu/NaY | 2.5 (2.2) | 0.3 (0.8) | 0.37 | 73 |
| Pt-Cu/NaY | 2.4 (2.1) | 0.6 (1.6) | 0.77 | 56 |
| Pt-Cu/NaY | 2.4 (2.1) | 0.8 (2.1) | 1.0 | 50 |
| Pt-Cu/NaY | 2.4 (2.1) | 2.4 (6.5) | 3.1 | 24 |
| Cu/NaY, pH 7 | — | 0.8 (2.1) | — | 0 |
| Cu/NaY, pH 5 | — | 0.8 (2.1) | — | 0 |
| Cu-Pt/Na ^a | 2.4 (2.1) | 0.8 (2.1) | 1.0 | 50 |

^a Sample prepared starting from Cu/NaY, pH 7, calcined at 500°C in O₂ for 2 hr.

stirring. All the prepared catalysts contained about the same Pt loading, corresponding to about two ions per unit cell (uc).

The exchanged zeolite was filtered and washed until no Cl⁻ was detectable. At this point the Cu ions were exchanged from a solution of about 200 ppm of Cu(NO₃)₂ (from Aldrich) at room temperature for 4 hr. The copper solutions were added dropwise to prepare samples with the Cu/Pt ratios ranging from 0.3 to about 3.

In the second procedure the Cu ions were exchanged first and a calcination step at 500°C in O₂ for 2 hr was done before the exchange of the Pt ions. According to this procedure we prepared the catalyst with a Cu/Pt ratio equal to 1.0.

Cu/NaY was also prepared in two different ways. In the first, we followed the normal procedure, with the pH of the solution equal to about 7. The second preparation was done by adjusting the pH of the solution to 5, using a dilute solution of HNO₃. The slurry containing NaY in deionized water was prepared maintaining the ratio of 1 g of zeolite/100 ml of solution. Quantitative analysis of Pt and Cu was done by atomic absorption of the solutions before and after the exchange.

In Table 1 we report relative metal loadings, copper/platinum metal ratios, and corresponding number of atoms per unit cell for all samples.

Before any characterization or catalytic study the catalysts were calcined in O₂ from room temperature to 300°C at a heating rate of 0.5°C/min and a flow rate of 1000 ml/min/g of catalyst. Then they were kept at 300°C first for 2 hr in O₂ and then 1 hr in Ar or He. Under these conditions, after the decomposition of the ammine complex, the Pt ions were placed in the supercages (13, 16). For the copper ions, it has been reported that at this relatively low calcination temperature the major portion of the ions should be located in the supercages, while the samples calcined at 500°C should contain only copper ions in sites I and I' (18). Upon rehydration the Cu²⁺ ions remain localized in sites I and I' (18).

B.2. XRD

X-ray diffraction (XRD) patterns of the samples after the calcination step and after reduction in H₂ were recorded by means of a Rigaku X-ray diffractometer using CuK α radiation (Ni filtered). The spectrum of pure NaY, recorded under the same experimental conditions, was used as reference.

B.3. XPS

X-ray photoelectron (XPS) spectra were taken on an ESCALAB spectrometer with AlK α or MgK α radiation working at constant transmission energy (50 eV). The binding energy reference was chosen as the Si(2p) line at 102.9 eV (19). Samples were prepared by pressing the zeolite in a stainless-steel die. The samples were studied after calcination and after the TPR/TPD experiments. The spectra were accumulated in a multichannel pulse height analyzer and then analyzed using a computer program for smoothing, background subtraction, and curve fitting of the peaks. The samples after TPR/TPD experiments were reduced for 5 min in H₂ at 500°C in the

ESCALAB cell to eliminate the effect of air exposure and then transferred to the analysis chamber under UHV conditions.

B.4. TPR/TPD

The apparatus used for the temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) experiments was already described in a previous paper (20). The calcined catalysts were cooled to -80°C in Ar and then the atmosphere was changed to 5% in H_2/Ar . For TPR a flow rate of 25 ml/min and a heating rate of $8^{\circ}\text{C}/\text{min}$, up to 530°C , was used. The TPD spectra were recorded by flowing Ar over the reduced catalysts which had been cooled to room temperature in H_2/Ar , using the same parameters as those in the TPR experiments.

