NOTE

Gallium–Aluminum Mixed Oxides as Supports for Ni–Mo Catalysts: Characterization and Reactivity for Cumene Cracking and Thiophene HDS Reactions

Mixed oxide supports (especially silica/alumina) have been studied for many reactions. However mixed oxides of gallium and aluminum have been studied only very little and, in particular, not much work has involved investigation of their HDS and hydrocracking activities. Recently though, gallium has been shown to have valuable catalytic properties, including increased hydrogenation capability, when added to zeolites (1–3). The aim of the present work was to investigate mixed oxides of gallium and aluminum as supports for hydrotreating catalysts.

The supports were prepared by adding aqueous ammonia to solutions containing the desired amounts of aluminum and gallium chloride until pH 9 was reached, and allowing overnight precipitation. The precipitate was washed until free from chloride, then dried in air overnight and at 110°C for another night. The sample was then calcined by drawing air through it at 500°C for 4 h.

Initially, cumene cracking experiments were carried out on the supports themselves, with no added metals, to see whether the added gallium does indeed influence the properties of the support surface. The mixed oxide support (0.150 g, 80–100 mesh) was sandwiched between layers of quartz wool in a continuous-flow microreactor reactor (i.d., 15 mm), and activated by passing helium gas for 90 min while it was held at 500°C. The temperature of the reactor was then reduced to 400°C and cumene was passed over the catalyst in a stream of helium from a presaturator held at ~10°C. The products were analyzed every 20 min during the 4-h duration of the experiment by an on-line gas chromatograph equipped with a TCD detector. Metal-loaded catalysts (similar to commercial alumina-based hydrotreating catalysts) were then tested. NiO and MoO_3 were added to the supports by the incipient wetness method, to give 15 wt% MoO_3 and 3 wt% NiO; the catalysts were calcined at 500°C for 4 h, sulfided (10% H_2S in H_2 for 90 min at 500°C), and cumene hydrocracking and thiophene HDS reactions were carried out. In both cases, hydrogen was used as a carrier gas.

Sulfur analyses were performed on a LECO Sulfur Determinator SC 132. Nitrogen BET surface area measurements were made on a Micromeritics Model 2200 analyzer.

IR spectra of self-supporting 20-mg wafers were recorded on a Nicolet 8000 FTIR at a resolution of 2 cm^{-1}. Powder XRD studies were carried out using a Norelco X-ray diffractometer with graphite monochromated Fe$K\alpha$ radiation. Further details of the testing procedures are given elsewhere (4).

As shown in Table 1, the surface areas for the mixed gallium–aluminum oxides all are larger than that of γ-alumina, while that of the pure gallium oxide is much smaller. As seen in Fig 1, a sharp X-ray pattern characteristic of α-gallia (5) was obtained for the pure gallium oxide, while the broad lines seen for the mixed oxides all resemble the pattern seen for γ-alumina. It is known that extensive series of solid solutions of aluminum and gallium oxides can be formed (6, 7), and it appears from the X-ray and surface area results that these mixed oxides resemble γ-alumina much more than they resemble α-gallia.

Upon the addition of metals, there is a decrease in the surface area of the support, as can also be seen in Table 1. With the exception of the pure gallium oxide (which has a much lower surface area than the other samples) this decrease becomes larger as the gallium content increases. The probable explanation for these observations is that the introduction of gallium to the alumina disrupts the structure slightly, creating small pores that cause the mixed oxides to have a larger surface area than does alumina itself. When metals are added, these small pores are more easily blocked, so the decrease in surface area is larger.

The integrated intensities obtained for the infrared absorbance spectra of the various samples in the O–H stretching region are also given in Table 1. The most noticeable observation is that this absorption decreases with increased gallium oxide content. Since the integrated absorbance in this region of the spectrum should be proportional to the concentration of surface O–H groups; this implies that the number of available O–H groups decreases as the gallium content of the support increases.

