Preparation Effects in Zeolite-Supported Metal Catalysts: Influence of Decomposition/Reduction on Ru Particle Size

I. INTRODUCTION

Ruthenium is a highly active catalyst for numerous reactions, such as CO hydrogenation (*1, 2*). When supported in zeolites, highly dispersed ruthenium catalysts may be obtained which offer enormous potential in the control of product selectivity (*3–5*). Besides their shape-selective properties, zeolites possess ion-exchange capabilities which may be used not only to introduce the active metal but also to generate bifunctional catalysts. The nature of the neutralizing cation in the zeolite greatly affects its bifunctional properties (*6, 7*).

A very successful method for preparing highly dispersed zeolite-supported Ru catalysts is by ion-exchange of the zeolite with ruthenium hexammine chloride, $Ru(NH_3)_6Cl_3$ (*8–11*). 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 (*11–13*). 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% (*11–14*); however, decomposition in flowing hydrogen always gave lower dispersions (*15*). 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, however, only the Na form of Y-zeolites was used. The influence of the nature of the neutralizing alkali cations remaining after ion-exchange on the success of preparing highly dispersed zeolite-supported metal catalysts has not been addressed to date.

The ability to prepare highly dispersed zeolite-supported metals having comparable dispersions and metal distribution is crucial in understanding the effect of other variables and in making full use of all the benefits of zeolites as supports. This note 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.

II. EXPERIMENTAL

Alkali cation (Li, K, Rb, and Cs) Y-zeolites were prepared by ion-exchange of NaY-zeolite supplied by Strem Chemicals with an aqueous solution of ultrapure alkali nitrates (from Alfa Products). The composition of the parent zeolite NaY and the other alkali zeolites, as determined by atomic absorption spectroscopy, is given in Table 1. RuY catalyst precursors were prepared by ion-exchange of $Ru(NH_3)_6Cl_3$ with these alkali zeolites and the ammonium form (80% exchanged, obtained from Strem Chemicals). A detailed description of the ion-exchange procedure is given in Ref. (*6*). After drying in air for 24 h at 323 K, the resulting ruthenium catalyst precursors were decom-

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TABLE 1

Dehydrated Unit Cell Composition of
Alkali Zeolites (6)

Zeolites	Composition
NaY[a]	$Na_{52}(AlO_2)_{52}(SiO_2)_{140}$
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	$Na_{17.2}Rb_{34.8}(AlO_2)_{52}(SiO_2)_{140}$
CsY	$Na_{16.7}Cs_{35.3}(AlO_2)_{52}(SiO_2)_{140}$

[a] Starting material.

posed 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, 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 (11). The catalysts were maintained at 673 K for 4–5 h. 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). Details of the procedures for characterization can be found elsewhere (6, 10).

III. RESULTS AND DISCUSSION

Hydrogen chemisorption measurements were used to calculate average Ru crystallite sizes and dispersions for the various catalysts as described in (10). Although such determinations have been found to compare favorably with TEM measurements (10) for Y-zeolites, suppression of irreversible hydrogen chemisorption may be significant for zeolite-supported ruthenium catalysts prepared by ion-exchange (16). Thus, H$_2$ chemisorption alone may not al-

ways be reliable for characterization. Although CO adsorption cannot be used for determination of ruthenium dispersion, since its stoichiometry is a function of the metal particle size (17), consideration of CO/H and CO/Ru$_{(total)}$ ratios may be used to indicate H$_2$ chemisorption suppression (16).

The results of H$_2$ and CO chemisorption for the various Ru catalysts decomposed under vacuum are given in Table 2 and those decomposed in flowing helium are given in Table 3. 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. In the case of RuHY a consideration of CO/H and CO/Ru$_{(total)}$ ratios suggests that the metal dispersion in this catalyst was in effect lower than that of the other Ru catalysts but perhaps better dispersed than determined by hydrogen chemisorption alone. All the catalysts may in fact have slightly higher dispersions since some hydrogen chemisorption suppression is suggested for ion-exchanged RuY catalysts (16). It is known that catalysts prepared in this manner contain most of the Ru inside the zeolite pore system (10). A discussion of why such highly dispersed catalysts can exhibit average Ru

TABLE 2

Characteristics of Catalysts Decomposed under
Vacuum

Catalyst	Ru (wt%)	D^a (%)	d_p^a (Å)	CO/H ratio	CO/Ru$_{(total)}$ ratio
RuHY	3.8	30	28	3.5	1.1
RuLiY	3.4	53	16	3.7	2.0
RuNaY	3.8	67	12	3.7	2.5
RuKY	3.2	52	16	3.4	1.8
RuRbY	3.6	49	17	3.7	1.8
RuCsY	3.7	56	15	3.6	2.0

[a] Dispersion (D) and average Ru particle size (d_p) determined using irreversible hydrogen chemisorption at room temperature.