B.5. H_2 Chemisorption

Measurements of hydrogen chemisorption at room temperature were carried out in a vacuum system with a Datametric pressure transducer whose reference side was evacuated at 10^{-5} Torr. The calcined catalysts were reduced in flowing H_2 for 2 hr at 300 or 450°C . They were then purged in Ar for 15 min at the reduction temperature, cooled to room temperature, and evacuated at 10^{-5} Torr. H_2 was admitted and its pressure increased from 30 to 180 Torr. After the isotherm for total adsorption was determined, the samples were evacuated at room temperature, and a second adsorption isotherm was measured. The difference between the two adsorption measurements, extrapolated to zero pressure, represents the strong chemisorption of hydrogen.

B.6. Catalytic Tests

Methylcyclopentane (MCP) conversion was carried out in a continuous-flow micro-reactor at atmospheric pressure as described previously (12). The experimental conditions were as follows: 250°C , a flow rate of 50 ml/min, and a H_2/MCP ratio of about 18. The amount of zeolite used in every experiment was about 0.1 g. The total

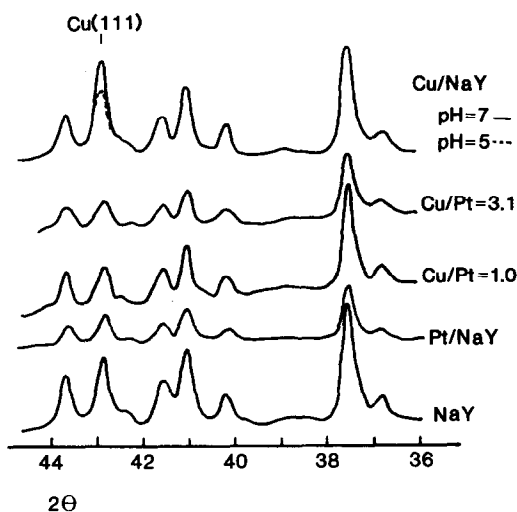


FIG. 1. XRD patterns of NaY, Pt/NaY, Cu/NaY (prepared at pH 5 and 7), and Pt-Cu/NaY samples (with Cu/Pt = 1.0 and 3.1), after reduction in H_2 at 450°C for 2 hr.

conversion was always under 20%. Reaction products were analyzed by an on-line HP 5794A gas chromatograph equipped with a 50-m crosslinked methyl silicone fused silica capillary column and a FID detector.

C. RESULTS AND DISCUSSION

C.1. X-Ray Diffraction

XRD patterns of the samples were recorded after calcination and after reduction in H_2 for 2 hr at 300 or 450°C . All calcined samples showed only the XRD features of the NaY zeolite. With the reduced samples we were able to detect a metal phase only for the Cu/NaY sample prepared at pH 7. In Figure 1 the XRD spectra of a series of samples reduced at 450°C are shown. These results indicate that under our experimental conditions in the Pt/NaY and Pt-Cu/NaY samples after reduction very small metallic clusters are formed with dimensions less than 40 \AA . Our result for Cu/NaY prepared at pH 7 is in agreement with previous literature data (21). After reduction the Cu(111) reflection is present (see Fig. 1) indicating the formation of large metal particles on the

external surface of the zeolite. The sample prepared at pH 5 does not present the Cu(111) reflection after reduction, suggesting that no metal phase can be formed or that reduced metal atoms form very small clusters entrapped in the zeolite matrix.

The color of the Cu/NaY sample prepared at pH 7 after reduction was reddish while the sample prepared at pH 5, which is actually acidic Cu/NaHY (see under XPS Analysis), was white. As previously reported by Petunchi and Hall (22), this difference in the color of the two samples could be an indication of complete reduction in the case of Cu/NaY and formation of Cu^+ ions in the case of Cu/NaHY. This is confirmed by our TPR data (vide infra).

C.2. XPS Analysis

The experimental binding energies of the XPS peaks for the Pt–Cu/NaY samples with Cu/Pt = 1.0 in the calcined and reduced form show the presence of Pt($4f_{7/2}$) peaks at $E_B = 73.2$ eV (Pt^{2+}) and at $E_B = 71.7$ eV (Pt^0), respectively. These data are in agreement with previous results reported by Védrine *et al.* (19) for Pt/NaY. The Cu($2p_{3/2}$) peak for the same samples was constant at $E_B = 932.7$ eV, and no satellite peaks were present. This indicates that Cu is reduced to either Cu^{1+} and/or Cu^0 . It was not possible to distinguish between these by measuring the Cu (L_3VV) Auger transition, for which a chemical shift of about 2 eV would permit an unambiguous assignment (23), because the Cu loading of our samples was too low to determine this Auger peak whose intensity amounts only to about 20% of the photoelectron peak. The oxidation state of the Cu in our samples has, however, been identified by TPR as is shown below.

