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Hydrogen Reduction of Ga–Pt Loaded HZSM-5

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Catalysts containing 1.2, 3.1, 6.1, and 10.0 g Ga as $Ga(NO_3)$ per 100 g HZSM-5 prepared by incipient wetness impregnation have been subjected to hydrogen reduction at 848 K in a microbalance and the reduction rates and capacities compared with identical materials further impregnated with 0.5 g Pt as $Pt(NH_3)_4\,(NO_3)_2$ per 100 g HZSM-5.

Weight loss stoichiometry suggests that supported $Ga(NO_3)_3$ is converted to Ga_2O_3 upon calcination in 3% O_2 in He while weight loss stoichiometry upon hydrogen reduction at 848 K in all cases can be correlated (within certain bounds which are discussed) as $Ga_2O_3 + 2H^+Z^- \rightarrow 2Ga^+Z^- + 3H_2O$, where Z^- is the anionic zeolitic framework. The addition of Pt does not increase the total amount of Ga_2O_3 which can be reduced even in cases where the cation capacity of the zeolite limits the reduction reaction but does increase the maximum rate of Ga_2O_3 reduction.

INTRODUCTION

Gallium-loaded HZSM-5 catalysts have received considerable interest for the conversion of light paraffins to aromatics since their incorporation in the Cyclar process (*1*). Our recent investigations on mechanical mixtures of Ga_2O_3 with HZSM-5 (*2, 3*) and $Ga(NO_3)_3$ impregnated on HZSM-5 (*4*) have shown that the materials undergo reduction when subjected to hydrogen treatment in a microbalance. For mechanically mixed catalysts, we have shown that a propane feedstock can also promote reduction (*2, 3*). Since several investigations in the open literature report the addition of transition metals to Ga containing zeolites as being effective in promoting catalytic performance for light paraffin aromatization (*5–8*), we report here a comparative study on the reduction of gallium and gallium/platinum-doped HZSM-5.

EXPERIMENTAL

Nine different catalysts formulations were prepared using Union Carbide MFI zeolite (SiO_2/Al_2O_3 = 40) as a base. This material is equivalent to HZSM-5 in the fully protonated form. Four of the nine materials were prepared by loading the HZSM-5 with $Ga(NO_3)_3$ via incipient wetness addition of an aqueous solution of $Ga(NO_3)_3$ such that the elemental gallium content was 1.2, 3.1, 6.1, or 10.0 g Ga/100 g zeolite. These four materials were then dried in air for 3 h at 393 K along with a sample of the HZSM-5 base. Half portions of each of the four $Ga(NO_3)_3$ loaded materials and the HZSM-5 base were then additionally impregnated via incipient wetness addition of 0.5 g Pt/100 g zeolite as $Pt(NH_3)_4(NO_3)_3$ and dried at 393 K for 3 h. All materials were then placed in a desiccator for at least 48 h. We refer to these materials as xGa–yPt/HZSM-5, where x and y are the Ga and Pt loading in g/100 g zeolite, respectively.

A Perkin–Elmer TGA-7 microbalance was used to detect weight change upon thermal and reagent gas treatment of these materials. Calcination was accomplished first by treatment from 313 to 880 K at 20 K/min then hold at 880 K for 2 h using 125 cm^3/min of a 3% O_2/97% He mixture. A flow of 125 cm^3/min of pure He was established, the sample cooled to 848 K, then after equilibration at 848 K for 1 min, 25 cm^3/min of H_2

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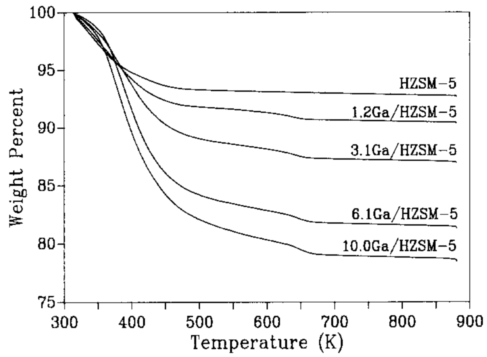

FIG. 1. Weight loss curves for Ga(NO$_3$) impregnated HZSM-5 during calcination.

was substituted for 25 cm^3/min of the He flow so that the overall purge rate remained 125 cm^3/min. An isothermal reduction curve is thus obtained.

