

## Pinacol Rearrangement on SAPO Molecular Sieves

Fadhil A. Jabur, Vladimir J. Penchev and Cvetana P. Bezoukhanova\*

University of Sofia, Faculty of Chemistry, FAX 35-92-62-28-08, 1, J. Bourchier Ave, Sofia 1126, Bulgaria

It has been found that the silicoaluminophosphate molecular sieves SAPO-37 and SAPO-5 are very active in pinacol rearrangement, while SAPO-11 and SAPO-34 showed rather low activity most probably due to pore constraints.

Crystalline silico-aluminophosphates are a relatively new class of molecular sieves, that combine different structures and pore dimensions with variation in acidity. They offer new opportunities as improved catalysts for petrochemical and organic synthesis<sup>1,2</sup> It is considered that their acidity is weak by comparison with zeolites, but their selectivity is superior. Recently we have compared the activity of Y faujasites with that of H ZSM-5 zeolites in pinacol rearrangement.<sup>3</sup> We have found, that the faujasites' activity in this reaction is superior to that of HZSM-5; an advantage of HZSM-5 was its high resistance to coke formation.

The aim of the present investigation was to compare the activity of SAPO molecular sieves in pinacol conversion. Four silicoaluminophosphates with different compositions and pore dimensions were used (Table 1).

SAPO-37 has a faujasite geometry, similar to Y zeolites with a 1.3 nm diameter of the supercages<sup>4</sup> and 0.74 nm diameter of the twelve-membered ring openings. The structure of SAPO-34 closely resembles that of the natural zeolite chabazite, whose framework consists of distorted hexagonal prisms linked together by four-membered rings to form a large ellipsoidal cavity.<sup>5</sup> Each ellipsoidal cavity is interconnected to six similar cavities through an eight-membered oxygen ring with an opening diameter of about 0.4 nm. SAPO-11 has a structure of AEL-type with void volume consisting of nonintersecting elliptic ten-membered ring pores of 0.39 × 0.63 nm diameter.<sup>6</sup> The topology of SAPO-5 is AFI, consisting of nonintersecting twelve-membered ring pores with a free diameter of 0.73 nm.

The SAPO samples were prepared as described in ref. 7 by heating a mixture of reagents usually of the same molar composition, *i.e.* 2R:0.1–0.4 SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>:P<sub>2</sub>O<sub>5</sub>:50 H<sub>2</sub>O., where R is the corresponding template molecule. The composition of SAPO samples is presented in Table 1. TG, DTG and DTA methods were employed for characterization of the materials used as catalysts.<sup>8</sup>

Reagent grade pinacol (Fluka) was added to the molecular sieve, which was previously pressed, crushed, sieved to 8–14 mesh, activated at 723 K under an air flow and cooled to the reaction temperature. The experiments were performed in a round bottomed flask fitted with a thermometer and an efficient reflux condenser. Samples from the reaction mixture were analyzed periodically by GC on a 2 m column of silanized chromosorb W 60-80 mesh with 15% DC 550 at 373 K using FID. IR spectra and reference substances were used for the identification of the products.

It is well established<sup>9</sup> that the dehydration of 1,2-diols

proceeds in the presence of strong acids *via* a carbenium ion and with migration of the substituent to a neighbouring carbon atom. The formation of a carbonyl compound is accompanied by some elimination. Concentrated sulfuric acid is the usual catalyst. It has been shown<sup>3</sup> that acidic zeolites are also active catalysts.

Our experiments with SAPO molecular sieves showed (Fig. 1) that some of these are also good catalysts for pinacol conversion. The most active was the faujasite isotype SAPO-37, which gives 49% conversion in 90 min. Similar activity is

