Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 100 (2005) 355–361

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Isomerization of *n*-butane to isobutane over Pt-SAPO-5, SAPO-5, Pt-H-mordenite and H-mordenite catalysts

Narendra Kumar [a,*], Jose Ignacio Villegas [a], Tapio Salmi [a],
Dmitry Yu. Murzin [a], Teemu Heikkilä [b]

[a] *Laboratory of Industrial Chemistry, Process Chemistry Centre, Åbo Akademi University, FIN-20500 Turku/Åbo, Finland*
[b] *Department of Physics, University of Turku, FIN-20014 Turku/Åbo, Finland*

Abstract

Aluminium sulphate, sodium aluminate, aluminium oxide and pseudo-boehmite were used as sources of aluminium in the synthesis of SAPO-5. The samples were characterized using XRD, SEM, XRF, FTIR and nitrogen adsorption. The formation of SAPO-5 phase, morphology, surface area and catalytic properties were found to be influenced by the source of aluminium used in the synthesis. The sample synthesized using pseudo-boehmite as a source of aluminium showed most phase pure silicoaluminophosphate, whereas syntheses using aluminium phosphate or sodium aluminate only formed quartz and berlinite. The FT-IR spectra exhibited the presence of Brønsted and Lewis acid sites in the Pt-SAPO-5, SAPO-5, Pt-H-mordenite and H-mordenite catalysts. Modification of SAPO-5 and mordenite by Pt impregnation did not influence the structures of these catalytic materials. The Pt-H-mordenite and H-mordenite catalysts with stronger Brønsted acidity exhibited higher conversion of *n*-butane and yield to isobutane than Pt-SAPO-5 and SAPO-5 catalysts with weak acid sites. Introduction of Pt in SAPO-5 and mordenite played a positive role in the isomerization of *n*-butane to isobutane.

Keywords: SAPO-5; Mordenite; Pt-SAPO-5; Pt-mordenite; *n*-Butane; Isomerization

---

1. Introduction

Synthesis of aluminophosphate (AlPOs) in the early 1980s by Wilson et al. [1] led to the increase in the new structures of microporous materials such as silicoaluminophosphate (SAPO), metal modified aluminium phosphate (MeAPO) and metal modified silicoaluminophosphate (MeAPSO) [2]. The aluminophosphate molecular sieves have univariant framework composition with Al/P = 1, wide range of pore sizes and structures. The framework of AlPOs is neutral and does not have ion-exchange property. The introduction of silicon in the framework structure of $AlPO_4$-5 results in the formation of silicoaluminophosphates, SAPO-5, having mild acidity and ion-exchange property. SAPO-5 has uni-dimensional pore systems consisting of cylindrical channels formed by 12-membered rings with a diameter of 0.80 nm [3]. SAPO-5 has very good thermal and hydrothermal stability and has potential applications as acid catalysts in hydroisomerization, propene oligomerization, cracking of *n*-hexane and xylene isomerization [4–6].

As compared to aluminosilicate type of zeolite such as mordenite, synthesis of silicoaluminophosphate requires mild acidic or mild basic pH and templates are amine or quaternary ammonium ions. Sources of silica and alumina have been reported to influence the phase purity, crystallinity, acidity and morphology of aluminosilicate type of zeolites [7–9]. There are, however, only a few studies published in the open literature on the influence of aluminium sources on the synthesis of silicoaluminophosphate (SAPO) type of molecular sieves [8]. Influence of synthesis variables of SAPO-5 on the catalytic performances has been reported [10]. Reaction of *n*-butane to isobutane is important from industrial and academic point of view. Several authors have studied reaction of *n*-butane to isobutane over acidic catalysts [11–13]. Garin et al. [14]

---

[*] Corresponding author. Tel.: +358 22154555; fax: +358 22154479.
E-mail address: nkumar@abo.fi (N. Kumar).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.10.023

has reported the use of *n*-butane as a test reaction for evaluating the relative acidic property of H-mordenite and ZrO_2/SO_4 catalysts. Isomerization of *n*-butane to isobutane over Pt-zeolite catalysts proceed via bifunctional reaction mechanism.

In this work we have studied the influence of alumina source on the physico-chemical and catalytic properties of SAPO-5. The reaction of *n*-butane to isobutane was used as a test reaction to investigate the catalytic property of Pt-SAPO-5 and SAPO-5. Furthermore the catalytic activity and selectivity to isobutane over Pt-SAPO-5 and SAPO-5 are compared with strong acidic H-mordenite and Pt-mordenite catalysts in order to investigate the role of acid sites, structure of zeolites and Pt sites in isomerization of *n*-butane.

