

Heterocyclic compounds from allyl alcohol over molecular sieves

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Abstract

The conversion of allyl alcohol on SAPO molecular sieves (37, 34, 11 and 5) and H ZSM-5 zeolite at 523–623 K and WHSV = 5.1 h⁻¹ results in the formation of diallyl ether, propanal, 2-methyl-2-pentenal and also tetrahydropyran-2-carbaldehyde and 2-oxepanone probably obtained from intermediate acrolein. The catalytic action of the molecular sieves used corresponds to the presence of Brønsted acid sites and basic sites activating the dehydration, dehydrogenation, aldol condensation, Diels–Alder reaction and ring expansion. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: SAPO; H-ZSM-5; Acid–base sites; Diels–Alder; Acrolein; 2-Oxepanone

1. Introduction

The synthesis of aluminophosphate based molecular sieves is a considerable progress in the preparation of non-corrosive acid catalysts. Their initial use in petroleum refining and petrochemical processes [1] was followed by application as catalysts in Friedel–Crafts alkylation [2] and dehydration reactions [3,4]. The catalytic activity of SAPO molecular sieves was attributed to their acid properties related to the existence of hydroxyl groups on the crystal surface acting as Brønsted acid sites. The proof that the strength of these acid sites is comparable with that of sulfuric acid [3] directed our attention to the conversion of allyl alcohol. In the presence of H ZSM-5 zeolite, allyl alcohol showed a variety of products formed on the acidic and basic active sites of the catalyst [5,6].

Some of the reactions, namely the formation of diallyl ether and of hydrocarbons [6] are undoubtedly related to the action of the Brønsted acid sites, while the formation of propanal and its aldol condensation to 2-methyl-2-pentenal [7] might proceed also with the participation of basic sites. In our earlier investigations on the conversion of allyl alcohol on H ZSM-5 zeolite [5] the formation of acrolein was suggested and it was confirmed by other authors [6] for zeolites, containing alkali metal cations.

The aim of the present investigation is to compare the catalytic activity of SAPO molecular sieves towards allyl alcohol with that of H-ZSM-5 zeolite.

2. Experimental

The characteristics of the molecular sieves SAPO-37, SAPO-34, SAPO-11 and SAPO-5

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used in the present investigation are given in Ref. [3]. Before the experiments the pressed, crushed and sieved to 1.25–2.50 mm particle molecular sieves were heated under an air flow to 723 K for 4 h, then 3 h at 823 K for the template decomposition. The used catalysts were regenerated under an air flow at 823 K before each experiment and then cooled to the reaction temperature; 623, 573 or 523 K. A flow reactor containing 0.5 g of the catalyst was used. Reagent grade allyl alcohol was introduced via injector with $WHSV = 5.1 \text{ h}^{-1}$ in N_2 atmosphere. The reaction products were analyzed each 15 min by GC with FID on a 2 m column of silanized chromosorb W 60–80 mesh with 15% DC 550 at 313 K. Hewlett Packard GC MS was used for the identification of the reaction products.

3. Results and discussion

The conversion of the allyl alcohol on SAPO molecular sieves at 573 K (Fig. 1) depends on the pore dimensions of the molecular sieves and

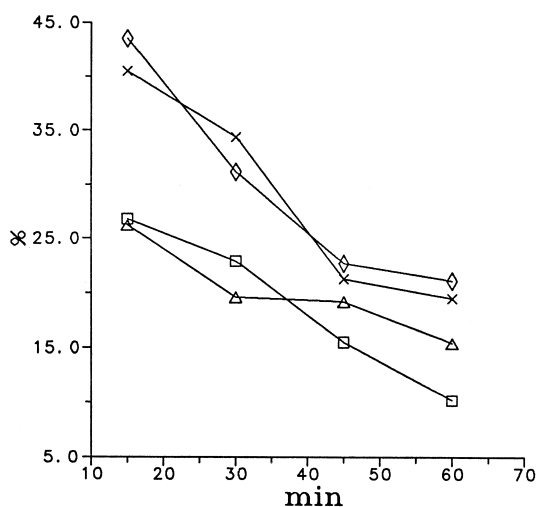


Fig. 1. Allyl alcohol conversion (%) at 573 K in the presence of SAPO-37 (◇), SAPO-34 (□), SAPO-11 (△) and SAPO-5 (×).

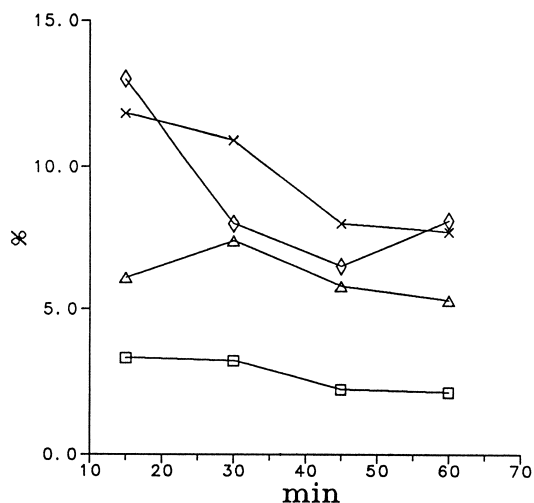


Fig. 2. Propanal (%) at 573 K in the presence of SAPO molecular sieves (see Fig. 1 for the legend).

those with larger openings are more active. The most active is SAPO-37 with 1.3 nm diameter of the faujasite supercages, followed by SAPO-5 with AFI topology and 0.73 nm free diameter of the pores. Less active is SAPO-34 with 0.4 nm opening diameter of the cavities and SAPO-11 with AEL structure having an elliptical pore opening of $0.39 \times 0.63 \text{ nm}$. The highest quantity of the propanal is formed on SAPO-5 (Fig. 2). Diallyl ether and 2-methyl-2-pentenal are present among the reaction products, too. Acrolein was not detected although it might precede the propanal appearance. The GC and GC-MS analysis revealed the presence of heterocyclic compounds (Fig. 3), tetrahydropyran-2-carbaldehyde and 2-oxepanone. Similar reaction products are obtained also in the presence of H ZSM-5 zeolite ($\text{Si}/\text{Al} = 50$) (Fig. 4). The formation of these heterocyclic compounds by the contact of allyl alcohol with zeolite molecular sieves is not yet described in the literature.

