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Catalytic Dehydrogenation of Iminodibenzyl to Iminostilbene on Mn_2O_3-SnO_2

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Catalytic dehydrogenation of iminodibenzyl to iminostilbene was carried out at 550°C on a binary oxide system of Mn_2O_3–SnO_2. Maximum activity was observed at an Mn_2O_3–SnO_2 ratio of 8:2; conversion was 40%, selectivity 82%. Mn_2O_3–SnO_2 catalyst dispersed on MgO and modified with K_2CO_3 gave 80—90% conversion and 82—88% selectivity. The relation between activity and the physical properties of catalysts was studied.

Keywords——vapor-phase reaction; carbamazepine; iminodibenzyl; iminostilbene; dehydrogenation; manganese oxide-stannic oxide catalyst

Carbamazepine, an anticonvulsant drug listed in the Japanese Pharmacopoeia X, has been synthesized *via* a liquid phase reaction from iminodibenzyl(10,11-dihydro-5*H*-dibenz-[*b*,*f*]-azepine) (1) to iminostilbene (5*H*-dibenz-[*b*,*f*]-azepine) (2) in three steps. Iminostilbene has also been obtained directly from iminodibenzyl on Pd,[1] Ni[2] and Fe_2O_3[3] by adopting a vapor-phase reaction procedure. However, these catalysts have some shortcomings with respect to conversion, selectivity and durability in prolonged operation. We examined the activity of various oxide catalysts, using a flow reactor under atmospheric pressure, and found that a binary catalyst composed of Mn_2O_3 and SnO_2 shows good activity at 550°C. We now report the activity and physical properties of a series of binary catalysts.

Experimental

Procedures for Catalytic Dehydrogenation——Heat-melted iminodibenzyl was introduced at a constant rate of 2.5 g/h *via* a dropping funnel into a quartz flow reactor (18 mm i.d. and 250 mm in length) equipped with a preheater of the same size. A mixture of nitrogen and steam was used as the carrier; it was introduced at 550°C into the preheater at 25 ml/min for N_2 and 0.75 ml/min for H_2O. As the reaction proceeded, orange crystals became attached to the inside wall of the trap. After 1 h, the products were washed out with ethyl acetate; upon removal of the ethyl acetate by evaporation, 2.2—2.3 g of solid product was obtained.

Product Analysis——The products were analyzed gas-chromatographically (Hitachi Ltd., type 063) using OV-17 (1.5 m) and PEG 20M (0.5 m) as column packing materials and He (30 ml/min) as the carrier. The retention times were 4.9 min for acridine, 8.1 min for iminodibenzyl, 9.2 min for 9-methylacridine, and 10.6 min for iminostilbene.

Preparation of Catalysts——Oxide catalysts were prepared from metal nitrates. Aqueous nitrates were adsorbed on the carrier in a water bath and the products were calcined at 600°C for 5 h in an electric furnace. Stannic oxide was prepared from stannous oxalate by calcination in air. All catalysts were crushed and passed through a 4—7 mesh sieve before use. Palladium-on-charcoal catalyst was prepared from palladium chloride adsorbed on cylinders of charcoal (2 mm i.d., 5 mm in length).

Surface Areas of Catalysts——The specific surface areas of a series of Mn_2O_3–SnO_2 catalysts were measured according to the BET method. A catalyst (0.2—0.5 g) was placed in a sample tube attached to a vacuum system and heated at 200°C for 1 h under reduced pressure (10^{-3} mmHg). Then N_2 (purity 99.99%) was adsorbed on the catalysts at liquid nitrogen temperature and the adsorption isotherm was measured.

X-Ray Analysis of the Powdered Catalysts——The X-ray patterns of powdered catalysts were obtained by the use of Ni-filtered $K\alpha$ radiation, with a Geigerflex D-3C diffractometer (Rigaku Denki Ltd.). The ASTM file was used to identify the crystal structures of the catalysts.

Results and Discussion

Dehydrogenation of Iminodibenzyl on Various Oxide Catalysts

The dehydrogenation of iminodibenzyl to iminostilbene was carried out with various oxide catalysts mounted on kieselguhr. In the initial period, their activities were examined for 1 h at 550°C with respect to conversion and selectivity. Iminostibene, 9-methylacridine(3) and acridine (4) were obtained as reaction products (Table I).

