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High Performance of Fe–K Oxide Catalysts for Dehydrogenation of Ethylbenzene to Styrene with an aid of ppm-order Pd

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Abstract Styrene is manufactured industrially through catalytic dehydrogenation of ethylbenzene on Fe–K oxide-based catalysts. It was invented by Süd-Chemie Group that the activity of the industrial ethylbenzene dehydrogenation catalysts (Styromax) based on the oxides of Fe and K is highly promoted by the addition of small amount (hundreds ppm-order) of precious metals such as Pd. The present work is intended to elucidate the role of Pd on the Fe–K catalyst empirically by use of a periodical pulse technique from a mechanistic point of view. The oxidative dehydrogenation was faster than the simple dehydrogenation, and it proceeded by consuming the surface lattice oxygen in the catalyst. The lattice oxygen was subsequently supplied from steam. Palladium added to the Fe–K oxide catalysts was found to enhance the rate of regeneration (supplying) of the lattice oxygen, although it hardly changed the rate of dehydrogenation of ethylbenzene or consumption of surface lattice O^{2-} anions. This study demonstrated that steam works not only as a diluent but also as a reactant to form hydrogen and lattice oxygen.

Keywords Effect of Pd · Oxidative dehydrogenation of ethylbenzene · Lattice oxygen · Fe–K catalyst

1 Introduction

Catalytic dehydrogenation of ethylbenzene is important for the manufacture of styrene monomer, which is the raw material for polystyrene, ABS resins, synthetic rubbers, etc. Fe–K mixed oxide catalysts have been applied for dehydrogenation of ethylbenzene. The Fe–K based mixed oxide catalyst can be further modified by addition of other promoters such oxides as MgO, CeO_2 and MoO_3 [1, 2].

Several authors have investigated the reaction mechanism of dehydrogenation of ethylbenzene on the Fe–K mixed oxide catalyst. Miura et al. [3] investigated dehydrogenation of alkylbenzenes over an Fe_2O_3–K_2CO_3–Cr_2O_3 catalyst by means of isotope exchange experiments. According to them, dissociation of α-hydrogen is the first step followed by dissociation of β-hydrogen, which is the rate-determining step or post rate-determining step. They concluded that the α-hydrogen is dissociated as a proton on a basic site because the exchange rate decreases in the sequence of toluene > ethylbenzene > cumene. Addiego et al. [4] examined catalyst surfaces after reaction using infrared spectroscopy. They have confirmed that styrene produced from ethylbenzene is bonded to the catalyst surface through the vinyl group.

Miura et al. [5] investigated the chemical properties of active sites for dehydrogenation of ethylbenzene using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). They have showed that the active surface of the catalyst is covered with $KFeO_2$ which is the stable phase during dehydrogenation of ethylbenzene, in agreement with Addiego [4], Mühler [6], and Hirano [7]. Hirano [2] reported the relation between the activation energy for styrene formation and the basicity of the catalyst. The rate of styrene formation increased and the activation energy decreased concomitant with a decrease in electronegativity of the added transition metal oxide. Cerium oxide was found to be the best promoter for accelerating styrene formation. Jebarathinam et al. [8] demonstrated that the desorption of styrene was the rate-determining in the case

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of a catalyst of weak basicity; the formation of styrene was the rate-determining for a catalyst of weak acidity. Zhu et al. [9] investigated transient kinetic experiments for Fe–K catalyst by on-line mass spectroscopy, and they revealed that the initial high activity for the dehydrogenation of ethylbenzene was originated from the fully oxidized iron (Fe^{3+}), and subsequently the yield of styrene decreased due to the reduction of iron.

Recently, it was reported that addition of small amounts of Pd or Pt enhances the activity of Fe–K based catalysts [10]. This work is intended to clarify the role of added Pd in relation to the reaction mechanism of dehydrogenation of ethylbenzene on Fe–K mixed oxide.

