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SELECTIVE FORMATION OF STYRENE AND HYDROGEN FROM ETHYLBENZENE OVER MoO_3/MgO CATALYSTS

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The catalytic conversion of ethylbenzene into styrene and hydrogen has been studied over various supported molybdenum catalysts. MoO_3/MgO catalysts exhibited remarkably high activity, selectivity, and resistivity against sulfur species even in the absence of additives. The relationships between the surface structure and the catalytic activity of the MoO_3/MgO catalysts were also studied by XPS.

The selective conversion of paraffins into olefins belongs to the challenging problems in the chemical industries. In addition, the reaction for hydrogen production has great importance in the use of coal as a clean energy source.

Processes for converting ethylbenzene to styrene are of increasing importance because styrene is an essential raw material for the preparation of many products. In the catalytic dehydrogenation of ethylbenzene, it is desirable to obtain as high yields of styrene and hydrogen.

There are many studies on the oxidative dehydrogenation of ethylbenzene over solid catalysts in the presence of oxygen or steam.[1-9)] Recently, Haag et al.[10)] pointed out that carbonyl sulfide was a highly selective reagent for the oxidative dehydrogenation of simple paraffins and alkylbenzenes and high yields of simple olefins and styrene were obtained with MgO and SiO_2 catalysts.

While studying the function of catalyst in connection with the catalytic dehydrogenation of ethylbenzene, it has been found that molybdenum oxide catalysts supported on MgO show higher activity and selectivity even in the absence of additives, such as steam, at lower temperatures than those employed in the literatures.[1-9)]

The following procedures were used in this study. Supported molybdenum oxide catalysts were prepared as follows. MgO used as a support was prepared by calcining $Mg(OH)_2$ at 600°C for 5 h. Other supports used were Al_2O_3(JRC-ALO-2), SiO_2(Nakarai Chem. Ltd.), TiO_2(JRC-TID-1), ZrO_2(Nakarai Chem. Ltd.), and active charcoal(Analytical Grade, Art. 2186). Catalysts were prepared by impregnating these supports with solutions containing required amounts of ammonium paramolybdate. The water was evaporated to dryness at 90°C under stirring, followed by drying at 110°C for 18 h and calcining at 550°C for 5 h in air.

The dehydrogenation reactions of ethylbenzene were carried out in the presence or absence of CS_2 over the supported molybdenum oxide catalysts(usually 0.07 g) at

500°C under atmospheric pressure using a conventional fixed-bed flow reactor. The products were mainly styrene and hydrogen with small amounts of benzene, toluene, and light hydrocarbons.

XPS spectra were measured at room temperature on a Hitachi 507 photoelectron spectrometer using $AlK\alpha_{1,2}$ radiation. All binding energies were referred to the contaminant carbon[C(1s)=285.0/eV]. The accuracy in the determination of the binding energy values was estimated to be ±0.2/eV. The surface state of the prereduced catalyst was compared with that of the nontreatment(oxidic) catalyst. Some part of the reaction for the XPS measurements were undertaken after one of the two kinds of pretreatment at 500°C for 1 h: (a) nontreatment(oxidic) in which the catalyst was contacted with a reaction mixture, ethylbenzene/N_2(ethylbenzene: 2.34 $\times 10^{-3}$ mol/min. g cat.), (b) prereduction with H_2(126 ml/min).

Table 1. Dehydrogenation of ethylbenzene over the MoO_3 supported*a catalysts

support	MgO	Al_2O_3	TiO_2	SiO_2	ZrO_2	Charcoal
conversion/%	8.1(1/h)*b 5.7(6/h)	16.5(1/h) 8.7(6/h)	6.4(1/h) 3.7(2/h)	2.5(1/h) -	2.4(1/h) -	17.1(1/h) 4.6(4/h)
selectivity/%*c	89.8(1/h) 90.1(6/h)	94.1(1/h) 93.5(6/h)	94.4(1/h) 92.2(2/h)	89.1(1/h) -	85.6(1/h) -	93.5(1/h) 92.5(4/h)

Reaction was carried out at 500°C under atmospheric pressure($P_{E.B.}$; 8.265×10^{-3} Pa, P_{N_2}; balance).

