Catalytic dehydrogenation of iminodibenzyl to iminostilbene. A comparison of potassium-promoted manganese, iron and cobalt oxide catalysts

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The dehydrogenation of iminodibenzyl (10,11-dihydro-5-dibenz[b.f]azepine) to iminostilbene (5H-dibenz[b.f]azepine) was investigated over potassium-promoted oxides of manganese, iron and cobalt. Both unsupported oxides as well as corresponding oxides supported on magnesium oxide were examined. Catalytic tests were carried out in a continuous fixed-bed reactor in the presence of steam in the temperature range of 400–550°C and at atmospheric pressure. Unsupported, potassium-promoted iron oxide proved to be the most suitable catalyst for the dehydrogenation of iminodibenzyl, yielding iminostilbene with 80% selectivity at nearly 100% conversion.

Keywords: dehydrogenation of 10,11-dihydro-5-dibenz[b.f]azepine; 5H-dibenz[b.f]azepine; iminodibenzyl; iminostilbene; catalytic behaviour; manganese oxide; iron oxide; cobalt oxide; promotion; potassium

1. Introduction

Iminostilbene is an important intermediate in the production of carbamazepine, an anti-epileptic drug [1]. Iminostilbene (5H-dibenz[b.f]azepine, IS) can be produced by dehydrogenation of iminodibenzyl (10,11-dihydro-5H-dibenz[b.f] azepine, IDB) using various catalysts and reaction conditions [2–10] (scheme 1).

Supported palladium on carbon [2,3], nickel on kieselgur [4], Raney-cobalt [5] and various supported compounds on chromia, vanadia, cobalt and copper were reported [4–6] to be suitable catalysts for the iminodibenzyl dehydrogenation. In a cyclic reduction–oxidation process iron oxide is used at 400–450°C as an oxidation agent, which has to be oxidized in an additional step with air or oxygen [7]. Unpro-

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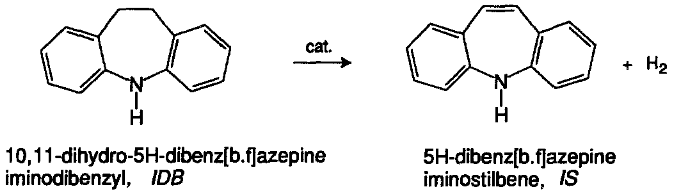


Scheme 1.

moted oxides of several transition metals, such as Pd, Ni, Co, Fe, Mn, Sn, Zn, Cr and Ce, supported on kieselgur, have been studied in the presence of steam at 550°C [8]. Manganese, iron and cobalt oxides were found to exhibit highest activity, while Zn and Sn oxides showed best selectivities. The promotion of a Mn_2O_3–SnO_2 catalyst with K_2CO_3 improved the activity and the selectivity compared to the unpromoted system [8].

Recently, we reported the dehydrogenation at 550–600°C over potassium-promoted iron oxide [9,10]. In these studies we have elucidated the effect of the iron oxide precursors [9], the roles of steam and of the potassium promoter [10]. The observed overall reaction behaviour was influenced by contributions from heterogeneous (catalytic) and homogeneous (non-catalytic) reactions. The homogeneous reaction pathway became prominent at high space times and/or high temperatures (above 600°C). Potassium-promoted catalysts prepared from different iron oxide phases, hematite, maghemite and magnetite, showed all similar selectivities to iminostilbene, indicating that the choice of the iron oxide precursor had no significant influence on the selectivity of the final potassium-promoted iron oxide catalyst. The behaviour of all potassium-promoted iron oxide catalysts was strongly influenced by the steam/iminodibenzyl ratio in the feed. Both selectivity to iminostilbene and conversion of iminodibenzyl increased with higher steam/iminodibenzyl ratios [9]. Potassium promotion of the iron oxides improved strongly the activity of the catalysts [10].

To our knowledge, there exists no comparative study of the suitability of potassium-promoted transition metal oxides for the dehydrogenation of iminodibenzyl to iminostilbene. This prompted us to study the catalytic behaviour of Mn, Fe and Co oxides promoted with potassium. Both unsupported oxides as well as corresponding oxides supported on magnesium oxide have been investigated.

