Topical Report

Molecular Sieves as Catalysts for Methanol Dehydration in the LPDME™ Process

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Summary

Several classes of molecular sieves were investigated as methanol dehydration catalysts for the LPDME™ (liquid-phase dimethyl ether) process. Molecular sieves offer a number of attractive features as potential catalysts for the conversion of methanol to DME. These include (1) a wide range of acid strengths, (2) diverse architectures and channel connectivities that provide latitude for steric control, (3) high active site density, (4) well-investigated syntheses and characterization, and (5) commercial availability in some cases.

We directed our work in two areas: (1) a general exploration of the catalytic behavior of various classes of molecular sieves in the LPDME™ system and (2) a focused effort to prepare and test zeolites with predominantly Lewis acidity. In our general exploration, we looked at such diverse materials as chabazites, mordenites, pentasils, SAPOs, and ALPOs. Our work with Lewis acidity sought to exploit the structural advantages of zeolites without the interfering effects of deleterious Brønsted sites. We used zeolite Ultrastable Y (USY) as our base material because it possesses a high proportion of Lewis acid sites. This work was extended by modifying the USY through ion exchange to try to neutralize residual Brønsted acidity.

We confirmed that many molecular sieves possess very high intrinsic activity for methanol dehydration to DME. However, no molecular sieve catalysts were found that provided a combination of activity, stability, and compatibility with methanol catalyst superior to our existing LPDME™ catalysts. Therefore, we concluded that zeolites and related molecular sieves are not suitable for use in the LPDME™ process.

Most materials deactivated very rapidly even in the absence of methanol catalyst. This deactivation was caused by formation of nonvolatile hydrocarbons via a Brønsted acid catalyzed mechanism. We had some success in suppressing this deactivation by eliminating Brønsted acid sites through ion exchange, but at the cost of activity.

Molecular sieves with weaker Brønsted acidity, such as SAPOs, ALPOs, and boron-substituted zeolites, were not active enough, deactivated rapidly, or exhibited both behaviors. We were not able to find materials that could trade off balance activity and stability.

Using different molecular sieve structures significantly altered the activity and deactivation behavior. Catalysts with one-dimensional channel systems generally had much lower, but more stable, activity. In addition, in some cases these materials also appeared to have a less deleterious effect on the methanol catalyst. Three-dimensional channel structures favored high activity. However, even using zeolites with very constrained channels (such as chabazite or zeolite rho) did not suppress deactivation appreciably.

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1 BACKGROUND

1.1 Interest in DME and Liquid-Phase Technology

The commercial importance of dimethyl ether (DME) has increased considerably in recent years as more attention has been focused on deriving fuels and chemicals from synthesis gas. In addition to a small but well-established market as a propellant, DME is being considered for such diverse applications as IGCC power generation[1], diesel fuel[2], fuel additives, home fuel applications, and vinyl acetate production. DME is extremely clean-burning and does not form peroxides as do higher ethers. Furthermore, by converting methanol to DME, one can drive a syngas-to-methanol reaction beyond the typical thermodynamic limitations (equations 1-3). The synergy is completed by reaction (3), the water gas shift reaction, which prevents the buildup of water by converting it back to the reactants required for methanol synthesis. Fortunately, reaction (3) is also catalyzed by the methanol synthesis catalyst.

$CO_2 + 3H_2 = CH_3OH + H_2O$ (1) Methanol Synthesis
$2CH_3OH = CH_3OCH_3 + H_2O$ (2) Methanol Dehydration to DME
$H_2O + CO = CO_2 + H_2$ (3) Water Gas Shift
$3H_2 + 3CO = CH_3OCH_3 + CO_2$ (4) Net DME Reaction[3]

Liquid-phase technology is particularly well-suited to capitalize on these advantages in that it provides the heat transfer capacity that is needed to operate at higher conversion per pass. Air Products has been involved for roughly 15 years in a DOE-sponsored program exploring environmentally clean routes from coal to fuels and chemicals via liquid-phase processes. This program has produced liquid-phase technology for producing methanol, in which the use of a slurry bubble column reactor permits higher conversion per pass and greater flexibility in syngas feedstock composition. This work culminated in the commissioning of the world's first commercial-scale liquid phase methanol (LPMEOH™) plant, which produces 260 tons per day of methanol at Eastman Chemicals' Kingsport, Tennessee facility. In 1991 the liquid-phase DME (LPDME™) process was developed, using a methanol synthesis catalyst and a methanol dehydration catalyst together in a slurry bubble column reactor. This process was demonstrated at the DOE-owned, Air Products-operated pilot facility at LaPorte, Texas, using gamma alumina as the dehydration catalyst. Although the LPDME catalyst system using gamma alumina did not demonstrate sufficient life for commercial application, the pilot trial did demonstrate the significant boost in syngas conversion that is afforded by the simultaneous formation of dimethylether.

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[1] (a) D. M. Brown, B. L. Bhatt, T. H. Hsiung, J. J. Lewnard, and F. J. Waller, *Catalysis Today*, 8 (1991) 279-304. (b) J. J. Lewnard, T. H. Hsiung, J. F. White, and D. M. Brown, *Chemical Engineering Science*, 45 8, 2735 (1990).

[2] (a) T. H. Fleisch and P. C. Meurer, *Fuel Tech. & Management*, July/August 1996, 54. (b) P. J. A. Tijm, F. J. Waller, B. A. Toseland. and X. D. Peng, "Liquid-Phase Dimethyl Ether™," "A Promising New Diesel Fuel," Energy Frontiers International Conference, Alaska, July 1997.

[3] Under hydrogen-rich conditions, the water gas shift reaction (3) does not proceed as readily, so the net reaction is better represented as $4H_2 + 2CO = DME + H_2O$.

1.1.1 Development of LPDME™ Catalysts

It is generally accepted that acid catalysts are the best materials for the dehydration of methanol to dimethylether and that either Brønsted or Lewis acids are capable of performing this reaction. For example, gamma alumina is a very effective catalyst for this reaction, and it is believed that most of the acid sites on this catalyst are of the Lewis type. However, there is no consensus in the scientific community as to whether the sites will be converted to Brønsted sites in the presence of water. Similarly, Klier and coworkers (among others) have shown H-mordenite to be a very effective methanol dehydration catalyst.[4] Although H-mordenite is expected to be a strong Brønsted acid, the possibility remains that small amounts of Lewis acidity resulting from nonframework aluminum in the zeolite could be providing some or most of the activity.

Although gamma alumina is an excellent catalyst for the water gas shift reaction on its own, when it is placed in the presence of a $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst in the LPDME process, both catalysts undergo a fairly rapid, irreversible deactivation. We have conducted very thorough experimentation into the cause of this deactivation. This work has been documented elsewhere.[5] The salient findings may be summarized as follows:

- Intimate contact between the two catalysts is necessary for deactivation to occur.
- Electron microscopy with EDS provided some evidence that copper and/or zinc were transferred from the methanol synthesis catalyst to the alumina.
- The rate of deactivation of the methanol synthesis catalyst depends on the bulk syngas composition. A less hydrogen-rich feed (Shell-type syngas) caused faster deactivation.

Further work showed that this deactivation of the catalyst system is not limited to gamma alumina. In tests of over 25 materials, only one catalyst was identified that would demonstrate both reasonably high activity and compatibility with the methanol synthesis catalyst. This material, an amorphous, nonstoichiometric aluminum phosphate oxide, has been patented[6] and extensively developed. After we reviewed this work, we concluded that the presence of strong acid sites and/or Brønsted acid sites on the dehydration catalyst is critical for the catalyst deactivation mechanism.

1.2 Motivation to Look at Zeolites for LPDME™

Molecular sieves offer a number of attractive features as potential catalysts for the conversion of methanol to DME. These include (1) a wide range of acid strengths, (2) diverse architectures and channel connectivities that provide latitude for steric control, (3) high active site density, (4) well-investigated syntheses and characterization, and (5) commercial availability in some cases. On the negative side, molecular sieves also are typically predominantly Brønsted acids. However, this Brønsted acidity can be modified through several routes. The physical structure of the zeolite (bonding arrangement and angles) affects the strength of the acid sites. Ion exchange of the cations in

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[4] K. Klier, Q. Sun, O. C. Feeley, M. Johansson, and R. G. Herman, *11th International Congress on Catalysis – 40th Anniversary, Studies in Surface Science and Catalysis*, Vol. 101, 601 (1996).

[5] X. D. Peng, B. A. Toseland, and R. P. Underwood, *Catalyst Deactivation 1997* (C. H. Bartholomew and G. A. Fuentes, ed.) p. 175, Elsevier Science B.V. (1997).

[6] US Patent 5,753,716, X.D. Peng, G. E. Parris, B. A. Toseland, and P. J. Battavio (assigned to Air Products and Chemicals, Inc., Allentown, PA), May 19, 1998.

the zeolite can be used to attenuate the acidity. Removal of aluminum atoms from the framework of the zeolite can create nonframework aluminum in the structure that is believed to generate Lewis acidity. Also, substitution of heteroatoms into the zeolite framework can profoundly affect the strength of the framework acid sites.

Our interest in molecular sieves was particularly driven by two factors. The first was the existence of patents teaching zeolitic catalysts for gas-phase methanol dehydration to DME. The second was our own screening work using the zeolite chabazite. We found that this catalyst achieved an 82% conversion of methanol to DME, virtually driving the reaction to equilibrium. From this experiment, it was clear that the activity of this zeolite was of at least an order of magnitude greater than that of the materials with which we had been working previously.

1.3 Approach and Objectives

We directed our work on zeolites as LPDME catalysts in two areas: (1) a general exploration of the catalytic behavior of various classes of zeolites in the LPDME™ system and (2) a focused effort to prepare and test zeolites with predominantly Lewis acidity. In our general exploration, we wanted to learn what range of methanol dehydration activity we could extract from molecular sieve catalysts. We also wanted to arrive at a broad understanding of how factors such as external surface acidity, acid site strength, channel connectivity and size, cation exchange, and the presence of heteroatoms would impact the activity and stability of these catalysts. In this work, we looked at such diverse materials as chabazites, mordenites, SAPOs, and ALPOs. Our work with Lewis acidity sought to exploit the structural advantages of zeolites without the interfering effects of deleterious Brønsted sites. We used zeolite Ultrastable Y (USY) as our base material because it possesses a high proportion of Lewis acid sites. This work was extended by modifying the USY through ion exchange to try to neutralize residual Brønsted acidity.

