Catalysis of the formation of ϵ-caprolactam from cyclohexanone oxime by tungsten oxide solid acids

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The synthesis and characterization of a new solid acid, tungsten oxide/silica gel, is described and different procedures for its preparation compared. Characterization includes the combined calorimetric and adsorption isotherm analysis, cal-ad, providing equilibrium constants, enthalpies and amounts of the different acid sites on the solid. The solid acid is shown to catalyze the Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam. Competing pathways that depend on strength and the industrial significance of this intermediate for Nylon 6, make this an ideal reaction to show the relationship between acid catalysis and solid acidity. The utility of the cal-ad procedure in probing catalytic reactivity is illustrated by comparing the acidity of the original catalyst, the regenerated catalyst and a catalyst prepared by conventional means. The strength and number of acid sites correlate to selectivity and activity.

Keywords: acid catalysis, silica supported tungstic acid, caprolactam, isomerization of cyclohexanone oxime, cal-ad, solid acidity

1. Introduction

Research from this laboratory has led to the synthesis of solid acids and the characterization of solid acidity by a combined calorimetric and adsorption analysis referred to as cal-ad [1]. The relationship between acid strength and activity of acid catalyzed reactions is being studied and acid strength thresholds and upper limits for various acid catalyzed reactions are being determined. Recently we reported the characterization of a novel solid acid consisting of tungsten oxide supported on silica gel [2] prepared from the hydrolysis of WCl_6, referred to as SG-W. The acid strength of this material was determined by cal-ad which provides a measure of the acid strength and quantity of the acid sites [1]. When slurried in cyclohexane an enthalpy of interaction with pyridine of -31.7 kcal mol^{-1} results corresponding to an acid of moderate strength. The solid contains 0.068 mmol g^{-1} of these acid sites and 0.41 mmol g^{-1} of a weaker, -16.2 kcal mol^{-1} acid site. The acidity was not great enough to isomerize pentane but did catalyze the dehydration of propanol. Supported tungsten oxide catalysts have been reported to isomerize butene to isobutene [3].

It was of interest to expand the types of catalyzed reactions that can be correlated to acid strength. Ideal reactions for this purpose are those which produce different products from competing reaction pathways that depend on acid strength. It is also ideal to use industrial significant reactions for such investigations.

We decided to investigate the isomerization of cyclohexanone oxime, an important chemical intermediate used for the production of ϵ-caprolactam, which is the monomer of Nylon 6. Commercially, it is synthesized by a liquid phase Beckmann rearrangement of cyclohexanone oxime using sulfuric acid. The commercial process uses stoichiometric amounts of sulfuric acid and results in the formation of 1 to 5 tons of ammonium sulfate by-product per ton of ϵ-caprolactam produced. Being 47th on the list of industrial chemical production, the environmental consequences of this process are significant and have motivated [4] research to find a greener process. Solid acid catalysis of the Beckmann rearrangement of cyclohexanone oxime in the gas phase would be a viable green alternative.

Solid acid catalysts for the gas phase rearrangement of cyclohexanone oxime to ϵ-caprolactam [5–9] are reported but all lead to a rapid decline in selectivity in short time due to coking [6]. Coking is reported to be acid strength dependent. Strongly acidic aluminas catalyze formation of side products which cause coking leading to decreased caprolactam selectivity [6] compared to less acidic aluminas. This reaction is ideal for incorporation into acidity–activity studies because the potential exists of defining optimal acidity limits and ranges that give high selectivities and similar ranges that minimize coking.

SG-W leads to high activity for the vapor phase rearrangement of cyclohexanone oxime to ϵ-caprolactam without a substantial decline in activity or selectivity for 40 h. This catalyst's activity, deactivation, and regeneration were monitored and these properties are compared to cal-ad measures of the acidity providing insight about catalyst reactivity and deactivation. Comparisons are made between of the acidity and activity of materials from different preparative methods for supporting

WO_3. The effect of catalyst pore structure, reaction temperature, contact time, and cyclohexanone oxime carrier solvent were also investigated.