2. Experimental

2.1. PREPARATION OF CATALYSTS

2.1.1. *MgO-supported manganese, iron and cobalt oxide catalysts promoted by potassium*

The MgO-supported catalysts were prepared according to the synthesis description reported in refs. [11,12]. Doubly distilled water was used for the preparations.

Magnesium oxide (3.2 mm pellets, >98%, Alpha Products) was crushed and particles from 0.5–0.8 mm sieve fraction were calcined at 1027°C for 24 h. The magnesium oxide support was impregnated using incipient wetness method with solutions of complexed metal ions (Mn(II), Fe(III), Co(II)) with ethylene diamine tetraacetic acid (EDTA). The catalysts were prepared with transition metal loading of 1.9 wt%, based on the magnesium oxide support. A suspension with an equimolar ratio of the corresponding metal salts (manganese(II) nitrate tetrahydrate (Fluka, purum>98%), iron(III) nitrate nonhydrate (Fluka, puriss.>99%), cobalt(II) nitrate hexahydrate (Fluka, purum>98%)) and ethylene diamine tetraacetic acid (EDTA, Fluka, puriss. >99%) was dissolved in water by adding concentrated ammonia (Fluka, puriss. 25%) until a pH of 6–7 was reached. The complexed metal solution was added dropwise to the magnesium oxide support and subsequently the particles were dried at room temperature for 30 min and then at 90°C for 2 h at 50 mbar in a rotavapor (Büchi). The metal EDTA / MgO precursor was calcined in several subsequent steps at 150°C / 2 h, 200°C / 1 h, 250°C / 1 h, 300°C / 1 h and finally at 700°C for 18 h in an electric furnace under air.

The potassium promoter was added by impregnating the magnesium oxide supported metal oxides with a solution of potassium carbonate in water using the incipient wetness method. The catalysts (K / Mn oxide on MgO, K / Fe oxide on MgO, K / Co oxide on MgO), prepared with a 1.2 wt% potassium loading, were dried in the rotavapor in the same way as described above and finally calcined at 850°C for 18 h.

2.1.2. *Unsupported manganese, iron and cobalt oxide catalysts promoted by potassium*

The unsupported manganese, iron and cobalt oxide catalysts were prepared by precipitation of the corresponding metal hydroxides. Doubly distilled water was used for the preparations. 0.3 mol of the metal oxide precursor salt (magnanese(II) nitrate tetrahydrate (Fluka, purum>98%), iron(III) nitrate nonahydrate (Fluka, puriss.>99%), cobalt(II) nitrate hexahydrate (Fluka, purum>98%)) were dissolved in 200 ml water and the solution dropwise added under vigorous stirring to 200 ml water at 80°C. The pH of the suspension was kept constant at 11 by adding 8 wt% potassium hydroxide (Sigfried, puriss.) solution. Subsequently, the suspension was stirred for further 2 h at 80°C for pH 11 and then filtered. The product was resuspended twice in 100 ml water, filtered and dried at 120°C and 125 mbar for 18 h. The dried oxides were crushed to particle sizes > 0.25 mm. Potassium promotion was carried out by dissolving appropriate amounts of potassium carbonate in water. The amount of K_2CO_3 was adjusted to obtain a potassium content of ca. 6 wt% (based on total catalyst weight). The resulting pastes were kneaded for 15 min, divided into small portions and dried at 120°C and 125 mbar for 18 h. The potassium-promoted metal oxides were calcined at 800°C for 18 h (K / Mn oxides, K / Co oxides) or at 950°C for 5 h (K / Fe oxides) and finally crushed to a sieve fraction of 0.5–0.8 mm.

Assignments, textural and chemical properties of all catalyst samples are listed in table 1.

2.2. CATALYST CHARACTERIZATION

Catalysts and catalyst precursors were characterized by means of powder X-ray diffraction (XRD), nitrogen adsorption, Hg-porosimetry and atomic absorption spectroscopy (AAS). The XRD measurements were carried out on a Siemens D5000 diffractometer using Cu Kα radiation in step mode between 20 and 65° 2θ, with a step size of 0.01° and 5 s per step. The diffractometer was equipped with a Cu secondary monochromator and a scintillation detector.