Autoreduction of Cu^{2+} ions to Cu^+ in NaY zeolite after thermal treatment *in vacuo* or in an inert dynamic atmosphere was reported by Jacobs *et al.* (24). Our results for the Cu/Pt = 1.0 and Cu/NaY samples, prepared at the two different pH values, show that the same process occurs when

the sample is under vacuum in the presence of ionizing radiation.

For the sample with Cu/Pt = 1.0 the intensity ratios between the Cu($2p_{3/2}$) and Pt($4f$) peaks are equal for the calcined and the reduced catalysts. This suggests that bimetallic clusters with constant composition are formed. A similar result for the reduced Pt–Cu/NaY sample was previously reported by Tebassi *et al.* (5).

For the two monometallic Cu samples the Al($2p$)/Si($2p$) intensity ratio is constant and, within experimental error, close to the theoretical value. The Na($2s$)/Si($2p$) intensity ratio for the sample prepared at pH 5 is about 30% less than that obtained for the sample prepared at pH 7. This shows that protons replace Na^+ ions during exchange at pH 5. Therefore, this sample will be referred to as Cu/NaHY. The Cu/Si intensity ratio does not depend on the pH of the solution.

From the intensity ratios and the cross sections reported by Scofield (25) atomic ratios can be calculated. Within 15% these values are in agreement with the values of the chemical analysis. These results are summarized in Table 2. From the Na/Si atomic ratio the unit cell formula of Cu/NaHY is calculated to be $\text{Cu}_{2.1}\text{Na}_{32.6}\text{H}_{19.2}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}$.

C.3. TPR and TPD Spectra

C.3a. Monometallic samples. In Fig. 2 TPR spectra are displayed for Pt/NaY, Cu/

TABLE 2

Atomic Ratios by XPS for Cu/NaY Samples (Prepared at pH 7 and 5) and the Bimetallic Sample with Cu/Pt = 1.0

| Sample | Na/Si | Al/Si | Cu/Si | Pt/Si | Cu/Pt |
|--------------|-------|-------|-------|-------|-------|
| Cu/NaY, pH 7 | 0.36 | 0.34 | 0.014 | — | — |
| Cu/NaY, pH 5 | 0.24 | 0.36 | 0.015 | — | — |
| Theor. | 0.38 | 0.41 | 0.015 | — | — |
| Cu/Pt = 1.0 | | | | | |
| Calcined | 0.36 | 0.35 | 0.018 | 0.018 | 1.0 |
| Reduced | 0.33 | 0.35 | 0.016 | 0.016 | 1.1 |
| Theor. | 0.35 | 0.41 | 0.015 | 0.015 | 1.0 |

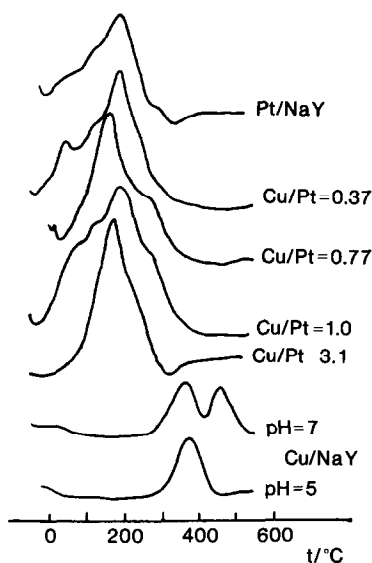
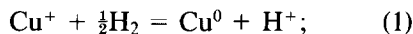


FIG. 2. TPR spectra for the monometallic Pt/NaY, Cu/NaY (prepared at pH 7 and 5), and the bimetallic Pt-Cu/NaY samples.

