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AEROGEL CATALYST MODIFICATION TO IMPROVE CATALYTIC STABILITY DURING THE NITROXIDATION OF PROPYLENE

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Résumé - L'introduction de MgO ou de Fe₃O₄ dans l'aérogel binaire NiO/Al₂O₃ augmente très notablement la stabilité du catalyseur dans la nitroxydation du propylène.

Abstract - By introducing MgO or Fe₃O₄ into a binary NiO/Al₂O₃ aerogel the catalytic stability in the nitroxidation of propylene may be dramatically improved.

INTRODUCTION

The nitroxidation of propylene over nickel oxide alumina aerogel catalysts, the combination of nitric oxide and propylene to form acrylonitrile, was first reported by Zidan, et al. in 1977 /1/. Recently, during an investigation of the mechanism of this reaction /2/, attempts were made to understand the nature of deactivation which occurred and to understand how it may be controlled by aerogel catalyst modifications /3/. Work has continued to model the rate of deactivation and to quantify the deactivation process which will be discussed below.

The nitroxidation reaction is :

The product, acrylonitrile, is an important monomer used in further processing for the manufacturing of acrylic fibers, nylon-66, and several other polymeric compounds.

EXPERIMENTAL

Aerogel catalysts synthesis

The reference catalyst was a 1:1 atomic ratio of Ni to Al aerogel. The aerogel was formed by autoclaving a mixture of 5 % nickel acetate tetrahydrate in methanol and 12.5 % aluminum-tri-sec-butoxide in sec-butanol. The procedure was as follows : a solution of 12.5 % aluminum-tri-sec-butoxide in sec-butanol was carefully made up and capped. A second solution of 5 % nickel acetate tetrahydrate in methanol was made up. Additional water, required for the hydrolysis of the alumina, was added to the second solution.

Then the proper amount of the second solution was rapidly added to first solution which would give a resultant atomic ratio of Ni to Al of 1:1. An aluminum hydroxide precipitate formed immediately while the Ni ions remained in solution (the alcogel). This mixture was then placed into an autoclave and supercritically dried. The Ni ions deposited onto the alumina during the drying process. The final product was greyish black. X-ray and Raman analysis showed the composition to be amorphous alumina, nickel oxide and a surface nickel ions.

Other atomic ratios of Ni to Al investigated were 0.05, 0.2, 0.4, 0.6, and 0.86. Another modification examined in the preparation of the 0.86 Ni to Al aerogel was the addition of ammonia to solution 2 before addition to solution 1. The color turned from green to blue for this solution, and the resultant aerogel had higher surface area of 426 m²/g versus 360 m²/g for the 0.86 material without ammonia. Further, evaluation of this aerogel showed tremendous activity for the cracking of propylene to methane with no activity for nitroxidation. Electron micrographs of this catalyst after testing showed a "peppered" surface indicating the agglomeration of Ni atoms into clusters. These agglomerations were not seen on the reference catalyst.

Further aerogel modifications investigated were the substitution of magnesium or iron for a portion of the nickel content. Specific compositions made were 0.2 Mg:0.8 Ni:1.0 Al and 0.2 Fe:0.8 Ni:1.0.

The magnesium and iron solutions used in the alcogels solutions were 5 % magnesium acetate tetrahydrate in methanol and 5 % ferric acetylacetonate in methanol.

Experimental test unit

The experimental test unit consisted of a quartz reactor, a reactant mixture panel, and an analytical section. The quartz reactor was designed as an up flow reactor catalyst bed. An aerogel catalyst (0.2 g) was placed between two quartz fritted disks (volume approximately 10 cm³) which kept the catalyst inside the quartz reactor. The reactor was heated by a quartz tube oven. All reaction measurements for this work were conducted at a catalyst temperature of 410°C ($\pm 2^\circ\text{C}$).

The reactant gas feed mixture was 2 cc/min nitric oxide, 18 cc/min propylene (CP grade), and 10 cc/min helium (1:9:5 NO:C₃H₆:He). These flow rates were constant for all evaluations except in the evaluations where moisture was added when (0.2 Fe:0.8 Ni:1.0 Al and 1:1 Ni:Al) helium was passed through a packed column with water. The saturated helium was then blended with the feed mixture at a rate of 10 cc/min. All aerogel catalysts received similar pretreatments of pure oxygen (30 cc/min) at 410°C for 24 hours. Thirty minutes prior to a run, the oxygen flow was switched to pure helium to prevent any explosions before switching to the propylene reactant mixture.

