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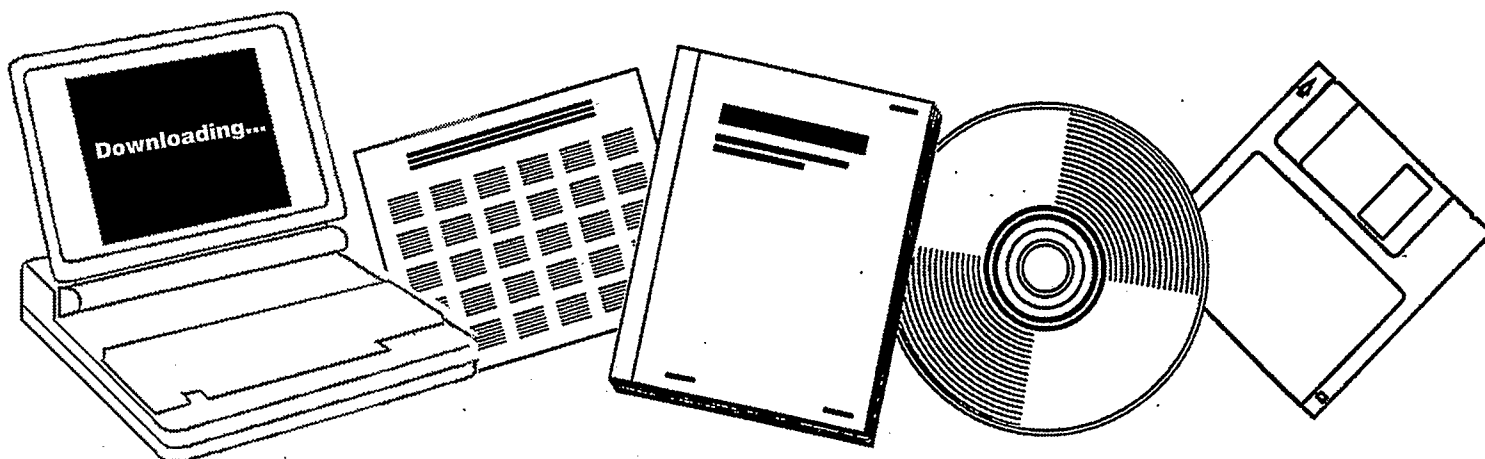
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**DESIGN OF A HIGH ACTIVITY AND SELECTIVITY
ALCOHOL CATALYST. ELEVENTH QUARTERLY
REPORT, FEBRUARY 7, 1993--MAY 7, 1993**

**DELAWARE UNIV., NEWARK. CENTER FOR
CATALYTIC SCIENCE AND TECHNOLOGY**

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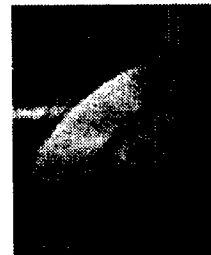
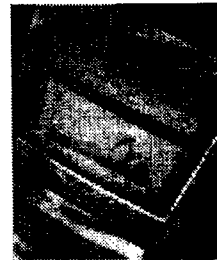
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**DESIGN OF A HIGH ACTIVITY AND
SELECTIVITY ALCOHOL CATALYST**

**Eleventh Quarterly Report for Period
February 7, 1993 to May 7, 1993**

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Ammonia TPD of Potassium Doped γ -Al₂O₃ Catalysts

The apparatus used for ammonia saturation and TPD testing outlined in the last quarterly report has been modified to avoid repeated injections of NH₃ to saturate the packed bed of sample, as the saturation breakthrough was difficult to determine accurately. In this new configuration, the break through is more apparent as the character of the gas eluted from the column can be monitored continuously while the feed stream is switched from He to NH₃ in He. Figure 1 below depicts a schematic representation of the current configuration of the NH₃ saturation and TPD apparatus.