2. Experimental

2.1. Synthesis and characterisation of SAPO-5 using aluminium sulphate, aluminium oxide, pseudo-boehmite and sodium aluminate, Pt-SAPO-5 and Pt-mordenite

The synthesis of SAPO-5 was carried out as mentioned in Ref. [9] with some modifications. The reagents used in the synthesis were phosphoric acid (Merck, 85 wt.%), hydrated aluminium oxide (Vista, 74.2 wt.% Al_2O_3 and 25.8 wt.% H_2O), fumed silica (Aldrich), tri-*n*-propylamine (Merck) and distilled water. A gel solution was prepared and poured into a Teflon coated stainless steel autoclave and the synthesis was carried out at 473 K for 24 h under static condition. The product was washed with distilled water and dried at 373 K for 12 h. The organic template was removed from the sample by calcination at 823 K for 6 h. The effect of aluminium sources in the synthesis of SAPO-5 was studied using sources of alumina: sodium aluminate (Riedel-de-Häen), aluminium sulphate (Merck), aluminium oxide (La-Roche) and pseudo-boehmite (Alta Vista). The samples synthesized with sodium aluminate, aluminium sulphate, aluminium oxide and pseudo-boehmite were designated as SAPO-5-SA, SAPO-5-AS, SAPO-5-AO and SAPO-5-PB, respectively. The effect of aluminium sources on the physico-chemical properties was studied by keeping all the synthesis parameters the same and varying the sources of aluminium.

NH_4-mordenite zeolite was obtained from Zeolyst International with Si/Al ratio 20 and calcined in a muffle oven to obtain H-mordenite. SAPO-5-PB synthesized using pseudo-boehmite as source of aluminium was used for modification with Pt. 2 wt.% Pt-H-mordenite and 2 wt.% Pt-SAPO-5 catalysts were prepared by impregnation method using aqueous solution of hexachloroplatinic acid. The mordenite catalysts were designated as Pt-H-MOR-20 and H-MOR-20. The in situ reduction of Pt-SAPO-5 and Pt-mordenite catalysts was carried out at 723 K prior to the catalyst testings.

The phase purity and the structure of SAPO-5 were determined by an X-ray powder diffractometer (Philips pW 1830). The morphology of SAPO-5 was investigated using a scanning electron microscope (Cambridge Leica 360) and the surface area was determined by a Sorptometer 1900 (Carlo Erba Instruments). The Si/Al ratio was investigated using an X-ray fluorescence spectrometer (Siemens SRS 303).

The acidic properties of SAPO-5, Pt-SAPO-5, H-mordenite and Pt-H-mordenite catalysts were studied by FT-IR spectrometer of adsorbed pyridine. The acidity of investigated samples was measured by infrared spectroscopy (ATI Mattson FT-IR) using pyridine ($\geq$99.5%, a.r.) as a probe molecule for qualitative and quantitative determination of both Brønsted and Lewis acid sites. The samples were pressed into self-supported pellets (10–15 mg/cm^2). Pyridine was first adsorbed for 30 min at 373 K and then desorbed in vacuo at different temperatures (523, 623 and 723 K) to obtain a distribution of acid site strengths. All spectra were recorded at 373 K with a spectral resolution of 2 and 4 cm^{-1}. Spectral bands at 1545 and 1450 cm^{-1}, respectively, were used to identify Brønsted (BAS) and Lewis acid sites (LAS). The amount of BAS and LAS were calculated from the intensities of corresponding spectral bands using the molar extinction coefficients reported by Emeis [15]. The Brønsted and Lewis acid sites can be distinguished by the bands of chemisorbed pyridinium ion at 1545 cm^{-1} and coordinatively bonded pyridine at 1455 cm^{-1}, respectively [16]. The band at 1490 cm^{-1} is usually associated with pyridine adsorbed on both Brønsted and Lewis acid sites.

2.2. Catalyst testing

Reaction of *n*-butane (99.9% AGA) to isobutane over Pt-SAPO-5, Pt-H-MOR-20 and H-MOR and SAPO-5 catalysts was studied in a fixed-bed micro-reactor at atmospheric pressure. The Pt modified catalysts were pre-treated in flow of hydrogen for 2 h at 723 K and a mixture of *n*-butane (20%) with hydrogen (80%) as a carrier gas was allowed to react with the catalysts. The products analyses were carried out on-line using a gas chromatograph (Varian 3700) equipped with a flame-ionisation detector (FID) and a capillary column (50 m × 0.32 mm ID fused silica PLOT Al_2O_3–KCl).