Gas analysis of the effluent gas stream was done by two gas chromatographs and a quadrupole mass spectrometer. For analysis of hydrocarbons, a gas chromatograph equipped with a FID was used. Initially, the FID chromatograph was a Perkin Elmer Model 3920 with a 1/8" O.D. 2 m column packed with Porapak QS. Later a Hewlett-Packard Model 5890 gas chromatograph was used. Oven temperature for the gas chromatographs was set isothermally at 120°C. Sampling was done with 1 cc gas chromatograph sample loop placed in line with the effluent reactor lines. Attached to the Hewlett-Packard chromatograph was a Hewlett Packard Model 3393-A integrator.

For analysis of nitric oxide, oxygen, carbon dioxide, and other inorganic gases, an Antek Model 300 gas chromatograph with TCD was used. This chromatograph had a 1/4" O.D. 2.5 m column packed with Porapak QS. It was operated isothermally at 120°C. Further details about the gas chromatograph operating conditions are presented in /2/.

Deactivation analysis - Relevant equations

The modelling of the deactivation reported below can be described by a concentration independent deactivation site balance : i.e.,

$$dS/dt = -k_d S \quad (2)$$

where S is the concentration of active sites per gram of catalyst and k_d is the deactivation rate constant. The lower k_d , the more stable the catalyst. Defining activity, a, as the ratio of the rate at any time (t-t_p) to the peak rate observed at time t_p and assuming that rate is proportional to the concentration of active sites then the following activity equation results :

$$da/dt = -k_d a \quad (3)$$

which integrates to :

$$a = r/r_{\text{peak}} = \exp(-k_d t_d) \quad (4)$$

where r is the rate of acrylonitrile formation in moles/g/sec and t_d = (t-t_p) is the time after the peak activity was observed. t_d = 0 is the time when the rate of formation to acrylonitrile equals the maximum. Thus, k_d for various aerogels and run conditions can be determined by least squares analysis for the r/r_{peak} vs. t_d data and qualitative comparison

can be made.

Results and discussion

The evaluation of 1:1 Ni to Al aerogel catalyst for nitrooxidation of propylene is as shown in Fig. 1. Focusing on the top curve in Fig. 1 which represents results for the reference catalyst, 1:1 Ni to Al, the first 20 minutes of the run shows a surface oxidation adjustment period.

Because the aerogel is oxidized with pure oxygen for a period of 24 hours prior to testing, the surface contains a surplus of oxygen which oxidizes propylene to carbon dioxide. As the run continues, the catalyst is reoxidized by nitric oxide which introduces nitrogen to the surface and propylene becomes more preferably oxidized to acrylonitrile. Further, partial oxidation is preferred over total oxidation because the mixture is severely oxygen lean (1 to 9 for NO to C_3H_6). Product distribution after 20 minutes was approximately 74 % acrylonitrile, 26 % acetonitrile, and 8 % carbon dioxide. Product distribution continued to improve to values of approximately 90 % acrylonitrile, 5 % acetonitrile, and 5 % carbon dioxide by the end of a 3 hour evaluation.

The discouraging result was a 45 % decline in acrylonitrile production over the three hour test period from its peak value.

Nickel is a known hydrocracking catalyst and a product of cracking is surface carbon and carbon filaments which grow on the surface. Carbon deposition was confirmed in post testing by passing a 5 % oxygen in helium mixture over the catalyst and detecting carbon dioxide. Further, catalyst examination by electron micrographs confirmed the presence of carbon filaments with metallic nickel centers. Therefore, decreasing nickel content was the initial approach investigated for stability improvement.

Figure 1. Rate of Formation of Acrylonitrile as a Function of Time over NiO/Al_2O_3 Aerogel Catalysts with Different Nickel to Aluminum Atomic Ratios.

The influence of Ni to Al ratio on catalyst stability is shown in Table 1 and Figure 1 for 4 levels of Ni to Al ratios. For the ratios of 0.2, 0.4, and 1.0 Ni to Al, percent activity retained over three hours is similar at 56 %, 59 %, and 58 %, respectively and k_d ranged from 0.142 to 0.191 hr^{-1} . Further, the peak activity per gram of nickel was similar

for the three ratios at 2.52, 2.82, and 3.27 $\mu\text{moles/g Ni sec}$. These results suggest the active site that is related to NiO. However, evaluation of the 0.05 Ni to Al ratio gave a different trend. First its overall activity was superior to the 0.2 Ni to Al aerogel and further it nearly matched the activity achieved with the 0.4 Ni to Al aerogel. Its peak activity per gram of nickel was 16.27 moles/g Ni sec . The 0.05 Ni to Al aerogel had poorer selectivity, however. It was nevertheless a more stable material retaining 69 % of its activity over a 3 hour run. The results suggest that the active site for nitroxidation is more than just NiO and that the support, alumina, plays a role.

Influence of Mg and Fe on catalyst stability

An aerogel catalyst was made with 0.2 Mg substituted for 0.2 Ni to give a resultant aerogel composed of 0.2 Mg:0.8 Ni:1.0 Al. This catalyst gave the best stability over a three hour period with no loss in activity over three hours.