The BET surface areas of the catalysts were measured with an Omnisorb 100 (OMI-CROM) instrument using nitrogen adsorption at 77 K in the relative pressure range $0.05 \leqslant p/p^0 \leqslant 0.2$. A cross-sectional area of 0.162 nm^2 was assumed for the nitrogen molecule. Pore volume and pore-size distributions of the catalysts were determined by mercury porosimetry using a Carlo Erba 2000 porosimeter and assuming a contact angle of 130° and cylindrical pores.

The potassium and iron contents of the catalysts were determined by atomic absorption spectroscopy (AAS). Carbonate contents were measured by photometric titration of the CO_2 formed after acidification of the samples. Water contents were determined by Karl-Fischer titration after drying of the catalysts at 180°C.

2.3. CATALYTIC MEASUREMENTS

The catalytic tests were performed in an integral type continuous tubular fixed-bed reactor with 3 g of catalyst in the range of 400–550°C and at atmospheric pres-

Table 1
Textural and chemical properties of potassium-promoted manganese, iron and cobalt oxide catalysts

Catalyst	Chemical composition (wt%)					Textural properties		
	transition metal	K	CO_3^{2-}	H_2O [a]	Mg	BET surface area [b] ($m^2\,g^{-1}$)	pore volume [c] ($cm^3\,g^{-1}$)	mean pore size [c] (nm)
K/Mn oxides	63.9	6.34	0.46	0.61		8.6	0.36	140
K/Fe oxides	64.0	6.09	0.02	1.69		4.6	0.46	220
K/Co oxides	65.4	5.64	3.33	2.27		13.2	0.43	70
K/Mn oxide on MgO	1.81	1.10	0.24	0.24	52.4	3.0	0.24	170
K/Fe oxide on MgO	1.90	1.25	0.08	0.83	52.7	3.0	0.23	150
K/Co oxide on MgO	1.54	1.25	0.14	0.58	53.1	2.9	0.24	160
MgO support					54.8	3.3	0.27	150

[a] After additional drying at 180°C.
[b] Determined by nitrogen adsorption.
[c] Determined by mercury porosimetry.

sure. 1–5 g/h molten iminodibenzyl and 0.05–0.5 g/min bidistilled water yielding to a steam/iminodibenzyl ratio of 50–300 mol/mol were vaporized and fed into the reactor. The solid reaction products were condensed in a trap at room temperature and analysed by gas chromatography. Beside iminodibenzyl (IDB) and water, the condensate contained iminostilbene (IS), 9-methylacridine (MAC), acridine (AC) and small amounts of aniline and indole. The vent gas contained hydrogen as major component, and minor amounts of CO_2, CO, CH_4. Further details about the apparatus and the product analysis were reported in ref. [9].

3. Results and discussion

3.1. CATALYST PROPERTIES

The chemical and textural properties of the catalysts used in the comparative study are listed in table 1. The chemical analysis of the unsupported catalysts (K/Mn oxides, K/Fe oxides and K/Co oxides) indicates that the potassium content (based on total catalyst weight) varied between 5.64 and 6.34 wt%. The carbonate contents of the iron oxide and manganese oxide catalysts were significantly lower than that of the potassium-promoted cobalt oxide. XRD analysis (fig. 1) showed that the potassium-promoted iron and manganese oxide catalysts contained cryptomelane (KMn_8O_{16}), potassium-β''-ferrite ($K_2O{\cdot}5Fe_2O_3$) and potassium-β-ferrite ($K_2O{\cdot}11Fe_2O_3$). It is well known from the literature that the formation of potassium polyferrites occurs at temperatures above 900°C [13], whereas potassium manganese oxide phases are formed in the temperature range of 600–800°C [14] under simultaneous evolution of CO_2. In addition to these peaks, hematite (α-Fe_2O_3) and hausmannite (Mn_3O_4) were detected in the catalyst samples (fig. 1). The high carbonate content of 3.33 wt% of the promoted cobalt oxide catalyst (table 1) is explained by the fact that the catalyst consisted mainly of Co_3O_4 and amorphous K_2CO_3. The XRD analysis of the cobalt oxide catalyst (fig. 1, bottom) showed no evidence for crystalline ternary potassium metal oxide phases, which were observed with manganese oxide and iron oxide systems.

The unsupported catalysts possessed BET surface areas (table 1) of 4.6–13.2 m^2/g. The shapes of the nitrogen adsorption isotherms and the hysteresis type could be classed to II and H3, respectively, according to the IUPAC nomenclature [15].