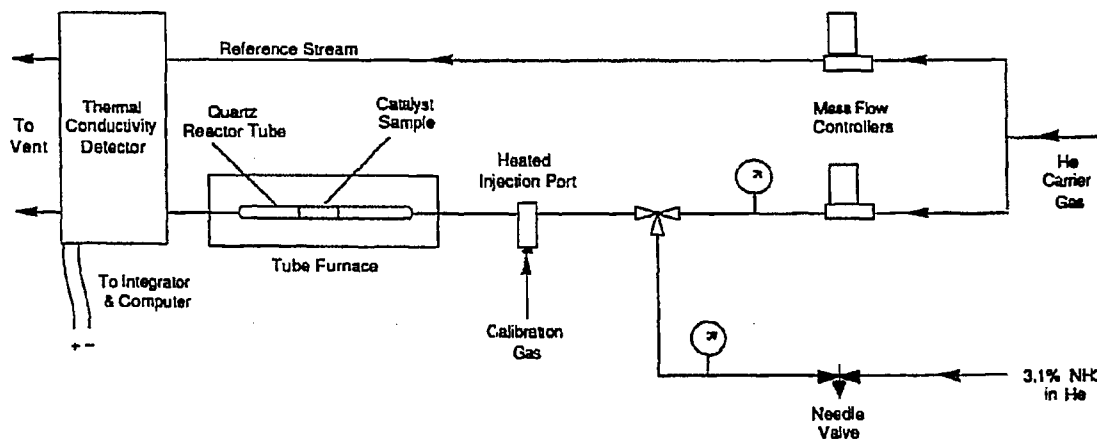


Figure 1. Modified TPD Configuration

The experimental protocol for the improved experimental configuration is as follows:

- (i) Approximately 0.3 g of 60 x 100 mesh sample—either γ -Al₂O₃ or Rh-Mo/ γ -Al₂O₃ doped with KNO₃—is loaded into a 9 mm I.D. quartz reactor tube and placed in a tube furnace.
- (ii) The sample is allowed to equilibrate to 50°C and is then dehydrated by ramping to 400°C at a rate of 7°C/min and soaking at 400°C for 50 min under flowing He.

- (iii) The sample is then cooled to 50°C, the carrier gas is switched from He to NH₃ in He, and the gas eluted from the column is monitored with an on-line thermal conductivity detector (TCD).
- (iv) When the baseline of the chromatogram has shifted and leveled off, indicating that the column is saturated with ammonia, the carrier is switched back to pure He and the temperature programmed desorption is begun.
- (v) The sample is ramped from 50 to 400°C at 7°C/min and then soaked at 400°C. The resulting desorption of ammonia from the surface of the sample is monitored by the TCD and is manifest as a series of peaks indicating ammonia-binding surface sites of different strengths (binding energies).

A representative chromatogram for the saturation and TPD of γ -Al₂O₃ is depicted in Figure 2. Note that off-line gas chromatography with a mass selective detector indicates that peak A in the figure is merely a TCD artifact of the valve adjustment needed to switch He to NH₃ in He carrier gas at the start of the saturation phase of this experiment, i.e. the gas eluted from the column contains no NH₃ before the first 20 min have elapsed.

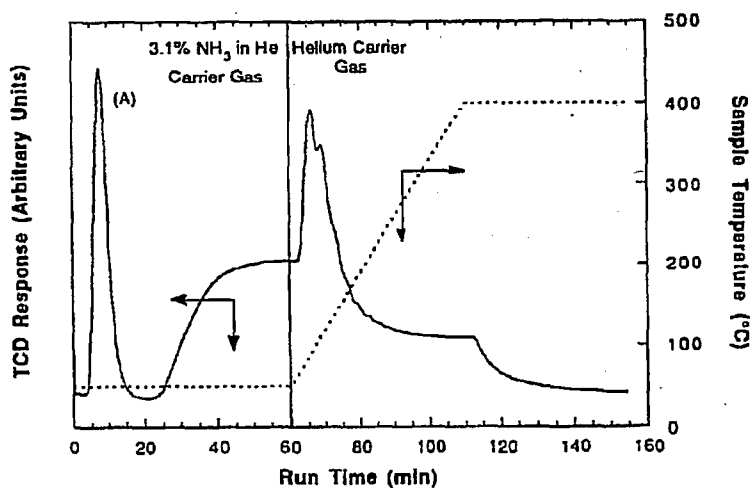


Figure 2. Saturation and TPD chromatogram for γ -Al₂O₃. Note that peak A is an artifact of the experimental protocol and is not significant.