NaY, Cu/NaHY, and a number of bimetallic samples with different Cu/Pt ratios. The TPR profile of Pt/NaY is in agreement with previous results obtained in this laboratory (13, 16). After calcination in O_2 at $300^\circ C$ the Pt^{2+} ions remain in the supercages; their reduction is completed at $300^\circ C$. For the Cu-containing samples the TPR profiles depend on the acidity of the zeolite. As mentioned above, the Cu/NaY, prepared at pH 7, is nonacidic, but Cu/NaHY, prepared at pH 5, has exchanged Na^+ ions against protons. The TPR spectrum of Cu/NaY shows two peaks at 370 and $460^\circ C$. The hydrogen consumptions correspond to $H/Cu = 1.2$ and 0.8 , respectively, and the sum of both peaks corresponds to complete reduction from Cu^{2+} to Cu^0 . In the spectrum of Cu/NaHY the second peak is missing; the first peak corresponds, again, to $H/Cu = 1.2$. After the TPR, Cu/NaHY is white, while the reduced Cu/NaY is pink-violet. In accordance with results by Herman *et al.* (21) and Petunchi and Hall (22) we assume that the peak at $370^\circ C$ corresponds to reduction of Cu^{2+} to Cu^{1+} with 20% of the Cu becoming Cu^0 . The second peak for Cu/NaY is

then assigned to the final reduction of Cu^{1+} to Cu^0 . This process does not occur for Cu/NaHY under the conditions of our TPR experiment. We, therefore, assume that an equilibrium is established,



i.e., the Cu^0/Cu^+ ratio at given temperatures should increase with $\sqrt{P_{H_2}}$, but decrease with the concentration of protons in the zeolite. This assignment is confirmed by the TPD spectra in Fig. 3. Although no hydrogen is chemisorbed by Cu at room temperature, the Cu/NaY sample shows an intensive hydrogen evolution at temperatures near $500^\circ C$; this evolution is absent for Cu/NaHY. Evidently this TPD peak does not represent a true desorption of previously adsorbed hydrogen, but at high temperatures and negligible hydrogen pressure the equilibrium (1) is shifted toward the left; i.e., zeolite protons reoxidize Cu atoms, and entropy is increased by release of gaseous hydrogen. An analogous reoxidation by protons of metal atoms in small zeolite cages had been observed in this lab for Pt/NaY and Ni/NaY (13, 11). We have also compared TPR spectra of the present samples after reoxidation in O_2 at $500^\circ C$ for 1 hr. For Cu/NaHY, hydrogen consumption is larger in the second than in the first TPR.

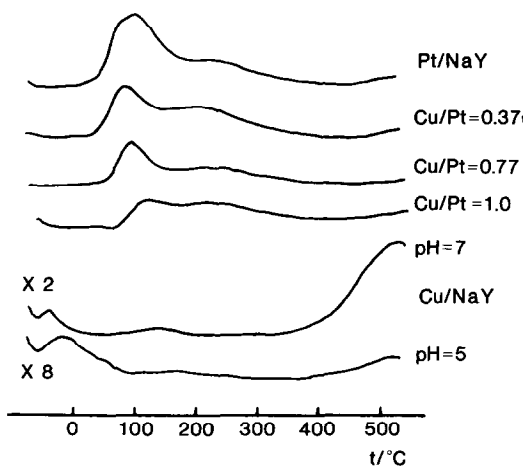


FIG. 3. TPD spectra for Pt/NaY, Cu/NaY (prepared at pH 7 and 5), and bimetallic Pt-Cu/NaY samples.

This suggests that after reoxidation part of the Cu^{1+} ions have migrated to supercages where they are reduced more easily. A similar result was reported by Petunchi and Hall (22). For Cu/NaY the spectra suggest that reoxidation results in the formation of CuO. This CuO is well dispersed and is reduced at a much lower temperature ($\approx 150^\circ\text{C}$) than unsupported CuO ($\approx 310^\circ\text{C}$).