2 Experimental

2.1 Catalysts

Catalysts used in this study were commercially available Fe–K catalyst (constituents: Fe_2O_3, K_2O) and Pd/Fe–K catalyst. The particle size was in the range of 0.50–0.70 mm. They were pretreated for 3 h prior to reaction under the following conditions: temperature, 873 K; H_2O/H_2, 12 mol mol^{-1}. The structure of catalysts was observed by an XRD measurement (RINT2000; Rigaku Corp.). After pretreatment of the catalyst and under working state of reaction, the predominant structure of catalysts was Fe_3O_4, which was not reduced further. Addition of Pd hardly changed the oxidation state of Fe in the catalyst.

2.2 Apparatus

The reactor used in this study comprised a quartz tube (12-mm i.d.) containing the catalyst bed, which was fixed by quartz wool. A type K thermocouple enclosed in a quartz thermowell of 3-mm outer diameter was positioned inside the catalyst bed for accurate measurement of the catalyst temperature.

2.3 Activity Tests

Catalytic activities, selectivities, and stabilities were first examined in a conventional fixed bed flow reactor. The charged catalyst weight was 1.0 g. Reactions were carried at 873 K at atmospheric pressure in the presence of steam; the molar ratio of steam to ethylbenzene was 12 and WHSV was 1.2 g h^{-1} g-cat^{-1}. Ethylbenzene and H_2O were fed separately using a micro feeder and a micro pump, respectively. Liquid products such as ethylbenzene, benzene, toluene, and styrene were analyzed using off-line flame ionization detection (FID) gas chromatography (GC8A; Shimadzu Corp.) with a capillary column of DB210 (0.25 mm × 30 m) using N_2 as a carrier gas at 373 K. Tetralin was used as an internal standard substance. Gaseous products such as H_2, CO, and CH_4 were analyzed using off-line thermal conductivity (TCD) gas chromatography (GC8A; Shimadzu Corp.) with a 3 mm × 2 m stainless steel column packed with an active carbon (60/80 mesh) using Ar as a carrier gas at 393 K.

2.4 Periodical Pulse Experiments

In periodical pulse experiments, the reactants of ethylbenzene and H_2O were supplied alternately to the catalyst bed. The period of each pulse was 600 s. The charged catalyst weight was 1.0 g. Ethylbenzene and H_2O were supplied using a bubbler with He as a carrier gas. The molar ratio of ethylbenzene to He was 1/20; the total flow rate was 7.8×10^{-2} mol h^{-1}. The molar ratio of H_2O to He was 1/8, and the total flow rate was 8.4×10^{-2} mol h^{-1}. Reaction temperature was 783 K. The product composition at the reactor outlet was monitored continuously using an on-line quadrupole mass spectrometer (HPR20; Hiden Analytical Ltd.). Calibration of mass spectrometer signals was based on prepared mixtures of known composition. For all periodical experiments, the gas-phase composition was calculated from the mass signal at the following m/e 2 (H_2), 4 (He), 18 (H_2O), 78 (styrene), and 91 (ethylbenzene).

3 Results and Discussion

Activities of Fe–K and Pd/Fe–K catalysts were tested in the fixed-bed flow reactor. Figure 1 shows the conversion of ethylbenzene for these catalysts. Conversion of ethylbenzene (EB) was increased from 23% to 32% by the addition of small amount of Pd. These catalytic activities were stable for 3 to 5 h at least. Selectivity to styrene (Sty) was 96% on all the catalysts. Benzene and toluene formed as by-products with selectivities of 1.7% and 2.2%, respectively.

Figure 2 shows the effect of Pd concentration for the initial catalytic activities on styrene dehydrogenation. From these data, the effect of the addition of Pd seems to be saturated at a few hundred ppm of Pd on the surface of catalyst. To elucidate the role of such small amount of Pd on the Fe–K mixed oxide catalyst for the ethylbenzene dehydrogenation, we carried out periodical pulse experiments. These experiments were performed with alternative supplies of ethylbenzene and H_2O as described in the Sect. 2.4. We supplied H_2O to oxidize the catalyst reduced under dehydrogenation reaction conditions. We investigated the catalytic performance in the early period of dehydrogenation reaction and oxidation of reduced catalyst by H_2O.

