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Catalytic conversion of butadiene to ethylbenzene over the nanoporous nickel(II) phosphate, VSB-1

Jong-San Chang,[ab] Sang-Eon Park,*[b] Qiuming Gao,[a] Gérard Férey[c] and Anthony K. Cheetham*[a]

[a] *Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA. E-mail: cheetham@mrl.ucsb.edu*

[b] *Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology (KRICT), P.O. Box 107, Yusung, Taejon 305-606, Korea. E-mail: separk@pado.krict.re.kr*

[c] *Institut Lavoisier, UMR CNRS 173, Université de Versailles Saint Quentin, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France.*

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The large-pore nickel(II) phosphate, VSB-1, shows excellent selectivity (> 80%) for the dehydrocyclodimerization of butadiene to ethylbenzene at 400 °C; conversion to 4-vinylcyclohexene and oligomeric byproducts is < 5% in each case.

The widespread utility of aluminosilicate zeolites in the field of shape-selective catalysis[1] has led to a quest for other families of nanoporous materials that might exhibit catalytic activity. In spite of the enormous amount of work that has been done in this area,[2] only two other families of materials, the aluminum phosphates[3] and the titanosilicates,[4] have yielded molecular sieves with exciting catalytic properties. For example, SAPO-34, an $AlPO_4$ with the chabazite structure, is being exploited for the conversion of methanol to olefins,[3] and the titanosilicate, TS-1, is a very effective for selective oxidations using hydrogen peroxide.[4] Attempts to make nanoporous transition metal phosphates have led to the discovery of many new phases, *e.g.* V–P–O,[5] Fe–P–O[6] and Co–P–O,[7] but, as is the case with most non-silicate open-frameworks, the poor thermal stability of these systems leads to the collapse of the pore structures on activation, thus rendering them unsuitable for applications that require porosity. Recently, however, we described the first example of an open-framework nickel phosphate, VSB-1 (Versailles/Santa Barbara-1),[8] whose porosity can be readily accessed by low temperature calcination. The structure is stable to *ca.* 550 °C. In the present work, we show that this phase is catalytically active in the dehydrocyclodimerization of butadiene to ethylbenzene.

VSB-1 was prepared as a green powder from a hydrothermal reaction at 180 °C for 6 d between nickel(II) chloride hexahydrate and phosphoric acid (85% by weight) in the presence of ammonium fluoride. Further details are given in ref. 8. This new material has a large unidimensional channel composed of 24 NiO_6 and PO_4 polyhedra, and the free diameter of the channel is estimated to be 8.8 Å (Fig. 1). Its surface area and chemical composition are 82 $m^2\ g^{-1}$ and $Ni_{18}(HPO_4)_{14}(OH)_3F_9(H_3O/NH_4)_4\cdot 12H_2O$, respectively.[8] Zeolite NaX (Si : Al = 1.40, S_{BET} = 875 $m^2\ g^{-1}$), used for comparison of the catalytic activity, was obtained from Fluka Chemie AG.

The cyclodimerization of 1,3-butadiene to 4-vinylcyclohexene (VCH) and its dehydrogenation to ethylbenzene or styrene (Scheme 1) could provide an attractive route for styrene production and is regarded as an interesting alternative to the classical ethylbenzene dehydrogenation process.[9] VSB-1 and NaX were investigated for this reaction. The catalytic runs were carried out in a fixed-bed, vertical flow quartz reactor mounted inside a tubular furnace at 400 °C and atmospheric pressure. After the catalyst had been placed in the reactor it was heated up to 450 °C in an oxygen flow for 4 h for activation and to remove any adsorbed species. The reactor was then purged with helium for 1 h at the same temperature and cooled down to the desired reaction temperature. 1,3-Butadiene (99%, Matheson) was delivered with a constant flow (typically 3 ml gas min^{-1}) and preheated to 200 °C and mixed with helium (10 ml min^{-1}) in a baffled gas-phase mixer within an oven at 200 °C. Product gases were analyzed downstream by on-line gas chromatograph (HP 5890II) with a flame ionization detector (FID). The capillary column (J&W, DB-WAX) of the gas chromatograph allowed the separation of the products.

Fig. 2 shows the conversion of butadiene *via* Diels–Alder cyclodimerization at 400 °C over VSB-1 and NaX. The thermal (non-catalytic) conversion of butadiene to 4-vinylcyclohexene or ethylbenzene in a Pyrex-filled glass reactor under the same conditions as our catalyst testing was less than 1%. We find that NaX gives very high butadiene conversion, at least initially [Fig. 2(*b*)], but very poor selectivity for cyclodimerization (< 30%). The main products over NaX are oligomeric ones such as polyalkenes, presumably due to residual acidity in the zeolite at high temperatures.