Two classes of experiments were performed. In "Dehydration" experiments, we fed a dilute stream of methanol in nitrogen to a slurry containing only the molecular sieve. The activity of the catalyst for dehydrating methanol to DME was measured directly. In "LPDME™ Runs," syngas was fed to a slurry containing both the molecular sieve and methanol synthesis catalyst. This experiment measured the effectiveness of the molecular sieve catalyst in the actual LPDME™ process. It differs from the dehydration experiment in two key ways: (1) the potential for interaction between the two catalysts and (2) higher concentrations of hydrogen, carbon monoxide, and carbon dioxide and a lower level of water present in the reactor. Further details of these two types of experiments are given in Sections 6.4 and 6.5.

2 RESULTS

2.1 Summary

- We confirmed that many molecular sieves possess very high intrinsic activity for methanol dehydration to DME. However, no molecular sieve catalysts were found that provided a combination of activity, stability, and compatibility with methanol catalyst superior to our existing LPDME™ catalysts.
- Most materials deactivated very rapidly even in the absence of methanol catalyst. This deactivation was caused by formation of nonvolatile hydrocarbons via a Brønsted acid catalyzed mechanism. We had some success in suppressing this deactivation by eliminating Brønsted acid sites through ion exchange, but at the cost of activity.
- Molecular sieves with weaker Brønsted acidity, such as SAPOs, ALPOs, and boron-substituted zeolites, were not active enough, deactivated rapidly, or exhibited both behaviors. We were not able to find materials that could trade off balance activity and stability.
- Using different molecular sieve structures significantly altered the activity and deactivation behavior. Catalysts with one-dimensional channel systems generally had much lower, but more stable, activity. In some cases, these materials also appeared to have a less deleterious effect on the methanol catalyst. Three-dimensional channel structures favored high activity. However, even using zeolites with very constrained channels (such as chabazite or zeolite rho) did not suppress deactivation appreciably.

Therefore, we conclude that zeolites and related molecular sieves are not suitable for use in the LPDME™ process.

2.2 Chabazites

Chabazite is a medium-pore zeolite with a three-dimensional channel structure. We tested these materials on the premise that they would contain high activity for methanol dehydration while maintaining physical segregation between the methanol catalyst and acid sites.

The very high activity of H-chabazite was confirmed in methanol dehydration experiments. Figure 1 shows the conversion of methanol to DME as a function of time on-stream. Two things are clear from this graph: (1) H-chabazite is a very potent catalyst for methanol dehydration and (2) even in the absence of S3-86, the chabazite deactivates rapidly. The initial activity was so high that the conversion of methanol to DME was essentially at equilibrium. Therefore, the slow initial decrease in conversion is actually a significant loss in activity. This can be seen if one uses a simple rate law to back out a rate constant (see Section 6.4). A graph of this rate constant versus time on-stream is shown in Figure 1. This graph shows that the rate of activity loss was basically constant throughout the experiment. Because the spent chabazite was black while the fresh catalyst was white, we suspected that carbon or hydrocarbon deposition was the cause of the activity loss. ^{13}C NMR (Figure 2) confirmed the presence of unsaturated hydrocarbons on the catalyst. Similar residues were identified on the spent catalyst from dehydration experiments using H-mordenite and a partially Mg-exchanged Y. Conversely, γ-alumina, which showed stable activity in the dehydration experiment, showed very little unsaturated hydrocarbon in the NMR.

Schulz and coworkers have reported that Brønsted acid sites in zeolites can catalyze the formation of nonvolatile hydrocarbons at temperatures as low as 250°C[7]. The mechanism they proposed proceeds via a sorbed DME intermediate (Figure 3). Thus it is reasonable to assume that once formed on a Brønsted site, DME can either desorb as product or undergo further methylation to form the "low temperature coke" precursor. In the dehydration experiment with chabazite, we observed a greatly increased yield of C1-C3 hydrocarbons during the last stages of catalyst deactivation, consistent with Schulz's mechanism.

When the same H-chabazite was tested in the LPDME™ experiment, the high activity for methanol dehydration was not observed (see Figure 4). We believe that there is a very rapid interaction between the methanol catalyst and the chabazite during either the reduction of the methanol catalyst or the initial phases of heat-up under synthesis gas. We postulated that if this interaction was occurring primarily on the external surface of the zeolite and was inhibiting further access to the interior of the particles, we could stabilize the catalytic activity by passivating the external surface. The external surface was passivated by selective dealumination using malonic acid, which is sufficiently large to be excluded from the pores of the zeolite. As seen in Figure 4, this treatment only resulted in a slight delay in the deactivation process. We thus concluded that the interaction was not occurring only on this surface.

We also tested a chabazite that was still in its as-synthesized, potassium-exchanged form. This chabazite has much less Brønsted acidity, and we anticipated that Lewis acidity from nonframework aluminum might contribute sufficient activity for methanol dehydration. As can be seen in Figure 4, the chabazite deactivated almost completely. However, the methanol catalyst was more stable in this experiment than in the case of the H-chabazite.

A comparison of methanol dehydration experiments using H-chabazite with and without methanol catalyst present demonstrated that the methanol catalyst does not contribute measurably to the deactivation of the chabazite. In this experiment, the standard dehydration experiment was run except that methanol catalyst was also added to the reactor. The deactivation rate of the chabazite was measured at 170, 190, and 210°C and compared to that measured without methanol catalyst (see Table 1). After that phase of the experiment was completed (24 hours), the feed was switched to Shell-type syngas, thereby establishing standard LPDME™ conditions except for the temperature. The methanol synthesis rate constant was much lower than we had obtained at 210°C using γ-alumina. This suggests that the methanol catalyst had deactivated under the previous 24 hours of interaction with the chabazite under methanol feed. Both catalysts remained fairly stable over a 68-hour period under this condition. Increasing the reaction temperature further to 250°C rapidly deactivated the chabazite and the methanol catalyst.

Table 1: Rates of Chabazite Deactivation With and Without Methanol Catalyst

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[7] H. Schulz, W. Böhringer, and S. Zhao, Proc. 9th International Zeolite Conference, Montreal 1992, Eds. R. von Ballmoos et al., Vol. 2, p. 567 (1993) Butterworth-Heinemann, a division of Reed Publishing (USA).

Temperature	Chabazite Alone	Chabazite + MeOH Catalyst
170°C	-1.89 % per hour	-1.76 % per hour
190°C	-1.78 % per hour	-1.80 % per hour
210°C	-1.73 % per hour	-1.10 % per hour

These experiments show that under methanol/nitrogen feed in the temperature range 170-210°C, the methanol catalyst does not harm the zeolite, but the zeolite does harm the methanol catalyst. At higher temperatures, there seems to be the onset of low-temperature coking of the chabazite as well as accelerated detrimental interaction between the two catalysts.

We also attempted to stabilize the H-chabazite activity by sterically hindering the formation of low-temperature coke precursors in the cages. The approach was to predose the zeolite with a mixture of ammonia and methanol at 275°, producing sorbed methylamines on the Brønsted sites of the zeolite in the cages. These sorbed species take up considerable space in the cage, neutralize some the Brønsted acidity, and may themselves serve as methylating agents to convert methanol to DME. Because these molecules are bulky, we also expect that they will not easily escape from the cages. We tested this material under methanol dehydration conditions and found it to have comparatively low activity (D* of 1.3) but excellent stability. Increasing the reaction temperature to 270° boosted the D* to 2.2 without harming the stability. NMR analysis of the spent catalyst (Figure 5) showed that the amine distribution in the chabazite had been shifted to more methylated species (such as tetramethylammonium ion), but also showed that very little of the unsaturated hydrocarbons had been formed. Thus, the presence of the amines in the zeolite was highly effective at blocking the formation of this "low-temperature coke" and thus stabilized the activity of the zeolite. However, the combined steric effects and basicity of the amines quenched too much of the activity of the zeolite for this modified catalyst to be commercially useful for the LPDME™ process.

2.3 Mordenites

Like H-chabazite, H-mordenite is a strong Brønsted acid. Our hope was that since many of the strong acid sites lie within the channels of the zeolite, they would not be accessible to the methanol catalyst. Therefore, the intimate contact that may be required for deactivation would be minimized. We also postulated that this steric constraint might suppress the formation of nonvolatile hydrocarbons. As opposed to chabazite, which possesses medium-sized channel openings (3.8Å) but larger cages at the intersections of its three-dimensional channel structure, mordenite contains a one-dimensional array of 6.5Å x 7.0Å channels.

The mordenites we tested had much lower methanol dehydration activity than H-chabazite, but appeared to be stable under LPDME™ conditions. Similarly, the methanol catalyst was more stable than in the presence of chabazite. Thus, it appears that the mordenite structure was successful in inhibiting the methanol catalyst deactivation mechanism. The low activity was not due to interactions with the methanol catalyst, since we also observed low mordenite activity in the dehydration experiment (no methanol catalyst present). An Arrhenius study showed that the activation energy for the dehydration reaction was linear over the temperature range 210-260°C, providing no evidence that the reaction was diffusion-limited. The observed activation energy of roughly 30 kcal/mol is also reasonable for intrinsic kinetics. Therefore we have no proven explanation for the low rate. We also observed formation of a waxy material in runs using large pore zeolites such as mordenite or Zeolite Y. Two possible explanations for this are: (1) the mineral oil can gain admittance into the zeolite structure and is reacting or (2) the nonvolatile hydrocarbons formed in the zeolite are able to diffuse out of the zeolite and into the oil phase.

We tested three different mordenites. The first was an extruded material that we ground and screened before testing. The results were hard to interpret because this catalyst contained 20% γ-alumina binder, which contributed considerable activity. Subsequently, we tested two commercial mordenite powders. Dealuminated materials were used, on the hypothesis that these might possess some Lewis, rather than purely Brønsted, acidity due to non-framework aluminum. However, one material–from LaPorte Industries–did not show any extra-framework aluminum in the ^{27}Al NMR This material initially showed almost no dehydration activity, but gradually became active and eventually showed modest, very stable activity (see Figure 6). The methanol catalyst was also comparatively stable, deactivating at a rate of -0.061%/hr. The second sample, from Tosoh, showed significant nonframework aluminum in the NMR. However, this catalyst had virtually no methanol dehydration activity. The activity of the S3-86 was also a bit lower than usual and was not as stable as in the run with the LaPorte mordenite.

2.4 Pentasils

ZSM-5 is often the first choice in zeolitic catalysts because it possesses a three-dimensional network of moderately small channels (10-membered rings, ~5.5Å diameter). These channels offer excellent coking resistance without severely hindering molecular diffusion. Previous work in our group showed that ZSM-5 was a very active catalyst for LPDME™ but deactivated rapidly. Because of our understanding of the detrimental impact of having too much Brønsted acidity, we tried three approaches to attenuating the acidity of ZSM-5. None produced a viable LPDME™ catalyst.

The first approach was to passivate the external surface of the zeolite with phosphate.[8] The phosphated ZSM-5 had high activity, but readily deactivated while at the same time changing from white to black. Thus, it appears that the channels of ZSM-5 are not small enough to prevent the same nonvolatile hydrocarbon formation that poisoned the chabazite and mordenite.