C.3b. Bimetallic samples. For the bimetallic samples the reduction of all metal ions, Pt and Cu, is complete at about 300°C . It follows that reduction of copper ions is strongly catalyzed by the presence of platinum. The Cu TPR peaks at 370 and 460°C are shifted to much lower temperatures and merge with the Pt peak near 200°C . No intermediate formation of Cu^+ ions can be detected in the presence of Pt. As mentioned in the Introduction, this result shows that Cu ions are highly mobile in the zeolite at 250°C . As the calcination program used in the work was geared toward forcing the Cu ions into sodalite cages, while Pt ions were kept in supercages, it was of interest to see how reduction would respond to a different initial location of the ions. The results clearly show that the samples with Cu/Pt = 1.0, prepared according to the two different procedures, gave virtually indistinguishable TPR spectra, and show, again, that migration of copper ions between zeolite cages is rapid under these conditions. This conclusion is in accordance with results in the literature. Gallezot *et al.* (26) reported that for Cu/NaY the addition of pyridine, naphthalene, or butene at room temperature induced an important migration of the Cu^{2+} ions from sites *I* and *I'* to sites in the supercages where they can interact with the sorbed molecules. A similar result was reported by Maxwell *et al.* (27) for a Cu/NaY catalyst after adsorption of butadiene at room temperature. We conclude that in our bimetallic samples the copper ions migrate out of small cages and become reduced in contact with Pt clusters in the presence of H_2 .

The TPD spectra are also of interest. No

hydrogen is chemisorbed by the Cu; the H/Pt ratio is high (≈ 0.9) for pure Pt and decreases with increasing Cu content to 0.45 for Cu/Pt = 1.0. The TPD profiles show two maxima, the first at about 100°C and the second at about 200°C . It is remarkable that the position of the maxima does not depend on the Cu/Pt ratio. This confirms the conclusion that the "electronic effect" of Cu on the Pt-H bond strength is negligible. For very high Cu/Pt ratios the high-temperature peak is broadened.

C.4. H_2 Chemisorption

The results of hydrogen chemisorption, after H_2 reduction at 300 and 450°C for 2 hr, are reported in Fig. 4 and Table 3. The sample containing only copper does not chemisorb H_2 at room temperature. Measured H/Pt values of PtCu_x samples are always lower than those for Pt samples in accordance with previous work on Group VIII-Group IB alloys on a variety of supports. It thus appears that any adsorption of H atoms, spilling over from Pt to Cu atoms, may be disregarded for the conditions used here. The H/Pt values, conventionally termed "Pt dispersions," thus basically "count" the Pt atoms in the surface of the

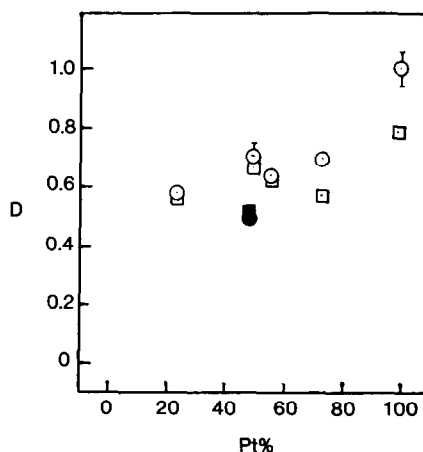


FIG. 4. Pt dispersion D ($= \text{H/Pt}$) by H_2 chemisorption at room temperature of Pt-Cu/NaY catalysts after reduction in H_2 for 2 hr at 300°C (\odot) and at 450°C (\square). Solid points represent the samples prepared from Cu/NaY, pH 7, calcined in O_2 at 500°C for 2 hr.

TABLE 3

Platinum Dispersion D ($= H/Pt$) of Pt-Cu/NaY Catalysts after Reduction with H_2 at 300 or 450°C for 2 hr by H_2 Chemisorption at Room Temperature

| Sample, Cu/Pt | D ($T_r = 300^\circ\text{C}$) | D ($T_r = 450^\circ\text{C}$) |
|------------------|-----------------------------------|-----------------------------------|
| 0 | 1.0 | 0.80 |
| 0.37 | 0.70 | 0.57 |
| 0.77 | 0.64 | 0.64 |
| 1.0 | 0.66 | 0.67 |
| 3.1 | 0.58 | 0.58 |
| 1.0 ^a | 0.51 | 0.50 |

^a From Cu/NaY, pH 7, calcined at 500°C in O_2 for 2 hr.

(bi)metallic particles; they will be used in calculating the turnover frequency (TOF) of MCP conversion.

