Catalysis Letters Vol. 109, Nos. 3–4, July 2006 (© 2006)
DOI: 10.1007/s10562-006-0072-4

Dehydrogenation of light alkanes over rhenium catalysts on conventional and mesoporous MFI supports

Anne Krogh Rovik,[a,b,]* Anke Hagen,[c] Iver Schmidt,[d] Søren Dahl,[d] Ib Chorkendorff,[a] and Claus Hviid Christensen[b]

[a]*Center for Individual Nanoparticle Functionality CINF, Department of Chemical Engineering and Department of Physics, NanoDTU, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*
[b]*Center for Sustainable and Green Chemistry, Department of Chemistry, NanoDTU, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*
[c]*Materials Research Department, Risø National Laboratory, DK-4000 Roskilde, Denmark*
[d]*Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark*

Recently, Re/HZSM-5 (Si/Al = 15) was shown to be an efficient catalyst for ethane dehydrogenation and aromatization at 823 K and atmospheric pressure. In this reaction, the major initial products were benzene, toluene and xylene (BTX), but increasing amounts of ethene were produced with time on stream due to deactivation of the catalyst. We show that by use of rhenium impregnated MFI supports with very few or no acidic sites (Si/Al > 500), highly selective ethane dehydrogenation catalysts are obtained with ethene selectivities of 98%. By use of mesoporous MFI supports (Si/Al >500) the lifetime of the catalyst appears to be slightly improved compared to conventional MFI crystals. The beneficial effect of a mesoporous MFI support is convincingly demonstrated in propane dehydrogenation, where both conversion and selectivities on the mesoporous MFI (Si/Al > 500) impregnated with Re are significantly higher than on Re supported on a comparable conventional MFI support.

KEY WORDS: dehydrogenation of light alkanes; rhenium; MFI zeolites; mesoporous zeolites.

1. Introduction

Dehydrogenation of light alkanes, such as ethane, propane, and butanes, into the corresponding alkenes has attracted significant attention since the alkenes constitute an important and versatile class of intermediates in the chemical industry. Today, ethene is mainly manufactured by steam cracking of naphta where yields of about 28 wt% are obtained [1]. About 80×10^6 tons of ethene are produced per year and ethene constitutes the feedstock for about 30% of all petrochemicals [2]. Direct catalytic dehydrogenation of ethane is currently of limited commercial interest. This is due to the fact that possible yields per pass are quite low as a consequence of thermodynamic constraints. This limits the conversion of ethane to 9 mol% at 823 K and atmospheric pressure. Furthermore, currently available catalysts have relatively short lifetimes. To overcome these limitations inherent in the direct catalytic dehydrogenation, focus has been on improving catalysts for the oxidative dehydrogenation of ethane [3,4].

For propane dehydrogenation, the situation is somewhat different since the direct dehydrogenation has achieved some success. The UOP Oleflex™ and Süd-Chemie CATOFIN® processes are used industrially in the production of propene by direct dehydrogenation. The catalysts used are Pt/Al_2O_3 and Cr_2O_3/Al_2O_3, and the reaction is performed at 873–973 K and 30 kPa with selectivities around 90% at conversions around 40% [1,4].

Recently, it was shown that rhenium impregnated on conventional H-ZSM-5 is an efficient catalyst for the conversion of ethane into ethene, aromatics, and hydrogen [5–8]. Due to higher intrinsic activity and slower deactivation Re/HZSM-5 is superior to the commonly described zinc ion-exchanged H-ZSM-5 used in the aromatization of ethane [6]. The slower deactivation is caused by less sublimation of the active metal and less coking of the rhenium catalyst.

Here, we focus on catalysts comprising rhenium metal supported on MFI zeolite. We systematically investigate the influence of the acidity and porosity of the zeolite support on the activity and selectivity in ethane and propane conversions. For ethane dehydrogenation we conclude that the reduction of the number of acidic sites on the catalyst gives highly selective and rather stable ethane dehydrogenation catalysts. Introduction of mesopores in the zeolite support has a clear effect on ethane conversion while the high ethene selectivity is unaffected. The presence of mesopores in the zeolite support also has a positive effect on conversion and selectivity as well as on the stability of the catalyst in the propane conversion.