3. Results and discussion

3.1. Pysico-chemical properties of SAPO-5-SA, SAPO-5-AS, SAPO-5-AO and SAPO-5-PB phase purity

The X-ray powder diffraction pattern of SAPO-5-AS synthesized with aluminium sulphate showed only two peaks (Fig. 1a) which were not of SAPO-5 type microporous materials. The identified crystalline phases by XRD were

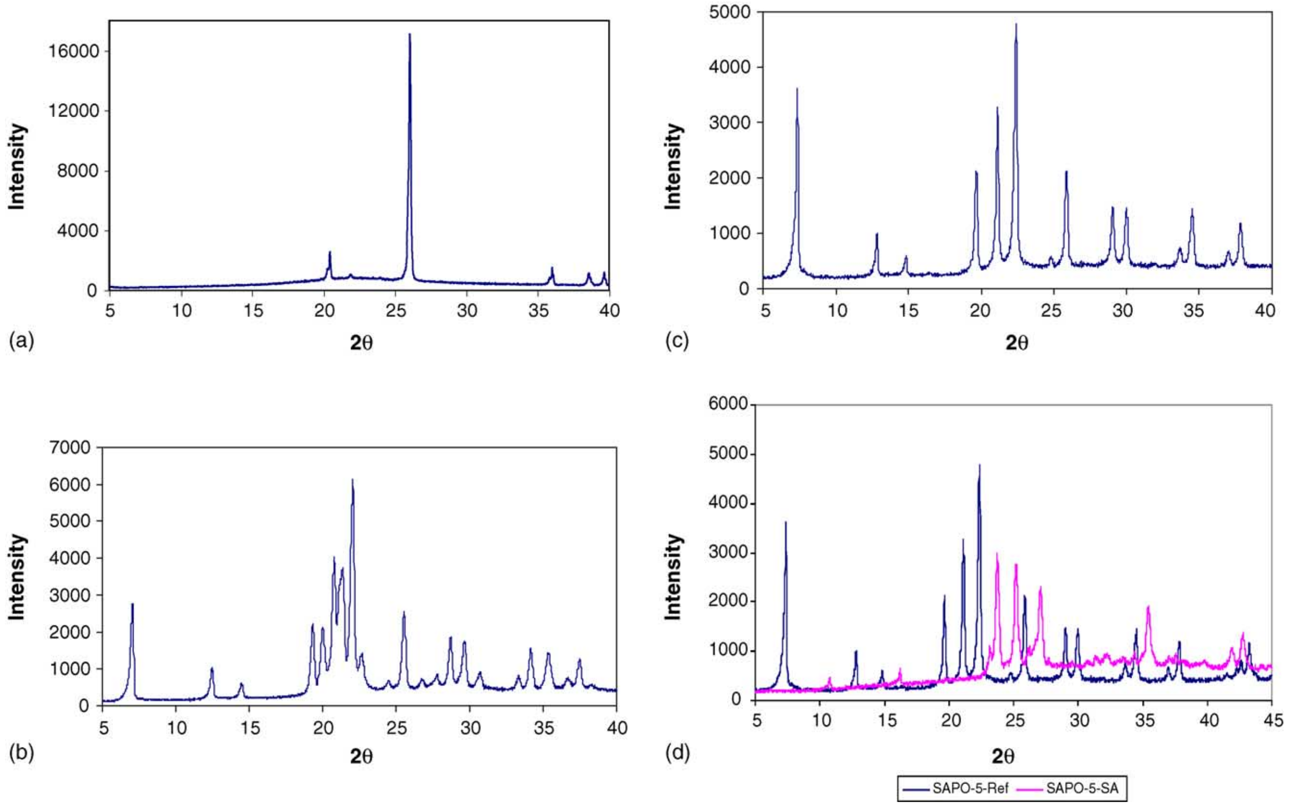

Fig. 1. (a) XRD patterns of SAPO-5-AS synthesized using aluminium sulphate. (b) XRD pattern of SAPO-5-AO synthesized using aluminium oxide. (c) XRD pattern of SAPO-5-PB synthesized using pseudo-bohemite. (d) XRD pattern of SAPO-5-SA synthesized with sodium aluminate and a reference SAPO-5 phase pure.