A Scintag PAD V goniometer with Peltier-cooled solid-state detector and Cu X-ray source operated at 45 KV and 35 ma was used to obtain X-ray diffraction spectra utilizing Cu$K\alpha$ radiation. Background subtraction and Cu$K\alpha_2$ stripping was accomplished on all spectra using the proprietary Scintag software.

RESULTS AND DISCUSSION

Figure 1 shows the weight changes associated with the calcination process for each of the Ga/HZSM-5 (no Pt) materials. The series of catalysts which contain 0.5 wt% Pt gave very similar results. Assuming that weight loss corresponds to the cumulative effects of dehydration of the zeolite host and conversion of Ga(NO$_3$)$_3$ to Ga$_2$O$_3$ (other authors also have assumed this conversion process (*9–11*)), we can compute a theoretical weight loss for each sample assuming that the hydration levels of each zeolite-based material are equivalent to the hydration level of the pure zeolite. Table 1 compares this calculation to the observed global weight loss. The agreement is quite good, certainly as good as can be expected when we consider that overall hydration levels may be different among the various materials.

X-ray diffraction, however, is unable to detect the appearance of any crystalline phase upon calcination, especially one which could be attributed to gallium oxide. Figure 2 compares the diffraction patterns for the base HZSM-5 to 10.0 Ga/HZSM-5, both of which have been calcined in 3% O$_2$/97% He at 880 K for 2 h. No reflections are apparent in the calcined 10.0 Ga/HZSM-5 which are not in the base HZSM-5 material. Several possible explanations include:

(1) Ga$_2$O$_3$ lines are hidden by HZSM-5 lines.

(2) Ga$_2$O$_3$ is an amorphous phase.

(3) Crystallites of Ga$_2$O$_3$ are so small that line broadening makes them virtually unobservable compared to baseline noise. Each of these possible explanations becomes more likely as the Ga content is lowered, but we have been able to detect β-Ga$_2$O$_3$ in weight fractions below 2% when mechanically mixed with HZSM-5 (*3*), so this is not a problem associated with overall sensitivity. Diffraction patterns for 1.2 Ga/HZSM-5, 3.1 Ga/HZSM-5, and 6.1 Ga/HZSM-5 along with the corresponding diffraction patterns for the Pt-containing materials are virtually identical to the 10.0 Ga/HZSM-5 material; no bands other than those attributable to HZSM-5 can be detected. Although this result creates some uncertainty in the assumption that Ga(NO$_3$)$_3$ is converted to Ga$_2$O$_3$ upon calcination, we proceed with this assumption since microbalance weight loss data are consistent with this assumption and because other nitrates are known to yield oxides upon calcination.

Figures 3 and 4 show the isothermal re-

TABLE 1

Weight Loss Analysis upon Calcination

Catalyst	Expected weight loss (%)	Observed weight loss (%)
1.2 Ga/HZSM-5	9.71	9.60
3.1 Ga/HZSM-5	12.96	13.01
6.1 Ga/HZSM-5	17.56	18.61
10.0 Ga/HZSM-5	22.27	21.46

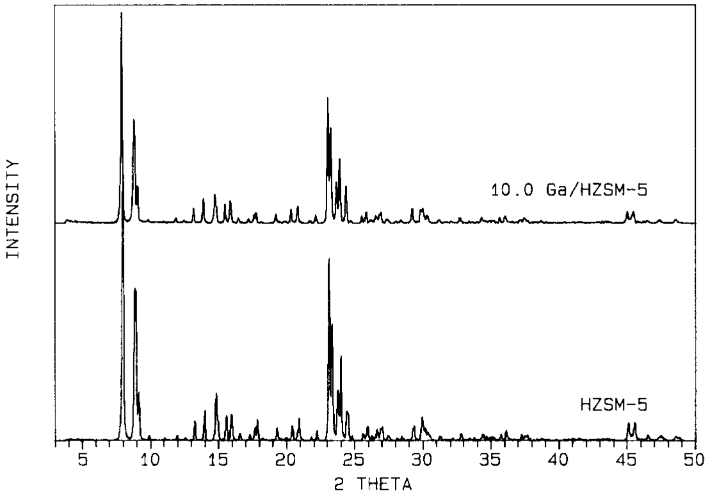

FIG. 2. X-ray diffraction patterns for HZSM-5 and 10.0 Ga/HZSM-5.