It is interesting that the H/Pt values for two Cu/Pt = 1.0 samples prepared in different ways are similar, but slightly lower for the sample in which Cu/NaY had been calcined in O_2 at 500°C for 2 hr to chase all Cu ions into sodalite cages. This is expected on the basis of our model which assumes that during reduction Pt particles are formed first and then act as nucleation sites for Cu atoms leaving sodalite cages. After their adsorption and reduction the Pt particle would be covered with Cu atoms, but subsequent reconstruction to the energetically most favorable atomic arrangement again brings Pt atoms to the particle surface, thus increasing the H/Pt value. The lower H/Pt value of the sample, which has initially all Cu ions in the sodalite cages would then indicate that reconstruction is not complete.

The most striking result of Fig. 4 is the approximately constant H/Pt value of ≈ 0.6 for a wide variety of Cu/Pt values and reduction temperatures. This result is similar to that obtained by Naccache and co-workers for Pt-Cu/NaY and Pt-Cu in ultra-stable Y zeolites (5, 6). We interpret this result by assuming that particles with 20% Cu have a surface composition of 40% Cu and 60% Pt in accordance with the well-known surface enrichment of such alloys.

Adding more Cu to such a particle by the mechanism described in the previous paragraph causes the particle to swell like an inflating balloon, but it does not change the ultimate surface composition appreciably. The particles with 80% Cu are just bigger, but have surface composition similar to that of the particles with 20% Cu. This interpretation is in agreement with our previous results on the growth mechanism. Reduction of a metal/zeolite system containing all reducible ions in the supercage, as is the case for Pt calcined at 300°C, results in small primary particles, which are electro-neutral and therefore migrate easily through the zeolite. After coalescence of similar particles a critical size is reached, where the metal particle is too big to traverse the cage windows, but is smaller than the cage diameter. This situation represents the final state for such monometal catalysts. In the case of (Pt + Cu)NaY, however, the particles can grow further by capture and reduction of Cu ions migrating out of the sodalite cages. The bimetallic particles thus can completely fill their cages or even bulge into adjacent cages. Such particles have been called "grape-shaped" (13, 16). While they grow, they remain, of course, subject to the thermodynamic principle of minimizing their surface energy, which in the case of Pt + Cu and a reduction temperature near 350°C appears to tend toward a 40 : 60 composition for Cu : Pt on the surface, while the composition of the interior of the particle may vary within wide limits.

C.5. MCP Conversion

Methylcyclopentane is one of the simplest molecules for which a significant structure sensitivity has been observed in its conversion selectivity. Very large changes in the ratio of the ring-opening products have been reported by Gault and co-workers (28) for Pt/Al₂O₃ catalysts of different dispersions. Another advantage of MCP is that the reaction pattern is characteristically dependent on the acidity of the

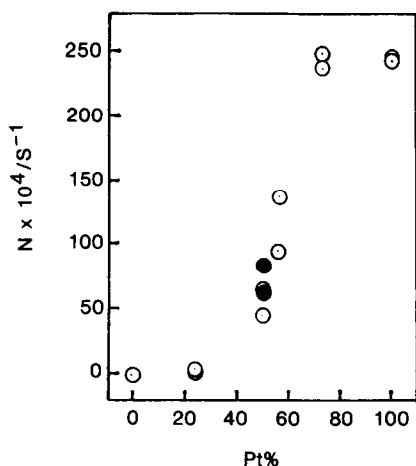


FIG. 5. Turnover frequencies for MCP conversion on Pt-Cu/NaY catalysts at 1 atm, $H_2/MCP = 18$, and $250^\circ C$ as a function of Pt atomic percent. Data after 5 min on stream. Solid points represent samples prepared from Cu/NaY, pH 7, calcined in O_2 at $500^\circ C$ for 2 hr.

support: for Pt/NaY, hydrogenolytic ring opening is the prevailing reaction at $250^\circ C$, but for the same metal on an acidic support, i.e., Pt/HY, ring enlargement to the six-membered ring molecules cyclohexane and benzene prevails, whereas ring opening is then only an insignificant side reaction (12). The present results show that addition of Cu to Pt/NaY alters both the activity per site and the selectivity. Both effects will now be discussed.

From Fig. 5 it is evident that the turnover frequencies, after 5 min on stream, for the disappearance of MCP decrease with increasing copper/platinum ratio in the catalysts. While the copper content increases to 50% the TOF is lowered about five times. The sample containing copper only is completely inactive under our experimental conditions.