that of quartz and berlinite. The absence of SAPO-5 could be attributed to SO_4 species present in the gel solution that inhibit the crystallisation process of SAPO-5. Aluminium salts have been reported to enhance the formation of unidentified condensed phases [8]. The X-ray powder diffraction pattern of SAPO-5-AO synthesized with aluminium oxide exhibited SAPO-5 phase (Fig. 1b), however other phases were also present at the 2θ values of 21°, 22°, 23°, 27°, 28°, 31° and 35°. The reason for this could be that highly pure Al_2O_3 consists of small particles, which are difficult to be dissolved, hence some other phases are formed because of the insolubility of Al_2O_3. The X-ray powder diffraction patterns of SAPO-5-PB synthesized with pseudo-boehmite exhibited crystalline (Fig. 1c) and phase pure SAPO-5. The phase purity characterisation of SAPO-5 by XRD is mentioned in Refs. [3,5,8–10]. The reason for this is the lower crystallinity of pseudo-boehmite, which is very reactive in the formation of SAPO-5. It has been reported by Bhattacharya et al. [8] that lower is the crystallinity of the boehmite, the higher is its reactivity towards SAPO-5 formation. The X-ray powder diffraction patterns of SAPO-5-SA synthesized with sodium aluminate exhibited phases other than that of SAPO-5 (Fig. 1d). A reference SAPO-5 phase pure XRD pattern is given in Fig. 1d. This could be attributed to the presence of sodium ions, which interfere with the nucleation, and crystallisation of SAPO-5 phase. The Si/Al ratio of SAPO-5-PB was determined to be 0.14.

3.1.1. Morphology

The scanning electron microscope of SAPO-5-PB showed crystals of circular shape with crater, typical for SAPO-5 types of materials (Fig. 2a). The crystal size distribution of SAPO-5-PB synthesized with pseudo-bohemite was 7–18 μm. Similar shapes of SAPO-5 have been reported in the literature [5]. Hence it was concluded from the scanning electron micrograph and XRD results that pseudo-boehmite as a source of aluminium was the most suitable for obtaining SAPO-5 crystals. The scanning electron microscope of SAPO-5-AO exhibited some crystals with spherical shape having craters, however, there were also crystals which were not of SAPO-5 types (Fig. 2b) indicating formation of other phases. The scanning electron microscope of SAPO-5-AS (Fig. 2c) and SAPO-5-SA (Fig. 2d) showed crystals of irregular shapes and were completely different from SAPO-5, indicating that use of alumino sulphate and sodium aluminate as sources of aluminium did not result in the formation of SAPO-5 type microporous materials. The presence of impurities in gel solution from the sources of aluminium and silicon has been reported to influence the morphology of the synthesized zeolite crystals [17]. It is