It has been suggested previously, for other catalysts, that incomplete sulfidation of the active species may affect the hydrodesulfurization activity (8–11). This does not appear to be the case for the materials studied in this work, how-
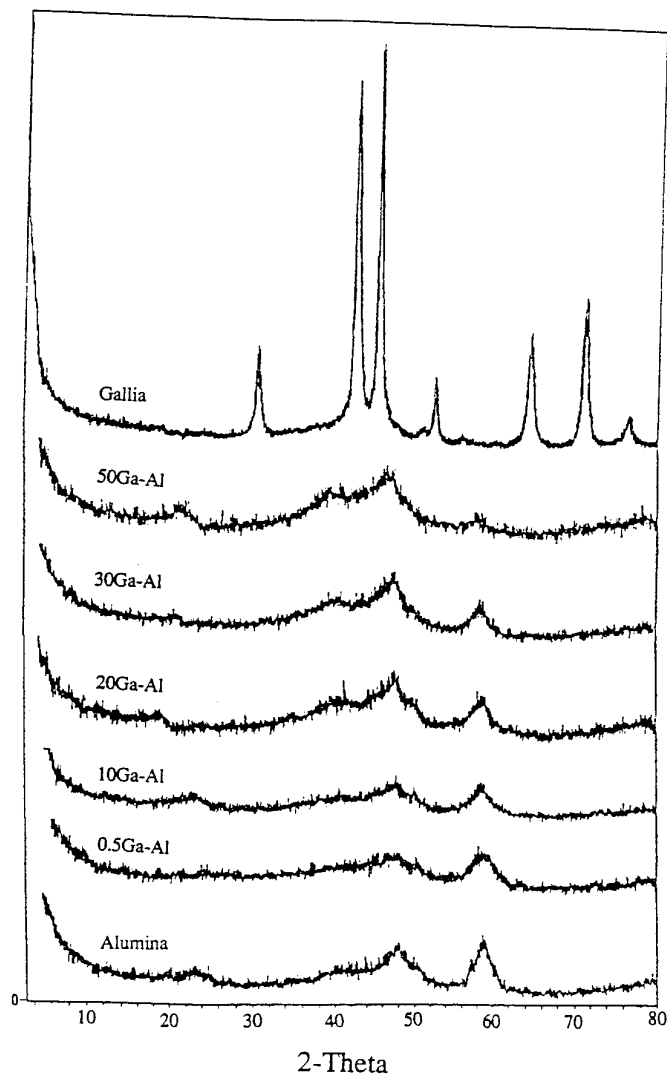
FIG. 1. X-ray powder patterns for the supports, without added metals, obtained with Fe$K\alpha$ radiation.

ever. The masses of sulfur in several of the Ni–Mo-containing catalysts were measured after sulfidation, but before the thiophene HDS experiments. The measured sulfur content was 7.6 wt% when the support was either pure Al_2O_3 or 3 Ga–Al, 9.7 wt% for the 20 Ga-Al, 12.7 wt% for the 50 Ga-Al, and 14.8 wt% for the pure gallium oxide. For those catalysts based on supports with zero or low gallium content, these values suggest virtually complete sulfidation of the nickel and molybdenum oxides. (If all of the 15 wt% MoO_3 and 3 wt% NiO were converted to sulfides, the expected sulfur content would be 8.0 wt% for each catalyst.) For those catalysts in which the support contains higher amounts of gallium (particularly the 50 Ga–Al and pure gallium oxide), the measured wt% S exceeds the expected 8%; apparently the support itself is being sulfided in these cases.

The results obtained after 4 h on stream in the cumene cracking and hydrocracking experiments are summarized in Table 2; the activities are virtually constant after this time. The cumene cracking results (carried out, as explained above, without metal additives) are quite interesting. Not unexpectedly (12), the alumina support containing no gallium was completely inactive for this reaction. However as the gallium content increased, the rate of conversion also increased, reaching a maximum for the support containing 20 wt% gallium oxide. The increased activities are not simply a surface area effect (cf. Table 1); a synergism must exist when gallium and aluminum form a mixed oxide phase. Similar experiments carried out on a physical mixture of gallium oxide and aluminum oxide having the same composition as the 20 Ga–Al showed that the physical mixture was much less active (rate = 6.39×10^{-8} mol g^{-1} s^{-1}), and also no benzene was formed. The physical mixture behaves as if the gallium oxide (which is active for dehydrogenation only, see Table 2) has simply been diluted by inactive aluminum oxide.

TABLE 1

Description of Catalysts

Mass % Ga_2O_3 in support	Catalyst designation	Surface area of support (m_2/g)		Loss in support surface area upon metals addition (m^2/g)	Intensity of OH bands in IR[a]
		No metals	Ni–Mo added[b]		
0	Al_2O_3	218	196	20	37.1
0.5	0.5 GaAl	242	221	21	41.6
3	3.0 GaAl	263	229	34	28
10	10 GaAl	281	236	45	35.3
20	20 GaAl	263	223	40	28.6
50	50 GaAl	252	172	80	27.5
100	Ga_2O_3	48	34	14	0

[a] Integrated area, baseline corrected, from 3810 to 3500 cm^{-1}.
[b] Normalized to mass of support, i.e., mass of NiO and MoO_3 subtracted from total sample mass prior to calculating specific surface areas.

TABLE 2

Cumene Cracking and Hydrocracking and Thiophene HDS Results

| Catalyst | Cumene cracking | | | | | Cumene hydrocracking | | | | | Thiophene HDS | |
	Rate[a]	B	MeS	EtB	Other	Rate[a]	B	MeS	EtB	Other	Rate[a]	%C[c]
		Selectivities (%)[b]					Selectivities (%)[b]					
Al_2O_3	0.00	0	0	0	0	4.20	23	34	6	37	21.5	0.7
0.5 GaAl	0.91	0	100	0	0	4.29	21	34	7	38	15.8	0.8
3.0 GaAl	3.63	0	100	0	0	5.92	32	19	12	37	11.6	1.0
10 GaAl	10.6	20	70	0	10	9.71	41	12	18	29	8.0	1.1
20 GaAl	18.6	15	71	0	14	11.2	45	9	23	23	6.6	1.4
50 GaAl	15.3	12	79	0	9	—	—	—	—	—	4.7	—
Ga_2O_3	12.3	0	100	0	0	4.31	77	17	6	0	3.6	0.0

[a] Rate is given in units of 10^{-8} mol g^{-1} s^{-1}.