A possible cause of the decrease in TOF is that larger Pt_n ensembles are required for the hydrogenolysis of MCP than for the simple adsorption of hydrogen. This is in accordance with numerous studies on hydrocarbon hydrogenolysis and will not be reiterated here. It is also certain that in Pt-

Cu alloys the Pt atoms maintain their individuality, because no electron transfer from one component to the other occurs (29). The question then arises why the TOF is not constant in the range of Cu/Pt ratios where the H/Pt ratio is approximately constant. Two possible causes can be considered. First, deactivation cannot be excluded. Although all bimetallic catalysts mentioned in Table 4 were prepared at pH 7, protons are introduced during the reduction of the metal ions. As the Pt content is kept constant for these samples, the highest metal load and, consequently, the greatest acidity after metal reduction, is expected for the sample with the largest Cu/Pt ratio, viz. 3.1; this sample contains about 18 protons per uc after reduction. Indeed ring enlargement, the typical acid-catalyzed reaction involving carbenium ions, is found to be largest for this sample, viz. 37%. A consequence of the introduction of Brønsted sites is that carbenium ions, known as notorious coke precursors, are easily formed at temperatures where the methylcyclopentane/methylcyclopentene equilibrium is established. Although we tried to minimize the effect of catalyst deactivation by basing TOF values on rates measured at 5 min on stream, it is conceivable that even in this short time the samples with higher metal load are significantly deactivated. Work is in progress in our lab to measure the amount of coke deposition by temperature-programmed oxidation.

A second possible cause of the precipi-

TABLE 4
Ring Enlargement and Cracking of MCP
on Pt-Cu/NaY

| Sample, Cu/Pt | Cyclohexane | Benzene | Cyclopentane |
|---------------|-------------|---------|--------------|
| 0 | 0.36 | 0 | 1.7 |
| 0.37 | 0.34 | 0 | 1.1 |
| 0.77 | 0.66 | 0 | 2.1 |
| 1.0 | 1.7 | 0 | 5.2 |
| 3.1 | 33.1 | 3.8 | 0 |

Note. Moles of product per 100 mol of MCP converted after 65 min on stream.

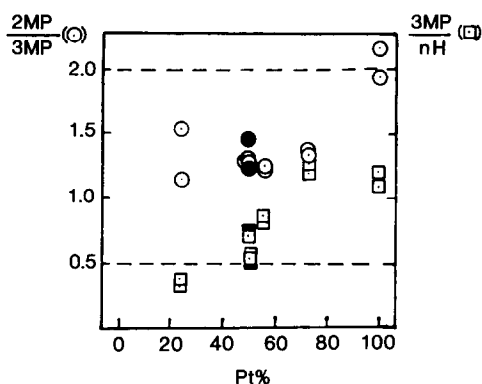


FIG. 6. 2MP/3MP and 3MP/ n H molar ratios as a function of Pt atomic percent. The statistical values are represented by the dotted lines; 2MP/3MP = 2 and 3MP/ n H = 0.5. The solid points represent samples prepared from Cu/NaY, pH 7, calcined in O₂ at 500°C for 2 hr.

tous decrease in TOF for samples with H/Pt = 0.6 could be due to the scattering of the actual composition of individual PtCu_x particles around the average composition. MCP hydrogenolysis probes for particles with large Pt ensembles on the surface. The number of such particles will steeply decrease as Pt atoms become more diluted in a Cu-rich surface.

As to the selectivity of ring opening, Gault and co-workers found with Pt/Al₂O₃ (28) that at Pt dispersions of the same order as that in our samples only a nonselective mechanism is operative, leading to a statistical product distribution for 2-methylpentane (2MP), 3-methylpentane (3MP), and n -hexane (n H) of 2MP:3MP: n H = 2:1:2 reflecting the number of C-C bonds in the C₅ ring leading to the particular product. Figure 6 shows the observed selectivity of MCP ring opening expressed as 2MP/3MP and 3MP/ n H ratios as a function of the copper content. The statistical values, viz. 2MP/3MP = 2 and 3MP/ n H = 0.5, are also included in the figure as dashed horizontal lines. The observations then can be summarized as follows:

1. The 3MP/ n H ratio for Pt/NaY exceeds the statistical value by a factor of 2, in

agreement with earlier results (12); with increasing Cu/Pt ratio it decreases toward the statistical value.

2. The 2MP/3MP ratio has the statistical value for Pt/NaY, in agreement with earlier results (12); with increasing Cu/Pt ratio it decreases significantly.