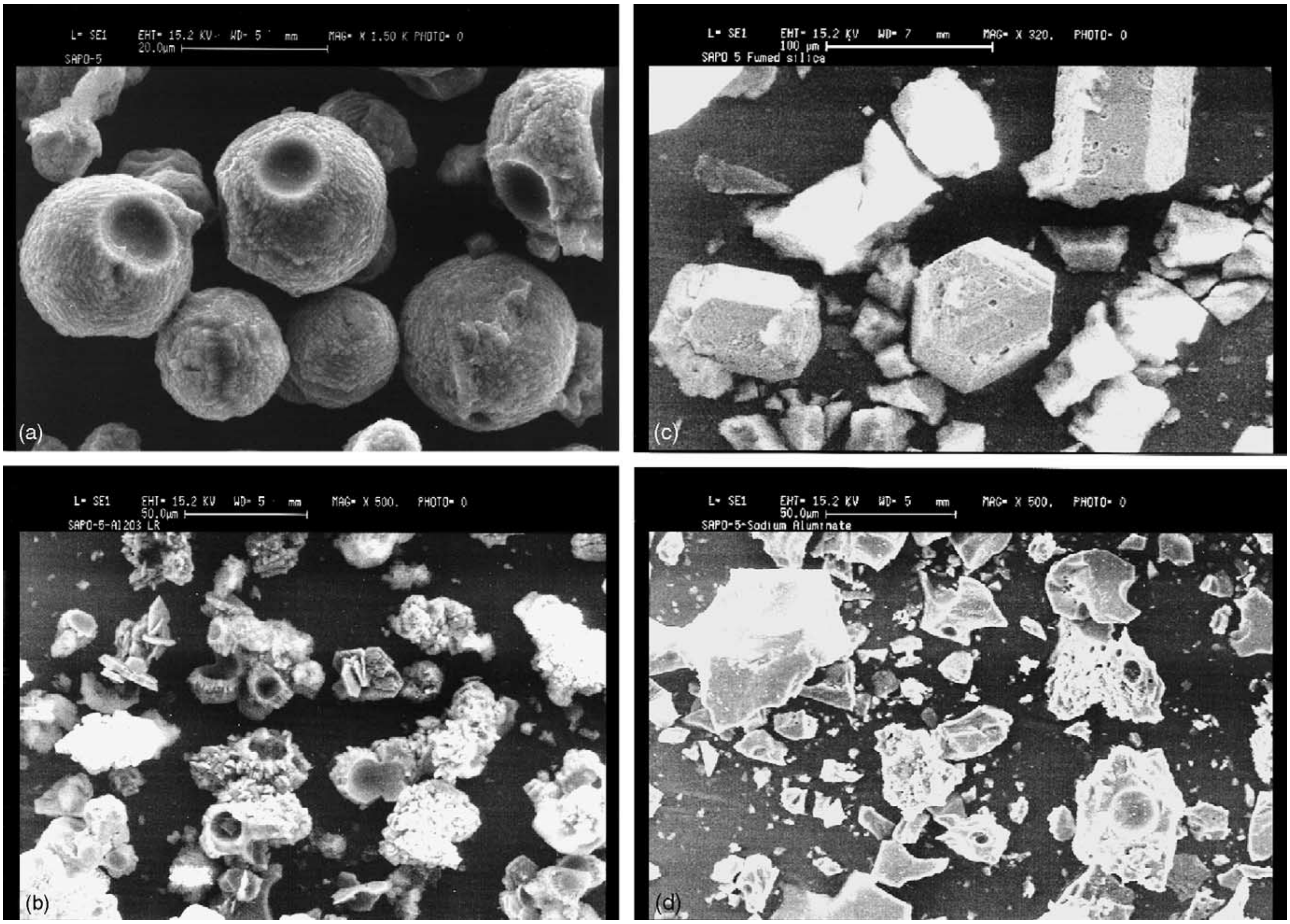

Fig. 2. (a) SEM micrograph of SAPO-5-PB synthesized with pseudo-boehmite. (b) SEM micrographs of SAPO-5-AO synthesized with aluminium oxide. (c) SEM micrograph of SAPO-5-AS synthesized with aluminium sulphate. (d) SEM micrograph of SAPO-5-SA synthesized with sodium aluminate.

very likely that sulphate or sodium ions present in gel solution from aluminium sulphate and sodium aluminate influences the synthesis of SAPO-5.

3.1.2. Surface area

The surface areas of SAPO-5-AO, SAPO-5-AS, SAPO-5-SA and SAPO-5-PB catalysts were determined by nitrogen adsorption using Dubinin method. The samples were out gassed at 573 K prior to the surface area measurements. The surface area of 354, 233, 50.8 and 4.3 m^2/g were determined for SAPO-5-PB, SAPO-5-AO, SAPO-5-AS and SAPO-5-SA, respectively (Table 1). SAPO-5-PB exhibited the highest surface area corroborating synthesis of phase pure SAPO-5. The adsorption–desorption isotherms of the samples SAPO-5-AO and SAPO-5-PB were of type II found for the zeolites and microporous materials [3,5,9]. Surface areas of the SAPO-5-AS and SAPO-5-SA catalysts prepared with aluminium sulphate and sodium aluminate, respectively, as aluminium sources were lower than that of SAPO-5-PB and SAPO-5-AO prepared with pseudo-boehmite and aluminium oxide. The reasons for lower surface areas for SAPO-5-AS and SAPO-5-SA are due to absence of SAPO-5 phase and micro-pores in these materials. The absence of SAPO-5 phase in SAPO-5-AS and SAPO-5-SA was confirmed by X-ray powder diffraction patterns.

Table 1
Synthesized samples, aluminium sources, surface area, Si/Al ratio, phases

Synthesized samples	Al sources	Surface area (m^2/g)	Si/Al ratio	Phases
SAPO-5-PB	Pseudo-bohemite	354	0.14	SAPO-5
SAPO-5-AO	Aluminium oxide	233	0.14	SAPO-5, berlinite,
SAPO-5-AS	Aluminium sulphate	50.8	0.14	Quartz, berlinite
SAPO-5-SA	Sodium aluminate	4.3	0.14	Quartz, berlinite