2. Experimental

2.1. Catalyst preparation

The SG-W catalyst is prepared by adding 80–200 mesh Davison silica gel to 0.5 mmol of WCl_6 per gram of silica in carbon tetrachloride. The solid product is treated with 1 M HNO_3, then deionized water and dried at 200°C in flowing air. The resulting SG-W catalyst is yellow. Further details concerning its preparation and characterization are reported [2].

Silica supported tungsten oxide was also prepared from ammonium tungstate [9,10]. A solution of ammonium tungstate corresponding to 10 wt% WO_3 per gram silica was prepared in water. Silica gel was added to the solution, and the water was evaporated. The resulting solid was calcined at 500°C in air to decompose the ammonium tungstate, producing a green solid whose color is characteristic of anhydrous tungsten oxide.

2.2. Reaction conditions

Unless noted otherwise, reactions of cyclohexanone oxime were carried out in a one time flow through reactor using the following conditions: 300°C, 0.5 g of catalyst, 8 wt% cyclohexanone oxime solution syringe pumped into the reactor at 1 ml/h with N_2 carrier gas flowing at 30 ml/min. Products were analyzed using gas chromatography and calibrated with known standards.

2.3. Surface characterization

Powder X-ray diffraction (XRD) studies were done using a Philips X-ray diffractometer and a 2θ range of 5 to 70. Scanning electron microscopy (SEM) analysis was done using a Joel 35C electron microscope with an acceleration voltage of 25 kV using several magnifications.

2.4. Cal-ad analysis of solids

Calorimetric titrations of the solids with pyridine were carried out using 1 g of catalyst slurried in cyclohexane. The cyclohexane and pyridine reagents were distilled over P_2O_5 prior to use. The heat evolved was measured after each injection of a known amount of pyridine solution. In the cal-ad process [1,11] an adsorption isotherm is also measured over the range of base additions used in the calorimetric titrations. The combined data from the calorimetric titration and adsorption measurements are analyzed simultaneously to determine accurate equilibrium constants, K_i's, moles of sites per gram, n_i's, and acid site strengths, ΔH_i's, for different acid sites on the solid. The subscripts (i) label the different sites, where $i = 1$ describes the strongest acid sites, and $i = 2$ the next strongest site, and so on. The cal-ad measurements are done in a non-interacting hydrocarbon solvent (cyclohexane) whose molecular mass is close to that of the donor (pyridine) in order to cancel out contributions from a dispersion component to the measured enthalpy [1].

2.5. UV-Visible spectroscopy

Measurement of the equilibrium concentration of pyridine in solution over the solid during the calorimetric titration experiment was determined by UV-Visible spectroscopy as described previously [1,11]. The UV-Visible spectra were obtained using a Perkin-Elmer Lambda 6 UV-Vis spectrophotometer and suprasil quartz cells.

3. Results and discussion

3.1. Catalyst characterization

Most supported tungsten oxide catalysts are prepared by using ammonium tungstate as the tungsten oxide precursor. The ammonium salt requires a calcination temperature of 500°C to decompose the ammonium salt. We have reported a low-temperature preparation of tungsten oxide on silica using WCl_6 [2]. The reaction between WCl_6 and silica's hydroxyl functionality yields a species whose formula is $W(OSG)_4Cl_2$, where SG is silica gel. The oxychloride species is treated with 1 M HNO_3 to hydrolyze the remaining chlorides and a yellow silica supported hydrated tungsten oxide species ($WO_3{\cdot}H_2O$) results, which will be referred to as SG-W. The SG-W catalyst was shown by cal-ad analysis to possess a greater amount of strong acid sites, n_1, than silica supported tungsten oxide made from ammonium tungstate (silica-WO_3). The strength of the strongest sites are comparable ($-\Delta H = 32 \pm 2$ and 28 ± 2 kcal/mol), but 6.5×10^{-5} mol/g of strong acid site (n_1) are found on SG-W, while only 1.6×10^{-5} mol/g of strong site (n_1) are found on the solid prepared from ammonium tungstate (silica-WO_3). The results from the cal-ad analysis of SG-W and silica-WO_3 are summarized in table 1. The strong acid site has an idealized structure illustrated by replacing Cl by OH and forming $WO_3{\cdot}H_2O$ with the strong acid site $(SiO)_{4-n}W(OH)(O^-)_{1+n}$ also functioning as an anchoring site. The weaker site is from the tungstic acid like proton. The complete characterization of the SG-W catalyst was described earlier [2]. SG-W has a BET surface area of 242 m^2/g. The greater number of acid sites on SG-W is reported to be due to better surface dispersion of tungsten oxide, as evidenced by XPS, BET and SEM [2]. Better dispersion decreases the average length of the tungstic acid like polymer and decreases the