Such products as ethylbenzene, styrene, H_2 and H_2O were detected by Q-Mass on the periodical pulse experiments. Surface lattice O^{2-} anions were consumed by the

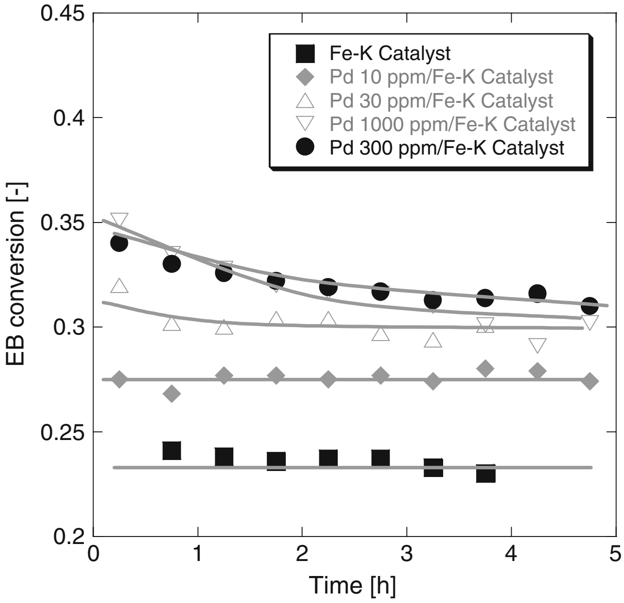

Fig. 1 Activities of Fe–K oxide catalysts with and without Pd. Catalyst pretreatment; H_2O/H_2: 12 mol mol^{-1}, 873 K, 3 h. Reaction conditions; temperature: 813 K, catalyst weight: 1.0 g, WHSV: 1.2 g h^{-1} g-cat^{-1}, steam/ethylbenzene: 12 mol mol^{-1}

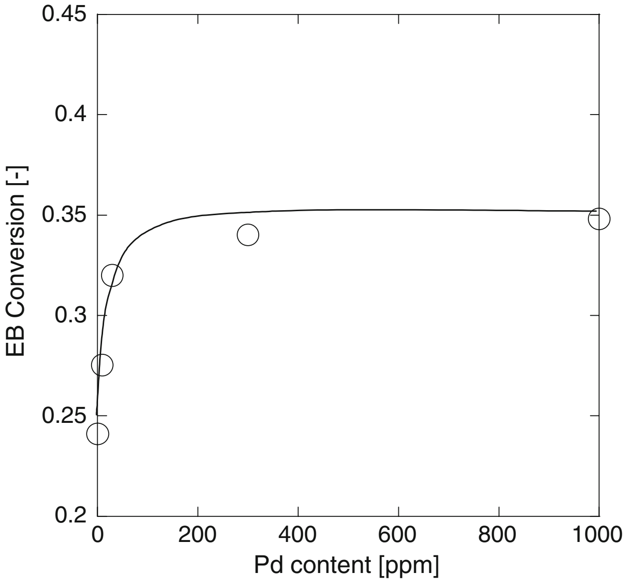

Fig. 2 Relation between the initial catalytic activity and Pd concentration. Catalyst pretreatment; H_2O/H_2: 12 mol mol^{-1}, 873 K, 3 h. Reaction conditions; temperature: 813 K, catalyst weight: 1.0 g, WHSV: 1.2 g h^{-1} g-cat^{-1}, steam/ethylbenzene: 12 mol mol^{-1}

ethylbenzene or produced H_2, thereby forming H_2O. Figure 3 shows the fraction of H_2O in produced hydrogen species ($[H_2O]/([H_2] + [H_2O])$) and the conversion of ethylbenzene when the pulse test was conducted on the Fe–K catalyst. Figure 4 shows the results for the modified Fe–K catalyst with small amount of Pd. Conversion of

