Oxidative Dehydrogenation of Aqueous Ethanol over the Molecular Sieve TS-1

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Aqueous ethanol undergoes oxidative dehydrogantion to acetaldehyde selectively over TS-1, in the presence of air, whereas acidic zeolites and TiO_2-impregnated silicalite-1 dehydrate ethanol to diethyl ether and alkenes.

The selective oxidative dehydrogenation of ethanol to acetaldehyde over mild oxidation catalysts such as Mo titanate[1] Fe molybdate[2] and alumina-supported metal ions[3] has been studied extensively. Recently, highly dehydrated silica[4] and silicalite[5] have also been reported to catalyse the conversion of ethanol to small amounts of acetaldehyde. Acidic zeolites convert ethanol to diethyl ether, alkenes and aromatic compounds depending on the conditions.[6–9] Transition metal-exchanged zeolites have a greater oxidation ability for conversion of ethanol to acetaldehyde, but lead to products of over-oxidation such as acids and carbon oxides.[8]

TS-1, a medium pore titanium silicate molecular sieve with the MFI structure, has been reported to catalyse the conversion of primary and secondary alcohols to aldehydes and ketones, respectively, in the presence of dilute hydrogen peroxide.[10,11] We now report the selective oxidative dehydrogenation of aqueous ethanol to acetaldehyde over TS-1 in the presence of air. Comparisons are made with silicalite-1 (S-1), TiO_2-impregnated S-1, ZSM-5 and Fe-ZSM-5. The latter two are typical acidic zeolites.

The detailed synthesis and characterization of S-1, TS-1, ZSM-5 and Fe-ZSM-5 have been reported elsewhere.[12] The TiO_2-S-1 sample was prepared by impregnating S-1 with $Ti(OBu)_4$ solution. The catalytic runs were carried out in a fixed-bed downflow-type reactor. Aqueous ethanol (10 wt%) was fed into the reactor at measured rates. Air was mixed with ethanol (O_2 to ethanol mole ratio of 1 : 1) before entering the heating zone of the reactor. The products were analysed by on-line GC (Shimadzu GC R1H).

The catalytic conversion of aqueous ethanol over all the catalysts is temperature dependent. As the temperature increases, the conversion of ethanol increases, reaching almost 100 wt% at temperatures of 553 (ZSM-5), 573 (Fe-ZSM-5), 648 (S-1 and TiD_2-S-1)and 673 K (TS-1). Under identical conditions of temperature (523 K) and space velocity

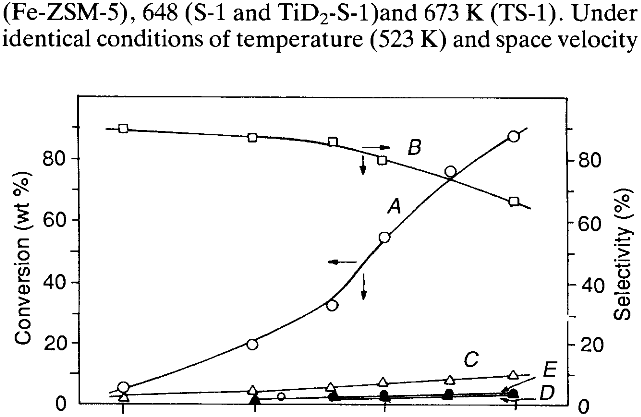

Fig. 1 Influence of temperature on conversion of ethanol (*A*) and selectivity for formation of acetaldehyde (*B*), ethylene (*C*), CO_2 (*D*) and acetic acid (*E*) on TS-1

Table 1 Product distribution at 30 wt% conversion of aqueous ethanol over MFI zeolites[a]

		Product distribution (wt%)					
Catalyst	Si/M ratio[b]	$CH_2{=}CH_2$	MeCHO	$MeCO_2H$	Et_2O	CO_2	Other
S-1	>3000	25.0	22.0	—	51.0	—	2.0[c]
TS-1	37	4.6	88.0	0.6	1.5	1.1	4.6[c]
S-1 + TiO_2	38	17.4	46.2	—	33.1	0.5	2.7[c]
ZSM-5	42	0.1	—	—	99.6	—	0.3[d]
Fe-ZSM-5	41	0.3	0.1	—	93.5	0.1	6.0[d]

[a] Feed = 10 wt% aq. ethanol; O_2(air)/ethanol mole ratio = 1. [b] M = Al, Ti or Fe. [c] Includes HCHO, HCO_2H, Me_2CO, CO and CH_4. [d] Includes C_3, C_4 and C_6 alkenes.

($1\ h^{-1}$), the activity follows the order: ZSM-5 > Fe-ZSM-5 > TiO_2-S-1 > S-1 > TS-1. The selectivity to different products, however, depends on the surface characteristics of the catalyst. Ethylene is the major product (>90 wt%) over S-1, whereas TS-1 yields acetaldehyde (>85% wt%). Fig. 1. presents the conversion of ethanol over TS-1 at different temperatures. At higher temperatures, other products like HCHO, $MeCO_2H$, CO and CO_2 are formed in small amounts.

In order to study the differences in product distribution, the catalysts are compared at 30 wt% conversion level (Table 1). Ethylene and diethyl ether are the major products over S-1. The incorporation of Ti^{4+} in the MFI framework (TS-1) shifts the selectivity to acetaldehyde, whereas TiO_2-impregnated S-1 still yields appreciable amounts of ethylene and diethyl ether. As expected, acidic ZSM-5 and Fe-ZSM-5 samples yield mainly diethyl ether and small amounts of alkenes. Diethyl ether has been reported to be an intermediate in the formation of ethylene over acidic zeolites.[13] While the observed difference in product selectivity could be accounted for by the use of acidic and neutral zeolites, the distinct advantage of having Ti^{4+} in the framework of TS-1 for selective one-step oxidation of ethanol to acetaldehyde is obvious from the above results.

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