The second approach was to substitute boron for the aluminum in the framework of the zeolite, thereby weakening the acid strength of the sites.[9] This catalyst had very low activity for methanol dehydration. The initial conversion of methanol to DME over this catalyst was roughly 7%, and it declined rapidly to 2%. This shows that boron incorporation goes too far in weakening the Brønsted acid sites. Unfortunately, there are very few elements that can be substituted into zeolite frameworks to produce an acidity between that resulting from aluminum and boron.[10] Of these few elements, iron is a potential methanol catalyst poison, and gallium is too expensive to be practical.

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[8] (a) H. de Lasa, L. Hagey, S. Rong, and A. Pekediz, *Chemical Engineering Science*, Vol. 51, No. 11, p. 2885 (1996); (b) A. Rahman, G. Lemay, A. Adnot, and S. Kaliaguine, *J. Catal.* 112, 453 (1988).

[9] (a) G. Coudurier and J. C. Védrine, *Pure & Appl.Chem*, Vol. 58, No. 10, 1389 (1986); (b) W. Hölderich, H. Eichhorn, R. Lehnert, L. Marosi, W. Mross, R. Reinke, W. Ruppel, and H. Schlimper, Proc. 6th International Zeolite Conference (D. H. Olson and A. Bisio Eds.) Butterworth, Guildford (1984) p. 545.

[10] C. T-W Chu and C. D. Chang, *J. Phys. Chem.* (1985) 89, 1569.

The third approach was to try to reproduce a Haldor-Topsøe patent[11], in which the strongest acid sites are neutralized by adsorption of ammonia at elevated temperature. The specific procedure involved three steps: (1) pretreatment at 550°C, (2) adsorption of ammonia at the desired temperature in the range of 250-650°C, and (3) subsequent desorption of the ammonia at the same temperature. The patent teaches that some small amount of ammonia remains adsorbed; this amounts to 545 ppm ammonia at the preferred temperature of 540°C. Calculations show this to correspond to about 5% of the available acid sites. The patent suggests that the stabilization is due to the presence of the residual ammonia on the very strongest Brønsted acid sites and that these are responsible for deactivation, while the remaining sites are selective for DME formation. However, we suspect that it is more likely that the initial 550°C treatment causes at least partial dealumination of the zeolite. The resulting nonframework aluminum could be providing the additional active sites for the DME reaction. The benefit of the ammonia treatment would be to neutralize any remaining Brønsted sites and/or very strong Lewis sites.

We performed a set of ammonia TPD experiments to understand this phenomenon better. In the first, the Haldor-Topsøe process was duplicated closely. A ZSM-5 with Si/Al of 50 was chosen, and the temperature of the ammonia treatment was 540°C. After the ammonia treatment, the sample was purged with nitrogen at 540°C, then cooled. Recognizing that the Topsøe work was done using a deep bed of catalyst, which would greatly enhance the opportunity for desorbing water to dealuminate the zeolite, we did a second run in which the 550°C pretreatment was conducted using helium that had been saturated with water at room temperature. A standard ammonia TPD experiment was then performed, in which the catalyst was saturated with ammonia at 100°C prior to a desorption via temperature ramping in helium. The two ammonia desorption curves are shown in Figure 7. The two broad peaks centered at around 200 and 400°C represent weak and strong acid sites, respectively. The sharp peak and noisy data in the range 500-550°C are artifacts of the way the TPD was performed and should be disregarded. The presence of a broad desorption centered at around 675°C suggests that there are some still stronger sites on which ammonia remains adsorbed even at 540°C. This suggestion supports the claim made in the patent. The addition of steam to the high-temperature pretreatment atmosphere appears to have had little effect.

We did not do any further testing of this material. The large amount of Brønsted sites giving rise to ammonia desorption between 300 and 500°C would be unaffected by the ammonia treatment and presumably still give rise to deactivation. We applied the same ammonia pretreatment procedure to γ-alumina and tested it under LPDME™ conditions. The results were very similar to what we had seen with unmodified γ-alumina. This reinforced our expectation that the pretreatment would not improve the performance of H-ZSM-5.

2.5 Zeolite Rho

Zeolite Rho was an attractive topography because it combines the small 8-membered ring channels of chabazite with a larger cage structure. The Rho was synthesized at Air Products. It was then calcined first at 250°C for two hours and then at 500°C for two hours. The purpose of this heat treatment was to partially dealuminate the zeolite, creating some Lewis acidity. We assessed the methanol dehydration activity of this sample in our standard dehydration experiment.

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[11] US Patent 4,536,485, J. Topp-Jorgensen (assigned to Haldor Topsøe A/S, Denmark, August 20, 1985).

The initial activity was so high that the conversion of methanol to DME was essentially at equilibrium. The catalyst rapidly deactivated, so that after 8 hours almost no activity remained. This behavior is similar to that of chabazite, suggesting that the Rho structure offers no benefit of the chabazite structure. Instead, it appears that the same Brønsted acid- catalyzed formation of nonvolatile hydrocarbons is causing deactivation.

2.6 ALPOs and SAPOs

SAPOs are mixed oxides of silicon, aluminum, and phosphorus that adopt microporous, well-defined crystal structures which are analogs of known zeolites. They are a logical choice as potential LPDME™ catalysts because they combine the ordered, microporous structure of zeolites with a more modest acid strength.

Our experiments showed that SAPOs can possess reasonably high activities for methanol dehydration. In LPDME™ testing, H-SAPO-34 displayed an initial dehydration rate constant similar to that of
γ-alumina. However, none of the SAPOs demonstrated high <u>and</u> stable activity. Furthermore, the methanol catalyst was not stable in the presence of either of the SAPOs we tested, but deactivated at a rate of roughly 0.4% per hour.

2.6.1 H-SAPO-34

H-SAPO-34 has the same structure as chabazite (3-dimensional channel structure, small eight-membered channel openings). We hoped to achieve the same molecular sieving effects, such as exclusion of the oil and methanol catalyst particles, with a weaker solid acid.

The H-SAPO-34 was synthesized at Air Products. We went straight to an LPDME™ experiment. During the first 15 hours of the run, more than 90% of the methanol synthesized over the S3-86 was converted to DME (Figure 8). While this was the highest DME selectivity we have seen, the productivity was not quite as high as that obtained with γ-alumina, because the rate of methanol synthesis was not as great. This means that the S3-86 was not as active in the presence of the SAPO as it was with alumina; presumably, some deactivation of the S3-86 occurred during the reduction or pre-reduction period (when the mixed slurry was stirred under nitrogen at room temperature).

After the first 15 hours, a brief period of rapid activity increase was seen in both catalysts, followed by precipitous deactivation of the SAPO-34. It is known that SAPO-34 is not hydrothermally stable. Therefore, a disintegration of the SAPO structure might have occurred, although it is not clear why this would happen suddenly after 15 hours of relatively stable operation. X-ray diffraction analysis of the spent catalyst showed that the SAPO had lost some crystallinity; however, some peaks due to crystalline SAPO were still observed. The S3-86 activity was never stable at any point in the run.

We repeated this test, this time using an initial reaction temperature of 240°C. The abrupt deactivation was again observed shortly after the temperature was raised to 250°C. The S3-86 clearly lost activity even during the initial period at 240°C. Low initial S3-86 activity was again observed. There was a general increase in the concentrations of small hydrocarbons produced over the SAPO-

34 during the first period of reaction, and during the period of rapid deactivation there was a discernible rise in the rate of production of these compounds. These observations are consistent with the nonvolatile hydrocarbon formation mechanism of Schultz and coworkers mentioned above. The rapid deactivation of SAPO-34 (and similarly, of H-chabazite) is therefore ascribed to the rapid methylation and subsequent cracking of carbocations laid down in the cages of the SAPO during the earlier portion of the experiment.

2.6.2 Commercial SAPO-34

We evaluated a commercial sample of SAPO-34. Because of the high activity of this catalyst, we initially tested it using a 95:5 ratio of methanol catalyst to SAPO-34. Nevertheless, the initial carbon selectivity was over 80% to DME (Texaco gas, 6000 GHSV, 750 psig). The SAPO deactivated rapidly but leveled off at a modest activity (k_D=3). The methanol catalyst stability did not seem to be affected by the presence of the SAPO. We added additional SAPO-34, bringing the ratio to 86.4:13.6, and observed a similar deactivation pattern but better DME selectivity. Then we added a considerable amount of SAPO-34 to attempt to establish a reasonable DME selectivity even after the initial SAPO deactivation. With this new catalyst ratio (66:33), we observed fairly rapid methanol catalyst deactivation.

Our conclusion is that SAPO-34 deactivates rapidly under LPDME™ conditions, probably due to nonvolatile hydrocarbon formation in the cages, but a residual level of activity is retained. However, when sufficient SAPO-34 is used to obtain acceptable DME selectivity, the methanol catalyst is not stable.

2.6.3 SAPO-11

When we tested the zeolites chabazite and mordenite, we found that the mordenite gave lower but more stable activity. SAPO-34 is isostructural with chabazite; SAPO-11 has a one-dimensional pore structure similar to mordenite, although the channels of the SAPO-11 are smaller than those of mordenite (6.7Åx4.4Å versus 6.5Åx7.0Å). Our hope was that we would again see more stable activity exhibited by a mordenite-like structure.

The SAPO-11 was tested in our standard LPDME™ experiment. Like mordenite, SAPO-11 provided low, stable activity. The methanol dehydration rate constant was roughly 75% that of the mordenite, reflecting either the lower acid strength of the SAPO catalyst or the more constrained channels. The methanol catalyst lost activity rapidly in the presence of the SAPO-11.

2.6.4 Co-SAPO-11

The objective was to determine whether incorporation of a transition metal (cobalt) in the SAPO-11 framework could increase its activity.

The Co-SAPO-11 was tested in the dehydration experiment (2000 L methanol/kg,hr). Initially, conversion was quite high (79%, close to equilibrium), but it fell to 25% in only 3 hours, and remained quite stable at this level for the remaining 24 hours of the experiment. This residual activity is lower than that of our present LPDME™ catalysts.

The difference in initial activity between the SAPO-11 and the Co-SAPO-11 shows that the cobalt either introduced considerable activity or retarded the rate of deactivation of the SAPO sufficiently to permit observation of the true initial activity. Nevertheless, the ultimate activity of both of these catalysts is too low for the LPDME™ process.

2.6.5 ALPO-5

ALPOs are zeolite analogs that are solely composed of aluminum, phosphorus, and oxygen. In theory they are neutral and contain no acid sites. However, imperfections in the atomic ordering–such as surfaces, grain boundaries, and point defects–could introduce some acid sites. To evaluate the intrinsic activity of these materials, we tested ALPO-5. This catalyst has a mordenite-like structure with one-dimensional, 12-membered ring channels.