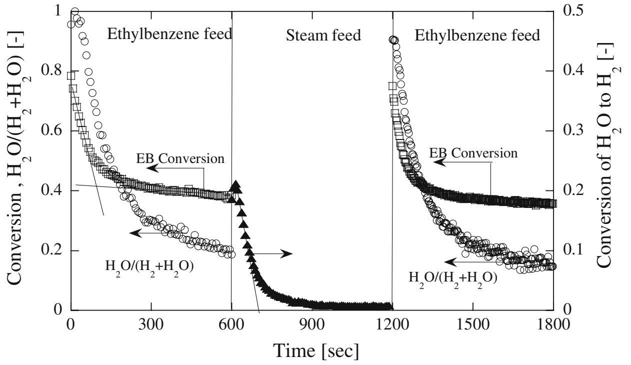

Fig. 3 Results for the periodical pulse reaction test with the Fe–K catalyst

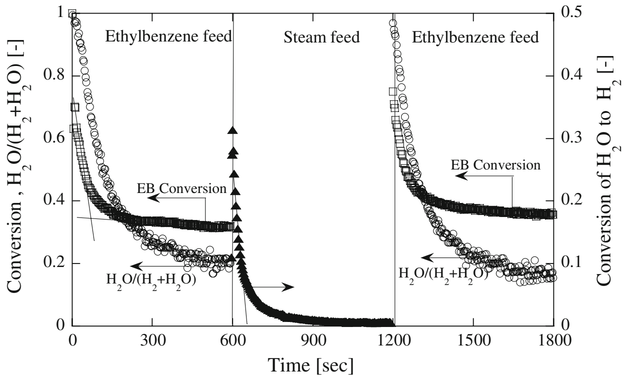

Fig. 4 Results for the periodical pulse reaction test with the Pd/Fe–K catalyst

ethylbenzene are defined as $[EB]/([EB] + [Sty])$, where EB is an abbreviation of ethylbenzene, and Sty means styrene, [EB], [Sty], $[H_2]$, and $[H_2O]$ are the amounts of these products at the reactor outlet.

The fraction of H_2O and the conversion of ethylbenzene showed a high value in the early period. This steep and straight decrease of ethylbenzene conversion from 0 s to 100 s could be attributed to the domination of oxidative dehydrogenation of ethylbenzene because the ratio of $H_2O/(H_2 + H_2O)$ was close to 1 at the early stage of the reaction. Oxidative dehydrogenation, by which styrene and H_2O were formed, competed with and progressed more rapidly than, the simple dehydrogenation which formed styrene and H_2. Afterward, the conversion of ethylbenzene and fraction of H_2O decreased and reached a steady state. Figure 5 shows the O^{2-} balance in the catalysts during these experiments. The amount of lattice O^{2-} anions that showed high reactivity is inferred to be 1.7×10^{-5} mol g^{-1}, which is about 25% of surface lattice O^{2-} anions from the BET surface area (ca. 2 m^2 g^{-1}). The amount of lattice O^{2-} anions decreased in a straight trend in 100–600 s, implying that the concentration of surface lattice O^{2-} anions reached a steady state and dominated by the bulk diffusion.

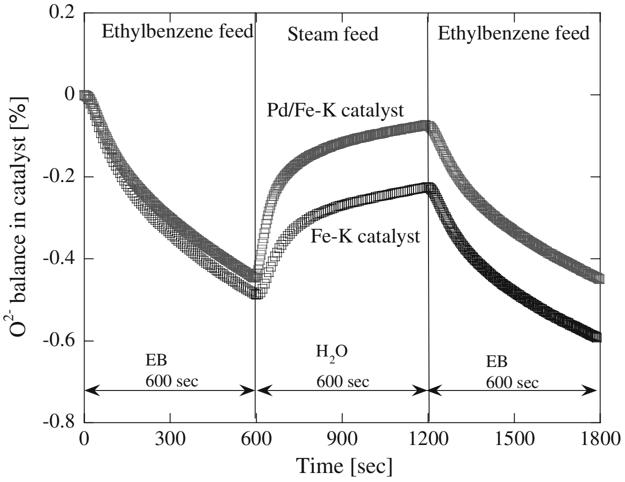

Fig. 5 Oxygen balance in the catalysts on the periodical pulse test

On the other hand, we found that the lattice O^{2-} anions that were consumed by ethylbenzene were regenerated by H_2O because H_2 was formed by the reaction with H_2O. The initial conversion of H_2O to H_2 was 20% at 600 s in Fig. 3, subsequently, it decreased. The rate of regeneration of lattice O^{2-} anions decreased from 1.7×10^{-7} mol s^{-1} g^{-1} to 4.1×10^{-8} mol s^{-1} g^{-1} at 700 s; then it reached the steady state. The amount of lattice O^{2-} anions that was regenerated before 700 s was 1.7×10^{-5} mol g^{-1}. The amount of lattice O^{2-} anions regenerated while H_2O reacted was 3.3×10^{-5} mol g^{-1}, which was 54% of the lattice O^{2-} anions consumed by ethylbenzene. The reactivity to ethylbenzene was mostly recovered by the oxidation with H_2O.

