4.0 CHARACTERIZATION OF ZEOLITE-SUPPORTED RU CATALYSTS

4.1 Chemical Composition and Structural Character of the Zeolites

The dehydrated unit cell composition of the various zeolites is given in Table 4.1. The metal loading of the ruthenium-exchanged zeolites is given in Tables 4.2 and 4.4 with the hydrogen chemisorption results. Except for LiY-zeolite, maximum amounts of exchange reported in the literature[81] were obtained for the other alkali zeolites. Chemical analysis after Ru exchange indicated that only 50% of the lithium exchanged remained in the zeolite. However, as will be seen in the following chapters, even this small amount of lithium was sufficient to produce noticeable changes in the acid-catalyzed secondary reactions occurring during CO hydrogenation.

The X-ray diffraction measurements showed that the samples were highly crystalline. Furthermore, as shown in Figure 4.1 which illustrates the X-ray powder patterns for the zeolite NaY, the structures of the zeolites were essentially unaffected by the various steps of catalyst preparation, reduction procedure, and reaction conditions. The slight variations in peak intensity observed after Ru exchange may be accounted for by differences in sodium content.[82] This is in agreement with the X-ray diffraction

Table 4.1 Unit Cell Composition of the Dehydrated Zeolites

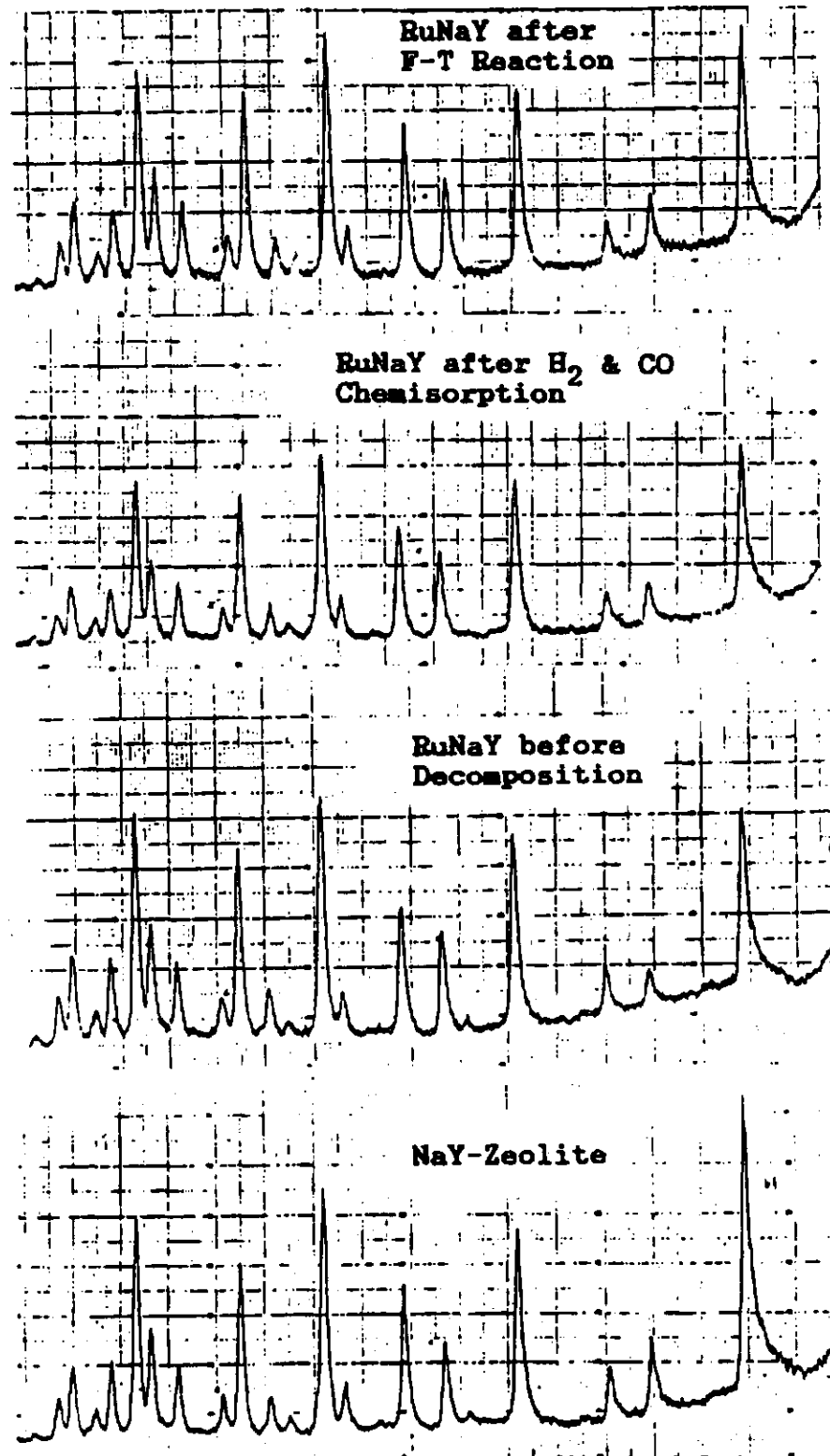| Zeolites	Composition
NaY	Na_{52} $(AlO_2)_{52}$ $(SiO_2)_{140}$
LiY	$Na_{36.4}$ $Li_{15.6}$ $(AlO_2)_{52}$ $(SiO_2)_{140}$
KY	$Na_{2.6}$ $K_{49.4}$ $(AlO_2)_{52}$ $(SiO_2)_{140}$
RbY	$Na_{20.3}$ $Rb_{34.8}$ $(AlO_2)_{52}$ $(SiO_2)_{140}$
CsY	$Na_{21.8}$ $Cs_{35.3}$ $(AlO_2)_{52}$ $(SiO_2)_{140}$
NaX	Na_{80} $(AlO_2)_{80}$ $(SiO_2)_{112}$
KL	$K_{7.9}(AlO_2)_{7.9}(SiO_2)_{28.1}$
Na-mordenite	$Na_{7.4}$ $(AlO_2)_{7.4}$ $(SiO_2)_{40.6}$