*a 13.0 wt%, nontreatment catalyst.

*b Time shown in the parenthesis represents the reaction time.

*c Selectivity is represented by styrene/reacted ethylbenzene.

The results of the catalytic activity and selectivity for the dehydrogenation of ethylbenzene over the supported molybdenum oxide catalysts are summarized in Table 1. The MoO_3 supported over MgO, Al_2O_3, and TiO_2 showed high activity and selectivity. Figure 1 illustrates the time-dependences of ethylbenzene conversion over the catalysts. The activity decreased gradually with increasing reaction time with all the catalyst systems examined here. In the cases of the MoO_3/MgO and MoO_3/Al_2O_3 catalysts, the activity reached steady states after deactivation, whereas in the case of MoO_3/C catalyst, its activity decreased more rapidly than those of the others. Since all the supports showed very low catalytic activity for the reaction, it is evident that the molybdenum oxides

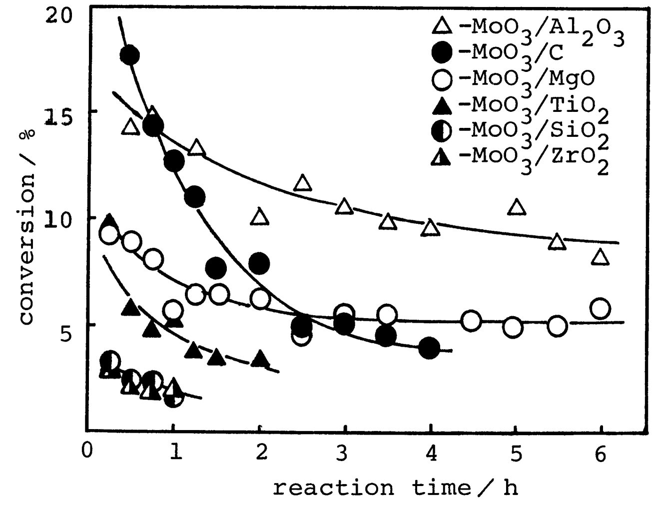

Fig.1. Time dependence of the conversion of ethylbenzene at 500°C upon the supported MoO_3(13 wt%) catalysts.

are active species. Although the MoO_3/Al_2O_3 catalysts showed the high activity and selectivity for the dehydrogenation of ethylbenzene, high boiling-point compounds, which were not analyzed further in this study, were concurrently produced in considerable amounts. They would be polymerization products of styrene catalyzed by acidic sites of the catalysts. However, no such products were detected for the MoO_3/MgO catalysts. This fact shows that MgO is an excellent support for the reaction.

The time-dependency of the catalytic activity for the reaction was examined by using the MoO_3/MgO catalysts containing different loading amounts of MoO_3(∿50 wt%). The higher the MoO_3 content, the faster was the activity decay observed. The conversion in the steady state(4 h) increased linearly with the MoO_3 loadings up to ca. 20 wt% and above that, no further increase was attained.

It is generally accepted that isolated molybdate in tetrahedral surroundings having strong interactions with Al_2O_3 is predominantly formed in a low-concentration range of supported MoO_3, while the amount of polymeric molybdate in octahedral surroundings having weak interactions with Al_2O_3 increases with increasing the loading amount of MoO_3 at the expense of tetrahedral molybdate.11-13) This suggests that tetrahedral molybdate and octahedral species can be expected for the MoO_3/MgO catalyst, too. This is further supported by the XPS spectra of the MoO_3/MgO catalysts with different loading amounts of MoO_3.