Based on results of periodical pulse experiments, we considered that the following three reactions progressed under reaction conditions with steam.

a oxidative dehydrogenation of ethylbenzene

$$C_8H_{10} + O^{2-}_{\text{lattice}} \rightarrow C_8H_8 + H_2O + 2e^-$$

b (simple) dehydrogenation ethylbenzene

$$C_8H_{10} \rightarrow C_8H_8 + H_2$$

c regeneration of lattice oxygen on the catalyst

$$H_2O + 2e^- \rightarrow H_2 + O^{2-}_{\text{lattice}}$$

Oxidative dehydrogenation is competitive with and faster than simple dehydrogenation; H_2O regenerates the surface lattice O^{2-} anions, showing high reactivity with ethylbenzene. The surface lattice O^{2-} anions are consumed by oxidative dehydrogenation of ethylbenzene and regenerated by H_2O and bulk diffusion of the lattice O^{2-}. Previous reports have determined that the role of H_2O is avoiding catalyst over-reduction [11]. However, in this work we consider that H_2O has a role of regenerating the surface lattice O^{2-} anions forming the highly active sites.

Comparing between Fe–K catalyst (Fig. 3) and Pd/Fe–K catalyst (Fig. 4), there was no appreciable difference on the conversion of ethylbenzene and the fraction of H_2O. The rate of consumption of the lattice O^{2-} anions on each catalyst showed the same value, which was 1.7×10^{-7} mol g^{-1} s^{-1}. The amount of the lattice O^{2-} anions showing high reactivity was 1.7×10^{-5} mol g^{-1}, which was 25% of the amount of surface lattice O^{2-} anions. Consequently, we conclude that added Pd changed neither the rate of dehydrogenation of ethylbenzene nor the amount of the lattice O^{2-} anions giving high reactivity.

On the other hand, when H_2O reacted, H_2 was formed. The initial conversion of H_2O to H_2 was increased from 20% to 30% by adding Pd to Fe–K catalyst at 600 s in Figs. 3 and 4. We found that surface lattice O^{2-} anions were regenerated promptly within 70 s. The initial rate of regeneration of the lattice O^{2-} anions was increased by adding Pd to reach 4.0×10^{-8} mol s^{-1} g^{-1}. At 670 s of run, regeneration of the lattice O^{2-} anions reached a steady state. The rate of regeneration of the lattice O^{2-} anions on Pd/Fe–K catalyst after 670 s, which was 4.1×10^{-8} mol s^{-1} g^{-1}, was similar to that on Fe–K catalyst, which was 4.1×10^{-8} mol s^{-1} g^{-1}. H_2O regenerated 83% of the lattice O^{2-} anions consumed by ethylbenzene after steam feed of 600 sec, the amount of which was 5.6×10^{-5} mol g^{-1}.

These results indicate that added Pd promoted the regeneration of lattice O^{2-} anions by H_2O although it does not affect the rate of dehydrogenation of ethylbenzene or the amount of the lattice O^{2-} anions giving a high reactivity. The amount of added Pd was 2.8×10^{-7} mol g^{-1}, which was 1.6% of the surface lattice O^{2-} anions giving a high reactivity. We have demonstrated that adding Pd

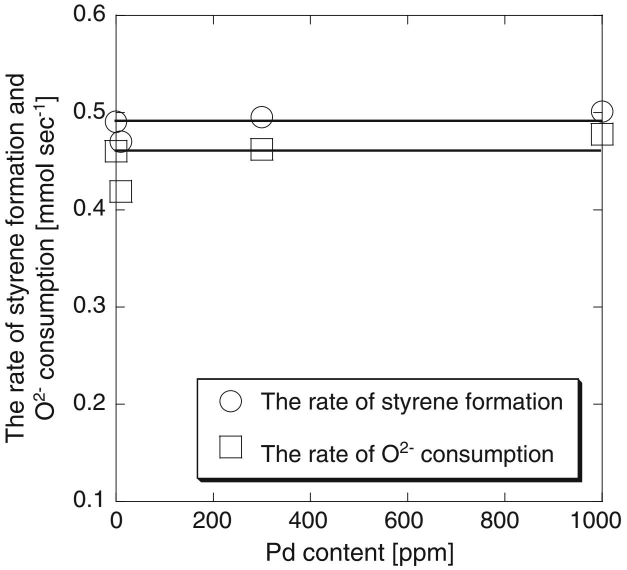

Fig. 6 The effect of Pd concentration on the rate of styrene formation and O^{2-} consumption

