Isomerization of styrene epoxide on basic solids

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The isomerization of styrene oxide has been investigated on mixed oxides obtained by calcination of hydrotalcites, rare earth phosphates and KF supported on alumina. All solids form β-phenylacetaldehyde. Basic catalysts deactivate rapidly or show a lower selectivity, most probably due to the formation of heavy products by aldolisation. ZnAl catalyst shows a selectivity towards β-phenylacetaldehyde $>98\%$ with no deactivation after 7 h on stream, in a flow gas phase process at 423 K.

KEY WORDS: styrene epoxide isomerization; hydrotalcites; phosphates; mixed oxides

1. Introduction

Styrene oxide is a well-known raw material utilized for the production of various chemicals. *E.g.*, β-phenylacetaldehyde is an important intermediate which offers a large range of use in manufacture of perfumes, pharmaceuticals and insecticides [1]. It can be obtained by rearrangement of the epoxide, commonly used to produce useful intermediates for organic synthesis. The catalysed reaction yields aldehydes on acids, whereas allylic alcohols would result in bifunctional acid–base mechanisms [2]. The isomerization of styrene oxide to β-phenylacetaldehyde is a difficult problem at the industrial scale, as recently reported by Hölderich and Barsnick [1]. The main problem is the occurrence of competitive side reactions of aldolisation giving 1,3,5-triphenylbenzene and coke with fast deactivation. The older solutions used thermolysis of the epoxide at 548 K in the presence of calcium sulfonate [3]. The phenylacetaldehyde yield was 44.7%, at 84% conversion, with 34.7% of heavy unidentified organics.

Other solutions have been recently proposed using zeolite catalysts. In that case a stabilisation of the α-carbocation favours the selectivity to aldehyde, and the zeolite shape selectivity hinders catalyst deactivation. Indeed Al or B containing MFI, and Cs–B-MFI were found to reach 98% yield at a $\text{WHSV} = 3\ \text{h}^{-1}$ in a gas-phase process at 573 K [4]. The lifetime was reported in subsequent patents to be very high at 573 K and much lower at 473 or 673 K, due to the occurrence of side reactions [5,6]. In the liquid phase this reaction was reported to give 93% yield in 5 h at 313 K in the presence of Nafion-H as catalyst [7]. The liquid phase reaction at 343 K with TS-1 as the catalyst reaches a yield $>95\%$ in 1 h, showing that the reaction requires only a weak acidity of the Lewis type [8].

Indeed mixed oxides or phosphates could exhibit both acido-basic centres due to the exposure of both cations and oxygens. The mixed oxides derived from hydrotalcites are known to adsorb CO_2, therefore show basic properties [9], but also exhibit some acidity considered as responsible for the dehydration of diacetonealcohol to mesityloxide in the aldolisation of acetone at low temperature [10,11]. The properties of hydrotalcites for aldolisation have recently been explored [12] and this work pointed out that hydroxylated solids are much more active for aldolisation. The acido-basic properties of rare earth phosphates have also recently been reported [13,14].

It was therefore interesting to check how these solids possessing acido-basic surface properties would catalyse the isomerization of styrene epoxide. It was supposed that a good catalyst for this reaction must not contain hydroxyls at the surface since aldolisation forms heavy products which can block the surface; therefore the solids were used after calcination at 723 K.

2. Experimental

2.1. Materials

Hydrotalcites of different compositions were prepared as described earlier by precipitation of a solution of chlorides at a constant pH [9]. Rare earth phosphates were prepared according to the procedures reported by Le Govic *et al.* [14]. This involves a dropwise addition of solutions of rare earth carbonates into a solution of phosphoric acid at 353 K.

KF/alumina was prepared as described earlier using SCP 350 γ-alumina provided from Rhône Poulenc (surface area 400 m^2/g) as support [15]. 15 g of alumina were poured into 150 ml of water containing the desired amount of KF (10 mmol-KF/g of support, referred to as KF10). Water was evaporated at 323 K, then the solid was dried at 383 K and calcined at 723 K just before use. One sample of KF on NaX

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Table 1
Chemical composition and textural properties of the mixed oxides

Sample	BET surface area (m^2/g)	Pore radius (nm)	Total pore volume (cm^3/g)
MgAl2,0	281	10–13	0.844
MgAl3,0	276	7–16	0.674
MgCr2,8	213	2–12	0.527
MgFe2,21	185		
ZnAl3,0	51	2–12	0.112
CoAl1,7	153	5–12	0.517

zeolite was also prepared by impregnation of 10 mmol of KF according to the same procedure.

All these solids were used after calcination at a temperature at which they are decarbonated and dehydroxylated. The standard temperature of activation was 723 K.