---

*To whom correspondence should be addressed.
E-mail: akrogh@fysik.dtu.dk

2. Experimental

Conventional H-ZSM-5 with Si/Al ratio of 116 was synthesized according to published procedures [9], but without impregnation of carbon black. In addition, conventional and mesoporous silicalite-1, having the same MFI structure as H-ZSM-5, were synthesized with a Si/Al ratio >500 [10]. Introduction of Re metal onto the zeolite support was carried out by incipient wetness impregnation with an aqueous solution of NH_4ReO_4 followed by drying and calcination at 773 K as previously described [6]. Concentrations of 2.8 wt% rhenium were obtained. Pelleting, crushing, and sieving of the catalysts ensured a particle size of 212–355μm. The catalyst particles were diluted prior to testing by mixing with an equal amount of quartz (400 mg) with the same sieve fraction. Testing was carried out in a plug flow reactor using a quartz reactor tube with an inner diameter of 3.7 mm. The length of the catalyst bed was 40–60 mm. The rhenium catalysts were activated for 1 h under a hydrogen flow of 675 ml(SATP)/h at 573 K in the reactor in order to reduce rhenium oxides and obtain metallic rhenium.

Catalytic tests were carried out at atmospheric pressure. The ethane flow was 550 ml(SATP)/h and the temperature 823 K. A volume of 75 mL(SATP)/h CO_2 was added as a standard to the effluent gasses which were analyzed by an on-line coupled Gas Chromatograph (HP6890A with a PONA column) equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID) in series. To avoid condensation of formed aromatics after the reactor or inside the GC, all piping and valves were heated to 473 K.

The propane dehydrogenation experiments were conducted at atmospheric pressure with a gas mixture containing 15 mol% propane in N_2. The total gas flow was 1800 ml(STP)/h, the temperature 823 K and 200 mg of catalyst was loaded in the reactor.

The conversions and selectivities were calculated from the FID results. Therefore only FID-detectable products are included. This excludes selectivities of possible coke deposits on the catalysts. The results from the FID are given in mole percent.

Nitrogen adsorption and desorption was performed at liquid nitrogen temperature on a Micromeritics ASAP 2010. Samples were outgassed in vacuum at 200 °C prior to measurement. Total surface areas were calculated using the BET method and pore volumes were determined by the BJH method (desorption).

3. Results and discussion

Rhenium impregnated on conventional H-ZSM-5 was recently shown to be a highly active catalyst in the conversion of ethane into ethene, aromatics, and hydrogen [5–7]. Similarly, preliminary reports of using Re/HZSM-5 for dehydrogenation and aromatization of propane have appeared [11, 12]. Re/HZSM-5 is a bifunctional catalyst where Re is responsible for the dehydrogenation of ethane to ethene and the acidic sites on the zeolite support are responsible for the further conversion of ethene into aromatics [13, 14]. Therefore, use of a Re catalyst supported on an MFI zeolite with low acidity is expected to favor the dehydrogenation reaction. This is investigated using a conventional HZSM-5 with Si/Al = 116 impregnated with 2.8 wt% Re as well as a conventional 2.8 wt%Re/silicalite-1. This silicalite-1 possesses a very low acid capacity (Si/Al > 500) according to NH_3-TPD and the only acidic sites are the weakly acidic silanol groups ($\equiv$ Si—OH).

Figure 1 shows that ethane conversions of around 2–0.5% and 4–2% are achieved and that the conversions are slightly decreasing within periods of 8 and 15 h. The rather low conversions obtained on both catalysts are partly a consequence of the thermodynamic equilibrium for the dehydrogenation of ethane of around 9 mol% at 823 K. Figure 1 shows that 2.8 wt%Re/HZSM-5 (Si/Al = 116) has a significantly higher conversion than 2.8 wt%Re/silicalite-1 (Si/Al >500). Figure 1 also shows that very high ethene selectivities of around 98% are obtained on the two catalysts after the initial period. The first 3 h on stream reveal a dramatic change in selectivity. In this period production of methane and hydrocarbons with 3 and 4 carbon atoms (C_3 and C_4) are detected. Also coking of the catalyst is observed and the active sites in the production of methane, C_3, and C_4 are hereby deactivated. The rate of deactivation of the two catalysts seem similar.