The presence of heterocyclic compounds is easily explained by the Diels–Alder reaction of acrolein formed after dehydrogenation of the starting allyl alcohol. The released hydrogen is added not only to form propanal, but to the 4H-2,3-dihydropyran-2-carbaldehyde. The tetra-

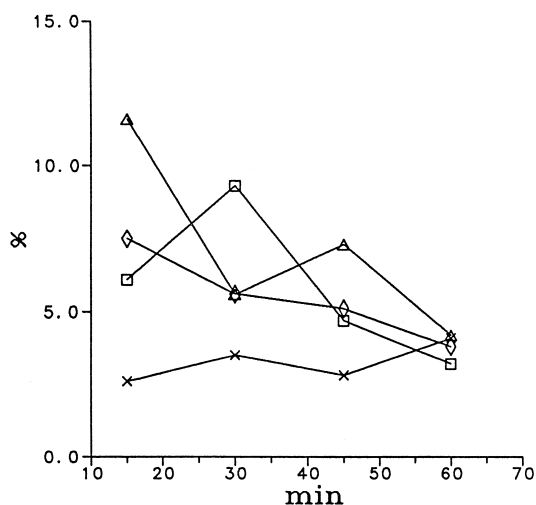
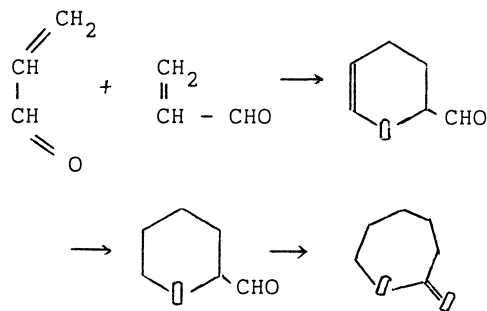


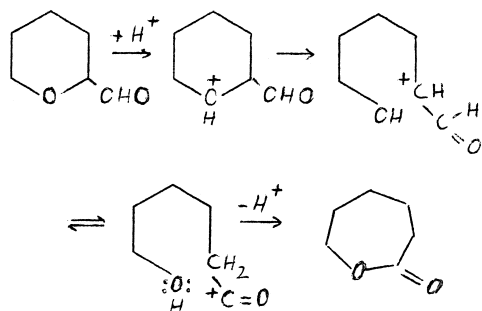
Fig. 3. Heterocyclic compounds (%) at 573 K in the presence of SAPO, molecular sieves (see Fig. 1 for the legend).

hydropyran-2-carbaldehyde is further isomerized to 2-oxepanone:



The zeolites were found to be active and regioselective catalysts in the Diels–Alder reaction [8,9]. Theoretical calculations [9] showed, that the complexation of adsorbed acrolein with a Lewis acid or its protonation stabilizes the transition state of the reaction. The enlargement of rings was also observed using zeolites as catalysts in the Beckmann rearrangement of ketoximes [10]. In the case of tetrahydropyran-2-

carbaldehyde the ring expansion may involve participation of Brønsted acid sites in protonation of the oxygen in the heterocycle and subsequent ring opening:



The carbenium ion formed may isomerize via hydrogen migration and then the positively charged carbon atom of the carbonyl group is neutralized by the free electrons of the oxygen from the HO-group, followed by proton abstraction and ring reclosure. All the positively charged species must be adsorbed on the negatively charged lattice.

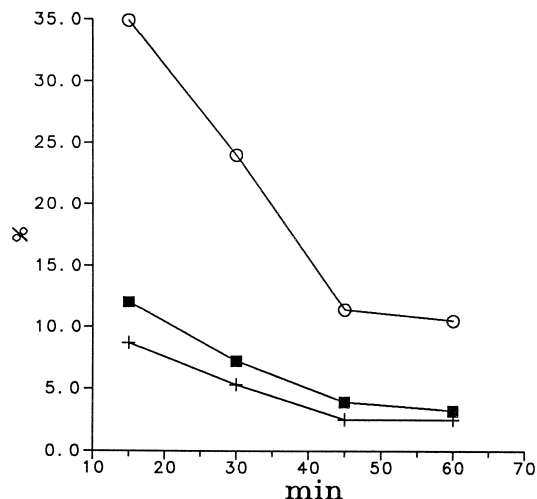


Fig. 4. Conversion of allyl alcohol in the presence of H-ZSM-5 (Si/Al = 50) (○), propanal (+) and heterocyclic compounds (■) formed at 523 K.

4. Conclusions

The acid–base properties of SAPO molecular sieves and of H-ZSM-5 zeolites enable their activity in different reactions with an unsaturated alcohol: dehydration, dehydrogenation, hydrogenation, aldol condensation of the carbonyl compounds, the Diels–Alder reaction and ring expansion.

The present results indicate that allyl alcohol converts to acrolein also in the absence of alkali cations in the catalyst. The dehydrogenation probably proceeds with the participation of acid–base pairs of active sites. The acid sites activate a fast Diels–Alder reaction of acrolein. The reaction product is saturated by the hydrogen available and afterwards partially converted into 2-oxepanone with the participation of the Brønsted acid site. The basic sites are important for the stabilization of all the positively charged species.

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