The ammonia adsorption and saturation data have been collected for a series of potassium doped alumina samples. This data is summarized in Table 1. The first sample listed in Table 1 is γ -Al₂O₃ (American Cyanimid) which was dehydrated by heating in air at 120°C and atmospheric pressure overnight for approximately 12 h prior to testing or use as a starting material for the second and third sample listed. The 8.2 and 11.9% potassium samples were prepared by impregnating two separate batches (~3 g each) of the dehydrated alumina with 2.63 M and 3.0 M aqueous solutions of KNO₃ to incipient wetness (~0.79 ml/g) and calcining in air and atmospheric pressure at 300°C overnight for approximately 12 h. The sample which ultimately had 11.9% potassium was reimpregnated and calcined with the 3.0 M KNO₃ solution a second time to achieve a higher potassium loading. The second impregnation was necessary due to the solubility limit of KNO₃ and the pore volume capacity of the alumina.

<u>Sample</u>	<u>NH₃-Sensitive Reversible^(a) Acid Sites Per 10,000 Å²</u>	<u>NH₃-Sensitive Irreversible^(b) Acid Sites Per 10,000 Å²</u>
γ -Al ₂ O ₃ (American Cyanimid)	143 ± 14	446 ± 30
8.2% K on γ -Al ₂ O ₃	90 ± 9	457 ± 27
11.9% K on γ -Al ₂ O ₃	84 ± 8	658 ± 40

(a) Reversible sites are defined as those NH₃-sensitive acid sites which desorb NH₃ upon heating to 400 °C.

(b) Irreversible sites are those sites upon which NH₃ irreversibly adsorbs below 400 °C, as determined by a mass balance of NH₃.

Table 1. Summary of Saturation and TPD Results for Alumina Samples

As Table 1 indicates, the calculated number of reversible acid sites interacting with NH₃ below 400°C drops considerably for the 8.2% and 11.9% potassium-doped samples compared to the native γ -Al₂O₃. "Reversible sites" are defined here as those which desorb NH₃ during the heating cycle of the samples which includes a maximum temperature exposure of 400°C.

Figure 3 also demonstrates the reduction in surface acidity with increased potassium loading. This figure depicts the TPD traces for the series of alumina samples and is parametric in potassium loading.