Table 1
Cal-ad analysis of fresh and regenerated SG-W catalysts

Catalyst	$-\Delta H_1$ (kcal/mol)	K_1 (ℓ/mol)	n_1 (mol/g)	$-\Delta H_2$ (kcal/mol)	K_2 (ℓ/mol)	n_2 (mol/g)
SG-W fresh	31.7	6.8×10^8	6.5×10^{-5}	16.2	7.1×10^2	4.1×10^{-4}
	±1.9	$\pm 1.5 \times 10^8$	$\pm 4.2 \times 10^{-6}$	±1.0	±359	$\pm 2.0 \times 10^{-4}$
SG-WO_3 [a]	27.4	1.2×10^9	1.6×10^{-5}	17.8	5.8×10^3	2.4×10^{-4}
	±2.4	$\pm 8.9 \times 10^8$	$\pm 1.9 \times 10^{-6}$	±2.5	$\pm 1.9 \times 10^3$	$\pm 1.0 \times 10^{-4}$
SG-W regen.	27.9	5.3×10^9	2.4×10^{-5}	18.0	2.4×10^3	4.6×10^{-4}
	±2.4	$\pm 3.3 \times 10^9$	$\pm 2.7 \times 10^{-6}$	±1.8	$\pm 1.6 \times 10^3$	$\pm 8.6 \times 10^{-5}$

[a] Prepared by calcination of $(NH_4)_2WO_4$.

relative number of weaker acid sites compared to strong anchoring sites.

3.2. Effect of solvent on the rearrangement of cyclohexanone oxime to caprolactam

The conversion of cyclohexanone oxime to ϵ-caprolactam over the SG-W catalyst was studied by feeding a solution of 8 wt% cyclohexanone oxime in benzene solvent. Initially, selectivity near 90% for ϵ-caprolactam resulted, but it declined to 78% after 10 h and 60% after 25 h of reaction, while the conversion of the oxime remained at 99% for the entire reaction time. The major product was caprolactam, and the other products are cyclohexanone and minor amounts of aniline, as found in other reports using solid acids for this reaction [4,5]. After 25 h the catalyst which was initially yellow in color was visually coked (black in color). Analysis gave 9.3% carbon and 1.1% nitrogen. The surface area decreased to 161.6 m^2/g, with loss of small pores.

The catalyst was treated at 500°C in air for 8 h to burn off the coke. The regenerated catalyst was retested at our typical conditions, and the results are shown in figure 1. The conversion of the oxime remained at 99% during the entire 20 h, but the initial selectivity of 85% dropped rapidly to 69% after 12 h and to 53% after 20 h. The amount of both carbon and nitrogen detected on the surface of the used catalyst increases with reaction time suggesting that polymerization of caprolactam followed by pyrolysis on the surface causes the selectivity decrease as proposed in the literature [4].

A sample of an amorphous SG-W catalyst, that was not HNO_3 washed to impart the crystallinity [2], was tested for caprolactam activity using the typical conditions. Initially, 93% conversion with 70% selectivity to caprolactam was found, which is poor compared to the 99% conversion and 90% selectivity to caprolactam for the HNO_3 washed SG-W catalyst. The acid wash is needed to obtain the strong acid site [2] and high selectivity for caprolactam.