The ALPO-5 was tested in the dehydration experiment. The initial conversion of methanol to DME was 24% (at 2000 L methanol/hr,kg feed rate), showing that the ALPO does possess a reasonable acidity. The catalyst deactivated gradually and stabilized at 13% methanol conversion. This activity is too low to be interesting for LPDME™ application.

2.7 Exchanged Ultrastable Y Zeolite

Because Brønsted acid sites catalyzed the formation of nonvolatile hydrocarbons, we investigated a series of molecular sieves containing primarily Lewis acidity. For this work we used Ultrastable Y Zeolite (USY) as our base material, because it possesses a large-pore, three-dimensional channel structure and considerable Lewis acidity contributed by non-framework aluminum. We demonstrated that exchanging the Brønsted sites with cations such as sodium, lanthanum, and cobalt stabilized the activity of the zeolite for methanol dehydration. However, these exchanged zeolites had only a fraction of the activity of the parent USY. Furthermore, they still produced unacceptable rates of methanol catalyst deactivation when they were tested in LPDME™ runs. Many of these zeolites likewise deactivated in the LPDME™ environment. We suspect that the cations are either too readily exchanged or that the zeolite framework is not sufficient to stabilize them in the desired oxidation state.

The USY samples we prepared are summarized in Table 2. The boron exchange was not successful, so no further testing of this sample was done.

Table 2: Elemental Analysis of Modified USY Samples

Sample	Si/Al	X/Al	$(Si/Al)_f$	Post-Run Color	Comments
USY	2.9	---	12	Black	Si/Al data suggests 25% of Al forms Brønsted sites
Na-USY	3.72	0.28		Black	
Cu-USY	3.46	0.31		Rusty	
Al-USY	5.99	---			^{27}Al NMR shows no Al^{3+}
$NH_4H_2PO_4$-USY	3.08	0.43		Black	
H_3BO_3-USY	3.11	0.04		---	Not Tested
USY + 2M HCl		---		---	X-Ray Amorphous

2.7.1 H-USY (Tosoh Ultrastable Y)

Testing was performed to determine whether using a zeolite with a higher ratio of Lewis to Brønsted acid sites would reduce the rate of deactivation via nonvolatile hydrocarbon formation. We obtained a sample of Tosoh USY with a bulk Si/Al of 2.9 and a framework Si/Al of 12. These ratios imply that roughly three-quarters of the aluminum atoms are "non-framework" and therefore do not give rise to Brønsted acid centers. Therefore, we expected this material to possess considerable Lewis acidity and relatively little Brønsted acidity.

To verify this, we obtained an ammonia TPD curve for this sample. Figure 9 compares this ammonia TPD with an H-ZSM-5 sample. The greater proportion of weaker Lewis sites in the USY is evident from the size of the peak at 200°C.

Figure 10 compares the methanol dehydration activity we observed using this material with the activity we previously reported for H-chabazite. As expected, the initial activity for the USY was lower than that of the chabazite. This reflects the much lower concentration of Brønsted sites and the comparatively low activity of the Lewis sites. The activity was much more stable than that of the chabazite. This shows that the low-temperature coking that caused the deactivation of the chabazite does not occur at a comparable rate on USY. However, there was continuous deactivation of the USY. One possible explanation for the steady deactivation is that the ongoing activity loss of the zeolite (0.28 % per hr) was due to nonvolatile hydrocarbon formation occurring on the residual Brønsted sites. This was supported by the subsequent experiment in which the Brønsted sites were neutralized by exchange with Na^+ (next section). The activity of the Lewis acid sites was low relative to Brønsted sites, as evidenced by the low activity of the USY compared with the initial activity of the chabazite. However, this may be partly due to the free access of the mineral oil into the pores of the Y-structure.

2.7.2 Na-USY (Na-Exchanged Tosoh USY)

Our intent in this test was to sodium-exchange USY to remove the residual Brønsted acid sites, leaving only the acidity associated with the NFA. This material was prepared by stirring the Tosoh USY with 1M $NaNO_3$ at 100°C overnight. The zeolite was then washed with water and dried at 110°C. XRD showed that the crystallinity of the parent material was retained. We evaluated this sample by slurrying it in Drakeol-10 and then feeding it 9% methanol in nitrogen at 250°C and 750 psig.

Methanol conversion was 34-37% and declined slowly over the remainder of the 170-hour run (Figure 11). In comparison, under equivalent conditions, the conversion over gamma alumina was 44%.

This sodium-exchanged USY was the first zeolitic catalyst we prepared with both reasonably high and reasonably stable methanol dehydration activity. These results strongly supported our hypothesis that Brønsted acid sites are the principal source of deactivation and that Lewis sites associated with non-framework aluminum are able to catalyze methanol dehydration. Although the activity level was still lower than that of γ-alumina, the stability prompted us to test this sample in an LPDME™ run.

Under LPDME™ conditions the Na-USY and the methanol catalyst deactivated rapidly. Isobutanol levels in the product increased from roughly 10 ppm (initially) to 75 ppm once the Na-USY was severely deactivated. The presence of alkali elements on methanol catalyst is known to promote isobutanol formation. This suggests that sodium ions are migrating out of the USY and onto the methanol catalyst. We focused our further work on identifying cations that would be more strongly held in the USY structure.

2.7.3 Al-USY (Aluminum-Exchanged Tosoh USY)

The goal in exchanging the USY with Al^{3+} ions was to increase the amount of non-framework aluminum in the zeolites while simultaneously eliminating Brønsted acid sites.

Elemental analysis of the sample showed that much of the original extra-framework aluminum of the USY was removed during the exchange process. The bulk Si/Al ratio before exchange was 2.9; after exchange the ratio was 6.0. This is probably due to the very acidic solution that must be used in the exchange process to keep the Al^{3+} in solution. It is not surprising that such a solution will also dissolve extra-framework aluminum within the zeolite structure. Later, we received ^{27}Al NMR results that did not show the presence of any Al^{3+} ions in the zeolite. Thus, it looks as if we did not achieve any exchange, but merely accomplished a mild acid wash, removing some of the extra-framework aluminum.

Results indicated that the aluminum-exchanged USY had an initial activity that was as high as the base USY. The activity loss was somewhat slower than for the base USY. However, the overall deactivation of the aluminum-exchanged USY was quite significant, showing that the aluminum exchange did not have the stabilizing effect on the activity that the sodium exchange had.

In conclusion, we were not successful in exchanging the H-USY with aluminum. The pH required to keep the aluminum ions in solution also dissolved the extra-framework aluminum in the zeolite. The performance of the resulting material did not differ appreciably from the unmodified USY.

2.7.4 Acid-Washed USY

Professor Wolfgang Hölderich (RWTH Aachen) reported that mild HCl treatment (pH=2) of USY produced a many-fold enhancement of its activity for α-pinene epoxide rearrangement.[12] His

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[12] W. F. Hölderich, J. Röseler, G Heitmann, and A. T. Liebens, *Catalysis Today* 37 (1997) 353-366.

explanation for this effect was that this is the optimal pH for removing amorphous silica. We suspected that we might observe similar effects in our system.

We tried washing the USY with 2M HCl (not pH 2, as intended) for 2 hours. XRD of the resulting sample showed complete loss of crystallinity. Perhaps the reason the structure was maintained in the case of the Al-exchange experiment, in spite of its comparable acidity and much longer exposure, was the presence of large amounts of aluminum in the solution. The ^{27}Al NMR of the acid-washed USY did show considerable Al^{3+}, so we proceeded with a test of its dehydration activity. In spite of the loss of crystallinity, the catalyst still showed dehydration activity comparable to the parent USY. The deactivation pattern was also similar.

2.7.5 Cu-USY (Copper-Exchanged Tosoh USY)

We proceeded on the assumption that Brønsted sites are deleterious to the methanol catalyst because they provide receptor sites for copper. Our intent was to block these sites with copper ions. The exchange was quite successful. However, in the methanol dehydration experiment, we observed very rapid deactivation of the zeolite. The bright rust color of the post-reaction slurry suggested that the copper had been reduced to Cu^0.

It appears that the zeolite cannot stabilize the copper in an oxidized state in the presence of a reducing atmosphere. However, the facility of the exchange process supports the theory that copper migration from the methanol catalyst to the Brønsted sites on the dehydration catalyst is the mechanism of deactivation in our LPDME™ process.

2.7.6 La-USY (Lanthanum-Exchanged Tosoh USY)

Once again, our intention was to “neutralize” Brønsted acid sites while possibly creating new Lewis sites active for methanol dehydration. Our reasoning in this treatment was that lanthanum should be much more strongly held than sodium and also may contribute additional Lewis acidity. Note that this is the same logic that prompted us to try aluminum exchange. The problem with aluminum exchange was that the conditions required for exchange caused serious loss of the extra-framework aluminum from the zeolite.

The lanthanum-exchanged USY was prepared via a multi-step exchange process designed to increase the extent of exchange and force some of the lanthanum into less accessible portions of the zeolite structure.

The La-USY demonstrated quite stable activity under an 8.5% methanol/nitrogen feed (Figure 11). The activity level was similar to that of the Na-USY, so the best performance we expected from it was similar to that of aluminum phosphate. The activity of gamma alumina is shown for comparison; this is a minimum target activity. The activity of an unmodified USY is also shown. After 120 hours on-stream under 8.5% methanol in nitrogen, we switched to an 8.5% methanol in Shell-type syngas feed to verify that the more reducing syngas environment would not cause stability loss under LPDME conditions. We did not observe any obvious change in stability.

Because the Co-USY (next section) was more promising, we did not test the La-USY under LPDME™ conditions.

2.7.7 Co-USY (Cobalt-Exchanged Tosoh USY)

We believed that cobalt could have advantages over lanthanum in that it is smaller and has a lower valence, which would facilitate exchange. Cobalt was also believed to have superior Lewis acidity. The cobalt-exchanged USY was tested in a simple methanol dehydration experiment and in a standard LPDME™ run.

As we had hoped, cobalt provided still higher activity than the lanthanum in the methanol dehydration test. The initial activity was on a par with what we have measured for gamma alumina. Unfortunately, this activity was not reflected in the LPDME™ performance. Although we did find that the cobalt-exchanged material was more stable than the sodium-exchanged material, neither the overall stability nor the steady-state activity comes close to that of aluminum phosphate. The steady-state methanol equivalent productivity of the cobalt-exchanged system was 16.5-17.0 gmol/kg,hr.

2.7.8 PO_4-USY

Another approach to modifying the acidity of the USY was to negate Brønsted sites by introducing phosphorous, anticipating that condensation reactions with the extra-framework aluminum might form an aluminum phosphate species in the zeolite.