[b] B = benzene, MeS = α-methylstyrene, EtB = ethylbenzene, "other" = mainly allylbenzene for cumene cracking, and n-propylbenzene for hydrocracking.

[c] Wt% carbon on surface after thiophene HDS reaction.

The major product of the cracking experiment in all cases was the dehydrogenation product, α-methylstyrene. Rather unexpectedly, however, significant amounts of benzene and other products (mainly β-methylstyrene and/or allylbenzene) were also formed. The appearance of such cracking and isomerization products suggests that the presence of gallium introduces an acidic functionality in addition to the anticipated enhancement of the dehydrogenation capability.

In the hydrocracking experiments, carried out over Ni–Mo-containing sulfided catalysts, cumene reactivity over the catalysts with gallium contents above 10 wt% is actually lower than in the cracking experiments, reflecting the inhibition of dehydrogenation in the H$_2$ atmosphere. However, there is still a very large difference between the catalysts supported on pure Al$_2$O$_3$ and those containing some gallium. While the selectivity for α-methylstyrene decreases as the Ga content increases, the amount of cracked and isomerized products (benzene, ethylbenzene, and propylbenzene) increases. The acidic sites which cause these products to form may be, at least in part, associated with -SH groups present at the edges of MoS$_2$ on the support (13, 14). However, the fact that the rate at which benzene is produced is substantially higher for the mixed oxides than it is for pure alumina confirms that the acidic sites generated on the support surface by gallium (and identified in the cracking experiments—see above) are also important.

The HDS experiments (Table 2) show that the rate at which thiophene is converted decreases rapidly as the gallium oxide content increases. The amount of coke deposited on the surface during this reaction increases with the gallium oxide content of the support, except for those catalysts supported on pure gallium oxide. However while
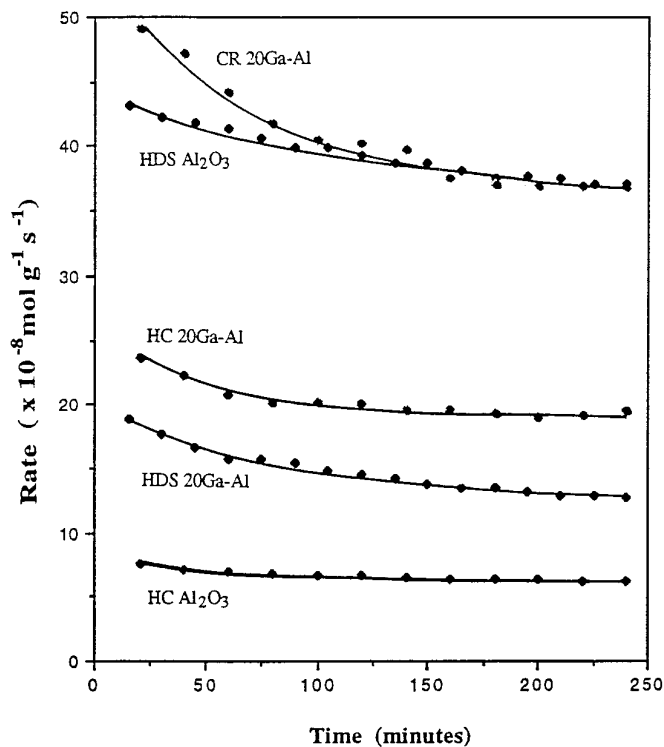
FIG. 2. Rate of cumene hydrocracking (HC) and thiophene HDS reactions at 400°C as a function of time for Ni–Mo catalysts supported on two different supports, alumina and the mixed oxide containing 20 wt% gallium oxide (20 Ga–Al). The rate for cumene cracking (CR) over the 20 Ga-Al support (no metals) is also given; this reaction does not proceed over pure alumina.

coke formation undoubtedly contributes to deactivation of the catalysts, it does not appear to be the primary cause of the differences in HDS activity between the catalysts. This is illustrated by the observation (see Fig. 2) that not only the final rates of thiophene HDS, but also the initial ones, are very different when the supports are alumina and a mixed oxide containing 20 wt% gallium oxide (20 Ga–Al). One possible explanation for the HDS results is that the dispersion of the active MoS_2 phase may be adversely affected by the decrease in the concentration of acidic surface hydroxyl groups as the gallium content increases (see Table 1).

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