In our previous study [9] dealing with various promoted iron oxides, we have shown that the BET surface area influences significantly the activity and selectivity of the catalysts for the iminodibenzyl dehydrogenation. In order to eliminate this factor in the present comparative study we have prepared potassium-promoted manganese, iron and cobalt oxides supported on magnesium oxide (K/Mn oxide on MgO, K/Fe oxide on MgO, K/Co oxide on MgO), which had similar textural properties. The textural properties of the basic magnesium oxide support were adjusted

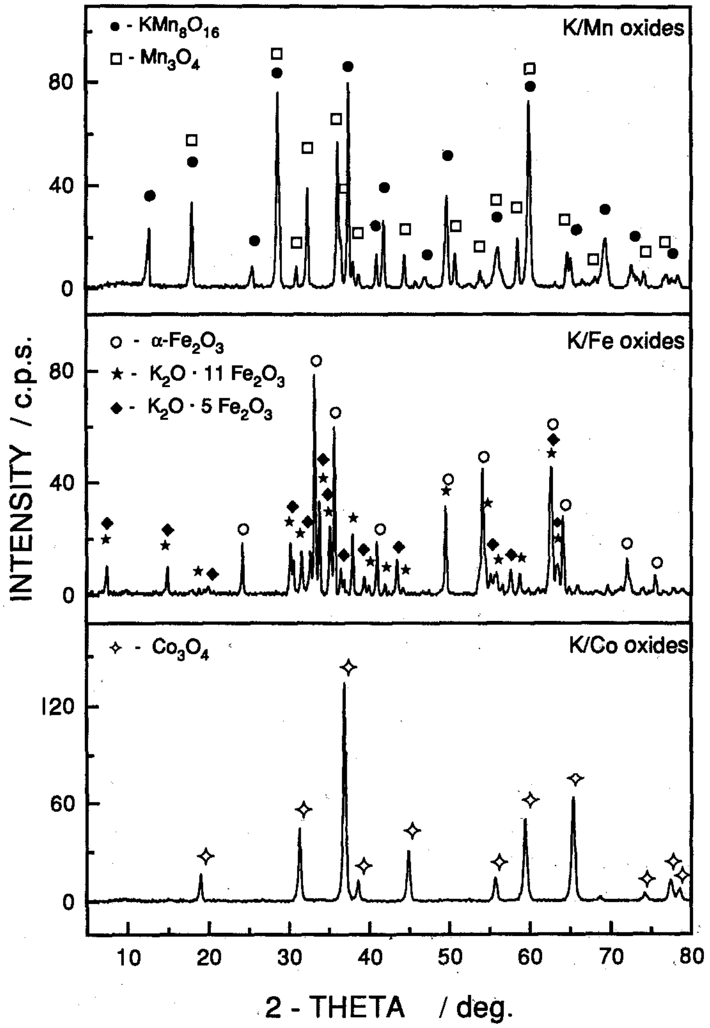


Fig. 1. X-ray diffraction patterns (Cu Kα) of unsupported, potassium-promoted manganese, iron and cobalt oxide catalysts.

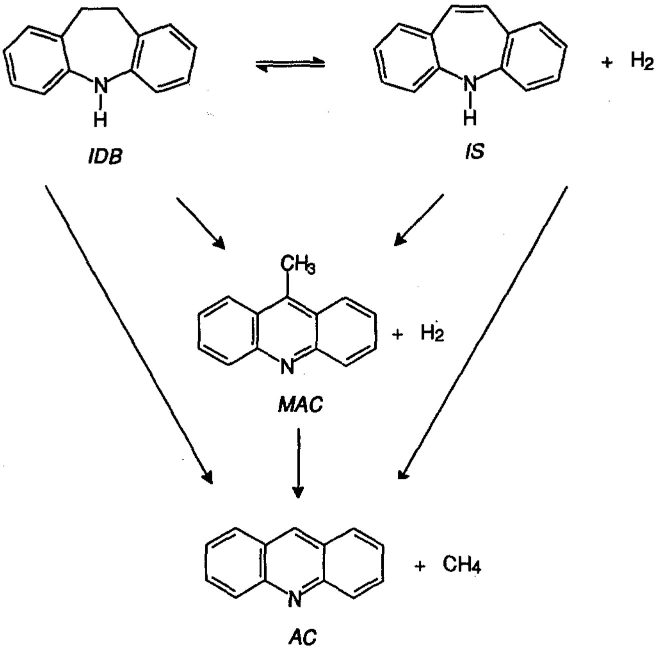
by thermal pretreatments (1027°C, 24 h). The results of the nitrogen adsorption and Hg porosimetry measurements confirmed that the final supported catalysts exhibited almost identical textural properties ($S_{\mathrm{BET}} \approx 3\ \mathrm{m}^2/\mathrm{g}$, table 1). XRD analysis of the supported catalysts were not conclusive with regard to phase composition due to the small loadings of transition metal oxide and potassium carbonate.