3.1.3. Acidic property

The Brønsted and Lewis acidities of the SAPO-5-PB, Pt-SAPO-5, Pt-H-MOR-20 and H-MOR-20 catalysts were determined by pyridine adsorption (FT-IR). All materials exhibited the presence of Brønsted acid sites (BAS) and Lewis acid sites (LAS). The FT-IR spectra of adsorbed pyridine over Pt-SAPO-5 and SAPO-5 showed the presence of Brønsted and Lewis acid sites indicating the substitution of Si^{4+} species in the framework of $AlPO_4$-5 and creating acid sites. It has been reported in the literature that the insertion of Si^{4+} in the framework of $AlPO_4$-5 creates weak acidity and ion-exchange property [8]. Considerable differences exist between the acidities of pure SAPO-5 and H-MOR-20 and their Pt-modified counterparts. Since SAPO-5 and Pt-SAPO-5 are materials with weak acid sites, Py molecules adsorbed on the surface were weakly bound to the material, thus desorption temperatures were lower, i.e. 423 and 523 K, than for the mordenite catalysts (523, 623 and 723 K). The Brønsted and Lewis acidity of SAPO-5 increased by loading the catalyst with Pt while the overall number of acid sites, both Brønsted and Lewis, were practically the same for Pt- and H-MOR-20. Although the total number of Brønsted acid sites (BAS), defined as the number of acid sites retaining Py at 523 K, is very similar between both H-MOR-20 and Pt-H-MOR-20, the relative stronger BAS, i.e., those which desorbs Py at 623 and 723 K, decreased severely to the point of non-existence when H-MOR-20 is modified with Pt. Furthermore, the strongest Lewis acid sites (LAS at 723 K) in all samples showed the same behaviour. These changes have been attributed to the interaction between the highly dispersed Pt particles and the acid sites. The dispersion of Pt in Pt-H-MOR-20 catalyst was measured to be 45.5% by CO chemisorption.

3.2. Catalytic property

3.2.1. Isomerization of *n*-butane to isobutane over Pt-SAPO-5, SAPO-5, Pt-H-MOR-20 and H-MOR-20 catalysts

The Pt-H-MOR-20 and H-MOR-20 catalysts exhibited higher conversion of *n*-butane and selectivity to isobutane than Pt-SAPO-5 catalyst (Fig. 3a and b). The explanation for this is the presence of stronger Brønsted acid sites in Pt-H-MOR-20 and H-MOR-20 aluminosilicate type of zeolite catalysts than aluminophosphate type of Pt-SAPO-5 catalyst. High conversion of *n*-butane over Pt modified mordenite catalyst has also been reported by in the literature.

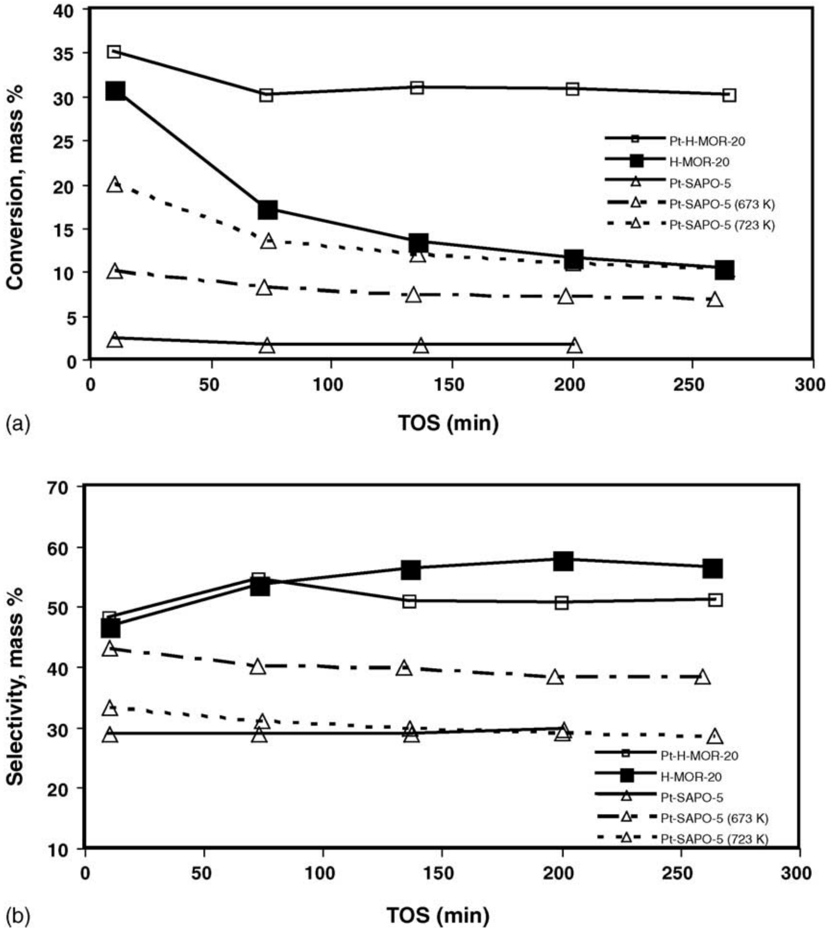

Fig. 3. (a) Effect of temperature and dilution on conversion of *n*-butane over Pt-H-MOR-20, H-MOR-20, Pt-SAPO-5 catalysts. (b) Effect of temperature and dilution on selectivity to isobutane over Pt-H-MOR-20, H-MOR-20, Pt-SAPO-5 catalysts.