We prepared this material by stirring the zeolite in a solution of $NH_4H_2PO_4$. Elemental analysis of the final material gave a P/Al ratio of 0.43, showing that considerable phosphorous was added.

The activity of this catalyst dropped very rapidly with time on stream. We suspected that the Brønsted sites might not have been affected by the phosphorous treatment. If the extra-framework aluminum is rendered inactive because of interactions with the phosphorous, then it makes sense that we observed faster activity loss.

2.7.9 H-SDUSY (Super-Dealuminated USY)

We demonstrated that deactivation of USY can be suppressed by exchanging the remaining Brønsted acid sites with cations such as sodium, cobalt, and lanthanum. Zeolyst International claims that its “Super-Dealuminated USY” has two orders of magnitude fewer Brønsted sites than typical USY materials. We reasoned that the exchange process might not be necessary to stabilize this material for LPDME™.

We tested a sample of this material under our standard LPDME™ conditions. The activity of the zeolite was very low. The initial carbon selectivity to DME was 2.5%, and it decreased to 1% after 125 hours on stream. However, the methanol catalyst showed roughly baseline deactivation in the presence of the zeolite. These observations suggest that there is not enough acidity remaining in the SDUSY to effect the desired chemistry.

3 DISCUSSION

It is evident from this work that, in general, catalysts from the zeolite family are not compatible with methanol catalysts under LPDME™ conditions. Furthermore, the strong Brønsted acid sites that naturally occur in these materials catalyze side reactions that cause the catalyst to deactivate. These observations seem to contradict numerous patents that teach the use of zeolites for methanol-to-DME or syngas-to-DME processes.

One possibility is that in a hydrogen-rich environment, the formation of nonvolatile by-products, such as low-temperature coke, is suppressed by competitive hydrogenation reactions. Because most of the literature focuses on syngas derived from natural gas, most of the work has been done under hydrogen-rich conditions. It would be straightforward for us to modify our standard dehydration experiment by using hydrogen-rich syngas in place of nitrogen. This would allow us to determine whether we can stabilize these active catalysts in this way.

The second key issue is deleterious interaction between the methanol catalyst and the molecular sieve. If this is due to the intimate contact between the two catalysts in the LPDME™ process, two strategies for using molecular sieves are apparent:

(1) *Design LPDME™ catalysts or reactors that minimize this interaction.* One example is a design in which the two catalysts are combined into a single particle with a stable interface. Alternatively, particles could be incorporated into a porous, attrition-resistant matrix. A third route would be to use some type of fixed-bed, liquid-phase design such as a trickle bed.

(2) *Investigate the performance of mixtures of methanol catalyst and molecular sieve in a fixed-bed, gas-phase reactor.*

Several classes of molecular sieves are attractive for LPDME™ applications but were not studied due to constraints of time or materials availability. These include:

(1) Zeolite Beta, which displays mild acidity.
(2) Titanosilicates, such as ETS-10 from Engelhard, which have a zeolite-like channel structure.

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Brent A. Aufdembrink (now with Cargill)
Gene E. Parris
Paula L. McDaniel

Outside Air Products
Wolfgang F. Hölderich (RWTH Aachen)
Eliot P. Hertzenberg (Zeolyst International)

5 FIGURES

Figure 1: Methanol Dehydration Over H-Chabazite at 2000 L Methanol/kg,hr

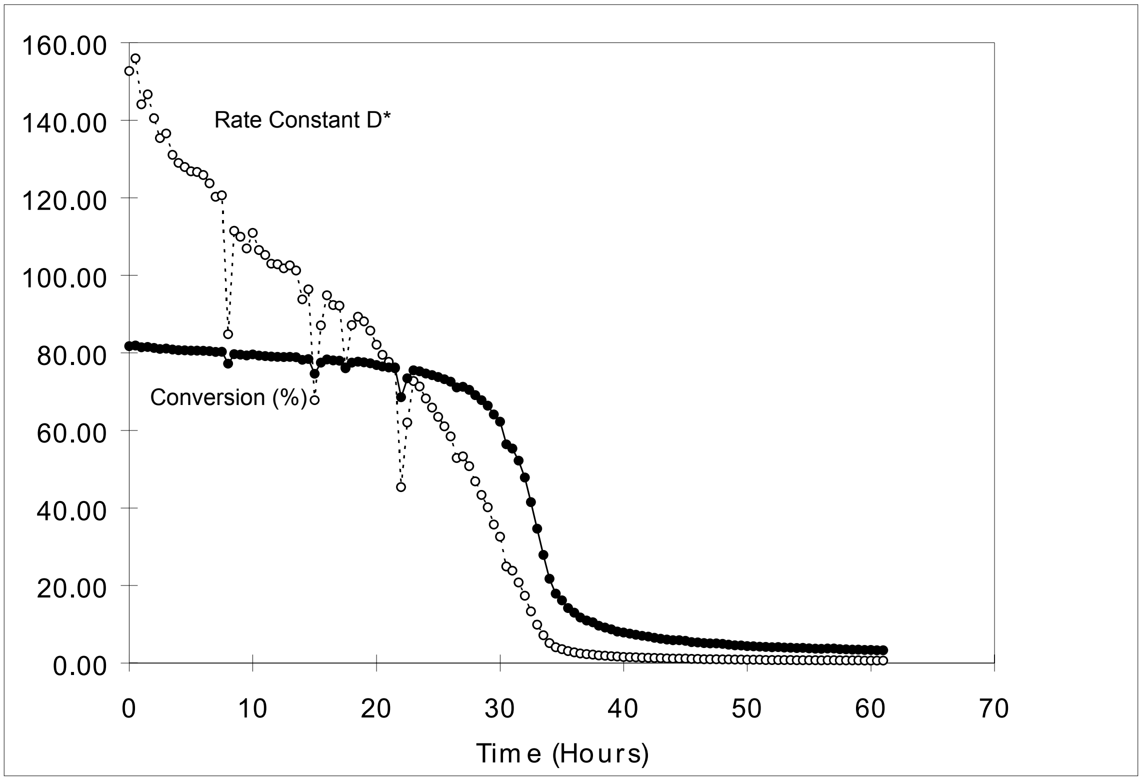
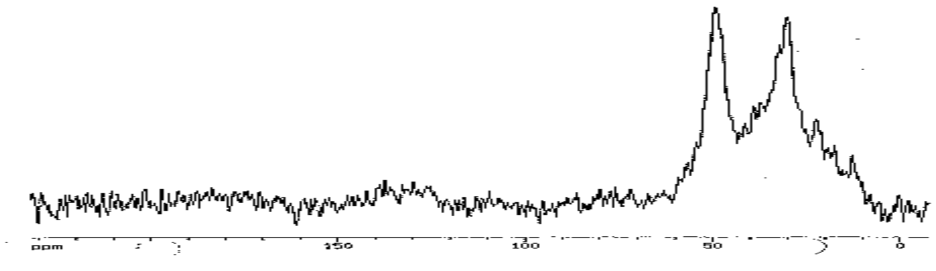
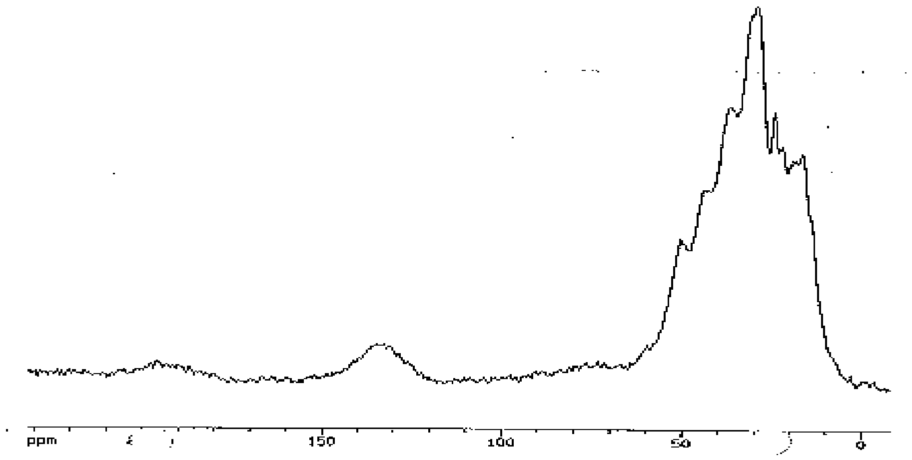


Figure 2: ^{13}C NMR Spectra of Spent Catalysts From Methanol Dehydration Experiments:

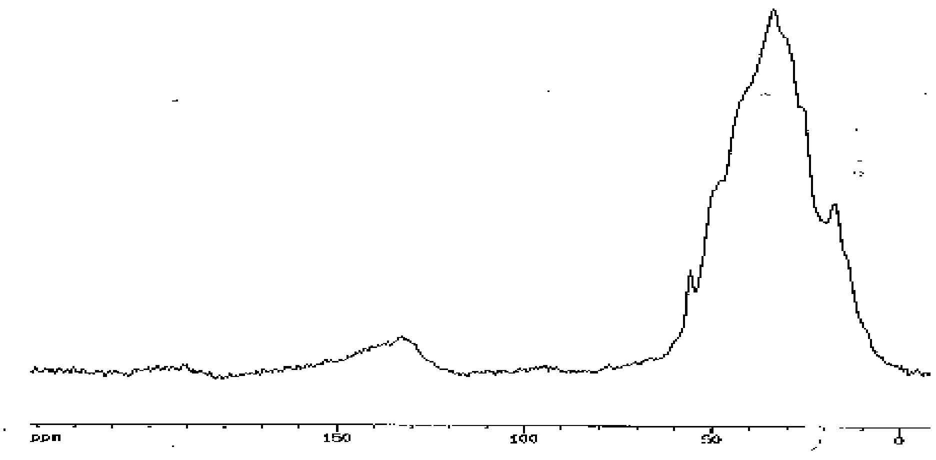
(a) γ-Alumina



(b) H-chabazite



(c) H-mordenite



Saturated hydrocarbons produce peaks in the range 10-60 ppm.
Unsaturated hydrocarbons produce peaks in the range 125-150 ppm.
Signal-to-noise ratio indicates overall peak intensity.