Figure 4.1 X-Ray Diffractograms of NaY and RuNaY at Various
Stages of Preparation and Use

results reported by Pearce et al.[83] for the Ru/Y-zeolite system.

Relatively high values of nitrogen physisorption capacities obtained for the various catalysts before and after Ru exchange and reduction also indicated preservation of crystallinity with no loss of internal surface area due to breakdown of the zeolite framework during the preparation and reduction of the catalysts.[84]

4.2 H_2 and CO Chemisorption

The hydrogen chemisorption measurements were used to calculate metal particle size and dispersion. however, H_2 chemisorption alone may not be very reliable for characterization when the metal is highly dispersed on acidic supports such as zeolites.[21] With such supports, the suppression of hydrogen chemisorption may be significant. CO chemisorption has also been shown to be inadequate for surface area determination, since the stoichiometry for CO adsorption varies with Ru particle size.[80,85] However, CO adsorption can be used to compare relative metal dispersions and the presence of H_2 chemisorption suppression, since suppression of CO chemisorption appears to be less significant than that of H_2.[21] From consideration of CO/H and CO/Ru$_{(total)}$ ratios, it is possible to tell whether suppression of hydrogen

chemisorption has taken place on Ru catalysts.

The results of H_2 and CO chemisorption for the various Y-zeolite-supported Ru catalysts are given in Table 4.2 and 4.3. Tables 4.4 and 4.5 list the results for the Ru/zeolite catalysts with different Si/Al ratios. The chemisorption isotherms for all the catalysts can be found in Appendix A. The Si/Al ratios of the zeolite supports, calculated from the AA analysis results are also listed in Table 4.4. As estimated by hydrogen chemisorption, the average diameters of the ruthenium particles, formed in the various alkali cation type Y-zeolites, were at or slightly above the upper limit of the supercage diameter (13 $\overset{o}{A}$). Several interpretations can be found in the literature to explain such relatively large particle sizes. First, it is known that RuO_2 is readily formed at ambient temperature in air from small metal particles and that it is highly mobile. Upon heating, the ruthenium dioxide may migrate to the external surface of the zeolite where larger crystallites could be formed.[13,83] If some metal exists as large particles on the external surface of the zeolite, an average metal particle diameter larger than the size of the zeolite pores would be calculated from chemisorption measurements, even though most of the metal might exist as very small particles inside the zeolite. Such a situation has been observed by TEM for highly dispersed Ru/NaY catalysts.[77]

Table 4.2   Characteristics of RuY-Zeolite Catalysts
Based on Hydrogen Chemisorption[a]

Catalyst	Ru (wt%)	H_2(irr.)[b] (μmol/g.cat.)	D[c] (%)	d_p[c] (A)
RuHY	3.8	56	30	28
RuLiY	3.4	90	53	16
RuNaY	3.8	126	67	12
RuKY	3.2	81	52	16
RuRbY	3.6	88	49	17
RuCsY	3.7	102	56	15
$RuSiO_2$	1.8	46	53	16

(a) Catalysts prepared by ion-exchange and decomposed under vacuum (except for $RuSiO_2$);
(b) Irreversible H_2 Chemisorption;
(c) Dispersion (D) and particle size (d_p) from H_2 chemisorption.