The effect of the solvent used to deliver the cyclohexanone oxime was varied while keeping all other conditions constant. The conversion of the oxime was 99% for all the solvents tested, but as shown in figure 2, the solvent has a dramatic effect on the selectivity of the reaction. The delivery solvents, methanol and acetonitrile increased the selectivity for ϵ-caprolactam as compared to methylene chloride and benzene. This increased selectivity with both methanol and acetonitrile is accompanied by a decrease in the amount of coke found on the catalyst to 4.5 wt% compared to the 9.3 wt% coke with

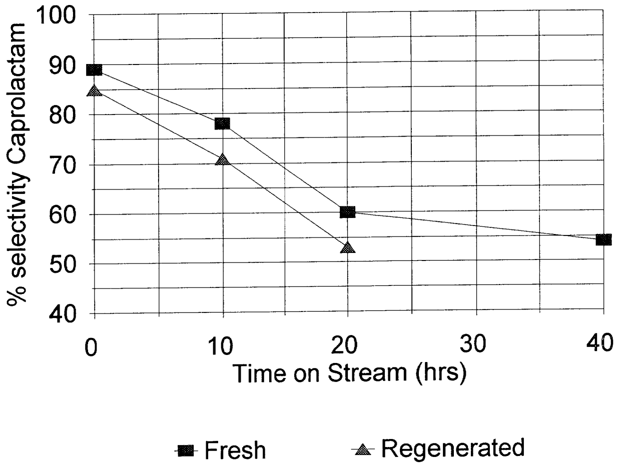

Figure 1. Caprolactam selectivity using the SG-W catalyst (0.5 g catalyst, 300°C, 1 ml/min feed of 8 wt% oxime in benzene solvent, and 30 ml/min N_2 carrier gas).

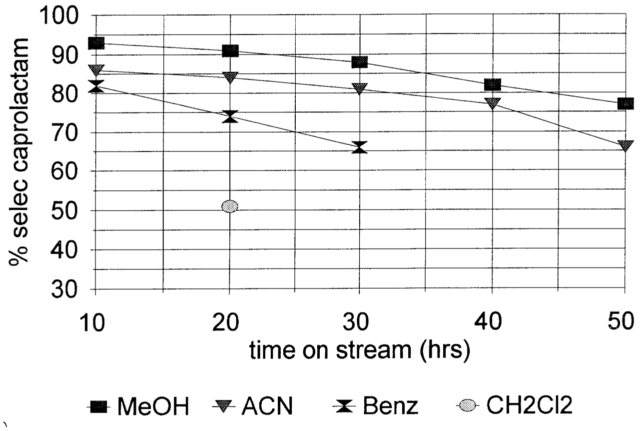

Figure 2. Effect of delivery solvent used in the cyclohexanone oxime feed (0.5 g catalyst, 300°C, 1 ml/min feed of 8 wt% oxime, and 30 ml/min N_2 carrier gas).

benzene and 12 wt% coke with methylene chloride. The trend parallels solvent basicity and suggests that either solvent decreases the acidity of the most acidic sites or, alternatively, basic solvents increase the desorption rate of ϵ-caprolactam, decreasing its contact time on the surface, and lowering the likelihood for acid catalyzed opening of caprolactam to form polymer on the catalyst surface.

The transformation of cyclohexanone oxime into ϵ-caprolactam has also been studied over TS-1 [12]. However, in order to obtain high conversion of oxime (100%) and high selectivity to ϵ-caprolactam (92%) higher temperatures, and longer residence times were required as compared to SG-W. TS-1 is a weak acid catalyst with an approximate $-\Delta H_1 = 14$ kcal/mol and its lower activity as compared to SG-W may be a reflection of its lower acidity.

3.3. *Effect of temperature and feed rate*

In order to relate acidity to activity, it is necessary to optimize conditions for running the catalytic reaction. The effects of temperature, oxime feed rate, and carrier gas flow rate were investigated using methanol as the solvent for 8 wt% cyclohexanone oxime with all other conditions the same as earlier. All reactions are compared after 10 h of reaction. When the N_2 flow rate was dropped to 10 ml/min, the selectivity to caprolactam dropped to 82% with 99% conversion of cyclohexanone oxime. Consistent with the solvent studies too long a residence time decreases selectivity via ring opening. Too short a contact time decreases the conversion, and also decreases the selectivity. Lower flow rates increase the residence time on the strong acid sites and lead to polymerization and eventually coke.

