Selective oxidative dehydrogenation of isobutane over unidimensional aluminophosphate molecular sieves ($AlPO_4$-5, $AlPO_4$-41, $AlPO_4$-25)

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Unidimensional aluminophosphate molecular sieves ($AlPO_4$-5, $AlPO_4$-41, $AlPO_4$-25) are found to be selective for the oxidative dehydrogenation of isobutane (2-methylpropane) to isobutene (2-methylprop-1-ene) and $AlPO_4$-5 with a twelve-membered ring pore shows relatively high conversion.

The production of gasoline octane enhancers (such as methylene *tert*-butyl ether (MTBE) has led to new commercial developments in isobutene production. Relatively abundant liquefied petroleum gas (LPG) contains mainly propane and butane and catalytic oxidative dehydrogenation of isobutane is a promising route to isobutene.[1–4] In this process, catalytic selectivity is the most important factor since for an alkane–oxygen mixture, thermodynamically favoured products are CO_2 and H_2O. Thus for this process, catalysts must be designed which effectively inhibit complete oxidation[5] and recently, metal fluoride promoted metal oxides and metal pyrophosphates have been studied.[6–8] Here, for the first time, we utilized aluminophosphate molecular sieves as catalysts for isobutane oxidative dehydrogenation.

$AlPO_4$-25 was obtained *via* calcination of $AlPO_4$-21 while $AlPO_4$-21 and $AlPO_4$-5 were synthesized by reacting aluminophosphate gels containing organic amines using procedures described in detail elsewhere.[9] For the synthesis of $AlPO_4$-41, aluminium triisopropoxide and phosphoric acid (H_3PO_4 85 mass%) were used as aluminium and phosphorus sources, respectively, diisopropylamine was the structure-directing template and triethylene glycol (TEG) was used as the solvent. A typical synthetic procedure involved the following steps: aluminium triisopropoxide was first slurried into an alcohol solvent followed by addition of an amine with stirring then phosphoric acid was added dropwise to the mixture. The resultant gel with molar composition 1.0 $Al(OPr^i)_3$: 1.8 H_3PO_4 : 6.5 TEG : 1.8 $NHPr^i_2$: 1.8 H_2O obtained after continuous stirring for 30 min was sealed in a Teflon-lined stainless-steel autoclave and heated at 180 °C under autogeneous pressure for 7 days. The products were filtered, washed with distilled water, and dried at ambient temperature. $AlPO_4$-5, $AlPO_4$-41 and $AlPO_4$-21 were characterized by X-ray powder diffraction, and shown to be pure phases as also corroborated by SEM. Thermal analysis on a Perkin-Elmer differential thermal analyser and on a Perkin–Elmer thermogravimetric analyser showed that the organic templates were lost at temperatures >300 °C, and $AlPO_4$-21 was converted into $AlPO_4$-25, as established by X-ray powder diffraction. By contrast, the inorganic skeletons of $AlPO_4$-5, $AlPO_4$-41 and $AlPO_4$-25 were stable up to 750 °C. After calcination to remove organic templates at 600 °C for 2 h, $AlPO_4$-5, $AlPO_4$-41 and $AlPO_4$-25 were further characterized by X-ray powder diffraction at ambient temperature, which indicated that their crystallinities were $>95\%$. Elemental analysis established that the calcined molecular sieves did not contain organic templates. The three calcined materials were further calcined at 250 °C at 10^{-3} Torr for 1 h and Brunauer–Emmett–Teller (BET) adsorption experiments on the calcined samples indicated type I adsorption isotherm behaviour, and the amount of adsorbed water was 26, 19 and 17 mass%, respectively, suggesting that in each the pores were accesible.[10]

The catalysts were then powdered. The catalytic activity and selectivity for oxidative dehydrogenation was determined by using a conventional flow system (fixed bed microreactor, 5 mm internal diameter) at a reaction temperature of 450–550 °C, 1 atm pressure and a space velocity of 4000 h^{-1}, with an isobutane : O_2 3 : 1 feed. 0.2 g of catalyst was employed and the products were analysed by on-line gas chromatography.

$AlPO_4$-5 was particularly active for the selective production of isobutene from the oxidation of isobutane with molecular oxygen. Isobutene selectivity was found to be higher than with pure or complex oxides (*e.g.* for a Y_2O_3 catalyst, isobutene selectivity = 37.1% with 34.5% isobutane conversion at 500 °C at a space velocity of 6000 h^{-1} without N_2 feed), and similar to multi-valence anion modified complex catalysts[6,7] and metal pyrophosphates.[8] Fig. 1 shows the results of catalytic oxidative dehydrogenation of isobutane over the prepared catalysts. The selectivity decreased with increasing temperature at above 450 °C, as found for Y_2O_3–CeF_3.[6] It is of interest that $AlPO_4$-41, which has a ten-membered ring unidimensional pore structure shows higher selectivity than $AlPO_4$-5 with twelve-membered ring pores or $AlPO_4$-25 with eight-membered ring pores, suggesting that the pore size of the molecular sieves affects the selectivity.

Conversion rates of isobutane are very different over these three aluminophosphate molecular sieves. $AlPO_4$-41 shows lower conversion rates, whereas $AlPO_4$-5 shows a much higher conversion of isobutane, even higher than found for Y_2O_3–CeF_3.[6,7] The conversion increased steadily with increasing temperature above 450 °C. The main byproduct was propene, however CO, CH_4 and CO_2 were also found. At 500 °C,

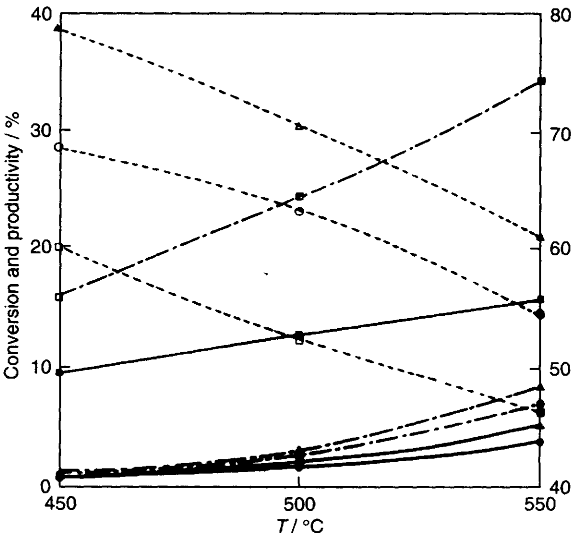

Fig. 1 Isobutane conversion (—·—), isobutene productivity (——) and isobutene selectivity (···) on the unidimensional aluminophosphate molecular sieves: (■) $AlPO_4$-5, (▶) $AlPO_4$-41 and (●) $AlPO_4$-25

isobutane conversion reached 24.6% over $AlPO_4$-5, with a selectivity of 52.32%, and the amount of isobutene obtained, 12.87%, is higher than found for multi-valence anion modified complex catalysts[6,7] or metal pyrophosphates,[8] and much higher than with Y_2O_3 (over Y_2O_3–CeF_3 10.9% isobutane conversion is observed).[6,7] Upon increasing the temperature to 550 °C, 16.41% isobutane is observed over $AlPO_4$-5. $AlPO_4$-41 and $AlPO_4$-25 show only poor yields of isobutene owing to their lower conversion rates.

Support of this work by the National Natural Science Foundation of China is gratefully acknowledged.

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Received, 24th April 1996; Com. 6/02875F