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Oxidative dehydrogenation of propane on zeolite catalysts

A. Kubacka[a], E. Włoch[a], B. Sulikowski[a,*], R.X. Valenzuela[b], V. Cortés Corberán[b,1]

[a] *Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Cracow, Poland*
[b] *Instituto de Catálisis y Petroleoquímica, CSIC, Campus UAM-Cantoblanco, 28049 Madrid, Spain*

Abstract

Oxidative dehydrogenation of propane has been studied on zeolite Na-Y, stabilized zeolite Y (USY) and ZSM-5. The supports with the faujasite structure were modified with boron, gallium and indium oxides and Ca, Mg, Sn, and Sb cations. The samples containing simultaneously In_2O_3 and Ga_2O_3 in the USY support were compared. A detailed analysis of the zeolite catalysts performance in the title reaction has been carried out. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative dehydrogenation; Propane; Faujasite; ZSM-5; Boron; Calcium; Magnesium; Gallium; Indium; Tin; Antimony

1. Introduction

In recent years there is a pronounced tendency in petrochemical industry to upgrade cheaper feedstocks, and in particular to use alkanes instead of more expensive olefins in many processes [1]. This may be exemplified by the selective oxidation of *n*-butane to maleic anhydride and transformation of ethane and propane to aldehydes, acids or nitriles. The oxidative dehydrogenation (OXD) of hydrocarbons is particularly useful, taking into account the fact that classical dehydrogenation requires much more energy (due to thermodynamic reasons) and is usually performed at temperatures exceeding 600°C. The OXD of alkanes seems to be a very promising process. There are, however, some obstacles to implement successfully such a process. First of all, the olefins formed are much more reactive than the starting alkanes, hence it is very difficult to carry out the dehydrogenation with required selectivity. This problem is connected closely with designing of a proper catalyst for the oxidative dehydrogenation of low molecular weight alkanes. A large number of catalysts have been studied in the OXD of alkanes. They encompass: mixed oxide catalysts (numerous systems containing vanadium [1]), different molybdates and recently zeolitic catalysts.

Two classes of materials that are used extensively as heterogeneous catalysts and for adsorption purposes are microporous (pore diameters <20 Å) and mesoporous (20–500 Å) inorganic solids. The large family of crystalline aluminosilicates (zeolites) and aluminophosphates belongs to the first class, while different inorganic solids to the second. The utility of these materials is due to their structure which allows molecules access to large internal pore system and react there. Major efforts were made in the chemistry of zeolites in order to control the accessibility of their channel system and the concentration of Brønsted acid sites. This can be achieved by affecting the composition of neutralizing cations and/or oxide(s) or other guest molecules located at the *extraframework* positions. It is also possible to manipulate the composition of the zeolitic framework itself, by *isomorphous* substitution of cations of boron, gallium,

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[*] Corresponding author. Tel.: +48-12-6395-127; fax: +48-12-425-1923.
E-mail addresses: ncsuliko@cyf-kr.edu.pl (B. Sulikowski), vcortes@icp.csic.es (V. Cortés Corberán).
[1] Fax: +34-91-585-4760.

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germanium, iron, titanium, vanadium and other onto the tetrahedral framework sites [2].

Our previous contributions were devoted to Ga-FAU [3], B-MFI, Ga-FER and B-BEA systems [4]. In this paper we will explore the oxidative dehydrogenation of propane on faujasite- and ZSM-5-based zeolite catalysts. We will analyse systematically the influence of cations (Mg^{2+}, Ca^{2+}, Sn^{2+}, Sb^{3+}) and oxide phases (Ga_2O_3, In_2O_3 and B_2O_3) dispersed in FAU and MFI type zeolites on their catalytic performance in the title reaction.

2. Experimental

2.1. Samples preparation

Zeolite Na-Y (Si/Al=2.47) was stabilized by a procedure obeying ammonium ion exchange (twice) and calcination under self-steaming conditions at 540°C for 4 h. The sample was ion-exchanged, calcined at 820°C and finally subjected to HCl leaching of aluminium (twice, using 0.1 and 0.2 M HCl) to yield the stabilized USY-ex sample with Si/Al=8.91 and Na/Al=0.003. ZSM-5 (Si/Al=47.6) was twice ion-exchanged with ammonium nitrate, calcined at 550°C and transformed into ammonium form by two additional treatments with NH_4NO_3. The ions of chosen metals were introduced into zeolitic matrices by using standard or contact-induced ion exchange (c.i.i.e.) procedures [5]. The samples containing magnesium and calcium were prepared by fourfold ion exchange from 10% solutions of corresponding nitrates. Na-Y zeolite was impregnated with boric acid solution to give two samples with B/Al=0.147 and 0.274. Tin and antimony were ion-exchanged from $SnCl_2$ and $SbCl_3$ solutions in ethyl alcohol. A series of zeolites modified with gallium and indium was prepared by using c.i.i.e. method [2,5]. The zeolite was ground in an agate mortar with β-Ga_2O_3 and/or In_2O_3. The mixtures were heated in a dry nitrogen flow to 400°C, reduced with hydrogen for 2 h and cooled to ambient temperature in an inert gas flow. The Ga1-USY-ex and In-USY-ex samples had Ga/Al=0.495 and In/Al=0.495. The samples containing both components had all Ga/Al=0.495, while the In/Al ratio was 0.164, 0.328 and 0.495, respectively. The samples were heated in a helium flow for few hours before the catalytic tests. They were checked routinely by XRD for crystallinity and presence of other phases.