Shown in Fig. 2 are the XPS spectra of the Mo(3d) level for the catalysts before and after the reaction or prereduction in a hydrogen flow. A shift in the Mo(3d) binding energy was apparently observed with the MoO_3/MgO(50 wt%) catalyst. Taking into account the binding energies of Mo(3d) level, Mo(VI)(Mo3d$_{5/2}$, 232.9 eV), Mo(V) (231.8), Mo(IV)(229.0), obtained by Patterson et al. and by us14,15) for MoO_3/Al_2O_3 catalysts and for SnO_2-MoO_3 catalysts,16) it is evident that Mo(VI) in the MoO_3/MgO (50 wt%) catalyst was reduced to Mo(IV) to much higher extents compared to that in the MoO_3/MgO(13 wt%) catalyst, when treated with hydrogen or used for the reaction. The results imply that easily reduced molybdenum species which would be polymeric octahedral molybdate is not an active species. Although it is difficult to decide the active species on the basis of the XPS data, isolated molybdenum species in tetrahedral surroundings would be the active species. Shown in Fig. 3 is the addition effect of CS_2 into the reactant on the performance of the catalyst. The catalytic reaction system containing CS_2 showed higher activity in the early stage of the reaction. However, the activities decreased drastically with increasing the reaction time and

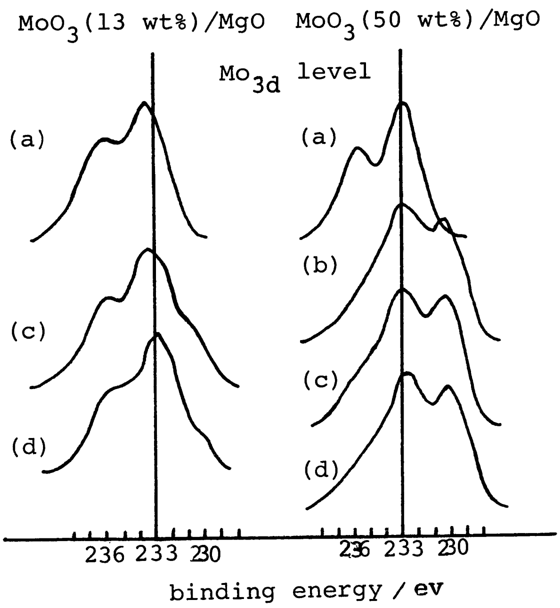

Fig.2. XPS spectra of Mo3d level for the MoO_3/MgO catalysts: (a) nontreatment; (b) used for reaction for 2 h; (c) used for reaction for 4 h; (d) prereduced in H_2 flow(126 ml/sec) at 500°C for 1 h.

approached the activity of the nontreatment(oxidic) catalyst. The deactivation of the catalyst would be due to a carbon deposited during the reaction. This means that the MoO_3/MgO catalyst is effective for the dehydrogenation reaction of ethylbenzene containing a small amount of sulfur species as impurities.

Further studies on the dehydrogenation of various paraffins over the present MoO_3/MgO catalysts are now in progress.

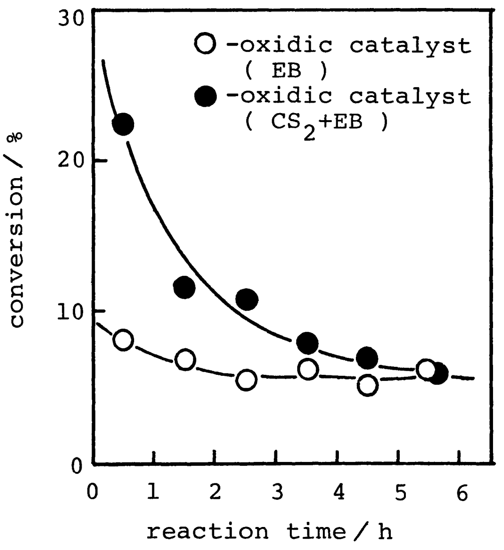

Fig.3. Addition effect of CS_2 into the reactant on the dehydrogenation of ethylbenzene at 500°C over the MoO_3 (13wt%)/MgO catalyst.

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