Figure 3: Mechanism of Low-Temperature Coking of Zeolite Catalysts Proposed by Schulz and Coworkers (9th International Zeolite Conference)

$CH_3OH + H^+ = CH_3\text{-}OH_2^+$

$CH_3\text{-}OH_2^+ + CH_3OH = (CH_3)_2OH^+ + H_2O$

$(CH_3)_2OH^+ + CH_3OH = (CH_3)_3O^+ + H_2O$

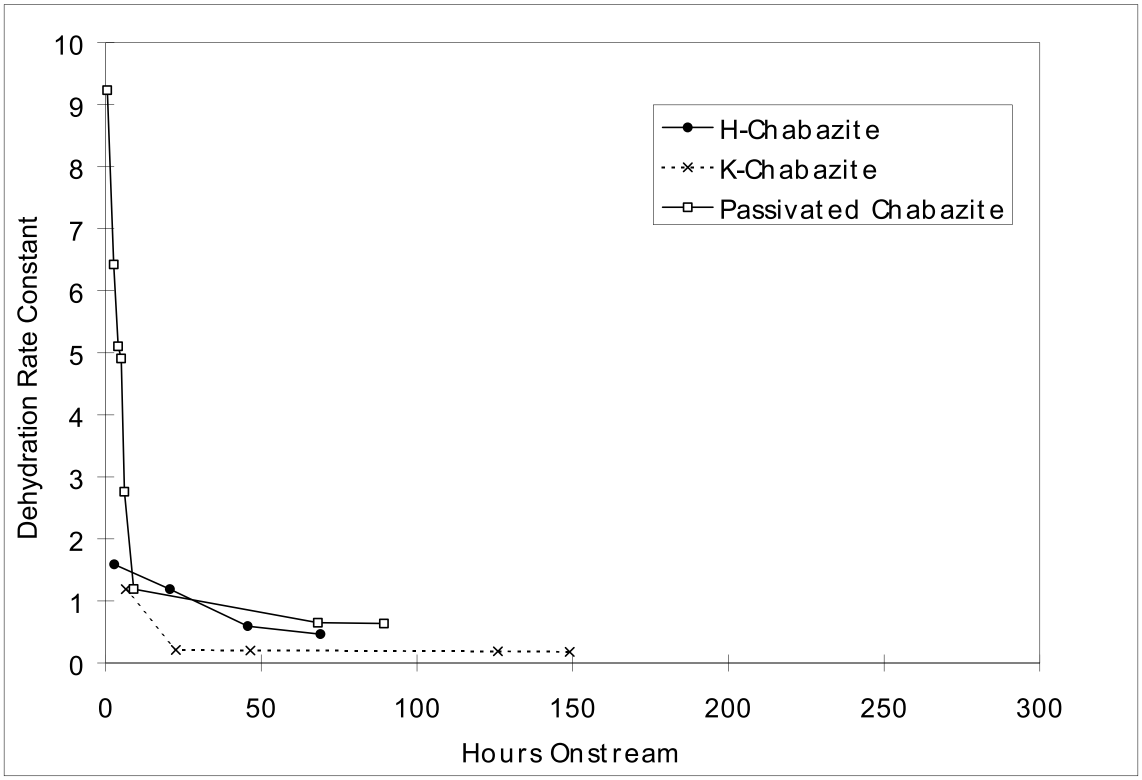
$(CH_3)_3O^+ = (CH_3)(C_2H_5)OH^+ = C_2H_4 + CH_3\text{-}OH_2^+$

$C_2H_4 + CH_3OH = CH_3CH{=}CH_2 + H_2O$

$CH_3CH{=}CH_2 + CH_3\text{-}OH_2^+ = CH_4 + {}^{+}\mathbf{CH_2CH{=}CH_2} + H_2O$

$^{+}\mathbf{CH_2CH{=}CH_2}$ is the primary intermediate for HC-deposit formation

Figure 4: LPDME™ Rate Constant Behavior Using Various Chabazites: (a) Methanol Dehydration; (b) Methanol Synthesis



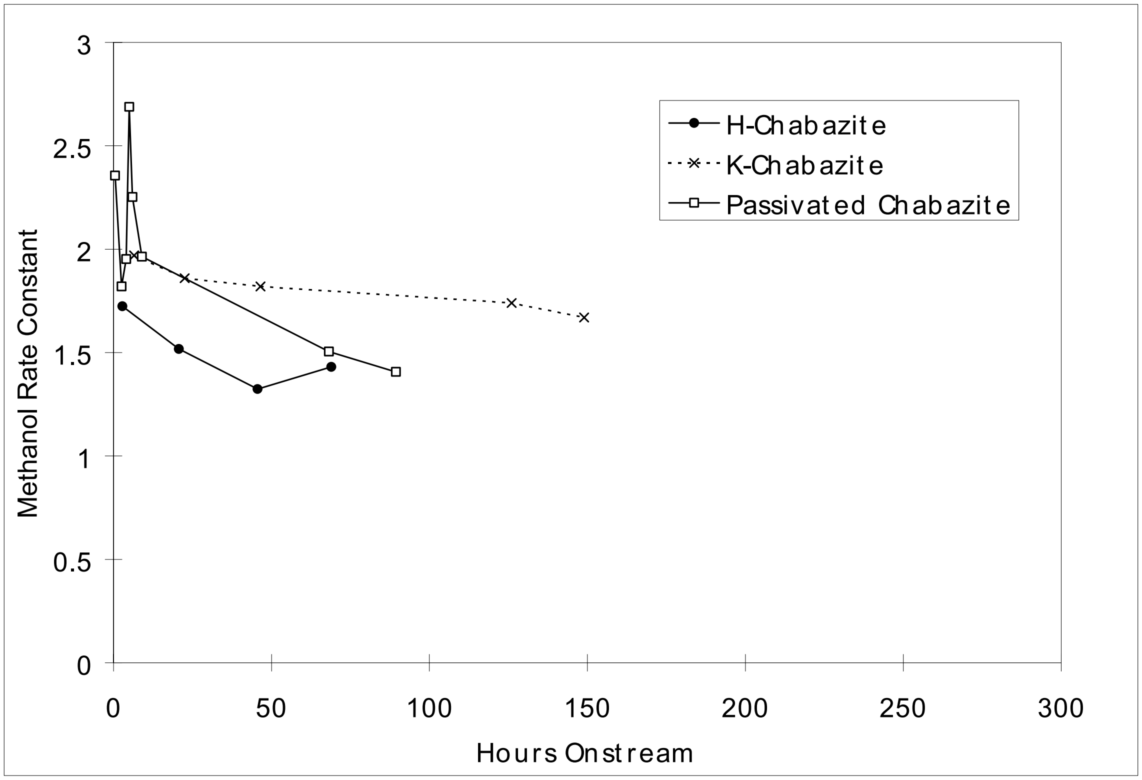


Figure 5: Effect of Preamination on the Distribution of Carbon-Containing Species in Chabazite During Methanol Dehydration

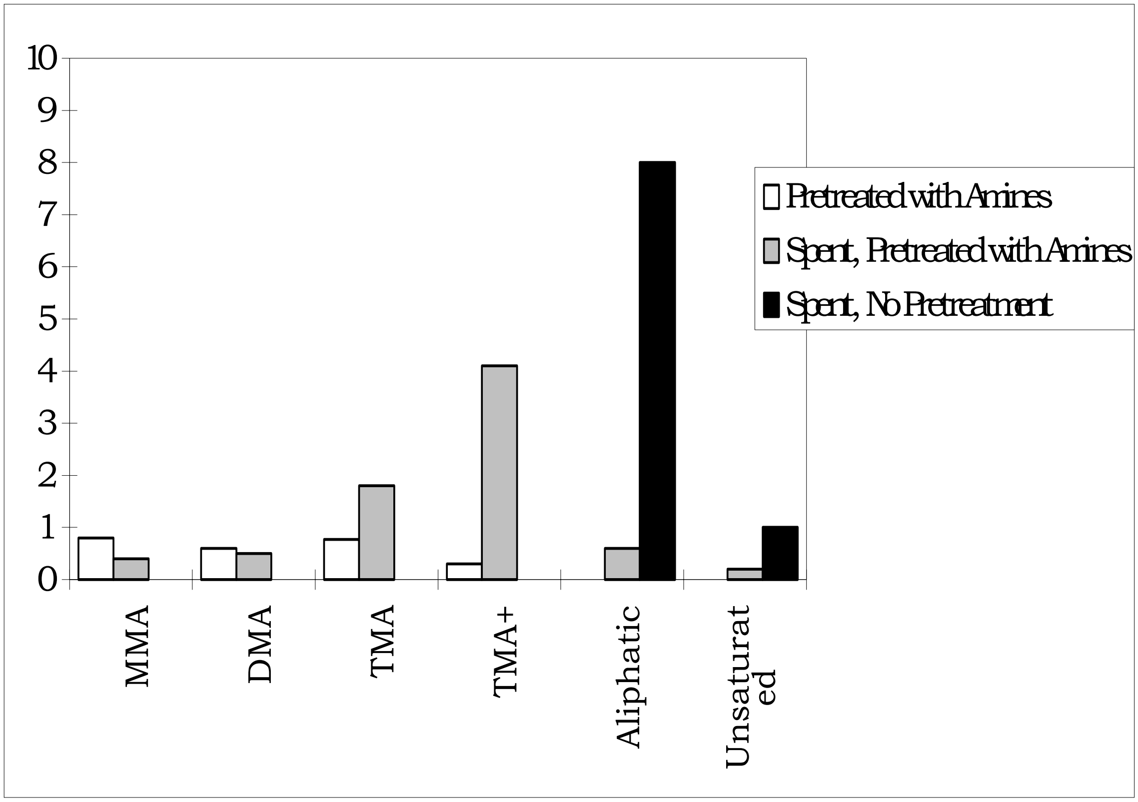


Figure 6: LPDME™ Rate Constant Behavior Using Mordenite (a) Methanol Dehydration (b) Methanol Synthesis