The variation of oxime feed rate was also investigated. Doubling the feed rate to 2 ml/min results in a drop of oxime conversion to 71%, but the selectivity to caprolactam remained at 90% after 10 h. A feed rate of 0.5 ml/min gives the same results for conversion and selectivity as the 1ml/min feed rate with methanol.

The reaction temperature was varied from 250 to 350°C with the products analyzed after 10 h of reaction. At 250°C the conversion of the oxime dropped to 50%, compared to 99% at 300°C, but the selectivity to caprolactam dropped only slightly to 89%. At 350°C the conversion of the oxime was still 99% but the selectivity to caprolactam decreases to 74%, compared to over 90% at 300°C. At 350°C the reaction products are noticeably yellow in color and an unidentified product appears. The effect of temperature is similar to that reported for other solid acids [5] and consistent with the dual path reactions described above.

3.4. *Catalyzed deactivation and regeneration studies*

Catalyst regeneration was studied using methanol as the cylcohexanone oxime delivery solvent using typical conditions. As shown in figure 2, the initial selectivity to caprolactam is over 90% and coking leads to a slow loss in selectivity. After 50 h the conversion was 99% but the selectivity to ϵ-caprolactam dropped to 76%. Calorimetric analysis of the deactivated catalyst shows that none of the strong acid sites remain giving a $-\Delta H_1 = 18.6$ kcal/mol. By heating the deactivated catalyst in air for 8 h, analysis showed that the coke is removed. The regenerated catalyst gives an initial conversion of 99% with 88% selectivity to ϵ-caprolactam. The decreased selectivity compared to the starting catalyst suggests that original acidity of the catalyst lost by coking is not completely restored by removal of coke by thermal oxidation. The failure to regenerate catalyst by high temperature oxidation was probed by a cal-ad analysis of the fresh and regenerated catalyst. The results are shown in table 1. A slight decrease in acid strength of the strongest site, $-\Delta H_1$, is observed in the regenerated catalyst, but of more significance is the loss in the number of strong acid sites, n_1, found. The fresh SG-W has 6.5×10^{-5} mol/g of strong acid site, while the regenerated SG-W has 2.4×10^{-5} mol/g. Further, cal-ad shows that the strong sites lost on the regenerated SG-W are converted to the weaker $-\Delta H_2$ site whose quantity has increased compared to the fresh SG-W catalyst. The dual reaction path model described above accounts for the acidity–reactivity observations.

The strongest (ΔH_1) site and the number of these sites, n_1, in the regenerated catalyst are similar to that reported for the SG-WO_3 catalyst prepared by thermal decomposition of ammonium tungstate on silica. This suggests that the high-temperature thermal oxidation of carbon during regeneration results in a solid that is similar to that obtained by thermal decomposition of ammonium tungstate. High temperatures lead to an irreversible loss of acid sites by dehydration and aggregation of tungsten species. High-temperature treatment [1a,13] of silica gel is reported to lead to irreversible dehydration of silanol groups (Brønsted acid sites). To investigate the possibility that the strongest sites of SG-W are responsible for the very high initial selectivity to ϵ-caprolactam, a solid prepared from thermal decomposition (500°C in air) of ammonium tungstate on silica, SG-WO_3, having the same loading of tungsten oxide as SG-W was used with the methanol delivery solvent and typical conditions. The resulting catalyst was found by BET to have a surface area of 218 m^2/g which is similar to that of the SG-W catalyst. The conversion of the oxime measured after 10 h was 99%, but the selectivity to ϵ-caprolactam was 86%. This selectivity is very close to the 88% selectivity at 10 h found for the regenerated SG-W catalyst when using methanol as the solvent.