duction curves for the Ga and Ga–Pt series, respectively. If the reduction stoichiometry (*3*) proceeds as

$$Ga_2O_3 + 2H^+Z^- + 2H_2 \rightarrow 2Ga^+Z^- + 3H_2O, \quad (1)$$

where Z^- is the anionic zeolite framework, we can compute the expected weight loss in each case and these results are given in Table 2 along with the observed weight declined. For the Pt-containing materials, we further expect $PtO + H_2 \rightarrow Pt + H_2O$ which gives an expected weight loss of 0.04%.

In Table 2, several important observations can be made. First, the ultimate degree of reduction for all four materials which contain 6.1 or 10.0 g Ga/100 g zeolite are very similar. This suggests that for these materials, the cation capacity of the zeolite limits the amount of reduction which can be obtained. If Ga^0 instead of Ga^+ is the product of reduction, we are unable to explain why only a limited amount of Ga_2O_3 may be reduced for the cases of high Ga loading. We could postulate that Ga_2O_3 crystallites can only be reduced to Ga^0 to a limited depth, but there are two reasons why this postulate is impossible. First, X-ray diffraction is unable to detect crystalline regions of Ga_2O_3 suggesting that there are no multiple layers

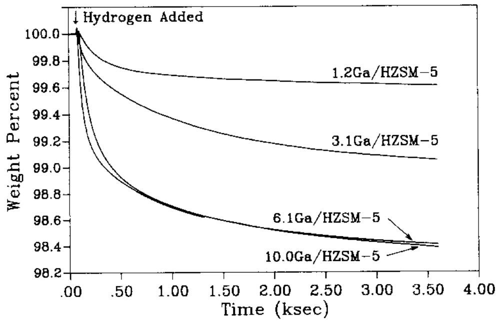

FIG. 3. Isothermal reduction curves for Ga/HZSM-5 catalysts at 848 K.

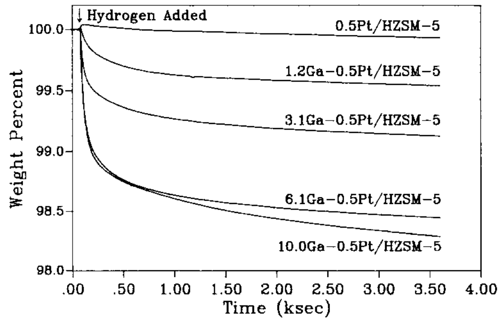

FIG. 4. Isothermal reduction curves for Pt containing Ga/HZSM-5 catalysts at 848 K.

TABLE 2

Stoichiometric Analysis for Hydrogen Reduction

Catalyst	Limiting reactant[a]	Expected weight loss (%)	Observation weight loss (%)
1.2 Ga/HZSM-5	Ga_2O_3	0.47	0.39
3.1 Ga/HZSM-5	Ga_2O_3	1.13	0.95
6.1 Ga/HZSM-5	HZSM-5	1.91	1.59
10.0 Ga/HZSM-5	HZSM-5	1.82	1.62
0.5 Pt/HZSM-5	—	0.04	0.07
1.2 Ga–0.5 Pt/HZSM-5	Ga_2O_3	0.51	0.46
3.1 Ga–0.5 Pt/HZSM-5	Ga_2O_3	1.17	0.87
6.1 Ga–0.5 Pt/HZSM-5	HZSM-5	1.95	1.55
10.0 Ga–0.5 Pt/HZSM-5	HZSM-5	1.86	1.71

[a] From Eq. (1).