According to our unpublished results, VSB-1 has much weaker acidity than zeolite NaX, so there is a reasonable expectation that oligomerization will be less than in the aluminosilicate. This behavior is confirmed in our experiments [Fig. 2(*a*)]. Steady state conversions are obtained after approximately 1 h and are sustained for at least 5 h. Although the activity of VSB-1 is relatively low, it exhibits high selectivity (> 90%) towards the cyclodimerization products, ethylbenzene and VCH. In particular, it is noted that VSB-1 shows remarkably high selectivity for ethylbenzene (82%). The

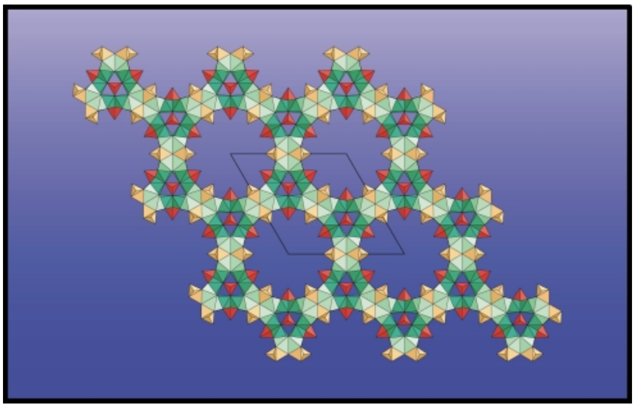
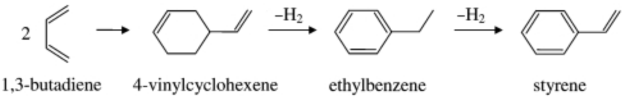


Fig. 1 A view of the structure of VSB-1 down [001]. NiO_6 octahedra and PO_4 tetrahedra are shown in green and red, respectively. The disordered sites are shown in light green and orange.



Scheme 1

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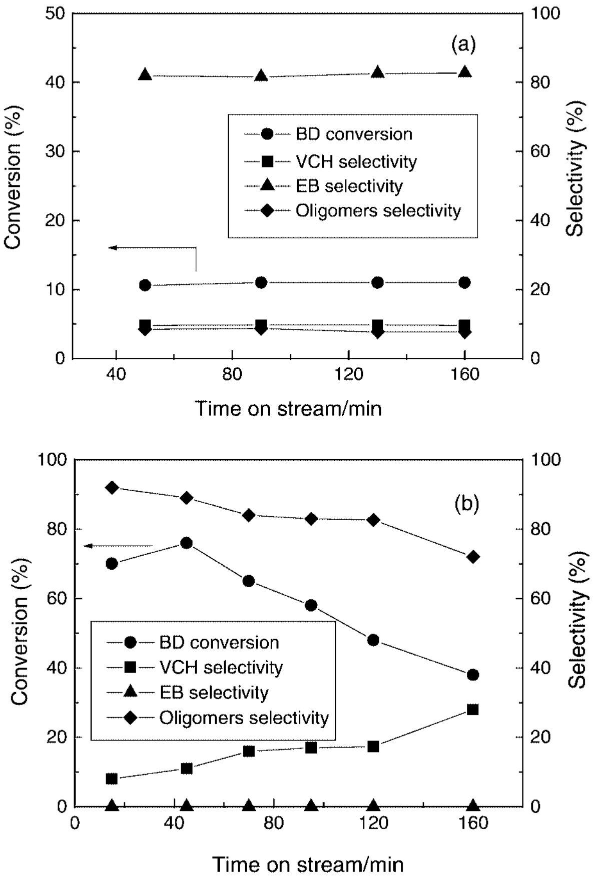

Fig. 2 The Diels–Alder cyclodimerization of 1,3-butadiene over (a) VSB-1 and (b) NaX. Reaction conditions: T = 400 °C, GHSV = 7800 h^{-1}, feed gas = 1,3-butadiene–helium (3/10). Notation: BD; 1,3-butadiene, VCH; 4-vinylcyclohexene, EB; ethylbenzene.

reaction certainly involves the cyclodimerization of butadiene to VCH followed by dehydrogenation to form ethylbenzene; that is, the whole process is better described as a dehydrocyclodimerization. In contrast, NaX did not produce any ethylbenzene or styrene. Interestingly, VSB-1 displays 2% selectivity to styrene at 425 °C (data not shown), but catalyst deactivation is observed at this temperature due to the deposition of oligomeric products.