The chemical interaction between reduced metal and zeolite is known to be weak, and the effect of alloying Pt with Cu is known to affect adsorption and catalysis predominantly by changing the concentration of multiatomic Pt ensembles on the surface, while any modification of the electronic characteristics of the adsorbing Pt atoms is negligible. None of these phenomena can thus explain the selectivity effects observed in the present study. Therefore it appears justified to attempt a speculative rationalization in terms of the geometry of the metal particles inside the zeolite channel system.

The lower than statistical ratio of n H formation on Pt/NaY was ascribed in a previous paper to the geometric constraints for MCP adsorbed on a Pt particle, which incompletely fills a supercage (14). Only in 50% of the approaches of an MCP molecule will the hydrogen atom at the tertiary carbon be pointing toward the metal surface, so that the Pt-C(tert.) bond which is required for ring opening toward n H can be formed. In the other 50% rollover is necessary for n H formation to occur, but this rollover is impossible in the narrow slit between Pt particle and cage ceiling. On the basis of this model it is expected that the deviation from statistics should disappear if particles become larger and fill the cage completely or bulge into adjacent cages. No geometric constraints will then impede rollover of molecules adsorbed at the exposed part of the metal particle. The observed change of 3MP/ n H toward the statistical value by adding Cu and thus producing cage-filling particles can thus be understood on the basis of this model.

Our second selectivity parameter, i.e.,

the ratio 2MP/3MP, is possibly even more relevant for the microgeometry of the catalyst system. Note that both molecules, 2MP and 3MP, are formed by cleaving a bond between two secondary C atoms; the chemistry is thus identical for both cases. Indeed, the ratio found by Gault and co-workers with Pt/Al₂O₃ with high metal dispersion and by ourselves with Pt/NaY was always close to the statistical value 2MP/3MP = 2. The present result that the 2MP/3MP ratio decreases with increasing Cu/Pt ratio from 2 to about 1.3 might also be rationalized in geometric terms. Before a MCP molecule reaches a (bi)metal particle it must diffuse through the narrow pore system of the zeolite and will be oriented with its long axis parallel to the pore axis. When a metal particle fills its cage, so that adsorption is only possible through the cage window, either the MCP molecule will hit the metal particle with its methyl group (no ring opening can result from this impact) or impact through the cage window will take place with the flat bottom end of the molecule. Formation of Pt-C bonds with these secondary C atoms will preferentially lead to the formation of 3MP. Orientation of hydrocarbon molecules in zeolites has also been proposed by Tauster and Steger as a potential cause of stereospecificity in reactions catalyzed by metal particles in zeolites (30).

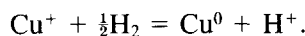
While these explanations are necessarily rather speculative at the present stage, it is noteworthy that a rationalization of the observed selectivity effects is possible by making exclusive use of the *microgeometry* of the metal/zeolite system. Work is in progress to test the above models with mono-metal Pt/NaY prepared by a method which results in larger cage-filling Pt particles than the method used here for Pt/NaY.

D. CONCLUSIONS

Some conclusions that emerge from this study are the following:

1. In Cu/NaY the reduction of copper

ions occurs in two discrete steps, but in Cu/NaY the second step, viz. complete reduction from Cu⁺ to Cu, is not observed. This indicates a reversible equilibrium:



2. The TPR peak characterizing the reduction of copper is strongly shifted to lower temperatures by the presence of Pt. Cu ions are assumed to leave the small zeolite cages and become reduced in contact with the Pt particles in the supercages. Bimetallic Pt_nCu_m particles are thus formed. Initially their surface consists of Cu; after reconstruction the H/Pt ratio is near 0.6.

3. The turnover frequency for MCP hydrogenolysis is low on Pt_nCu_m particles, because large Pt ensembles are required for this reaction. Moreover, protons introduced during metal reduction increase carbenium ion reactions, including ring enlargement and formation of coke precursors.

4. For metal particles smaller than the diameter of the supercages, the 3MP/*n*H ratio in MCP ring opening is two times the statistical value, presumably because of rollover limitation. For particles equal to or larger than the supercages the formation of 3MP is preferred, possibly due to orientation of impinging MCP molecules.

5. For larger metal loads, the acidity of the zeolite that is induced by metal reduction is sufficient to catalyze ring enlargement of MCP at the expense of the ring opening.

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