3.2. CATALYTIC TESTS

The global reaction scheme including major side reactions and by-products observed with potassium-promoted manganese, iron and cobalt oxide catalysts is presented in scheme 2. With all catalysts, 9-methylacridine and acridine were detected as major by-products in the reaction mixture. In addition small amounts (< 1%) of aniline and indole were found in the product mixture.

Table 2 compares the conversions of iminodibenzyl and selectivities to iminostilbene measured for the potassium-promoted manganese, iron and cobalt oxide catalysts. Activity and selectivity data collected under steady-state conditions are presented for three different experimental conditions: (I) 550°C, $W_{cat}/F_{IDB} = 2\ g_{cat}\ h/g_{IDB}$, steam/iminodibenzyl ratio 50 mol/mol; (II) 550°C, $W_{cat}/F_{IDB} = 2\ g_{cat}\ h/g_{IDB}$, steam/iminodibenzyl ratio 130 mol/mol and (III) 550°C, $W_{cat}/F_{IDB} = 0.6\ g_{cat}\ h/g_{IDB}$, steam/iminodibenzyl ratio 50 mol/mol. All catalysts showed a high initial activity which slowly declined and reached a steady-state after ca. 24 h on stream. The initial activity and selectivity after 2 h on stream are also listed in table 2. Fig. 2 illustrates for all catalysts the relationship between the selectivities to iminostilbene and the iminodibenzyl conversion for a constant steam/iminodibenzyl ratio of 50 mol/mol.

The best selectivity to iminostilbene combined with a high catalyst activity was obtained with the unsupported, potassium-promoted iron oxide catalyst. The selectivity of the unsupported manganese oxide was significantly lower than that of the iron oxide catalyst. The highest activity at 550°C was observed with the potassium-promoted cobalt oxide. However, the catalyst was unselective at 550°C, producing mainly 9-methylacridine, acridine, indole, aniline and unknown smaller



Scheme 2. The global reaction pathway, as suggested based on the observed product distribution. (IDB: iminodibenzyl; IS: iminostilbene; MAC: 9-methylacridine; AC: acridine.)

Table 2

Catalytic properties: conversion (%) of iminodibenzyl and selectivity (%) to iminostilbene of potassium-promoted manganese, iron and cobalt oxide catalysts for the three different conditions (I), (II) and (III) [a]

Catalyst	(I)				(II)		(III)	
	initial [b]		steady state [c]		steady state [c]		steady state [c]	
	conv.	sel.	conv.	sel.	conv.	sel.	conv.	sel.
K/Mn oxides	77.9	70.4	66.0	72.0	67.1	78.2	42.8	78.3
K/Fe oxides	76.0	78.5	71.0	77.7	95.5	83.5	51.6	83.0
K/Co oxides	100	0	100	0	–	–	–	–
K/Mn oxide on MgO	69.5	66.1	45.0	74.9	48.9	78.0	29.2	78.9
K/Fe oxide on MgO	65.4	76.2	48.2	75.3	59.7	80.1	29.7	79.9
K/Co oxide on MgO	54.4	76.7	40.0	77.3	54.9	83.2	21.9	81.8
MgO support	–	–	4.3	53.7	3.5	55.2	2.7	68.7
non-catalytic reaction [d]	–	–	3.0	43.0	2.3	47.1	1.0	40.5

[a] (I) $W_{cat}/F_{IDB} = 2$ h, steam/IDB ratio 50 mol/mol, temperature 550°C; (II) $W_{cat}/F_{IDB} = 2$ h, steam/IDB ratio 130 mol/mol, temperature 550°C; (III) $W_{cat}/F_{IDB} = 0.6$ h, steam/IDB ratio 50 mol/mol, temperature 550°C.