2.2. Characterizations

The chemical compositions were obtained by IPC analysis after dissolution of the samples. The structures were checked by XRD on a Siemens 5000 instrument. Surface areas and pore sizes were obtained from the adsorption–desorption isotherms of nitrogen at 77 K. The number and strength of the basic sites were characterised by the adsorption of CO_2 using calorimetry according to published procedures [16]. The results are reported in tables 1 and 2.

2.3. Reactions

Isomerization reactions were performed in the gas phase at 423 K, in a flow reactor operated at atmospheric pressure. A solution of styrene oxide (0.6 M) in toluene was introduced with a HPLC pump. The effluents were condensed in ice and analysed by GC on a Perkin–Elmer instrument equipped with a capillary column (30 m) coated with DB5.

3. Results and discussion

The solids were first decarbonated and dehydroxylated by heat treatment at 723 K. This treatment converts hydrotalcites into mixed oxides of MgO structure for MgAl, MgFe and MgCr hydrotalcites, and of CoO or ZnO structure for CoAl and ZnAl hydrotalcites. The phosphates crystallize in this treatment and show the XRD spectrum of the corresponding phosphate. KF/alumina is also crystallized to KF, with part of the fluoride reacting with the support to form K_2AlF_6. The surface areas of these solids are reported in tables 1 and 2. The textural properties of phosphates reproduce those reported earlier [13].

Table 2
Chemical compositions and surface areas of phosphates

Sample	% P	% M	S_{BET} ($m^2\,g^{-1}$)	Phase from DRX
$SmPO_4$	12.0	50.5	111	$SmPO_4$
$SmPO_4(NH_4^+)$	11.9	50.5	110	$SmPO_4$
$LaPO_4$[a]	12.4	54.0	266	$LaPO_4$

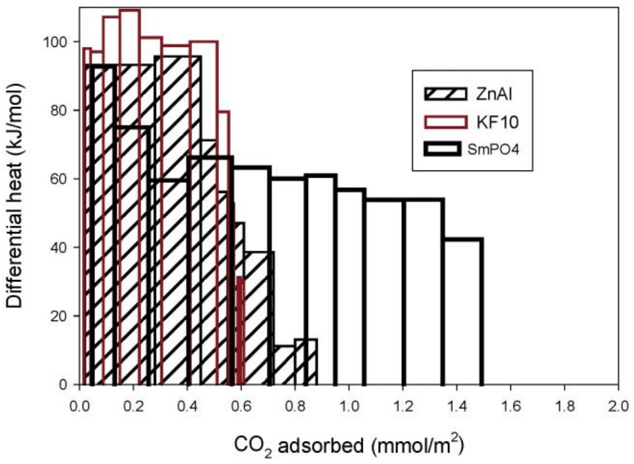

Figure 1. Differential heats of adsorption of CO_2 on ZnAl mixed oxide, KF10 and Sm phosphate.

The differential heat of adsorption of CO_2 on the mixed oxides obtained from hydrotalcites has been reported earlier [9]. The initial heat is relatively constant at about 110 kJ/mol whatever the solid and only the number of sites changes. As illustrated in figure 1, KF10 shows a lower heat of adsorption of about 100 kJ/mol and $SmPO_4$, taken as representative of the phosphates, shows an even lower heat of adsorption of about 80 kJ/mol. In the latter case the adsorption is indeed reversible.

The catalytic properties were measured at 423 K, with a flow of 40 ml/min and a weight of catalyst of 0.5 g (contact time of about 3 s). Since a high conversion of the epoxide is easily reached, the emphasis was put on selectivity and stability at full conversion. The products of the reaction were β-phenylacetaldehyde, phenylethanol, styrene and in some cases 1,4-diphenyl-2-butene. β-phenylacetaldehyde is the main product expected for the acid-catalysed isomerization of styrene oxide; therefore at 423 K, the surface exhibits mostly the reactivity of a solid acid. 1,4-diphenyl-2-butene, identified by GC-MS analysis, is an oligomer of styrene, formed by a protonic mechanism, thus showing that these solids possess some Brønsted acidity under the reaction conditions. Phenylethanol and its product of dehydration, styrene, can result from hydrogen transfer catalysed by either acids or bases. Their formation should also result in dehydrogenated products not detected in the gas phase and therefore transformed into coke. Phenylethanediol was also observed in trace amounts resulting from the hydration of the epoxide. The most reasonable source of water is the dehydration of the aldol made by self-condensation of the aldehyde.

The changes of catalytic properties are illustrated in figure 2 for KF/alumina. This solid was earlier shown to be a good catalyst for aldolisation, and the fast deactivation observed in this reaction is therefore attributed to the formation of heavy products retained at the surface. The same phenomenon occurs faster on KF/NaX (not shown).