Table 4.3   CO Chemisorption Results for RuY-zeolites[a]

Catalyst	CO (irr.)[b] (μmol/g.cat.)	CO/H	CO/Ru$_{(total)}$
RuHY	395	3.5	1.1
RuLiY	660	3.7	2.0
RuNaY	921	3.7	2.5
RuKY	562	3.4	1.8
RuRbY	632	3.7	1.8
RuCsY	713	3.6	2.0

(a) Catalysts prepared by ion-exchange and decomposed under vacuum;
(b) Irreversible CO Chemisorption.

Table 4.4   Characteristics based on H_2 Chemisorption for Ru/Zeolites with Various Si/Al Ratio[a]

Catalyst	Ru (wt %)	Si/Al Ratio	$H_2(irr.)$[b] (μmol/g.cat.)	D[c] (%)	d_p[c] (A)
RuNaX	3.0	1.4	79	54	16
RuNaY	3.8	2.7	126	67	12
RuKL	3.2	3.5	53	36	24
RuNaM[d]	3.2	5.5	39	26	32

(a) Catalysts prepared by ion-exchange and decomposed under vacuum;
(b) Irreversible H_2 Chemisorption;
(c) Dispersion (D) and particle size (d_p) from H_2 chemisorption;
(d) M = Mordenite.

Table 4.5   CO Chemisorption Results for Ru/Zeolites
with Various Si/Al Ratio[a]

Catalyst	CO (irr.)[b] (μmol/g.cat.)	CO/H	CO/Ru$_{(total)}$
RuNaY	921	3.7	2.5
RuKL	534	5.0	1.8
RuNaM[c]	343	4.3	1.1

(a) Catalysts prepared by ion-exchange and decomposed under
    vacuum;
(b) Irreversible CO Chemisorption;
(c) M = Mordenite.

Second, Pearce et al. (83) have observed by X-ray methods that, for ruthenium-exchanged zeolites pretreated under vacuum then reduced, up to 18% of the metal is atomically dispersed in the sodalite cages. Since, at room temperature, this ruthenium is inaccessible for hydrogen chemisorption, the average particle size calculated from hydrogen chemisorption is larger than the actual. Furthermore, localized destruction of the lattice to form cracks and holes has been observed by Verdonck et al.[13] Thus encapsulation of Ru clusters of intermediate size in these holes would also result in low dispersion being measured. Gustafson and Lunsford[86] have also suggested that in the presence of H_2 the mobility of Ru is increased, resulting in the agglomeration of Ru in several adjacent unit cells where the particles may be connected through the windows of the zeolite framework. This would render some portions of the metal particles inaccessible to hydrogen adsorption. Finally it has been reported that suppression of irreversible hydrogen chemisorption could be significant for most zeolite-supported ruthenium catalysts prepared by ion-exchange, resulting in an overestimation of the average particle diameter.[21] The concentration and strength of acidic hydroxyl protons (correlated with the Si/Al ratio) are suggested to be the reason for this hydrogen chemisorption suppression. Luckily, the CO/H ratio has been

shown to be a good indication of H_2 chemisorption suppression.[21] Furthermore, CO/H ratios have been found in previous studies[14,80] to be a function of particle size.

A comparison of the dispersions given in Table 4.2 with the CO/H ratios in Table 4.3 suggests that the dispersions of the ruthenium in the various Y-zeolites were high and similar, except for RuHY. The latter had higher concentration of acidic hydroxyl groups than the alkali cation neutralized zeolites. Thus, the suppression of hydrogen chemisorption would be expected to be more significant with RuHY, resulting in much higher CO/H ratio than that normally found for a dispersion of Ru of 30%.[80] A consideration of CO/Ru$_{(total)}$ for this catalyst suggests that the metal dispersion of this catalyst was in effect lower than that of the other Ru catalysts.