SEM for the fresh SG-W catalyst, and the SG-W catalyst after reaction and regeneration at 10,000× magnification shows that agglomeration of surface tungsten oxide species has occurred as shown in figure 3. BET

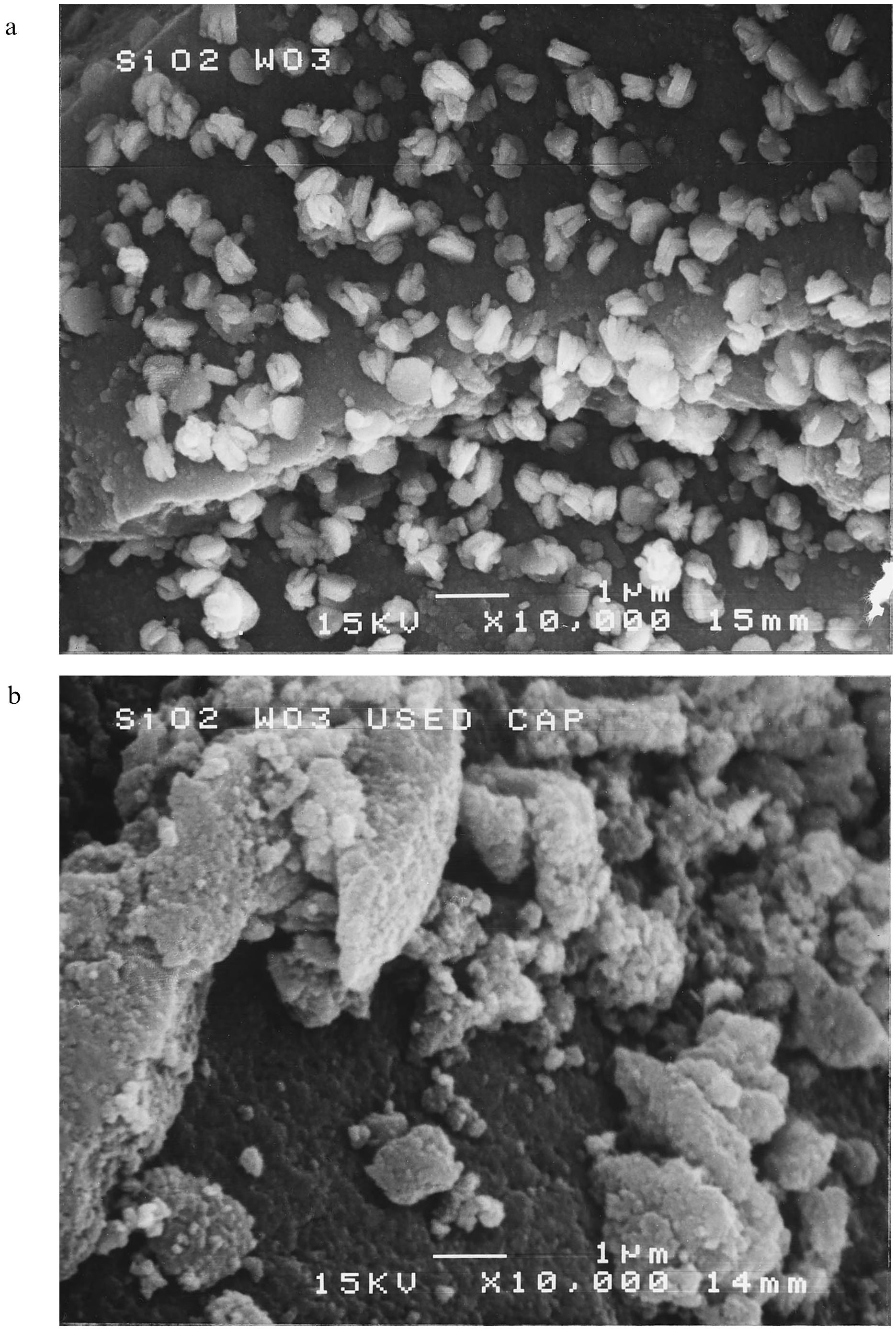

Figure 3. SEM micrograph of (a) fresh SG-W at 10,000× magnification, (b) regenerated SG-W at 10,000× magnification.