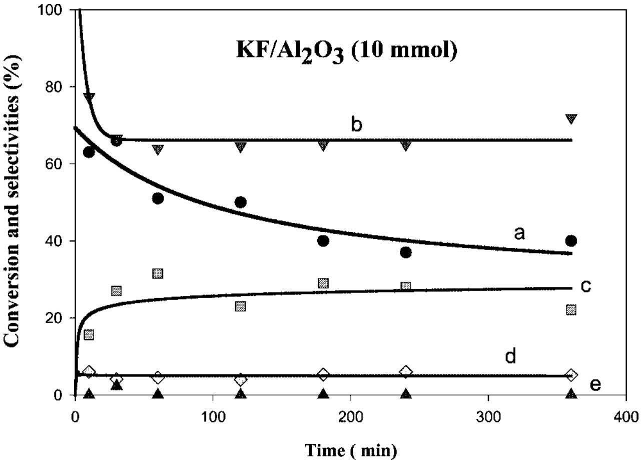

Figure 2. Variation of catalyic properties with time on stream for supported KF: conversion (a), and selectivities to β-phenylacetaldehyde (b), styrene (c), phenylethanol (d) and minor products (e).

The properties of the mixed oxides derived from hydrotalcites are reported in figure 3. With these mixed oxides the conversions reach 100%. With MgAl hydrotalcites the selectivity increases with time suggesting a slow poisoning of the stronger sites. No correlation appears between basicity as determined by CO_2 adsorption and conversion. Therefore, as expected, the reaction is not controlled by the basic properties. This can be further checked by the comparison of rare earth phosphates and supported KF. KF on Al_2O_3 (figure 2) or NaX deactivated steadily and showed a low selectivity (65–75%). Samarium phosphate has been reported to show acid properties when calcined at 773 K. The surface sites however show pure basic properties after treatment with an ammoniacal solution [14]. Here the selectivity and stability of $SmPO_4$ reported in figure 4 decrease upon treatment with NH_4OH, which increases basicity.

Activity is therefore not related to basicity; however the selectivity and stability are controlled by the basic strength of the surface, since the possible consecutive processes of aldolisation of the product in the presence of hydroxyls can account for the observed decay of activity with time on stream.

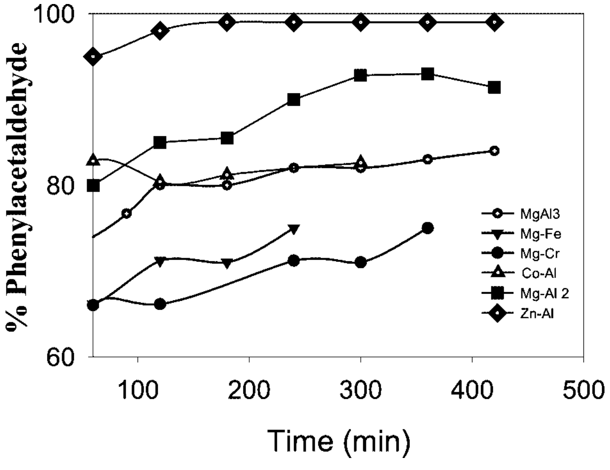

Figure 3. Yields of β-phenylacetaldehyde as a function of time at 423 K for the mixed oxides obtained from hydrotalcites.

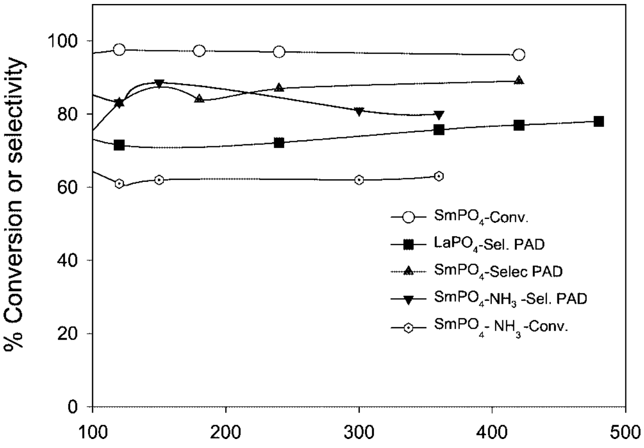

Figure 4. Variations of conversion (open points) and selectivities on samarium and lanthanum phosphates.

The best catalyst for this process is ZnAl mixed oxide reaching a yield >95% after 10 h on stream, with no sign of deactivation. ZnAl mixed oxides show a low basicity, are difficult to rehydrate [17] and consequently do not catalyse aldolisation or oligomerization of the epoxide. They are considered as Lewis acids [18], which agrees with the present results on the acid-catalysed isomerization of the epoxide in aldehyde.

In conclusion, these mixed oxides and phosphates calcined at 723 K show Lewis acid properties at 423 K. They could offer an alternative to microporous zeolites for the isomerization of styrene epoxide into β-phenylacetaldehyde. The large porosity of the solid precludes here any shape selectivity, so that a high activity is expected for bulky substrates of interest in fine chemistry.

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