The CO/H ratios obtained for RuKL and RuNa-mordenite (Table 4.5) suggest actually a significant suppression of hydrogen chemisorption on these catalysts. In agreement with the results repported by Wang et al.[21], such results would be expected for these two catalysts since, as correlated with the Si/Al ratio of the zeolite,[87] the acid strength of the hydroxyl groups formed on these supports would be much higher than on X- or Y-zeolite. This would at least partly explain the higher particle sizes calculated from H_2 chemisorption for these two catalysts. Any agglomeration of Ru in the zeolite channels may render some portions of the

metal particles inaccessible to adsorption. Such behavior would also result in an overestimation of the particle sizes calculated from H_2 chemisorption.

4.3 Effect of Decomposition/Reduction Conditions

4.3.1 Introduction

A very successful method for preparing highly dispersed zeolite-supported Ru catalysts is by ion-exchange of the zeolite with ruthenium hexammine chloride, $Ru(NH_3)_6Cl_3$.[12,13,77,83] The ion-exchange is followed, after drying, by the thermal decomposition of the Ru hexammine complex ion and reduction in hydrogen at 673 K of Ru to its metallic form. The state of dispersion of the metal has been shown to depend very much on the atmosphere under which this complex ion is decomposed and on the rate of temperature increase.[13,88-89] The decomposition (dehydration-deammination) methods invariably used to obtain highly dispersed catalysts have been by degassing either under high vacuum or in flowing helium, nitrogen, or hydrogen. It was found that decomposition under high vacuum or flowing helium gave equally high dispersions approaching 100%;[13,88-90] however, decomposition in flowing hydrogen always gave low dispersions.[86] The presence of water or oxygen was found to be the major factor leading to excessive

sintering of Ru in these catalysts. For these studies, only Na form of alkali Y-zeolites was used. The influence of the nature of the neutralizing cations remaining after ion-exchange on the success of preparing highly-dispersed zeolite-supported metal catalysts has not been addressed to date.

This section discusses the influence of the decomposition/reduction procedure on the physical characteristics of Y-zeolite-supported ruthenium catalysts when alkali cations other than sodium are used to neutralize the zeolite framework.

4.3.2 Experimental

Two series of RuY catalysts were prepared by ion-exchange of $Ru(NH_3)_6Cl_3$ with the alkali (Li, K, Rb, and Cs) Y-zeolites and the ammonium form as described in the previous chapter. After drying in air for 24 h at 323 K, the resulting ruthenium catalyst precursors were then decomposed using two different methods. The only difference between the two methods of decomposition was that one was carried out under a dynamic vacuum of 10^{-6} torr, as already described, while the other was carried out in flowing helium (UHP grade) which was first passed through a molecular sieve trap to remove water. A slow heating rate (0.5 K min^{-1}) up to 673 K was used in both cases during the catalyst decomposition, since such a slow rate is necessary in order

to maximize ruthenium dispersion.[13] The catalysts were maintained at 673 K for 4-5 hours. The samples were then reduced for one hour in hydrogen at that maximum temperature. Such procedures have been found to produce totally reduced Ru catalysts.

The two series of reduced catalysts were characterized by AA and chemisorption of hydrogen and carbon monoxide at room temperature (static gas volumetry), as described in the previous chapter.

4.3.3 Results and Discussion

Hydrogen chemisorption measurements were used to calculate the Ru average crystallite sizes and dispersions for the various catalysts. The results of H_2 and CO chemisorption for the various Ru catalysts decomposed under vacuum (Tables 4.2 and 4.3) have been presented in the previous section, and those decomposed in flowing helium are given in Table 4.6. From these results it can be seen that, except for RuHY, the decomposition of the ion-exchanged Ru hexammine complex ion under vacuum produced highly dispersed ruthenium catalysts whatever the nature of the neutralizing cation present in the zeolite. When the catalysts were decomposed in flowing helium, high ruthenium dispersions were obtained only when the neutralizing cations were sodium or potassium cations. With Y-zeolites

Table 4.6 Catalyst Characteristics from H_2 and CO
Chemisorption [*]

Catalyst	Ru (wt%)	D (%)	d_p (Å)	CO/H Ratio	CO/Ru$_{(tot.)}$ Ratio
RuHY	3.2	20	42	2.1	0.4
RuLiY	3.1	43	20	3.2	1.4
RuNaY	3.1	64	13	4.3	2.6
RuKY	3.2	50	17	1.5	0.8
RuRbY	3.2	20	42	2.6	0.5
RuCsY	3.2	34	24	2.7	0.9

[*] Catalysts decomposed in flowing helium.

containing other cations (H^+, Li^+, Rb^+, and Cs^+) much larger ruthenium crystallites were obtained under the same pretreatment conditions. Based on both hydrogen and CO chemisorption results, the larger crystallite sizes cannot be attributed to an overestimation due to hydrogen chemisorption suppression. The metal dispersion seems to be a function of the method of decomposition when the neutralizing cations are other than sodium or potassium. In order to make sure that the differences between the catalysts were not introduced during ion-exchange, the results were reproduced using, for some samples, the same batch of catalyst for both decomposition methods.