analysis of the used and regenerated catalyst shows slightly less surface area and pore volume as compared to the fresh SG-W catalyst, indicating that the agglomeration has not caused a significant blockage of the large pores on the silica. These studies support the proposal that agglomeration of tungsten oxide on SG-W results in the loss of strong acid sites which prevents complete regeneration of the SG-W catalyst. Earlier studies show [2] that the fresh SG-W catalyst has as the strongest sites those protons on tungsten anchored to silica, $(SiO)_{4-n}W(OH)(O^-)_{1+n}(WO_3{\cdot}H_2O)_x$. Regeneration increases x at the expense of tungsten in $(SiO)_{4-n}W(OH)$ environments.

3.5. *Effect of silica pore size*

Using the same conditions for synthesis, the tungsten oxide catalyst was prepared using WCl_6 on a silica gel support from Fisher which has different surface characteristics and porosity than the Davison support. The for-

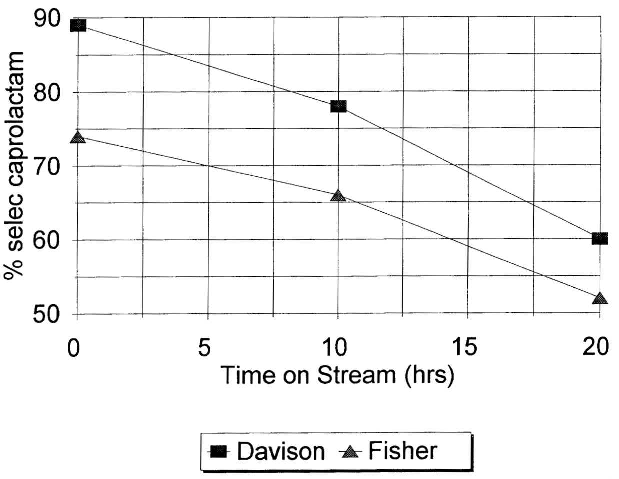

Figure 4. Effect of support porosity and surface area on caprolactam selectivity. Davison silica gel; surface area of 265 m^2/g and 175 Å average pore size. Fisher silica gel; 570 m^2/g and 28 Å average pore size.

mer has a surface area of 570 m^2/g and an average pore size of 28 Å, compared to Davison silica which has a surface area of 265 m^2/g and an average pore size of 175 Å. Consistent with other findings on the effect of support on caprolactam activity [3], the smaller pores lead to inferior selectivity to caprolactam with similar conversions of cyclohexanone oxime as shown in figure 4. This is attributed to longer retention times for ϵ-caprolactam on the stronger acid sites of porous solids.

4. Conclusion

The Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam, a valuable chemical intermediate is added to the series of acid catalyzed reactions whose reactivity is correlated to acidity. Conversion follows two different paths on the strong and weak acid sites. The acid sites of SG-W, whose $-\Delta H$ of interaction with pyridine is 32 kcal mol^{-1}, show high selectivity to ϵ-caprolactam while sites with acidities corresponding to 16 kcal mol^{-1} are less selective. With long residence times from low flow rates or poorly basic solvents, the 32 kcal mol^{-1} sites lead to extensive coking via polymerization of the products. The lifetime and selectivity of the catalyst can be affected by changing the oxime delivery solvent, with the most basic solvent methanol resulting in the least amount of coke formation and the longest catalyst lifetime of the solvents studied. Conditions are reported that permit a comparison of the reactivity of this rearrangement with acidities of new solid acids.

The catalyst prepared by WCl_6 hydrolysis has more strong acid sites and a better dispersion of tungsten oxide than conventional preparation methods using ammonium tungstate thermal decomposition. Cal-ad analysis of the fresh catalyst, regenerated catalyst and catalyst prepared from $(NH_4)_2WO_4$ demonstrate that the acidity and number of acid sites parallels selectivity to ϵ-caprolactam in the catalytic rearrangement. Porosity of the catalyst is shown to be an important factor influencing selectivity in addition to acidity.

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