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Characterization and Testing of Ga/HZSM-5 Prepared by Sublimation of $GaCl_3$ into HZSM-5

HZSM-5 supported Ga catalysts are known to catalyze the dehydrocyclodimerization of light aliphatic hydrocarbons to aromatic molecules. Several catalyst preparation methods have been described in the literature, including ion exchange (*1–4*), impregnation (*5*, *6*), physical mixing of HZSM-5 with Ga_2O_3 (*4*, *7*), and isomorphous substitution (*3*).

In the present Note we describe a method which makes use of sublimation of $GaCl_3$. It is motivated by two considerations:

(1) Recently it was shown by Feeley and Sachtler (*8*) that highly dispersed Pd/HY catalysts can be prepared by subliming $PdCl_2$ into HY. The physisorbed $PdCl_2$ in the zeolite cavities can easily be reduced with H_2 to Pd + HCl. The volatility of $GaCl_3$, in combination with its low boiling point (201°C) and appropriate molecular dimensions (5.5 × 7.5 $Å^2$) makes it a suitable candidate for this technique.

(2) Compensation of the positive charge of a multivalent cation in a zeolite of low Al/Si ratio by widely spaced negative charges leads to low Coulombic interaction energy (*9*). A much more stable situation can be attained by partial or complete hydrolysis of the multivalent cation; for instance, with gallium the reactions

$$GaCl_3 + H_2O = GaOCl + 2HCl \quad (1)$$

and

$$GaOCl_3 + H^+ = (GaO)^+ + HCl \quad (2)$$

would leave the Ga ion in its stable tripositive state, but three negative charges in the zeolite can be compensated by three positive ions, each in close proximity to its countercharge. Under reducing conditions the gallyl ion, $(GaO)^+$ (*4*), will be reduced to Ga^+. An additional advantage of this chemistry is that the amount of exchanged gallium is not longer limited to one-third of the negative charges of the zeolite framework as it is for Ga^{3+}. However, extensive hydrolysis will convert GaOCl into GaO(OH) which is dehydroxylated to Ga_2O_3 upon heating.

In the present work XRD, H_2-TPR, FTIR, high-resolution analytical electron microscopy (HRAEM), and detection of HCl by mass spectrometry (MS) and by titration with $AgNO_3$ have been used to identify the Ga species in the zeolite. In addition, CO-TPR has been used to distinguish $(GaO)^+$ from Ga^{3+} (*10*, *11*). During the TPR runs, the samples were heated to 800°C at a rate of 8°C/min and kept at this temperature for 1 h. After the first TPR run, the catalysts were reoxidized at 500°C. The same samples were subsequently subjected to a second TPR run. Catalysts prepared by sublimation are called *Ga/NaHZSM-5(Su)*; they are compared with samples prepared by ion exchange, as described by Davies and Kolombos (*2*), and called *Ga/NaHZSM-5(IE)*. Both types were made from NaHZSM-5 (Si/Al = 16), kindly provided by the Mobil corporation. The Na content of NaHZSM-5 is 0.60%; this catalyst was converted into the H-form where desirable.

The evolution of HCl upon heating the physical mixture of NaHZSM-5 and $GaCl_3$ was detected by MS; quantitative determination by titration after HCl absorption in an aqueous solution of NaOH by HCl or $AgNO_3$ showed that the amount of HCl de-

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tected was 92% of that expected on the basis of Eqs. (1) and (2). This lends support to the hypothesis that hydrolysis and interaction with zeolite protons take place. No damage to the zeolite structure or dealumination was detected by XRD. The FTIR spectra also confirmed the decrease in OH band intensity after sublimation. This suggests that Ga is mainly located in exchange positions inside the zeolite. Furthermore, the HRAEM results indicated that gallium is finely dispersed in the zeolite with an average particle size <5 Å. This again, shows that the nature of the prevailing Ga species is different from Ga_2O_3 (*12*). The TPR spectra show several peaks; we assume that, after heating in a carrier gas, the zeolite loaded with Ga by sublimination contains three gallium species, viz., Ga^{3+}, $(GaO)^+$, and Ga_2O_3.

We have attempted to differentiate between these by using TPR. Obviously, all three species will be reducible with H_2, but only $(GaO)^+$ and Ga_2O_3 can be reduced with CO. Further, the positions of the TPR peaks provide information; the general experience with zeolite-encaged oxide particles and ions is that the reduction of small oxide particles occurs at lower temperature than that of zeolite encaged ions (*13*). The IE and Su catalysts show unique TPR peaks which are absent in the profiles of impregnated catalysts. We attribute these peaks to the reduction of ionic Ga species. Finally, we have used the reversibility of reduction upon reoxidation with O_2 to differentiate between Ga_2O_3 and $(GaO)^+$. A temperature of 500°C was used for this reoxidation, because we had observed with impregnated catalysts that reoxidation of gallium suboxide to gallium trioxide is completed within less than 30 min at this temperature.