[b] After 2 h on stream.

[c] After 24 h on stream.

[d] Reactor in absence of catalyst.

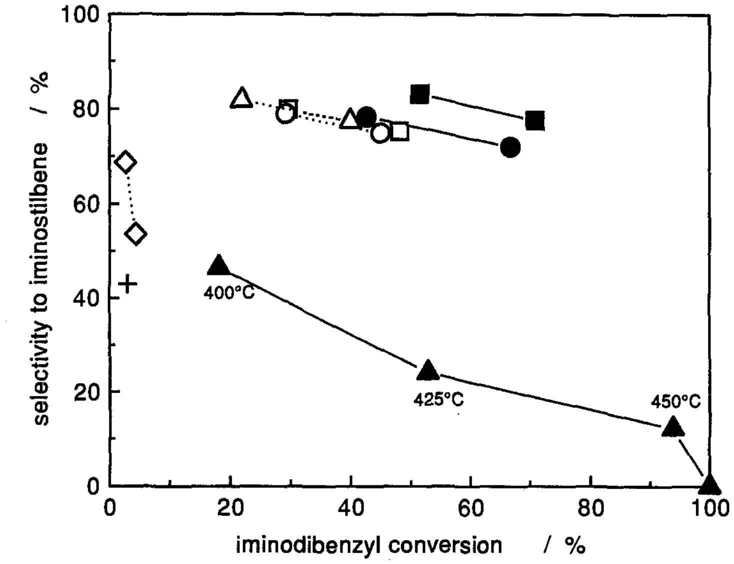


Fig. 2. Catalytic behaviour of unsupported and on magnesium oxide supported potassium-promoted manganese, iron and cobalt oxide catalysts. (■) Unsupported K/Fe oxides; (●) unsupported K/Mn oxides; (▲) unsupported K/Co oxides; (□) on MgO supported K/Fe oxide; (○) on MgO supported K/Mn oxide; (△) on MgO supported K/Co oxide; (◇) MgO support. Conditions: 550°C, steam/iminodibenzyl ratio 50 mol/mol, $W_{cat}/F_{IDB} = 0.6$ and 2 g_{cat} h/g_{IDB}. (+) Reactor without catalyst at $W_{cat}/F_{IDB} = 2$ g_{cat} h/g_{IDB}, steam/iminodibenzyl 50 mol/mol, 550°C.

fragments of iminodibenzyl. Note that the unsupported cobalt oxide catalyst produced iminostilbene only at temperatures below 450°C (fig. 2). The selectivity to iminostilbene measured for the iron oxide system was not reached by the potassium-promoted cobalt oxide under these conditions.

The comparative catalytic investigations indicate that the magnesium oxide supported transition metal oxides (fig. 2, open symbols) were significantly less active than the corresponding unsupported catalysts (solid symbols). Moreover, the best selectivity ca. 83% at a steam/iminodibenzyl ratio of 50 mol/mol of the unsupported iron oxide catalysts was not reached neither by the supported iron oxide nor by the supported manganese or cobalt oxide catalysts.

The supported catalysts showed similar behaviour independent of the nature of the deposited transition metal oxides. This is noteworthy particularly in the light that a remarkable increase of activity and selectivity was achieved by the impregnation of the magnesium oxide support with potassium and the transition metal oxides, as the comparison of the catalytic results obtained with the unloaded magnesium oxide support reveals. At a steam/iminodibenzyl ratio of 50 mol/mol and 550°C, a conversion of 2.7–4.3% and a selectivity of 54–69% were observed over the pure support material (table 2, fig. 2). Experiments without any catalyst in the reactor showed that iminodibenzyl was also converted (conversion 1–3%, table 2) by non-catalytic, homogeneous reactions to iminostilbene (selectivity 40–47%), 9-methyl acridine and acridine under the conditions chosen [9].

Table 2 indicates that the catalytic behaviour of the potassium-promoted manganese, iron and cobalt oxide catalysts is strongly influenced by the steam/iminodibenzyl ratio of the feed. A strong increase of activity was observed for the unsupported iron oxide and the magnesium oxide supported iron oxide and cobalt oxide, while the unsupported as well as the supported manganese oxides did only weakly show this effect.