TABLE 3

Characteristics of Catalysts Decomposed in Flowing Helium

Catalyst	Ru (wt%)	D^a (%)	$d_p{}^a$ (Å)	CO/H ratio	CO/Ru$_{(total)}$ 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

^{a} Dispersion (D) and average Ru particle size (d_p) determined using irreversible hydrogen chemisorption at room temperature.

particle sizes larger than the zeolite supercage dimensions is given elsewhere (6).

When the catalysts were decomposed in flowing helium, high ruthenium dispersions were also obtained when the neutralizing cations were sodium or potassium cations, consistent with the results of other workers (11–14). However, with Y-zeolites 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 catalysts were not introduced during ion-exchange, the results was reproduced using, for some samples, the same batch of catalysts for both decomposition methods.

Gallezot (18) has reported that heating zeolite-supported metals in the presence of certain gases may considerably enhance the mobility of the metal, leading to sintering. However, Fiedorow et al. (19) have shown that Ru is less susceptible than Pt or Rh to sintering in hydrogen. Pedersen and Lunsford (13) 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 was found to remain in the zeolite cavities even after the methanation reaction. However, this was determined only for the case where the remaining neutralizing cations were sodium.

Minachev et al. (20) 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 has been found to influence significantly sintering of the metal via formation of partially hydrolyzed species (11, 12). 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 (21). Hence, the dehydration of the catalysts may be a function of the nature of the neutralizing cations, especially in the 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 distribution 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 nonuniform 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 (6). Evidence for a nonuniform distribution of Ru in RbY- and CsY-zeolites has also been provided by a recent study of this series of catalysts by TPD of hydrogen (22). 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 Ru-NaY and RuKY is less sensitive to the procedure used by virtue 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 ruthenium 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 Fig. 1.

The decomposition of HY–zeolite-supported ruthenium catalysts 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
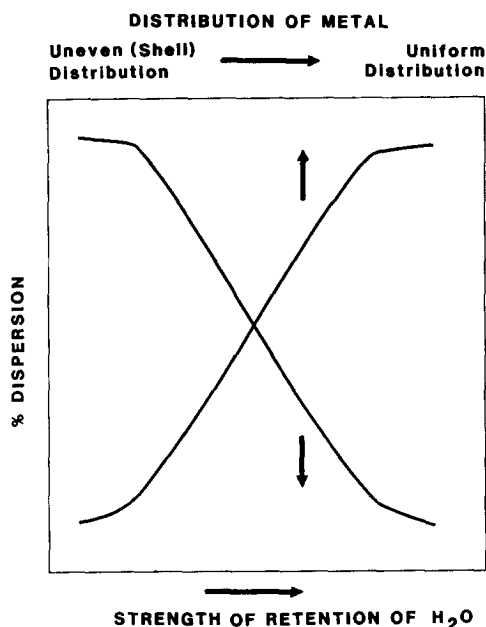

FIG. 1. Competing effects of Ru distribution and strength of water retention in zeolites on metal dispersion.

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 toward water which may result in partial hydrolysis of lattice aluminum (11). In addition, Gustafson and Lunsford (15) have suggested that residual NH_3 from the decomposition of $Ru(NH_3)_6^{3+}$ in NaY-zeolites may also enhance the mobility of ruthenium, resulting in the agglomeration of the metal in several adjacent supercages. This effect of NH_3 on Ru dispersion would, therefore, be more significant in RuHY since the zeolite used for the preparation of this catalyst is in the ammonium form. In this case the thermal decomposition of the catalyst would result in the release of NH_3 not only from the Ru hexammine complex ion but also from the zeolite itself.

IV. CONCLUSION

Zeolite-supported Ru catalysts prepared by ion-exchange of the zeolite with ruthenium hexammine chloride may be ther-

mally 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. When the catalyst precursor is decomposed under flowing helium, it appears that the metal dispersion is a function of two competing characteristics: the strength of interaction of the zeolite with water and the uniformity of Ru distribution in the zeolite crystallites. 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.

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