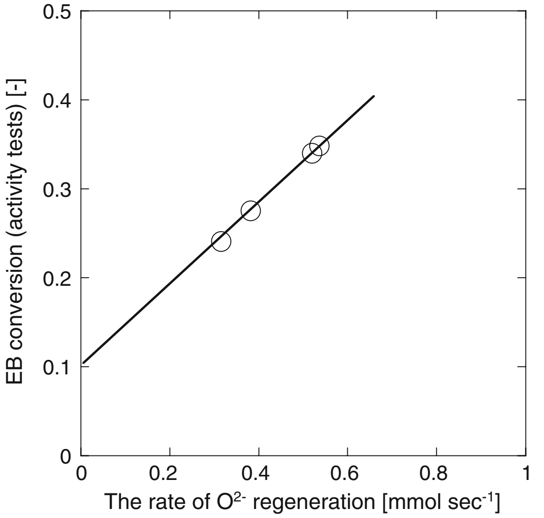

Fig. 7 The relation between the rate of lattice oxygen regeneration and steady-state conversion of ethylbenzene

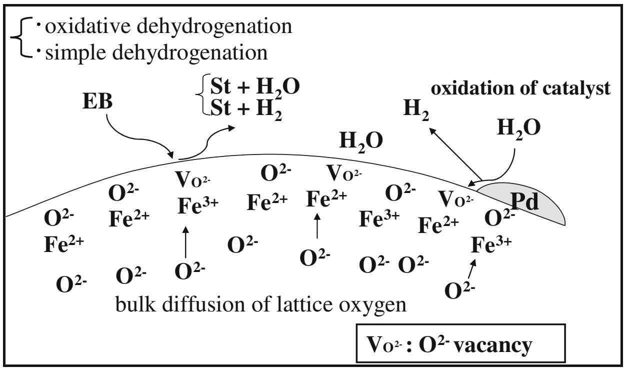

Fig. 8 Schematic image of oxidative dehydrogenation of ethylbenzene on the Pd/Fe–K catalyst

fewer than the surface lattice O^{2-} anions enhances the catalytic activity.

This conclusion was confirmed by the further experiments by changing the amount of Pd on the Fe–K catalyst. Figure 6 shows the relationship between Pd content on the Fe–K catalyst and the rate of styrene formation/O^{2-} consumption. As shown here, there is no particular effect of Pd addition on the Fe–K catalyst for the rate of styrene formation and O^{2-} consumption in/on the catalyst. Figure 7 shows the relation between the rate of lattice oxygen regeneration calculated by the periodic pulse experiments and the steady-state conversion of ethylbenzene observed in the continuous reactor. A linear relation between them confirms that the added Pd increases the rate of lattice oxygen regeneration in/on the Fe–K catalyst. Proposed reaction mechanism of this Pd/Fe–K catalyst for oxidative dehydrogenation of ethylbenzene is shown in Fig. 8.

4 Conclusion

We studied the effect of Pd on the activity of Fe–K mixed oxide catalyst for dehydrogenation of ethylbenzene. Results of periodical pulse experiments show that the oxidative dehydrogenation is competitive with and faster than simple dehydrogenation on the Fe–K mixed oxide. The amount of surface lattice O^{2-} showing a high reactivity with ethylbenzene is 0.14% of the total O^{2-} in the catalyst. We conclude that added Pd hardly changes the rate of dehydrogenation of ethylbenzene or the amount of surface lattice O^{2-} anions showing high activity. The surface lattice O^{2-}, which is regenerated by H_2O and Pd promotes the regeneration of surface O^{2-} by H_2O.

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