2.2. XRD

Powder X-ray diffraction patterns were acquired on a Siemens D5005 automatic diffractometer using Cu Kα radiation (55 kV, 30 mA) selected by a graphite monochromator in the diffracted beam. Silicon powder was used as an internal standard if necessary.

2.3. BET

Sorption of argon was measured in a volumetric sorption unit of standard design. The samples were outgassed at 350°C before the measurement.

2.4. Catalytic tests

A 250 mg-portion of catalyst particles (0.25–0.42 mm) was mixed with double amounts (by volume) of SiC chips (0.5–0.8 mm) and loaded into a down-flow quartz microreactor. Additional amounts of SiC were placed above the catalyst bed to decrease the undesirable gas phase reactions. The propane (99.5%)–oxygen (99.995%) mixture diluted with He (99.999%) was fed into the reactor to give a total flow of 100 cm^3/min. The propane:oxygen:helium ratio in the tests described here was 12:6:82 (by volume), to give W/F=9.204 $g_{catal.}$ h/gmol C_3. The conversion of propane was studied under steady-state conditions, which were established after 10–30 min on stream at given temperature. The conversion of propane was studied at temperatures 400–625°C under the atmospheric pressure. Substrates and products were analysed on-line with a Varian 3400 gas chromatograph equipped with a TCD detector. Two columns loaded with Porapak QS and molecular sieve were used for analysis. Mass and carbon balances were controlled carefully and kept within ±5% error.

3. Results and discussion

The as-prepared samples of zeolite Na-Y, USY-ex and ZSM-5 were, according to XRD, highly crystalline. ^{29}Si MAS NMR spectra of parent zeolite

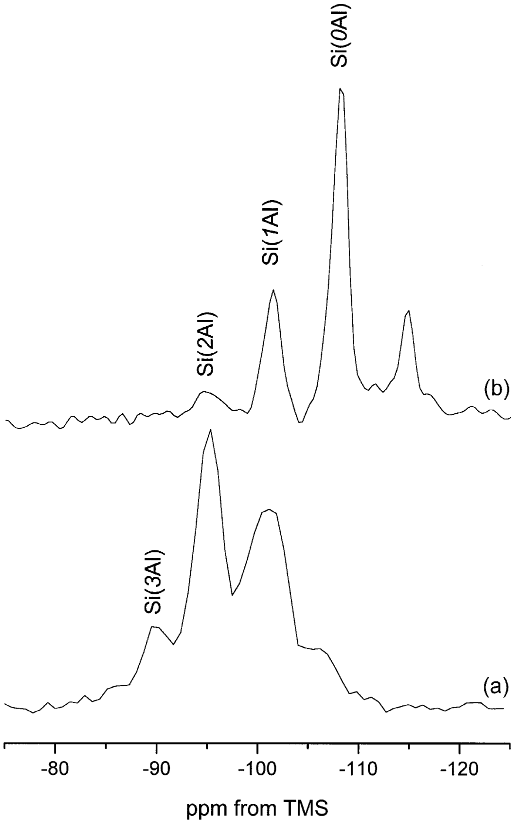

Fig. 1. ^{29}Si MAS NMR spectra of: (a) parent zeolite Y and (b) stabilized zeolite USY-ex.

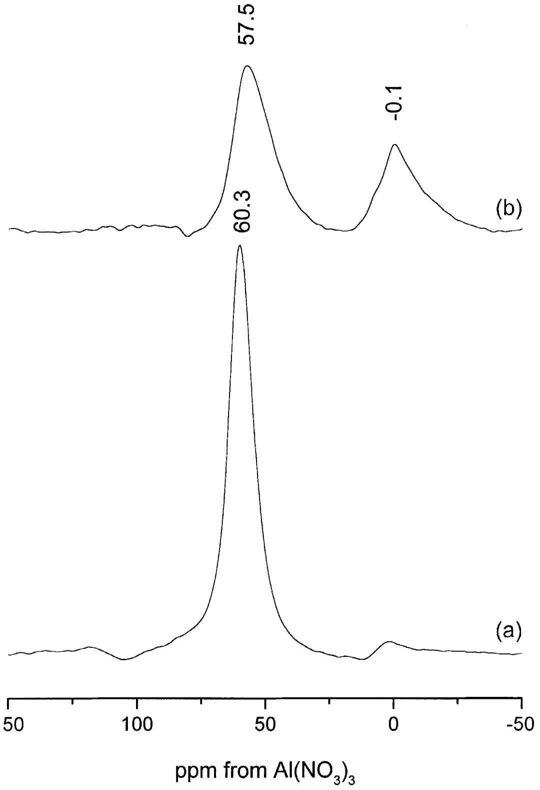

Fig. 2. ^{27}Al MAS NMR spectra of zeolites: (a) Na-Y and (b) USY-ex.