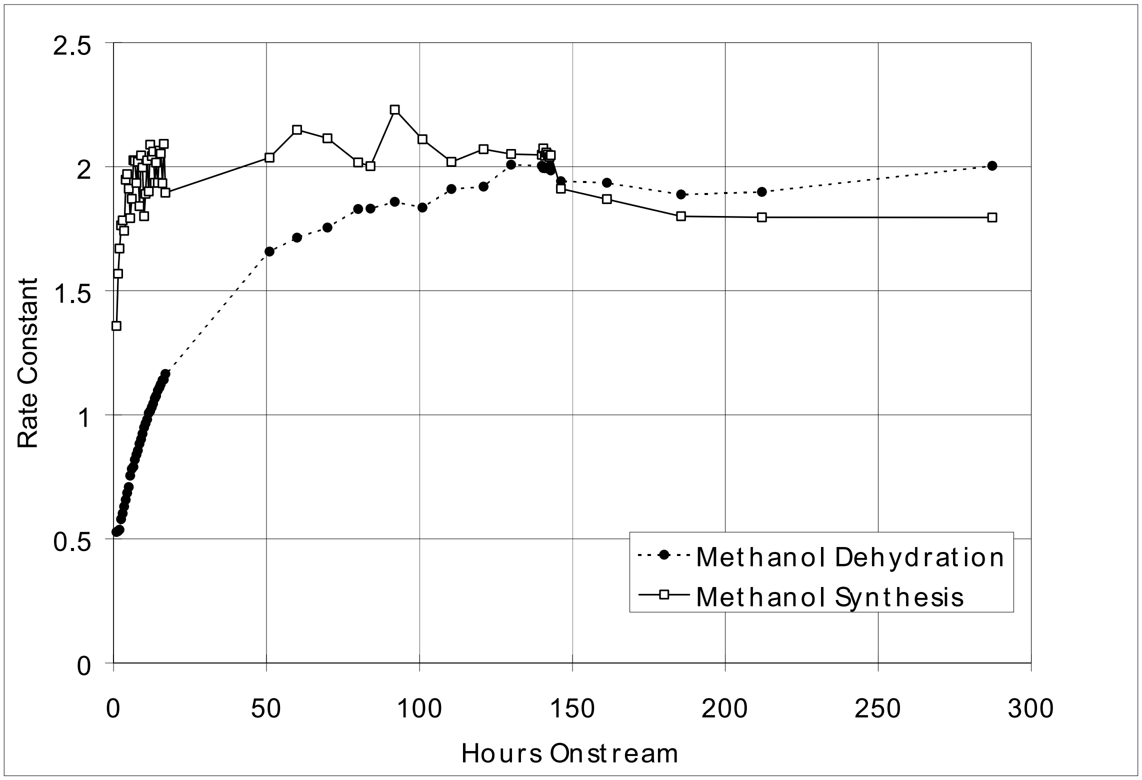


Figure 7: Ammonia TPD Data on Ammonia-Treated H-ZSM-5 Catalysts

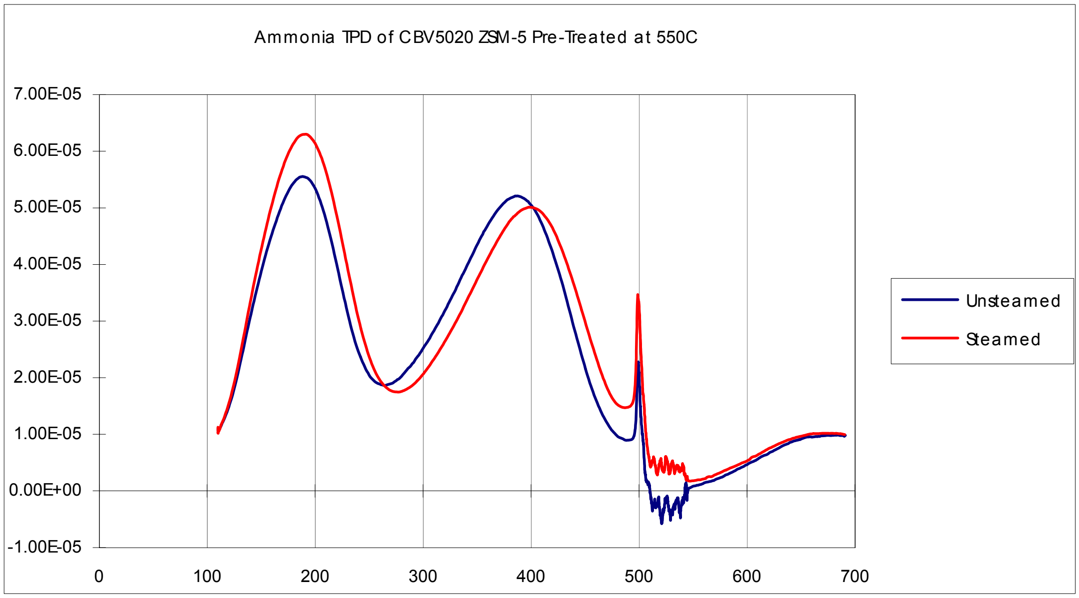
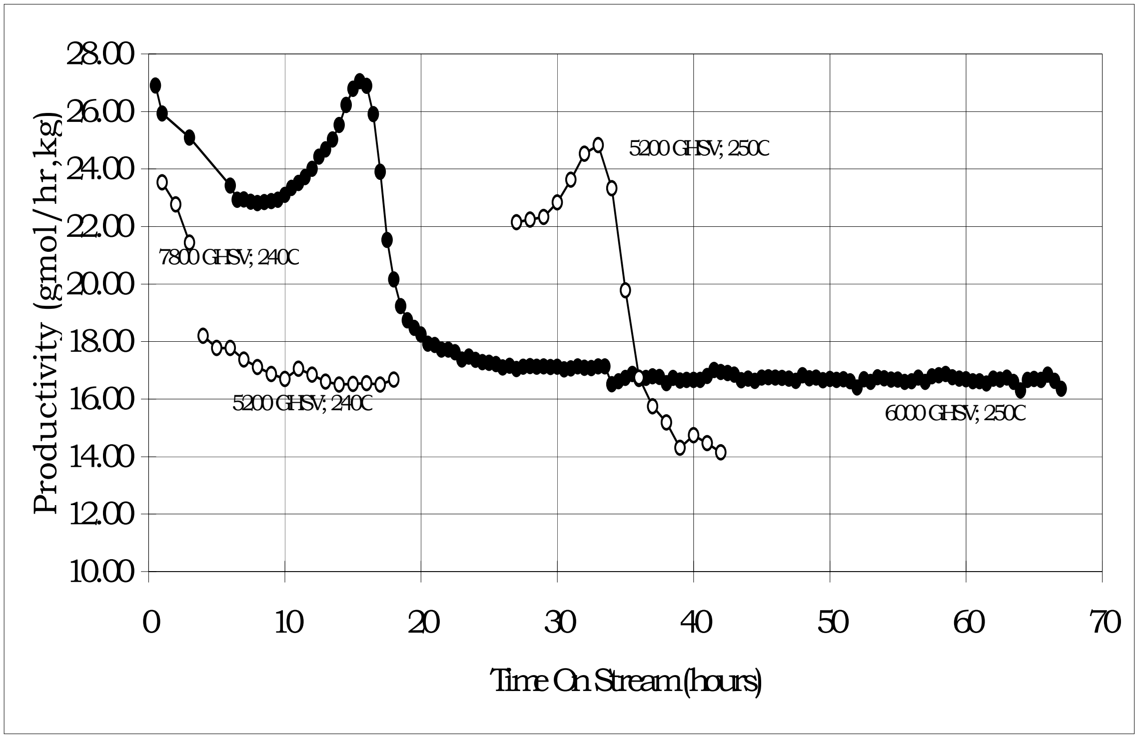


Figure 8: Data from Two LPDME™ Runs Using H-SAPO-34
(a) Methanol Equivalent Productivity



(b) Rate Constant History for the Second Experiment

Note that the calculated dehydration rate constant shown on this graph is artificially low because the water concentration has been set to zero. The dehydration reaction is close to equilibrium, so the rate constant is very sensitive to the water concentration.