Overall, the Mg containing aerogel had the lowest deactivation rate constant of 0.058 hr^{-1} . The explanation of why magnesium improved the stability is as follows. Catalytic activity for the cracking of hydrocarbons occurs over alumina-silica catalysts, and it has been shown that this activity is directly related to acidity level /4/.

The addition of basic magnesium (MgO) neutralizes acidity due to alumina and lowers cracking activity, therefore increasing stability. Thus, the deactivation process is partially related to the acidity of the aerogel.

Another aerogel catalyst was made with 0.2 Fe substituted for 0.2 Ni to give a resultant aerogel composed of 0.2 Fe:0.8 Ni:1.0 Al. This catalyst's stability was poorer than the Ni/Al aerogel ($k_d = 0.23 \text{ hr}^{-1}$). The motive to include iron in the aerogel catalyst was to provide an alternative to the Boudouard reaction ($2 \text{ CO} \rightarrow \text{C(s)} + \text{CO}_2$), a source of surface carbon, by promoting an alternative reaction path for CO via the water gas shift reaction, $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$. Further testing in which moisture was added to the feed showed a dramatic improvement in stability. k_d decreased by a factor 4 to 0.062 hr^{-1} and the catalyst rivals the stability of the Mg containing aerogel. However, in comparing the peak activity between the magnesium and the iron containing aerogels, the magnesium aerogel is about a factor 2 better.

Table 1 : Deactivation Constants for Various Aerogel Catalysts Investigated for the Nitroxidation of Propylene to Acrylonitrile.

Catalyst	Atomic Ratio of the Metallic Components	Moisture Content in the Reactant Feed ¹⁾	k_d hr^{-1}	Peak Activity ²⁾ $\times 10^{-8}$	Activity After 3 Hours $\times 10^{-8}$
NiO/Al ₂ O ₃	1:1	0.00	0.191	83.8	46.3
NiO/Al ₂ O ₃	0.4:1	0.00	0.142	50.3	30.0
NiO/Al ₂ O ₃	0.2:1	0.00	0.149	32.8	18.4
NiO/Al ₂ O ₃	0.05:1	0.00	0.160	45.2	31.1
NiO/(MgO + Al ₂ O ₃)	0.8:0.2:1	0.00	0.058	81.8	81.8 ³⁾
(NiO + Fe ₃ O ₄)/Al ₂ O ₃	0.8:0.2:1	0.00	0.230	83.2	53.0
NiO/Al ₂ O ₃	1:1	2.66	0.105	97.9	59.0
(NiO + Fe ₃ O ₄)/Al ₂ O ₃	0.8:0.2:1	2.66	0.062	41.6	31.4

1) k pa

2) g mole/cm³/g/sec

3) the activity was observed for 48 h

Since the addition of moisture to the feed stream improved the stability of iron containing aerogel an evaluation with moisture added was performed on the reference catalyst, 1:1 Ni/Al. The results of this modification was encouraging with the highest peak rate observed for any of the aerogels investigated and k_d decreasing from 0.191 hr^{-1} (table 1) to 0.105 hr^{-1} .

Carbon monoxide used as a molecular probe

Further evidence that the Boudouard reaction is the major source of deactivation was established by flowing a 5 % carbon monoxide in helium stream across the 1:1 Ni/Al aerogel at 410°C. The catalyst deactivated and k_d was 0.23 hr⁻¹. This value of the deactivation rate constant compares with the value for iron containing aerogel shown in Table 1. When a mixture of 5 % carbon monoxide and 5 % nitric oxide in helium was flowed across the catalyst the deactivation rate constant decreased by a factor of 2 to 0.12 hr⁻¹. The presence of nitric oxide provided an alternative path for carbon monoxide oxidation in which no carbon was deposited on the surface.

CONCLUSIONS

1. Stability of nickel oxide alumina aerogel catalysts is not directly related to Ni content. The deactivation rate constants, k_d , range from 0.160 to 0.191 hr⁻¹.
2. The introduction of magnesia into the nickel-oxide-alumina aerogel catalyst improved the stability, $k_d = 0.058$ hr⁻¹, by lowering the aerogel's surface acidity.
3. The introduction of iron into the nickel oxide-alumina aerogel catalyst decreased stability for a dry feed mixture, $k_d = 0.230$ hr⁻¹, and improved stability for a moist feed mixture, $k_d = 0.061$ hr⁻¹. This is because a suspected product intermediate, carbon monoxide, reacts via the Boudouard reaction in the first case depositing surface carbon and reacts via the water gas shift reaction in the second case.
4. Deactivation via the Boudouard reaction was further substantiated by flowing carbon monoxide across the catalyst and measuring a deactivation rate of 0.23 hr⁻¹.

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