Fig. 3 illustrates the influence of the steam/iminodibenzyl ratio on the iminodibenzyl conversion and the selectivity to iminostilbene for the unsupported manganese oxide and iron oxide, and the supported cobalt oxide catalysts. Note that the conversions of the unsupported iron oxide and the supported cobalt oxide increased more strongly than over the manganese oxide, when the steam/iminodibenzyl ratio was changed from 50 to 150 mol/mol. However, all catalysts showed a similar behaviour concerning the selectivity to iminostilbene. The selectivities increased with higher steam/iminodibenzyl ratio due to shorter space times of the reactants in the catalyst bed and in the reactor void space [9]. Note that in addition to the kinetic effects, the dehydrogenation equilibrium shifts towards the product side with a higher dilution of the feed, as discussed in ref. [9]. In contrast to the manganese and cobalt oxide catalysts the selectivity of the iron oxide passed through a maximum of ca. 80% for a steam/iminodibenzyl ratio of 150 mol/mol. Consecutive reactions of iminostilbene became prominent when the iminodibenzyl conversion approached 100% leading to a loss of selectivity.

In conclusion we can state that unsupported potassium-promoted manganese,

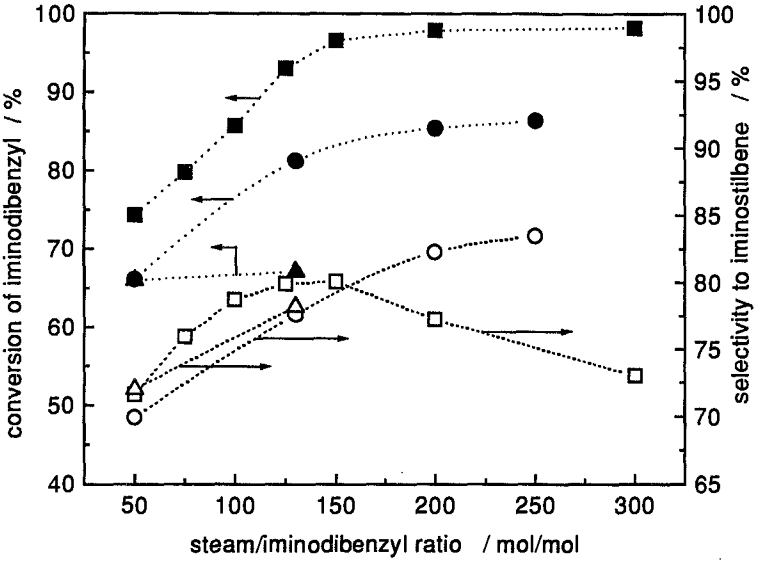


Fig. 3. Influence of steam/iminodibenzyl ratio on iminodibenzyl conversion and selectivity to iminostilbene. Conversion (■) and selectivity (□) for the unsupported potassium-promoted iron oxide catalyst at 550°C and $W_{cat}/F_{IDB} = 3\ g_{cat}\ h/g_{IDB}$. Conversion (▲) and selectivity (△) for the unsupported potassium-promoted manganese oxide catalyst at 550°C and $W_{cat}/F_{IDB} = 2\ g_{cat}\ h\ g_{IDB}$. Conversion (●) and selectivity (○) for the on MgO supported potassium-promoted cobalt oxide catalyst at 570°C and $W_{cat}/F_{IDB} = 3\ g_{cat}\ h/g_{IDB}$.

iron and cobalt oxides show significantly different catalytic behaviour for the dehydrogenation of iminodibenzyl to iminostilbene. When supported on magnesium oxide, the catalysts exhibit similar catalytic behaviour. A high catalyst activity, as reached with unsupported iron oxide, is essential for the dehydrogenation of iminodibenzyl to iminostilbene, because an enhancement of the conversion by changing reaction parameters (increase of contact time factor W_{cat}/F_{IDB} or temperature) leads to a significant formation of the by-products 9-methylacridine and acridine, due to an unfavourable contribution of unselective, homogeneous reactions [9]. Among the catalysts tested for the iminodibenzyl dehydrogenation the unsupported, potassium-promoted iron oxide proved to be most suitable due to its excellent performance under conditions of low steam/iminodibenzyl ratio (50 mol/mol, fig. 2). The catalytic behaviour of this catalyst is favourably influenced by the addition of steam to the feed, which results in yields of iminostilbene of ca. 80%.

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