CO-TPR profiles are shown in Fig. 1 for samples prepared by sublimation and conventional ion exchange. In agreement with the H_2-TPR data (not shown), the profiles indicate the presence of more than one Ga species, which is reducible with CO. The MS spectra confirm that CO_2 formation matches CO consumption. Deconvolution of the TPR spectra, a lower temperature (LT) peak attributed to Ga_2O_3 and a higher temperature (HT) peak assigned to $(GaO)^+$ ions, show that the sample prepared via sublimination of $GaCl_3$ has a higher $(GaO)^+/Ga_2O_3$ ratio than the sample prepared by aqueous ion exchange. We estimate this ratio to be 69/31 for the Su and 54/46 for the IE sample.

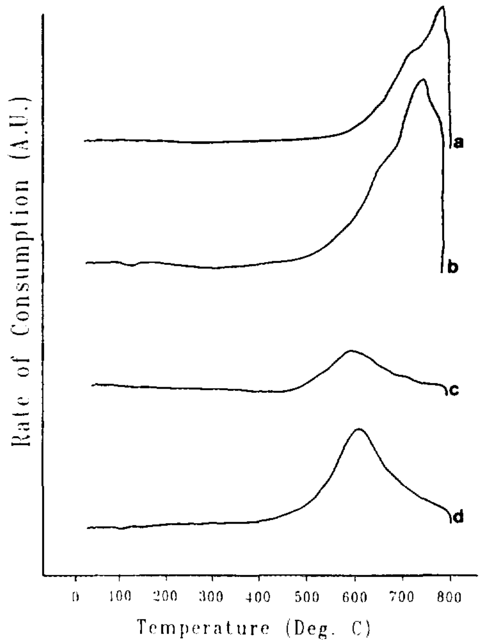

FIG. 1. First (a, b) and second (c, d) CO-TPR spectra of 1.32% Ga/HZSM-5 (Su) (a, c) and 3.10% Ga/NaHZSM-5 (IE) (b, d).

After reoxidation, samples were subjected to a second TPR test, either by H_2 or by CO. The results show TPR profiles markedly different from those obtained in the first reduction of the calcined samples. This conclusion holds irrespective of the reductant used in the first and second TPR, i.e., H_2 or CO. For illustration, the second CO-TPR profiles are shown in Fig. 1 for the Su and IE samples. Clearly, the HT peak is much smaller in the second CO-TPR than in the first CO-TPR. The LT peak is found at lower temperature in the second than in the

TABLE 1

Summary of TPR Results

Sample	H_2/Ga ratio from H_2-TPR		O/Ga ratio from CO-TPR		
	1st TPR	2nd TPR	A	B	C
3.10 Ga/NaHZSM-5(IE)	0.74	0.56	1.37	1.47	0.84
1.32 Ga/HZSM-5(Su)	1.12	0.82	1.14	1.44	0.44

Note. (A) After calcination, (B) after calcination/TPR/reoxidation, and (C) after calcination/CO-TPR/reoxidation.

first CO-TPR, indicating some oxide redistribution. In line with the general assignment of TPR peaks we conclude that Ga oxide can be reversibly reduced and reoxidized, but the $(GaO)^+$ ion, being the only ionic species reducible with CO, is incompletely regenerated in this redox cycle. This result is in line with expectations based on elementary chemistry (*14*): Ga_2O_3 particles are reduced to Ga_2O particles, which are easily oxidized by

$$Ga_2O + O_2 = Ga_2O_3, \qquad (3)$$

but $(GaO)^+$ ions which are reduced to Ga^+ with H_2 or CO will not be regenerated with O_2 because

$$2Ga^+ + O_2 = 2(GaO)^+ \qquad (4)$$

requires dissociation of O_2 on Ga^+ ions that are spaced far apart from each other. It is possible, however, that some $(GaO)^+$ ions adhere to Ga_2O_3 particles and that another fraction is reduced to Ga^0. Indeed, we observed almost complete reduction of finely dispersed $(GaO)^+$ from low loading Ga/HZSM-5(Su) (*15*). Reoxidation of Ga_n^0 particles with O_2 is expected to be easy, but will result in oxide particles, not gallyl ions.

On the basis of these assignments (Table 1), we estimate the distribution of the three Ga species in the Su sample after the first calcination to be $Ga^{3+} : (GaO)^+ : Ga_2O_3 = 0:7:3$. For the IE sample this ratio is 0:5:5.

We have tested the present Su catalyst for the aromatization of propane and compared them with samples prepared by incipient wetness impregnation and Ga-free HZSM-5. The activities and product distributions are given in Table 2.

TABLE 2

Comparison of Catalytic Performance

	HZSM-5	1.49% Ga/HZSM-5(IW)	1.47% Ga/HZSM-5(Su)
Conversion (%)	17.8	25.0	28.3
Products (wt%)			
$C_1 + C_2$	28.7	10.1	9.3
Olefins	28.1	9.2	7.1
C_4's	15.5	4.6	4.4
C_5^+ NA	2.7	0.6	0.6
Aromatics	22.4	67.7	70.6
H_2	0.6	7.8	8.0

Note. T = 530°C; WHSV = 20 h^{-1}; propane/Ar = 50/50.

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