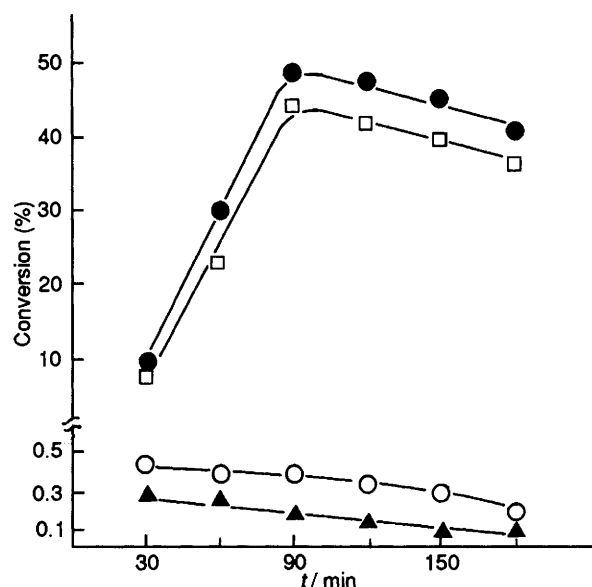


Fig. 1 2,3-Dimethyl-butane-2,3-diol (pinacol) conversion on SAPO molecular sieves at 423 K, catalyst: pinacol = 0.1:1 (m:m) SAPO-37 (●), SAPO-5 (□), SAPO-11 (○), SAPO-34 (▲)

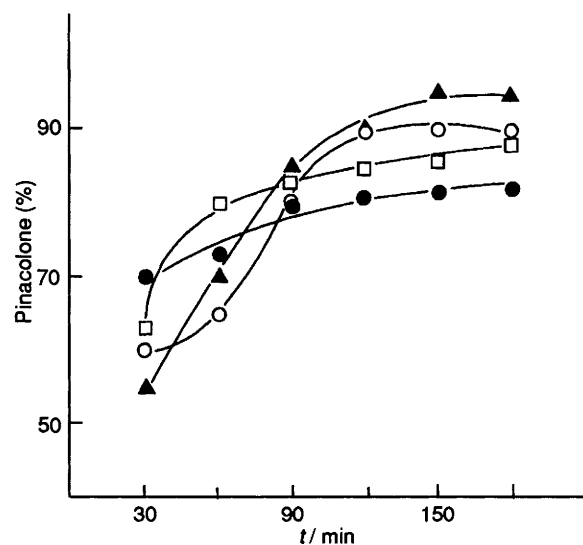


Fig. 2 Yields of pinacolone in the presence of SAPO

Table 1 Composition of molecular sieves used

Sample	Chemical analysis (mole fraction)			Template
	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub> (solid)	SiO <sub>2</sub>	
AlPO <sub>4</sub> -5	0.54	0.46	—	Tripropylamine
SAPO-5	0.48	0.39	0.13	Tripropylamine
SAPO-37	0.43	0.37	0.20	Tetramethylammonium + Tetrapropylammonium hydroxide
SAPO-11	0.40	0.55	0.05	Dipropylamine
SAPO-34	0.38	0.53	0.09	Isopropylamine

demonstrated by SAPO-5. The activities of SAPO-11 and SAPO-34 are much lower. Evidently the pore dimensions of the molecular sieve are important for the catalytic activity in this reaction, with similar materials being active in other reactions.<sup>1,6</sup>

As for other acid catalysts, the conversion of pinacol on SAPO molecular sieves proceeds in two parallel pathways, giving either a ketone or a diene (Fig. 2). The ratio between the two products does not depend considerably on the type of the molecular sieve used. Diene formation diminished as the reaction progressed while more pinacolone was produced. One possible explanation is that pinacolone formation requires one proton, while elimination of water to give the diene requires two protons.

The observed results are in accordance with the data on the catalytic activity of SAPO towards hydrocarbons.<sup>1,6</sup> On the basis of <sup>29</sup>Si MAS-NMR data it has been suggested, that SAPO-37 contains extremely active sites located at the boundaries between the domains of aluminosilicate and silicoaluminophosphate.

Access to the active sites depends on the dimensions of the reacting molecule and the size of the pores of the catalyst. The acidic sites of SAPO-37 and SAPO-5 are easily accessible for

pinacol, while diffusion in SAPO-11 and SAPO-34 with pore openings of less than 0.7 nm is very difficult.

Received, 11th March 1994; Com. 4/01451K

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