Unusual Performance for the Selective Oxidation of Ethane to Acrolein over Mesoporous SBA-15-supported Potassium Catalysts

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SBA-15 silica-supported potassium catalysts were first reported for the selective oxidation of ethane to aldehydes by using oxygen as oxidant. It was found that SBA-15-supported potassium catalysts exhibited very high yield of aldehydes, especially surprisingly high yield of acrolein in the selective oxidation of ethane. The SBA-15-supported catalyst with 2% loading of potassium showed the best performance for the partial oxidation of ethane to aldehydes. The highest yields of acrolein and total aldehydes (formaldehyde, acetaldehyde, and acrolein) were 2.5% and 5.2%, respectively, when the ethane conversion was 14.8% at the reaction temperature of 748 K.

Direct conversion of ethane to aldehydes by partial oxidation using oxygen is a big challenge in catalyst research on the effective utilization of light alkanes. The stability of ethane molecule is only inferior to that of methane molecule, and it is not easy to obtain aldehydes with yields higher than 2%[1] in the selective oxidation of ethane.

Researches on the conversion of ethane over transition metal mixed oxides were increasingly more and more since the oxidative dehydrogenation of ethane over Mo and V mixed metal oxides was reported firstly by Throsteinson[2] in 1978. In the most cases, the products of aldehydes were formaldehyde and acetaldehyde for the selective oxidation of ethane.[3,4]

At the end of the 1990s, Zhao and Kobayashi et al.[1,5] investigated the selective oxidation of ethane over the silica-supported low loading metal oxide catalysts modified by alkali metal (alkali/M/SiO_2, alkali:M:Si = 10:1:1000, molar ratio). Compared with the result of the direct selective oxidation of ethane over high loading catalysts (V:Si $\geqslant$ 1 wt %), a higher selectivity to aldehydes was obtained over the catalysts with highly dispersived and isolated active sites, and the acrolein was detected in the products. The highest yield acrolein of 1.2% was obtained over K-Fe/SiO_2 catalyst in the selective oxidation of ethane. The ethane conversion was very low over K/SiO_2 catalyst ($\approx$0.1%),[6] and the alkali metal, acted as a promoter rather than the active components, was introduced to the M/SiO_2 catalysts.

Since mesoporous molecular sieves possess well-ordered mesoporous channels and large surface areas, the active component may thus be tailored in their nano-order spaces. Very recently, SBA-15, a new type of ordered mesoporous material, has attracted much attention in the field of catalysis.[7–9] SBA-15 possesses a high surface area (600–1000 m^2/g) and is formed by a hexagonal array of uniform tubular channels with tunable pore diameters in the range of 5–30 nm. Given its thicker walls (31–64 Å), SBA-15 provides a thermal stability and hydrothermal stability that exceed those of the thinner walled MCM-41 materials. SBA-15 may be used as a promising catalyst support, particular for the reactions occurring at high temperatures.

This is the first report on the performance of K/SBA-15 catalysts, which are transition-metal-free and SBA-15-supported catalyst system, for selective oxidation of ethane to aldehydes, especially to acrolein.

In this study, the pure siliceous mesoporous SBA-15 was prepared according to a literature procedure using Pluronic P123 triblock polymer as template under acidic conditions.[10] A solution of P123:2 M of HCl:TEOS:H_2O = 2:60:4.25:15 was prepared, stirred for 20 h at 313 K, and then hydrothermally treated at 373 K for 48 h. The solid products were recovered by filtering off, then dried overnight at 373 K. SBA-15 formed after calcinations at 873 K for 5 h in air.

K/SBA-15 samples with different potassium loading (0.5–10 mol %) were prepared by impregnation of SBA-15 with aqueous solution of potassium nitrate, followed by drying at 353 K in oven for 14 h and calcining at 873 in air for 6 h.

Activity tests were carried out in a fixed bed flow reactor (quartz tube, 6 mm i.d.) under atmospheric pressure. The reactant gas mixture consisting of ethane and oxygen (C_2H_6:O_2 = 3:1, mol %) was passed through the catalyst of 0.3 g at a flow rate of 15 mL/min. Products were analyzed by gas chromatograph. Double FIDs were used to analyze mixed gas flowing from reactor: (a) 50 m PONA capillary column for separate of ethylene, ethane, acetaldehyde, and acrolein; (b) 1 m TDX-01 column to separate carbon monoxide, carbon dioxide, methane, formaldehyde, ethylene, and ethane. The later was equipped with a Ni-catalyzed methanizer.