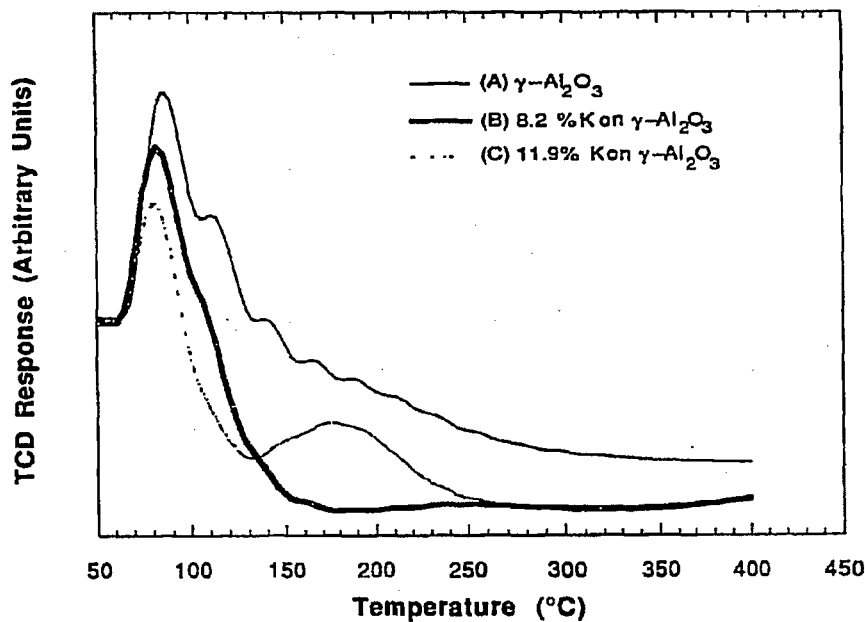


Figure 3. Ammonia TPD for Series of Potassium-Doped Alumina Samples

The TPD trace for native $\gamma\text{-Al}_2\text{O}_3$ has significant fine structure above 110°C associated with convoluted peaks representing NH_3 desorbing from the surface acid sites of increasing strength. This fine structure structure is greatly diminished when the loading is increased to 8.2% and 11.9% potassium. For the 8.2% potassium sample, only weaker acid sites are interacting with the NH_3 below 400°C , and such sites desorb NH_3 early in the temperature ramp. The 11.9% potassium sample again principally desorbs ammonia below 120°C . The sites associated with the second broad peak in Figure 3 for the 11.9% potassium trace between 150 and 250°C and the surprisingly large jump in "irreversible sites" for this sample listed in Table 1 may be an artifact

of the synthesis protocol for this sample which required two successive impregnation and calcination steps to the one required to make the 8.2% potassium sample. In the process of conducting the second impregnation the sample surface could have been partially rehydrated by the KNO_3 solution used to dope the surface—leading to both (i) the generation “reversible sites” attributable to the TPD peak between 150 and 250°C depicted in Figure 3 and (ii) the unusual jump in irreversible sites for the 11.9% sample listed in Table 1.

Rh-Mo/ γ - Al_2O_3 Assessments

In order to further examine the influence of molybdenum oxide promotion on the catalytic activity of alumina-supported rhodium catalyst, additional samples of Rh/ γ - Al_2O_3 and Rh-Mo/ γ - Al_2O_3 have been synthesized. The transition-metal precursors used to synthesize these samples were $\text{Mo}(\text{CO})_6$ and $\text{Rh}(\text{I})(\text{CO})_2(\text{acac})$. Metal carbonyls were chosen rather than metals salts in order to provide higher dispersions and more uniformly dispersed metal aggregates. The synthesis procedure for these samples followed a basic protocol which involved (i) slurring and degassing the alumina support in refluxing anhydrous heptane and cooling to room temperature, (ii) chemisorbing the first transition-metal carbonyl by adding it to the slurry and refluxing under flowing N_2 for 4 h and cooling to room temperature, (iii) filtering and mildly oxidizing the resulting catalyst in air and (iv) either calcining the resulting catalyst in air at 125°C overnight for approximately 12h, if it was intended to be monometallic, or repeating the chemisorption process in a fresh, degassed heptane slurry with the second metal and then calcining the resulting bimetallic sample. Using this basic approach, the alumina-supported samples described in Table 2 have been synthesized.

<u>Sample Name</u>	<u>wt% Molybdenum</u>	<u>wt% Rhodium</u>	<u>Rh/Mo Ratio</u>
<i>Monometallic</i>			
Rh-I	N/A	0.25	N/A
Rh-II	N/A	0.5	N/A
Rh-III	N/A	1.5	N/A
Rh-IV	N/A	3.0	N/A
<i>Bimetallic</i>			
Rh-Mo-I	1.5	0.25	0.167
Rh-Mo-II	1.5	0.5	0.333
Rh-Mo-III	1.5	1.5	1.0
Rh-Mo-IV	1.5	3.0	2.0

Table 2. Alumina-Supported Rhodium Monometallic and Molybdenum-Promoted Catalysts

The catalyst samples described in Table 2 will be tested for (i) the infrared (IR) activity of adsorbed CO, (ii) the rate of rhodium sintering and agglomeration via dynamic H₂ chemisorption experiments, (iii) catalytic activity for CO hydrogenation and, possibly, (iv) site structure sensitivity/insensitivity via comparing results of propylene hydrogenation and propane hydrogenolysis across the samples. The aim of this testing will be to examine the physically stabilizing and electronically synergistic effects of the molybdenum oxide promoter as a function of rhodium loading.

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