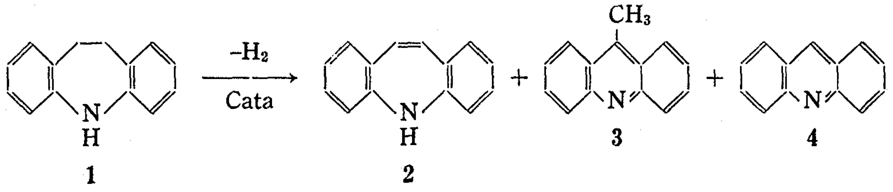

Table I. Dehydrogenation of Iminodibenzyl on Various Catalysts

Catalyst	$Q^{a)}$ (kcal/mol)	Time (h)	Conversion (%)	2 (%)	3 (%)	4 (%)
0.5% PdO–C	20.2	1	100	0	0	0
30% NiO–KG	57.3	1	100	0	0	0
30% CoO–KG	56.9	1	36.6	30.9	2.7	3.0
50% Fe_2O_3–KG	65.6	1	66.8	40.8	5.9	20.0
		2	37.2	27.6	3.4	6.2
50% Mn_2O_3–KG	76.4	1	40.3	33.3	4.3	2.7
50% SnO_2–KG	69.4	1	13.2	13.2	0	0
50% ZnO–KG	83.3	1	14.7	14.7	0	0
50% Cr_2O_3–KG	90.9	1	9.6	9.6	0	0
50% CeO_2–KG	130.1	1	7.6	7.6	0	0
50% MgO–KG	143.7	1	7.3	7.3	0	0

Reaction temperature, 550°C; feed rate, 2.5 g/h.

a) The value of Q is taken as $-\Delta H$ of the metal oxide divided by the number of oxygen atoms; "Kagaku-Bin-Ran," Maruzen Co., Ltd., Tokyo, 1975, p. 954.

The activities estimated under identical reaction conditions varied widely with the kind of metal oxide used, and the oxides could be divided into four groups. On PdO and NiO, the reaction was so violent that only gaseous decomposition products were obtained. Therefore, Pd on charcoal catalyst and Ni on kieselguhr catalyst were used under reduced pressure (0.2—0.5 mmHg) and at a lower reaction temperature.[1,2] The second group involved CoO, Fe_2O_3 and Mn_2O_3. These oxides showed strong catalytic activity; however, the activity of Fe_2O_3 decreased considerably after 1 h. In practical applications, these catalysts were calcined again in air and re-used.[3] Oxides of the third group, ZnO and SnO_2, gave lower conversions. On the other hand, the selectivity for iminostilbene was excellent. Oxides of the last group, CeO_2, Cr_2O_3 and MgO, were almost inactive. These tendencies are roughly in accord with the order of the enthalpy values distributed to each oxygen atom, denoted as Q in Table I, and this is in accord with a linear relationship observed previously between the activation energies and the Q values in the exchange reaction of oxygen on various oxides.[4] Therefore, oxides of moderate Q value (about 60—80 kcal/mol) are suitable for the dehydrogenation of iminodibenzyl. From the standpoint of activity, selectivity and durability, Mn_2O_3 was chosen as a suitable oxide for the reaction.

Dehydrogenation of Iminodibenzyl on Mn_2O_3-SnO_2

The dehydrogenation of iminodibenzyl on Mn_2O_3–kieselguhr was examined at various temperatures (Fig. 1). Conversion increased with increase in the reaction temperature from 500°C to 600°C. Above 575°C, the amounts of by-products such as 9-methylacridine and

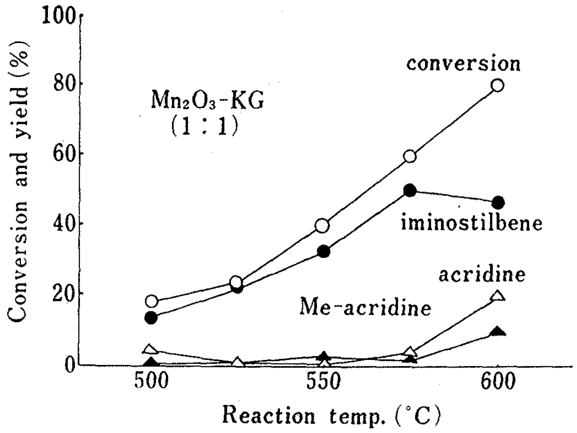

Fig. 1. Effect of Reaction Temperature on the Dehydrogenation of Iminodibenzyl on Mn_2O_3–Kieselguhr

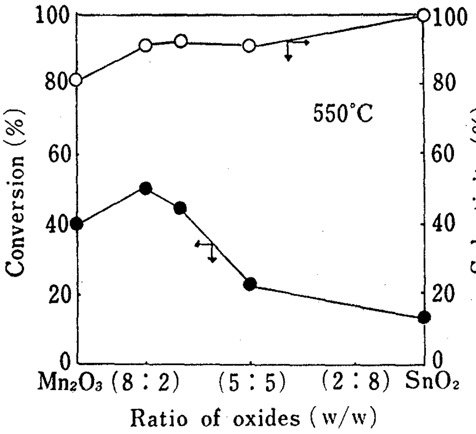

Fig. 2. Effect of SnO_2 on Conversion and Selectivity in the Dehydrogenation of Iminodibenzyl on Mn_2O_3–Kieselguhr

acridine increased considerably and the selectivity for iminostilbene decreased. Therefore, we used the catalyst at 550°C. To suppress isomerization, 20—30% SnO_2 was admixed with Mn_2O_3 as the second component, as we expected this to improve the selectivity. As shown in Fig. 2, maximum conversion and good selectivity were obtained at Mn_2O_3–SnO_2 ratios of 8: 2 to 7: 3.