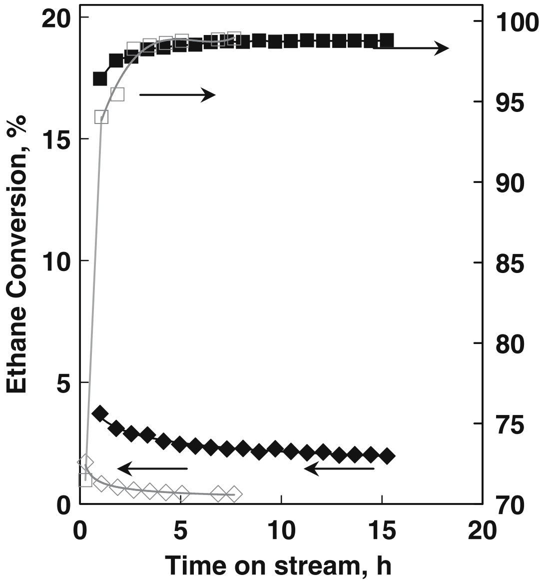

Figure 1. Ethane conversion (diamonds) and ethene selectivity (squares) on conventional 2.8 wt%Re/HZSM-5, Si/Al = 116 (filled) and on conventional 2.8 wt%Re/silicalite-1, Si/Al >500 (open) (823 K and atmospheric pressure).

It is previously reported [6] that rhenium impregnated MFI support with an even higher acid capacity (Si/Al = 15) gives an ethene selectivity of only 12% after 15 h on stream. It is therefore evident that by reducing the number of acidic sites we have hereby obtained a very selective catalyst.

In ethane dehydrogenation, it is obviously interesting to try to further improve the activity of the very selective Re/silicalite-1 catalyst. Previously, it has been seen that introducing mesopores into the microporous zeolite single crystals can increase the activity of the catalyst in ethene alkylation of benzene [16]. Here both conversions and selectivities to ethylbenzene increased on mesoporous ZSM-5 compared to conventional ZSM-5. Therefore, the influence of the morphology on the ethane conversion is studied on a conventional and a mesoporous 2.8 wt%Re/silicalite-1 (Si/Al > 500) (figure 2).

As seen in figure 2 the mesoporous 2.8 wt%Re/silicalite-1 is clearly more active than the conventional even though the acid capacities are identical. The acid capacities of both silicalites are measured by NH_3-TPD revealing an acid capacity corresponding to a Si/Al ratio of > 500. The acidic sites consist only of the weakly acidic silanol groups. Also the amounts of Re impregnated onto the silicalites are identical. Conversions decrease from 2% to 0.4% on the conventional catalyst while the conversions on the mesoporous decrease from 6.9% to 3% in the same period of time on stream. The conventional 2.8 wt%Re/silicalite-1 has an initial ethene selectivity of 71.5%, which increases to around 98.5% within a period of 3 h. The ethene selectivities increase from 89.5% to 99.6% on the mesoporous 2.8 wt%Re/silicalite-1. As in figure 1 an initial period with production of methane, C_3, and C_4 is observed. In these first 3 h coking of the catalyst is observed by which the active sites in the production of methane, C_3, and C_4 are deactivated.

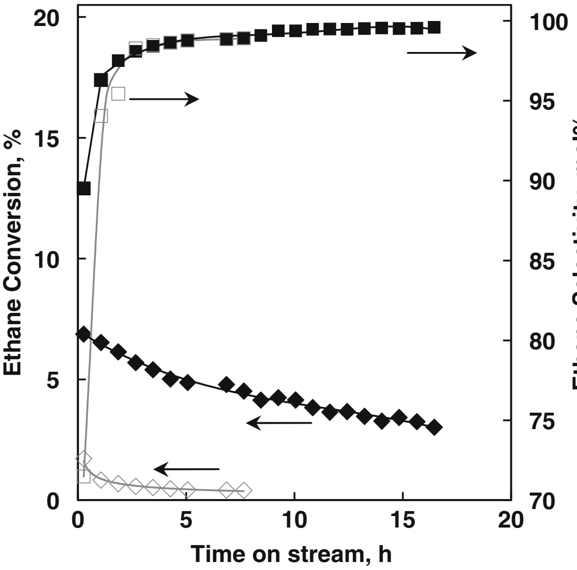

Figure 2. Ethane conversion (diamonds) and ethene selectivity (squares) on conventional (open) and mesoporous (filled) 2.8 wt%Re/silicalite-1, Si/Al > 500 (823 K and atmospheric pressure).