of Ga_2O_3 and, second, a comparison of silicalite (0.53 % Al_2O_3) and HZSM-5 (3.73% Al_2O_3) loaded with identical levels of Ga_2O_3 gave disparate reduction levels by a factor of over two (*3*). Equation (1), which was previously postulated (*3*), very neatly predicts the observed reduction limit. One of the primary reasons we have performed the research work reported here is to answer the question of whether or not Pt may be able to alter the observed reduction limit by catalyzing the reduction of Ga_2O_3 independent of the presence of the zeolite. Clearly, the addition of Pt does not (in this case) enhance the total amount of Ga_2O_3 which can be reduced and, therefore, we cannot attribute catalytic performance changes which have been reported to take place upon the addition of Pt (*6–8*) to enhanced degrees of Ga reduction. This result can probably be extended to the action of other transition metals such as Re and Rh (*5–7*) which have been used in light paraffin aromatization catalysts. In all of these cases, we must attribute changes in catalytic performance to the catalytic actions induced by the metal itself.

However, the expected degree of reduction of Ga_2O_3 in all eight cases is greater than the actual amount observed. Part of this disparity can be explained by the fact that reduction is not quite complete. Our extrapolation of the curves presented in Figs. 3 and 4 via fitting an exponential to the tail suggests that approximately 0.05 to 0.10 wt% further reduction could be obtained which represents about one-third of the dis-

TABLE 3

Maximum Rates of Weight Loss for Ga and Ga–Pt/HZSM-5 upon Reduction at 858 K

Material ID	Weight loss rate (wt%/ks)	Material ID	Weight loss rate (wt%/ks)
1.2 Ga/HZSM-5	1.4	1.2 Ga–0.5 Pt/HZSM-5	2.4
3.1 Ga/HZSM-5	3.7	3.1 Ga–0.5 Pt/HZSM-5	8.2
6.1 Ga/HZSM-5	7.9	6.1 Ga–0.5 Pt/HZSM-5	16.1
10.0 Ga/HZSM-5	12.2	10.0 Ga–0.5 Pt/HZSM-5	16.1

parity. We believe that the roots of the remainder of the disparity can be traced back to the salt impregnation process. When an aqueous salt is added to a zeolite via incipient wetness, although the purpose may be to impregnate the material and not to disturb the cation content of zeolite, there must be a certain degree of ion exchange, but we cannot really quantify the extent of the ion-exchange process and complete ion exchange of polyvalent cations with ZSM-5 is known to be difficult. However, any ion exchange which does take place results in HNO_3, which will be broken down in the calcination step. This reduces the number of H^+ ions which can participate in the Ga_2O_3 reduction stoichiometry given in Eq. (1). Therefore, for the cases where the zeolite is the limiting reactant, the total weight loss upon reduction will be less than that calculated by assuming that $Ga(NO_3)_3$ does not exchange, is converted exclusively to Ga_2O_3, and reduction proceeds via Eq. (1). When a small amount of ion exchange and impregnation occur concurrently, we should see a weight loss upon calcination larger than that predicted by the combined affects of zeolite dehydration and $Ga(NO_3)_3 \rightarrow Ga_2O_3$, but this "excess weight loss" would be of the order 0.1 to 0.4 wt% (expected weight loss on reduction minus observed weight loss on reduction) which is virtually unobservable compared to the overall weight loss upon calcination of 7–21 wt%.

Pt addition does, however, promote the rate of gallium reduction. Table 3 compares the maximum observed rate of weight loss for catalysts with and without Pt. This result may have ramifications related to catalyst activation procedures.

CONCLUSIONS

For Ga/HZSM-5 catalysts prepared by $Ga(NO_3)_3$ impregnation, the addition of Pt increases the rate of Ga reduction but does not promote more Ga reduction than the amount obtained over Pt free samples. Since the reduction of Ga has been linked to improved catalytic performance of similar materials (*2*, *3*), this result suggests that Pt-induced catalytic performance changes which have been reported by other researchers (*6–8*) cannot be attributed to a more highly reduced Ga state in Pt-containing materials. It is likely that this conclusion can also be extended to other transition metals such as Re and Rh.

Results of the H_2 reduction studies on Ga-impregnated materials presented in this paper also extend the stoichiometric theory developed for Ga_2O_3/HZSM-5 mechanical mixtures (*3*).

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