Gallezot[49] has reported that heating zeolite-supported metals in the presence of a gas may considerably enhance the mobility of the metal, leading to sintering. However, Fiedorow et al.[91] have shown that Ru is less susceptible than Pt or Rh to sintering in hydrogen. Pedersen and Lunsford[89] have also shown that, provided oxygen is excluded from the system, highly dispersed Ru catalysts may be obtained when an inert gas such as helium or nitrogen is used in the dehydration-deammination step prior to reduction in hydrogen. The ruthenium remained in the zeolite cavities even after the methanation reaction. However, this seems to be the case only when the remaining neutralizing cations are sodium or potassium.

Minachev et al.[92] have shown that reduction of

transition metals in zeolites is accompanied by migration of metal to the external surface of the zeolite crystals and that the reduction and migration processes depend on factors such as the chemical nature of the metal complex ion, the degree of ion-exchange, cation location, and the thermal stability of the structural hydroxyls. A possible influence of the nature of the remaining neutralizing cation may be attributed to the residual water in the zeolite. Residual water during reduction of the ruthenium hexammine complex ion in the zeolite was found to influence significantly sintering of the metal via formation of partially hydrolyzed species.[13,88] Hence, it has been suggested that only thoroughly degassed samples should be contacted with hydrogen.

The nature of the cation determines the degree of hydration of the zeolite and the interactions of water molecules with the zeolite lattice. Studies of adsorption of water on alkali zeolites have shown that the interactions of water molecules with the zeolite depend on the nature of the alkali cations present in the zeolite, the weakest interactions being observed in the presence of K, Rb, and Cs, and the strongest in the presence of Li.[93] Hence, the dehydration of the catalysts may be a function of the nature of the neutralizing cations, especially in presence of a gas which would tend to limit the diffusion of the

water out of the zeolite pores. When the decomposition is carried out under vacuum, the dehydration of the zeolite may be facilitated.

Since the strongest interactions of water molecules with alkali zeolites are found in the case of lithium, one would expect that ease of metal sintering would decrease in the order LiY > NaY > KY > RbY > CsY. Such an obvious correlation , however, would be greatly affected by any difference in metal dispersion throughout the zeolite. For the series of well-dispersed ruthenium catalysts, i.e., those decomposed under vacuum, the activation energy results for CO hydrogenation suggest that due to steric factors, a non-uniform distribution of Ru throughout RbY- and CsY- zeolites was obtained during ion-exchange, while Ru was initially more uniformly distributed throughout the zeolite crystallites for the smaller cation zeolites (see next chapter). If the Ru complex ions are situated in the external shell of the zeolite crystallites, their migration to the external surface would be more favored during decomposition and hence more sensitive to even low partial pressures of water vapor than when a more uniform dispersion of the Ru complex ions exists. Thus, it would appear that decomposition of RuNaY and RuKY is less sensitive to the procedure used by vertue of having both a more uniform distribution of Ru throughout the zeolite crystallites and only a moderate ability to retain water to higher

temperatures. RuRbY and RuCsY are more sensitive to the procedure used due to the fact that the Ru is more concentrated in the outer shell of the zeolite crystallites, while RuLiY is sensitive because of the retention of water to higher temperatures. The effect of these two competing characteristics on Ru dispersion is illustrated schematically in Figure 4.2.

The decomposition of HY-zeolite-supported ruthenium catalyst resulted in relatively low ruthenium dispersions compared to the alkali zeolite-supported catalysts, regardless of the decomposition method. Although a slightly better dispersion was obtained when the catalyst was decomposed under vacuum, the larger particle sizes obtained with this catalyst may be attributed to an effect of residual water. This zeolite is considered particularly sensitive towards water which may result in partial hydrolysis of lattice aluminum.[13]