The differences in activity of the conventional and the mesoporous 2.8 wt%Re/silicalite-1 could be attributed to different rhenium metal dispersions. TEM images from previous studies of Re particles on a conventional zeolite revealed crystal sizes of 2–10 nm [6], while crystal diameters on a mesoporous zeolite were 2–20 nm. Accordingly, the larger activity on the mesoporous 2.8 wt%Re/silicalite-1 observed in figure 2 is apparently not due to improved rhenium dispersion, since the dispersion on the mesoporous zeolite appears slightly lower than on a conventional zeolite.

N_2 adsorption isotherms of the reduced conventional 2.8 wt%Re/silicalite-1 shows a BET surface area of 367 m^2/g and a total micropore volume of 0.19 cm^3/g. Compared to this the conventional silicalite-1 without Re has a BET surface area of 390 m^2/g while the total pore volume is 0.20 cm^3/g. These pore volume measurements reveal a blocking of the micropores by the Re metal impregnated onto the zeolite. Since also NH_3-TPD concludes that the acid capacities and strengths are identical the differences in activity can most likely be attributed to a higher accessibility to the rhenium caused by the mesoporosity. This effect has also been observed by Melián-Cabrera *et al.* [17] where the accessibility in ion exchange in a ZSM-5 zeolite is improved by introducing mesopores.

Summarizing, the mesoporous catalyst has a considerably higher conversion, a longer lifetime and a slightly higher ethene selectivity compared to the conventional 2.8 wt%Re/silicalite-1.

To further study the influence of mesopores in the zeolite support, conversion of propane is investigated. Propane is interesting since the direct dehydrogenation has achieved some industrial importance. Conventional and mesoporous silicalite-1 are used as supports for 2.8 wt% Re. In figure 3 a significantly higher conversion is achieved on the mesoporous 2.8 wt%Re/silicalite-1 compared to the conventional one. The conversion on the mesoporous catalyst remains relatively constant (8%) during the whole testing period and the catalyst is therefore not significantly deactivated. The conventional 2.8wt%Re/silicalite-1 deactivates, however, with conversions decreasing from 5% to 2.6%. Also, the propene selectivities are around 95% on the mesoporous catalyst whereas the selectivities on the conventional catalyst are 85%. These results clearly demonstrate that the mesoporous catalyst has a much higher activity for propane conversion, a lower deactivation tendency as well as a much higher selectivity for the formation of propene.

Thus, it is clear that the introduction of mesopores has a larger impact on the propene selectivity and the propane conversions than on ethane selectivity and ethane conversions. The effect of increased olefin

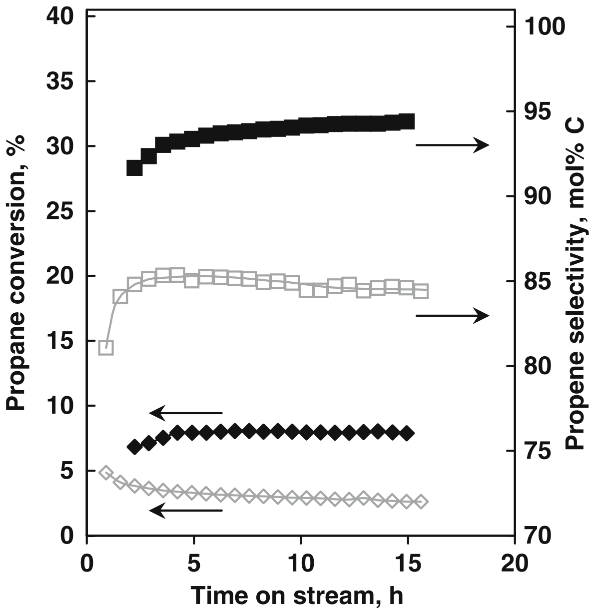

Figure 3. Propane conversion (diamonds) and propene selectivity (squares) on conventional (open) and mesoporous (filled) 2.8 wt%Re/silicalite-1, Si/Al > 500 (823 K and atmospheric pressure).

selectivity and the very low, almost absent, deactivation when using a mesoporous zeotype on catalytically dehydrogenation of hydrocarbons was recently patented [8].