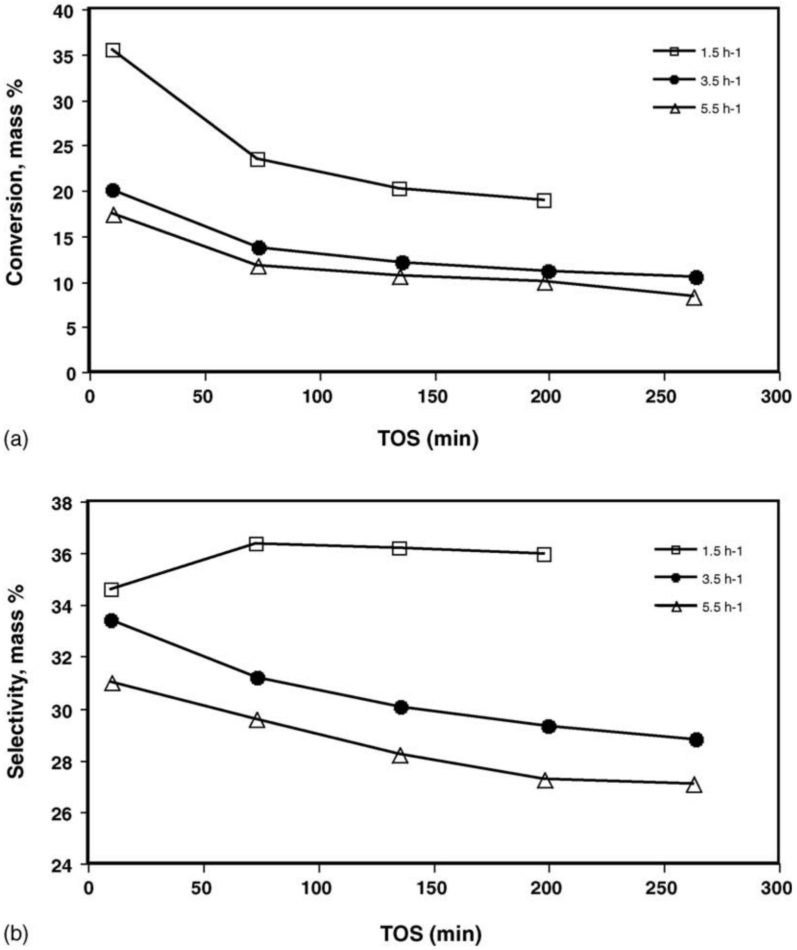

Fig. 4. (a) Effect of WHSV on the conversion of *n*-butane. (b) Effect of WHSV on the selectivity to isobutane.

SAPO-5 without Pt modification showed lower conversion of *n*-butane than Pt modified SAPO-5. The acidity investigation by FT-IR of adsorbed pyridine showed that the Pt-SAPO-5 and SAPO-5 catalysts have weaker Brønsted acid sites than Pt-H-MOR-20 and H-MOR-20 catalysts. The Brønsted acid sites in H-mordenite zeolite catalyst have been reported to be the active sites for conversion of *n*-butane to isobutane [14]. The H-MOR-20 and SAPO-5 catalysts without Pt modification exhibited lower *n*-butane conversion than their Pt modified counterparts indicating clearly the positive role played by Pt in the isomerization of *n*-butane via dehydrogenation and hydrogenolysis reactions over Pt sites to form olefins and then isomerization reaction. H-MOR-20 catalyst also showed deactivation with time on stream due to the coke formation on the strong acid sites. However, modification of H-MOR-20 by Pt decreased the deactivation process (Fig. 3a). Hence it was concluded that Pt sites played significant role in inhibiting the deactivation of Pt-H-MOR-20 catalyst during *n*-butane isomerization. The selectivity to isobutane over H-MOR-20 was similar to that of Pt-H-MOR-20 (Fig. 3b) because of decrease in conversion of *n*-butane with time on stream. A large number of active Pt and acid sites are situated in the channels of H-MOR and Pt-H-MOR-20, however, some of these sites are also on the outer surface of mordenite zeolite. Besides isobutane, other significant products formed over the H-mordenite and Pt-H-mordenite catalysts were methane, ethane, propane, pentane and octane. Some small amounts of ethene, propene and octenes were also formed.