4.2.4 Conclusion

Zeolite-supported Ru catalysts prepared by ion-exchange of the zeolite with ruthenium hexammine chloride may be thermally decomposed under high vacuum or in flowing inert gas. The decomposition method using vacuum has been shown to result in higher dispersions of the metal than when it is carried out in flowing helium, especially in the case for

zeolites containing neutralizing cations other than sodium or potassium. This appears to be related to the more efficient removal of water from the zeolite under vacuum. Two competing characteristics influence the dispersion of Ru when the catalyst precursor is decomposed in flowing helium: the strength of interaction of the zeolite with water and the uniformity of Ru distribution in the zeolite crystallites. As illustrated schematically in Figure 4.1, because of their optimal characteristics high dispersions of Ru are obtained in RuNa and RuKY-zeolites even when the Ru complex ion is decomposed in flowing helium.
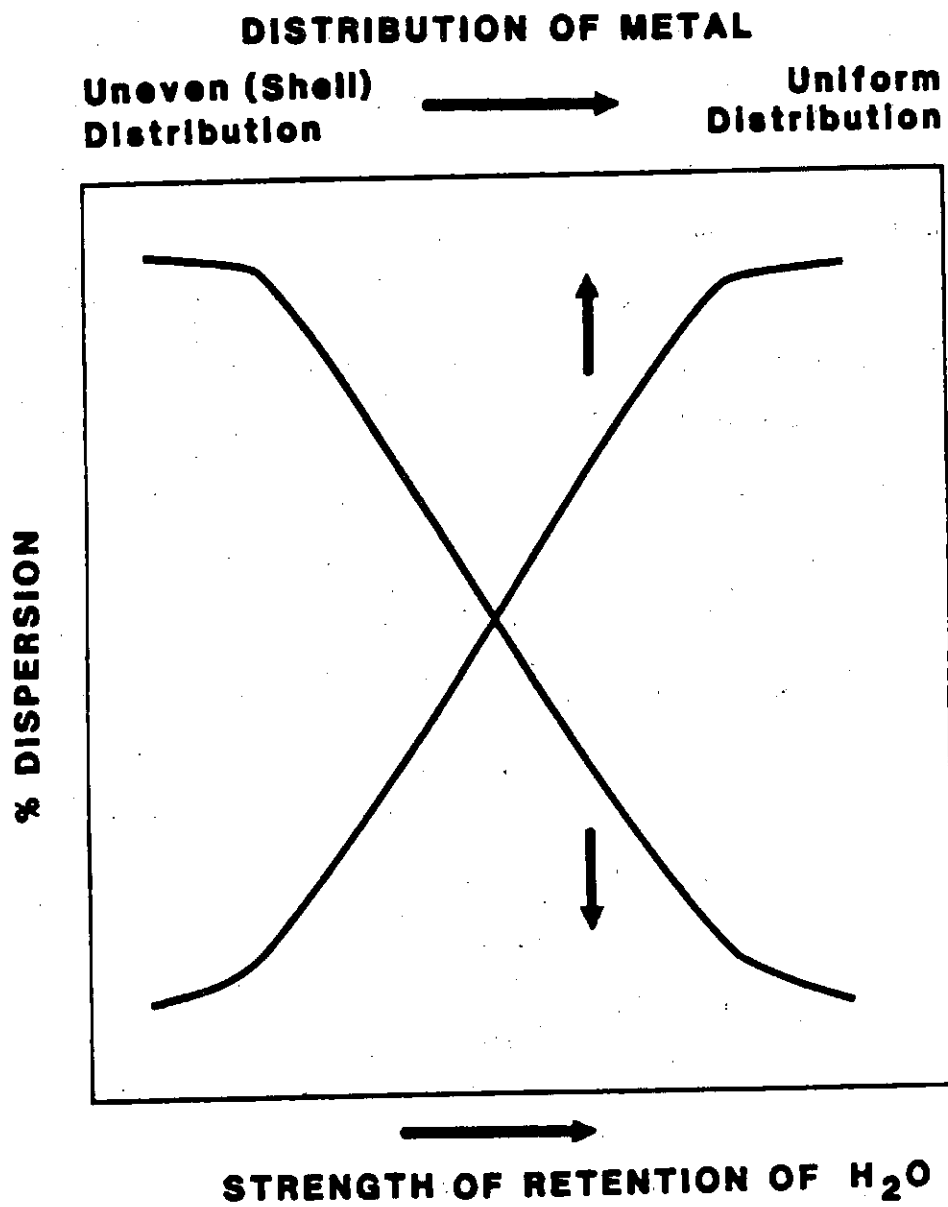
Figure 4.2 Competing Effects of Ru Distribution and Strength of Water Retention in Zeolites on Metal Dispersion