4. Conclusions

The influences of zeolite acidity and porosity on conversions and product distributions are investigated in ethane and propane dehydrogenation on rhenium catalysts.

It is clearly shown that low acid capacity is responsible for the very high selectivity of ethene (98–99%). This is in good agreement with the picture that the dehydrogenation takes place on the rhenium particles whereas acidic sites are mainly responsible for the aromatization reactions.

The introduction of mesopores into the silicalite-1 results in higher ethane conversions, longer lifetimes and slightly higher ethene selectivities compared to the conventional silicalite-1. This effect is not caused by better Re dispersion or a change in zeolite acid capacity or strength. Pore volume measurements reveal a blocking of the micropores by Re in the conventional HZSM-5. Thus the access to the active sites is increased by introducing mesopores into the zeolite structure. To further investigate the influence of the introduction of mesopores, the dehydrogenation of propane is studied. The results reveal a profound effect in using a mesoporous support since both higher conversions and higher selectivities are observed. The conversion of propane is more affected by the introduction of mesopores since propane and propene are more diffusion limited compared to ethane and ethene. Also, propane is easier cracked into ethane and methane than ethane into methane. Therefore, a change in retention time for the reactants in the zeolite pores will have a higher effect on the selectivity of propane dehydrogenation than ethane dehydrogenation. This is in accordance with the experimental observations.

In the dehydrogenation of light alkanes, using a rhenium impregnated mesoporous MFI zeolite support with low acid capacity therefore leads to very high alkene selectivities, higher conversions, and longer lifetimes compared to a conventional zeolite support with otherwise same characteristics.

Acknowledgments

Anne Krogh Rovik would like to thank Haldor Topsøe A/S and Copenhagen Graduate School for Nanoscience and Nanotechnology (CONT) for funding. Center for Individual Nanoparticle Functionality (CINF) and Center for Sustainable and Green Chemistry (CSG) are sponsored by the Danish National Research Foundation.

References

[1] *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed. (John Wiley & Sons Inc. 2005).

[2] K. Weissermel and H.-J. Arpe, *Industrial Organic Industry* (VCH, Weinheim, 1997).

[3] E.A. Mamedov and V.C. Corberán, Appl. Catal. A: General 127 (1995) 1.

[4] M.M. Bhasin, J.H. McCain, B.V. Vora, T. Imai and P.R. Pujadó, Appl. Catal. A: General 221 (2001) 397.

[5] L. Wang, K. Murata and M. Inaba, Catal. Today 82 (2003) 99.

[6] A. Krogh, A. Hagen, T.W. Hansen, C.H. Christensen and I. Schmidt, Catal. Commun. 4(3) (2003) 627.

[7] F. Solymosi and P. Tolmacsov, Catal. Lett 93 (2004) 7.

[8] I. Schmidt, A. Krogh, C.H. Christensen, Process for Catalytic Dehydrogenation and Catalyst Therefore (European Patent, No. EP1430949, December 10. 2002).

[9] C.J.H. Jacobsen, C. Madsen, J. Houzvicka, I. Schmidt and A. Carlsson, J. Am. Chem. Soc. 122 (2000) 7116.

[10] A.H. Janssen, I. Schmidt, C.J.H. Jacobsen, A.J. Koster and K.P. de Jong, Micropor. Mesopor. Mater. 65 (2003) 59.

[11] J. Guo, H. Lou, H. Zhao, L. Zheng and X. Zheng, J. Mol. Catal. A 239 (2005) 222.

[12] F. Solymosi, P. Tolmacsov and A. Széchenyi, Stud. Surf. Sci. Catal. 147 (2004) 559.

[13] A. Hagen and F. Roessner, Catal. Rev.-Sci. Eng. 42 (2000) 403.

[14] M. Guisnet and N.S. Gnep, Appl. Catal. A: General 146 (1996) 33.

[15] L. Wang, R. Ohnishi and M. Ichikawa, Catal. Lett. 62 (1999) 29 .

[16] C.H. Christensen, K. Johannsen, I. Schmidt and C.H. Christensen, J. Am. Chem. Soc. 125 (2003) 13370.

[17] I. Melián-Cabrera, S. Espinosa, J.C. Groen, B. v/d Linden, F. Kaptein and J.A. Moulijn, J. Catal. 238 (2006) 250.