To investigate these phenomena, physical properties of a series of Mn_2O_3–SnO_2 catalysts were studied. As shown in Table II, the specific surface areas of the binary catalysts were six to ten times larger than that of Mn_2O_3 or SnO_2 alone. The X-ray patterns of these catalysts are shown in Fig. 3. The peak at 2θ: 32.9° ($d=2.72$ Å) is attributable to Mn_2O_3; that of SnO_2 was observed at 34.0° ($d=2.63$ Å). On admixture of SnO_2 and Mn_2O_3, the peak intensities due to Mn_2O_3 decreased and the peak width increased. This tendency, which was more marked in the SnO_2 than the Mn_2O_3 peaks, suggests that a disturbance occurred in the crystallization of the oxides. Based on these results, we expected that the more finely Mn_2O_3 is dispersed, the more its activity would be enhanced.

TABLE II. Specific Surface Areas of Mn_2O_3–SnO_2 Binary Catalysts

Mn_2O_3–SnO_2–KG (Wt ratio)	Surface area (m^2/g)
10 : 0 : 10	3.6
8 : 2 : 10	23.6
7 : 3 : 10	35.4
5 : 5 : 10	36.9
0 : 10 : 10	9.9

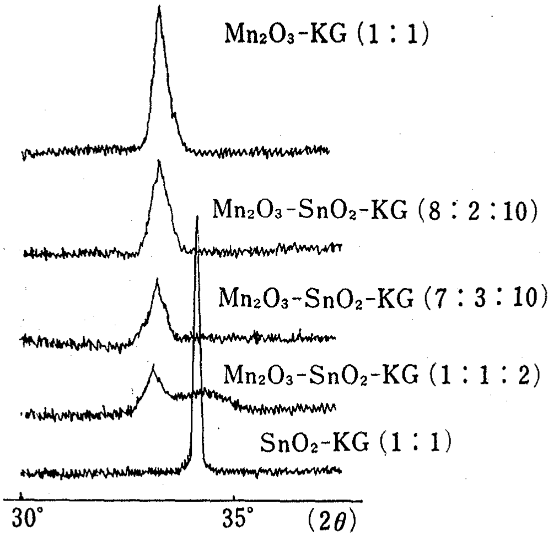

Fig. 3. X-ray Powder Patterns of Mn_2O_3–SnO_2 Binary Catalysts

Table III. Effect of Carriers of Mn_2O_3–SnO_2 on the Surface Area and Activity

Catalyst	Surface area (m^2/g)	Conversion (%)	Selectivity (%)
Mn_2O_3–SnO_2–KG	30.2	44.5	94.0
Mn_2O_3–SnO_2–MgO	68.0	71.5	86.4
Mn_2O_3–SnO_2–CaO	10.9	34.6	91.0
Mn_2O_3–SnO_2–SrO	19.5	27.6	94.5

Mn_2O_3: SnO_2: Carrier = 7: 3: 10; reaction temperature, 550°C.

Table IV. Effect of Reaction Time on the Dehydrogenation of Iminodibenzyl on Mn_2O_3–SnO_2 Catalysts

Catalyst	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)
Mn_2O_3–SnO_2–KG	600	1	86.2	54.5
(7: 3: 10)		4	76.3	67.0
		8	77.6	73.7
		12	63.8	64.2
K_2CO_3–Mn_2O_3–SnO_2–MgO	550	1	97.9	68.9
(1: 7: 3: 10)		4	90.3	83.3
		6	94.1	88.5
K_2CO_3–$CaCO_3$–Mn_2O_3–SnO_2	600	48	85.8	88.0
(1: 1: 2: 1)		105	86.0	84.1
		199	90.1	84.0

Effect of Carriers and Alkaline Compounds

Mn_2O_3–SnO_2 (7: 3) was mounted on such basic oxides as MgO, CaO, and SrO in place of kieselguhr (Table III). The activity was primarily affected by the specific surface area of the catalyst, and Mn_2O_3–SnO_2–MgO catalyst gave the best conversion. On the other hand, a lower selectivity was obtained. Frequently, when it takes place on the acidic sites of catalysts, isomerization is prevented by the addition of basic compounds.5) On K_2CO_3–Mn_2O_3–SnO_2–MgO catalyst, both the selectivity and the conversion were improved (Table IV). Based on these observations, we hypothesize that iminodibenzyl is tightly adsorbed on acidic sites and undergoes isomerization, and the turnover rate decreases. These acidic sites are neutralized by alkaline compounds. After continuous operation for 5 h, Mn_2O_3 (Partrigeite type) of Mn_2O_3–SnO_2–kieselguhr catalyst was reduced to MnO(Manganosite type), as determined by X-ray analysis. Although the conversion decreased gradually, the activity persisted for 12 h. On K_2CO_3–$CaCO_3$–Mn_2O_3–SnO_2 catalyst, about 85% conversion was maintained for 200 h at 600°C. Therefore, MnO is also an active oxide species for the dehydrogenation of iminodibenzyl.

References and Notes

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