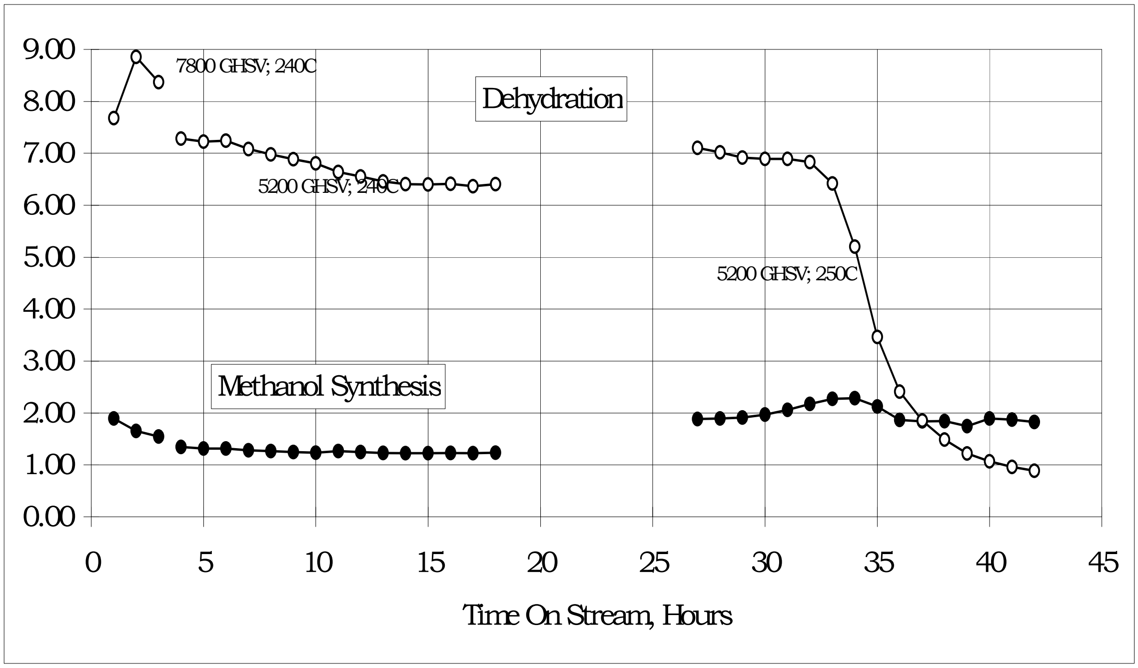


Figure 9: Comparison of the Acidities of Zeolite USY and H-ZSM-5 by Ammonia TPD

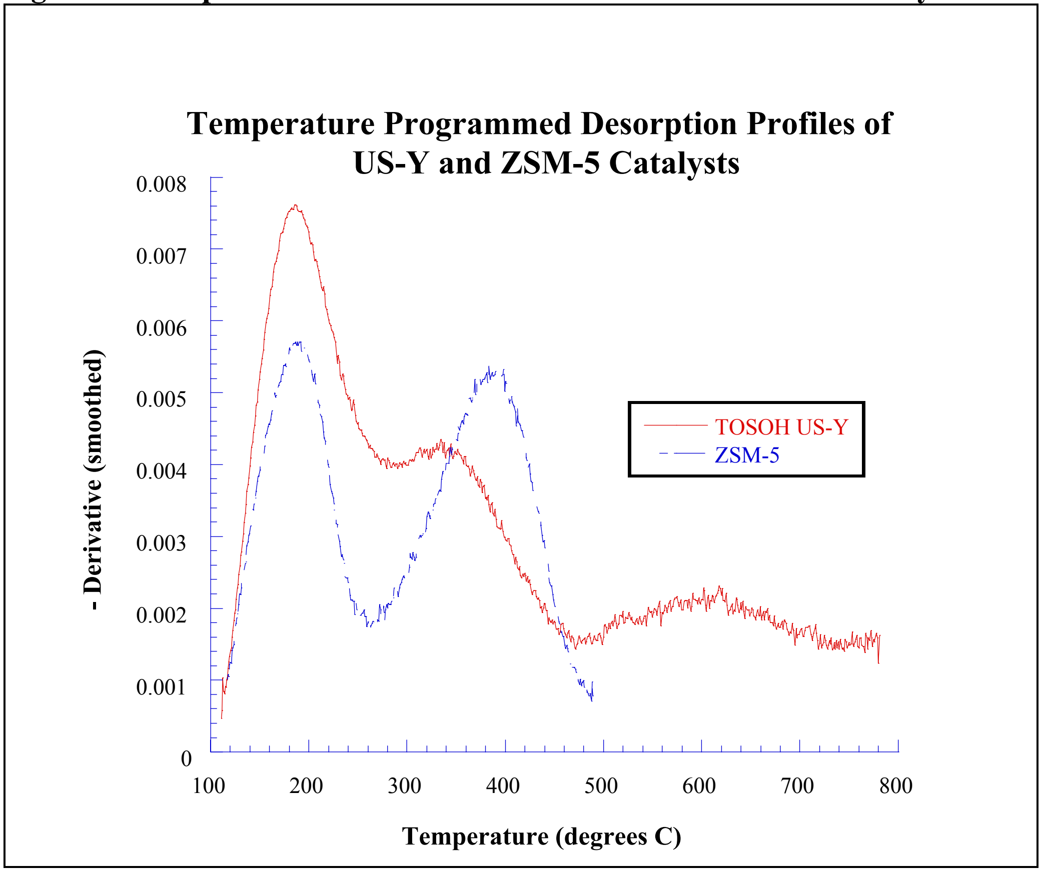


Figure 10: Changes in Methanol Dehydration Activity of USY and H-Chabazite at 250°C, 750 psig

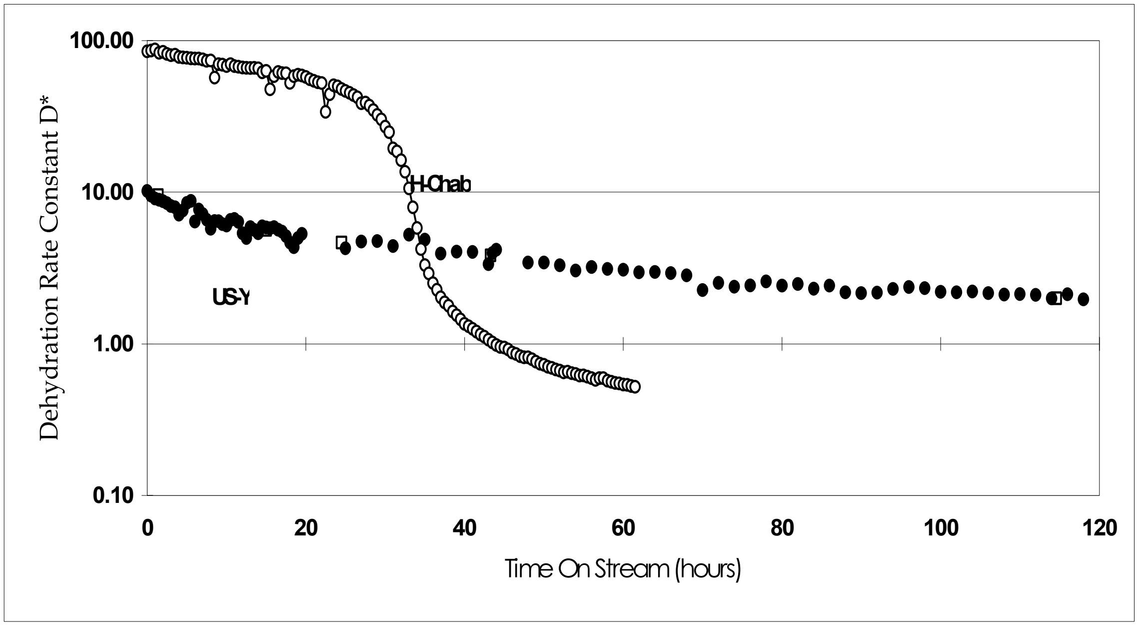
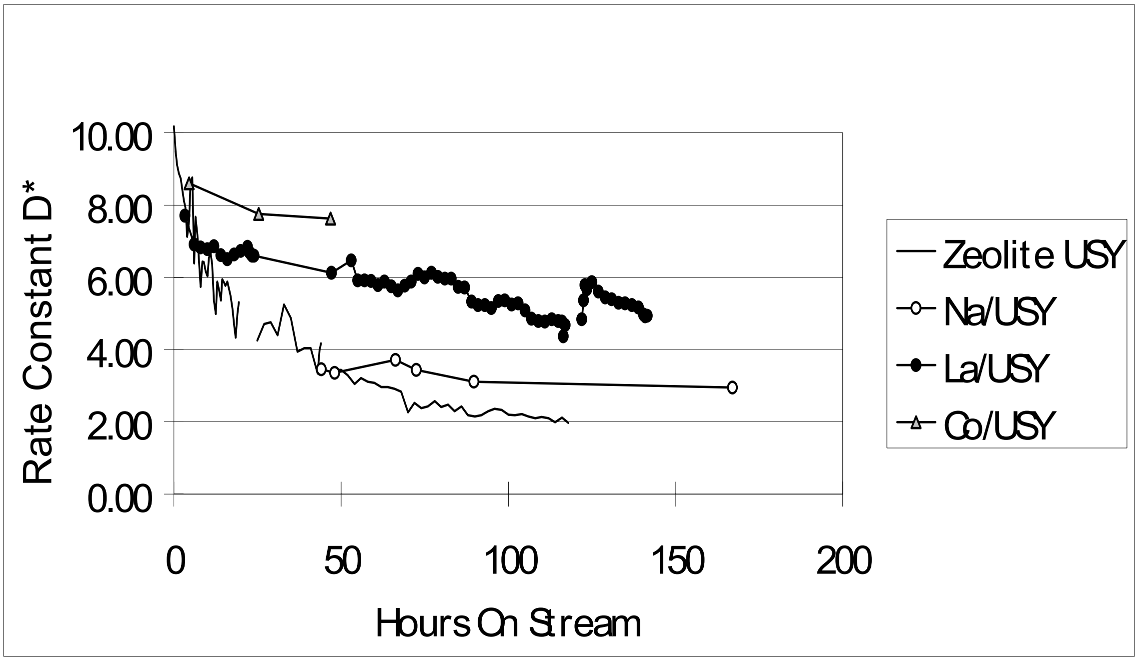


Figure 11: Changes in Methanol Dehydration Activity of Various Exchanged USY Zeolites at 250°C, 750 psig



6 APPENDIX: EXPERIMENTAL

6.1 Nuclear Magnetic Resonance Experiments

Solid-state ^{13}C CPMAS NMR was used to characterize carbon-containing species on spent catalysts. The experiments were performed at room temperature using a Bruker ASX-200 FT-NMR spectrometer equipped with a magic angle sample spinning multinuclear probe. The rotor material was zirconia. Glycine was used as an external reference.

Solid-state ^{29}Si and ^{27}Al MAS NMR were used to determine framework Si/Al ratios and the presence of non-framework aluminum. The experiments were performed at room temperature using either a Bruker ASX-2000 or a AM-500 FT-NMR spectrometer equipped with a magic angle sample spinning multinuclear probe. The rotor material was zirconia. TMS, $Al^{3+}(aq)$, and calcium hydroxyapatite were used as external references for silicon, aluminum and proton chemical shifts, respectively.

6.2 50 mL Microclave Reactor System

Most of the experiments described in this report were performed in our two 50 mL Microclave reactors, purchased from Autoclave Engineers. These reactors use a magnetically coupled drive that we operated at 1500 rpm. We have conducted experiments with these reactors to verify that our mixing is sufficient under our typical operating conditions and that the rates of chemical reaction are not mass transfer-limited.

The Microclaves share one analytical station, which consists of two gas chromatographs. One GC is used to measure hydrogen, CO, CO_2, and nitrogen using a thermal conductivity detector. A 13X molecular sieve column is used to separate hydrogen, CO, and nitrogen; the CO_2 is captured on a Poropak T column to prevent contamination of the 13X. Poropak Q is used to separate and analyze for CO_2. The other GC is used to measure organic molecules using a flame ionization detector and a capillary Hayesep D column.

6.3 Methanol Dehydration Experiments

These experiments were designed to evaluate the activity and stability of the catalyst for the dehydration of methanol in the absence of methanol catalyst and syngas. The 50 mL Microclave reactors were used. 1.2 grams of catalyst were slurried in 21 grams of mineral oil and fed 440 sccm of 9% methanol/nitrogen (2000 L methanol/kg,hr). The typical reaction conditions were 750 psig and 250°C. The reactor effluent was analyzed by gas chromatography. The reaction generally was highly selective to dimethyl ether, although a small amount of light alkanes was detected.

The activity of the catalyst was expressed either by the percent methanol conversion or as a rate constant. Because the atmosphere was essentially free of syngas, our standard LPDME™ rate laws did not apply. Instead, we defined a new rate law specific to this experiment.

$$Rate = D * f_{MeOH}^{2}\left[1 - \frac{f_{DME} f_{H2O}}{f_{MeOH}^{2} K}\right]$$

We did not do any experimentation to support this rate law. However, the data acquired with H-chabazite, which initially approached equilibrium methanol conversion, showed a fairly steady deactivation pattern when k_D* is plotted against time on-stream (see Figure 1). This shows that by accounting for approach to equilibrium, this simple rate law gives a better picture of the catalyst activity than conversion data alone.

6.4 LPDME™ Experiments

LPDME™ runs were conducted in the 50 mL Microclave reactor under conditions designed to approximate those in a commercial bubble column reactor. Methanol catalyst (2.4 grams) and molecular sieve dehydration catalyst (0.6 grams) were mixed with 21 grams of Drakeol-10 mineral oil and charged to the reactor. A 2% hydrogen in nitrogen feed was used to reduce the methanol catalyst over the course of a 20-hour temperature program. The reduction was essentially complete at 200°C. The reactor temperature was then increased to 250°C over five hours, as the feed was shifted to synthesis gas and the reactor was pressurized to 750 psig. A synthesis gas blend similar to that produced by a Shell-type gasifier (66% CO, 30% hydrogen, 3% CO_2, and 1% nitrogen) was used in these experiments. In addition to the bulk feed components, the product stream contained methanol, dimethyl ether, water, and traces of by-products (alkanes, alkenes, ethers, esters, and alcohols). The gas chromatographs were not equipped to measure water. However, data from our other labs has shown that the water gas shift is usually close to equilibrium in LPDME™ runs under carbon-rich syngas feeds.