The Diels–Alder cylcodimerization of 1,3-butadiene to VCH is a well-known thermally-initiated electrocyclic reaction, that is kinetically second-order in butadiene.[10] Neither acidic nor basic catalysts have been used successfully for this reaction.[11] In addition to homogeneous catalyst systems,[12] the cyclodimerization of butadiene has been found over large-pore molecular sieves such as CuY,[13] NaZSM-20,[11] NaBeta[11] and NaX.[13] The catalytic role of non-acidic zeolites in the Diels–Alder reaction has therefore been understood in terms of the ability of zeolites to concentrate hydrocarbons within their cavities.[11] Thus, by increasing the butadiene concentration inside the zeolitic pores relative to that in the external gas phase, the zeolite can enhance the rates of bimolecular reactions such as the Diels–Alder reaction. In the present work, the high selectivity of VSB-1 for the cyclodimerization may again be ascribed to the concentration effect within its large pore channel (8.8 Å). Moreover, the high selectivity towards ethylbenzene over VSB-1 points to the role of the Ni species within its open framework in the partial dehydrogenation step. This type of selectivity has been seen with other nanoporous materials containing transition metals, but not with acidic or basic catalysts. For example, a Ni-impregnated aluminum phosphate catalyst was reported to be active in the dehydrogenation of cyclohexane at 400 °C.[14]

Although the active sites for this reaction are unclear as yet, the high selectivity of VSB-1 for ethylbenzene highlights the bifunctional role of VSB-1. Another important feature of VSB-1 is its excellent stability. The catalytic performance is very stable over several hours, and, significantly, no appreciable deactivation is observed. The stability of VSB-1 is consistent with a previous report that it is thermally stable in air to 550 °C,[8] in contrast to most other open-framework transition metal phosphates. In the case of NaX, severe catalyst deactivation was noted as the reaction proceeded due to the formation and deposition of oligomeric cokes.

In summary, our work shows that the nanoporous nickel(II) phosphate, VSB-1, has some interesting catalytic properties, exhibiting good stability and high selectivity for ethylbenzene in the dehydrocyclodimerization of 1,3-butadiene. The catalytic performance is ascribed to the bifunctional role of VSB-1, *i.e.* the dehydrogenation ability of Ni species and the concentration effect of the nanoporous structure. Further studies are in progress to elucidate the active sites of VSB-1 for the cyclodimerization and dehydrogenation. In the light of earlier work that demonstrated the dehydrogenation of EB to styrene at temperatures as low as 250 °C,[15] we are also exploring the possibility that a single stage conversion of butadiene to styrene might be possible.

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Notes and references

1 M. E. Davis, *Chem. Eur. J.*, 1997, **3**, 1745 and references therein.
2 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268; G. Férey and A. K. Cheetham, *Science*, 1999, **283**, 1125.
3 B. V. Vora, T. L. Marker, P. T. Barger, H. R. Nilsen, S. Kvisle and T. Fuglerud, in *Fourth International Natural Gas Conversion Symposium*, ed. M. de Pontes, R. L Espinoza, C. P. Nicolaides, J. H. Scholtz and M.S. Scurrell, Elsevier, Amsterdam, *Stud. Surf. Sci. Catal.*, 1997, **107**, 87.
4 B. Notari, *Adv. Catal.*, 1996, **41**, 253; R. J. Saxton, *Top. Catal.*, 1999, **43**, 9.
5 V. Soghomanian, Q. Chen, R. C. Haushalter, J. Subieta and J. O'Connor, *Science*, 1993, **259**, 1596; T. Loiseau and G. Férey, *J. Solid State Chem.*, 1994, **111**, 416.
6 D. R. Corbin, J. F. Whitney, W. C. Fultz, G. D. Stucky, M. M. Eddy and A. K. Cheetham, *Inorg. Chem.*, 1986, **25**, 2280; H. M. Lin, K.-H. Lii, W.-C. Jiang and S.-L. Wang, *Chem. Mater.*, 1999, **11**, 519.
7 J. Chen, R. H. Jones, S. Natarajan, M. B. Hursthouse and J. M. Thomas, *Angew. Chem., Int. Ed.*, 1994, **33**, 639; P. Feng, X. Bu, S. H. Tolbert and G. D. Stucky, *J. Am. Chem. Soc.*, 1997, **119**, 2497.
8 N. Guillou, Q. Gao, M. Nogues, R. E. Morris, M. Herview, G. Férey and A. K. Cheetham, *C. R. Acad. Sci. Paris*, 1999, **2**, 387.
9 D. A. Hucul, *US Patent*, 5 336, 822, 1994.
10 R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 1965, **87**, 4388; D. Rowley and H. Steiner, *Discuss. Faraday Soc.*, 1951, **10**, 198.
11 R. M. Dessau, *J. Chem. Soc., Chem. Commun.*, 1986, 1167.
12 P. Heimbach, P. W. Jolly and G. Wilke, *Adv. Organomet. Chem.*, 1970, **8**, 29.
13 I. E. Maxwell, R. S. Downing and S. A. J. van Langen, *J. Catal.*, 1980, **61**, 485; I. E. Maxwell, *Adv. Catal.*, 1982, **31**, 1.
14 S. A. El-Hakam, A. A. El-Khouly and A. S. Khder, *Appl. Catal. A: Gen.*, 1999, **185**, 247.
15 Y.-S. Choi, Y.-K. Park, J.-S. Chang, S.-E. Park and A. K. Cheetham, *Catal. Lett.*, 2000, **69**, 93; R. Neumann and I. Dror, *Appl. Catal. A: Gen.*, 1998, **172**, 67.