The XRD patterns of bare SBA-15 and K/SBA-15 samples with different K loadings, the peaks (100), (110), and (200) indexed to hexagonal regularity of SBA-15[10] were sustained for the samples with the potassium loading up to 5 mol %, because of the collapse of mesoprous channels for the sample with 10% of potassium loading.

Table 1 showed the results of ethane selective oxidation over the K/SBA-15 catalysts at 723 K. No acrolein was detected over bare SBA-15. The selectivity to acrolein increased with the increasing of the K loading from 0.5 mol % to 3 mol %, and then it decreased with the further increasing of the K loading from 3 mol % to 10 mol %. The selectivity to acrolein increased remarkably when potassium loading was up to 2–3 mol % and the main products of aldehydes were acrolein and acetaldehyde, while the main products of aldehydes were formaldehyde and acetaldehyde over the low loading K/SBA-15 samples (K = 0.5–1.5 mol %). Acrolein was reported to be produced via the aldol-type condensation between formaldehyde and acetaldehyde.[6,11]

The apparent performances of the increasing of potassium loading over SBA-15 are summarized as follows: (a) To shift in carbon number of aldehydes from lower to higher in the distribution of the products; (b) To reduce of the CO_x selectivity

Table 1. Partial oxidation of ethane over the K/SBA-15 (K:Si $= x$:100, mol) catalysts at 723 K

K loading /mol %	Conv. /%C_2H_6	Selectivity/%					
		CO_x	C_2H_4	Aldehydes			
				HCHO	CH_3CHO	CH_2CHCHO	Total
Empty tube	0.01	100.0	0.0	0.0	0.0	0.0	0.0
0.00 (SBA-15)	14.3	85.5	4.7	8.4	1.40	0.0	9.8
0.50	5.3	69.0	9.0	14.5	4.60	2.9	22.0
0.75	6.7	64.3	9.7	11.0	11.1	3.9	26.00
1.00	6.9	62.3	7.6	8.5	16.4	5.2	30.1
1.25	8.4	58.5	7.0	9.0	18.9	6.7	34.5
1.50	8.5	56.8	7.0	11.2	16.6	8.4	36.2
2.00	9.2	44.5	6.2	6.8	19.4	23.2	49.3
3.00	4.4	43.0	3.4	4.6	21.5	27.5	53.6
5.00	4.9	49.0	3.3	3.6	17.2	26.9	47.7
10.00	3.5	50.5	3.7	5.5	16.1	24.2	45.8

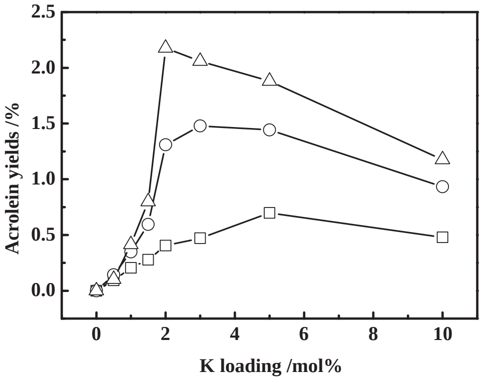

Figure 1. Effect of K loading amount on the acrolein yield over K/SBA-15 catalysts at ethane conversion of 2% (□), 6% (○), and 10% (△).

and to enhance of the aldehydes selectivity, especially the acrolein selectivity.

The influence of potassium-loading amounts on the catalytic performance of K-SBA-15 for ethane oxidation to acrolein was shown in Figure 1. There was a range of better acrolein yield at potassium loading of 2–5 mol %. The highest acrolein yield and the highest total aldehyde yield obtained were 2.5% and 5.2%, respectively, at the ethane conversion of 14.8%, over the sample with K/Si ratio of 2/100 at the reaction temperature of 748 K. The performance of K-SBA-15 for ethane oxidation to acrolein weakened with the collapse of mesoprous channels of sample with K loading of 10%, indicating the importance of the ordered organization at long range of the mesoporous structure.

In summary, the catalyst with appropriate potassium loading on the SBA-15 was a novel type of catalyst system for the selective oxidation of ethane to aldehydes, especially to acrolein.

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