The effect of temperature on the conversion of *n*-butane and selectivity to isobutane was investigated over Pt-SAPO-5 catalyst. It was observed that Pt-SAPO-5 catalyst exhibited increase in conversion of *n*-butane and selectivity to isobutane with increase in temperature (Fig. 3a and b). The Pt-SAPO-5 catalyst however, showed the highest selectivity to isobutane at temperature of 673 K (Fig. 3b). The effect of WHSV at 1.5, 3.5 and 5.5 h^{-1} on the conversion of *n*-butane and selectivity to isobutane was investigated over Pt-H-MOR-20 catalyst at 723 K. The Pt-H-MOR-20 catalyst showed increase in conversion of *n*-butane and selectivity to isobutane with decrease in WHSV (Fig. 4a and b). The Pt-H-MOR-20 catalyst at WHSV of 1.5 h^{-1} showed the highest deactivation, which could be attributed to large amount of coke formation in the pores of 8-membered rings of mordenite zeolite. The large amount of coke formation was confirmed by lower surface area determined for Pt-H-MOR-20 catalyst used at WHSV of 1.5 h^{-1} than the fresh catalyst.

4. Conclusions

The sources of aluminium used in the synthesis of SAPO-5 were found to influence the phase purity, morphology and surface area. SAPO-5 synthesized with pseudo-boehmite as a source of aluminium exhibited the most phase pure SAPO-5, the highest surface area and the presence of Brønsted and Lewis acid sites. SAPO-5 synthesized using aluminium sulphate and sodium aluminate as sources of aluminium did not result in the formation of SAPO-5 phase. The Pt-H-mordenite and H-mordenite catalysts showed higher conversion of *n*-butane, yield to isobutane and selectivity to isobutane than Pt-SAPO-5 catalyst indicating the major role of strong Brønsted acid sites in the isomerization of *n*-butane to isobutane. Pt modified SAPO-5 and mordenite catalysts exhibited higher conversion of *n*-butane, yield to isobutane and selectivity to isobutane than unmodified SAPO-5 and H-mordenite.

Acknowledgements

This work is part of the activities at the Åbo Akademi Process Chemistry Centre within the Finnish Centre of Excellence Programme (2000–2005) by the Academy of Finland.

References

[1] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannana, E.M. Flanigen, J. Am. Chem. Soc. 83 (1982) 1146.
[2] E.M. Flanigen, B.M. Lok, R.L. Patton, S.T. Wilson, in: Proceedings of the Seventh International Zeolite Conference, Tokyo, August 17–22, 1986, p. 205.
[3] M. Höchtl, A. Jentys, H. Vinek, J. Catal. 190 (2000) 419.
[4] N. Kumar, F. Klingstedt, L.-E. Lindfors, in: Proceedings of the Ninth Nordic Symposium on Catalysis (Book of Abstracts), Stockholm, Sweden, June 4–6, 2000, p. 111.
[5] J.M. Campelo, F. Lafont, J.M. Marinas, Zeolites 15 (1995) 97.
[6] P. Meriaudeau, V.A. Tuan, V.T. Nghiem, S.Y. Lai, L.N. Hung, C. Naccache, J. Catal. 169 (1997) 169.
[7] E.J.P. Feijen, J.A. Martens, P.A. Jacobs, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Weinheim, 1997, p. 311.
[8] A. Bhattacharya, J. Das, S. Mitra, S.K. Roy, J. Chem. Technol. Biotechnol. 54 (1992) 399.
[9] J.M. Campelo, F. Lafont, J.M. Marinas, J. Catal. 156 (1995) 11.
[10] T. Xiao, Li-dun, H. Li Nang, Appl. Catal. A: Gen. 130 (1995) 187.
[11] R.A. Asuquo, E.-M. Gabriele, J.A. Lercher, J. Catal. 155 (1997) 376.
[12] C. Bearez, F. Chevalier, M. Guisnet, React. Kinet. Catal. Lett. 22 (1983) 405.
[13] N.N. Krupina, A.Z. Dorogochinskii, N.F. Meged, V.I. Shmailova, React. Kinet. Catal. Lett. 23 (1983) 273.
[14] F. Garin, D. Andriamasinoro, A. Abdulsamad, J. Sommer, J. Catal. 131 (1991) 199.
[15] C.A. Emeis, J. Catal. 141 (1993) 347.
[16] G. Busca, Catal. Today 41 (1998) 191.
[17] E.G. Derouane, L. Baltusis, R.M. Dessau, K.D. Schmit, in: B. Imelik (Ed.), Catalysis by Acid and Bases, Elsevier, Amsterdam, 1985, pp. 135–146.