Na-Y and the dealuminated matrix are shown in Fig. 1. As seen, the signals correspond to five possible environments of a silicon atom Si (nAl; $n \leq 4$), where n denotes the number of aluminum atoms connected, via oxygens, to a central silicon atom. The parent sample Na-Y had 55.6 Al in the framework, as evidenced by ^{27}Al MAS NMR spectrum (Fig. 2a). After ultrastabilization procedure followed by acid treatment, the USY-ex support was obtained. Its XRD pattern revealed no loss of crystallinity. The contraction of the unit cell parameter was observed because the Si–O bond is shorter than the Al–O one (Table 1). Thus the ultrastabilization procedure led neither to the amorphization of the solids nor to a decrease in its sorption capacity. Most of the *extraframework* aluminium generated during hydrothermal treatment was removed. In the matrix 14 Al_F/unit cell were found by IR, XRD, ^{29}Si and ^{27}Al MAS NMR methods. As revealed by ^{27}Al MAS NMR, the matrix still contain 5.4 nonframework aluminium per unit cell, which has

Table 1
Characteristics of zeolites

Sample	Si/Al[a]	Lattice constant (Å)[b]	BET_{Ar} (m^2/g)	Al_F/unit cell (average)
Na-Y	2.47	24.690(2)	599	55.6
USY-ex	8.91	24.373(5)	599	14.0
ZSM-5	47.6	a=2.017, b=1.996, c=1.343	309	2.0

[a] Bulk, by wet chemical analysis (AA).

[b] Lattice parameters were calculated for the fully hydrated samples.

not been extracted by HCl. ^{29}Si MAS NMR spectrum of ZSM-5 (not shown) was characteristic for the MFI structure. Only tetrahedral framework aluminium was found in ZSM-5 by ^{27}Al NMR. In Table 1, the properties of zeolites used are listed.

Zeolitic supports have been modified with gallium and indium by extensive use of c.i.i.e. method [2,5]. Cations can usually be introduced into those solids by using aqueous solutions of corresponding salts. The standard ion exchange method has, however, many disadvantages. Large volumes of a salt solution are needed, and the whole procedure must be repeated several times. However, the amount of cations introduced into zeolite is not known, while an estimation of the ion exchange level from the corresponding isotherm requires tedious experiments or additional analysis by other methods. All of these can be avoided by performing c.i.i.e. This is performed by mixing a known amount of a salt (or oxide) with the ammonium or hydrogen form of zeolite at room temperature. The mixture is then calcined at elevated temperature, usually 300–500°C, in an inert gas flow. After evolution of HCl from the system, cations are inserted into the zeolite cationic positions. Provided that a salt is not volatile, the amount of cations is inserted into zeolite stoichiometrically. By using the c.i.i.e. method, the zeolites were modified by gallium(III) and indium(III)oxides. In some experiments two cations were inserted simultaneously into zeolite (Ga, In).

3.1. Zeolite Na-Y modified with boron

Oxidative dehydrogenation of alkanes was previously studied, *inter alia*, on B_2O_3 containing samples. Boron oxide was also used for modification of zeolites at framework and extraframework positions [2,6,7]. Our previous studies were denoted to MFI and BEA structure containing boron [4,8]. It seemed therefore of interest to carry out the OXD of propane on faujasite (FAU) type zeolite containing boron species. For this purpose Na-Y zeolite was mixed with solution of H_3BO_3 and calcined to give a zeolite with a dispersed amorphous B_2O_3 phase. Two samples, with the ratio B/Al=0.147 and 0.274, exhibited very low conversion of propane, one order of magnitude lower than found for the other samples described in this work. The conversion of propane was from 0.1% at 400°C to 1.3% at 550°C, with the selectivity to propene around 50% at 0.5–1.3% propane conversion and no cracking reactions. This is in a striking contrast with the behaviour of other boron-containing samples, [B]-MFI and [B, Al]-BEA. In both cases the conversion of propane was much higher (4–14% in the temperature range 475–600°C) [4]. We note that H_3BO_3 deposited on SiO_2 exhibited very low acidity [9]. Brønsted acidity was only found in the amorphous $Al_2O_3{\cdot}B_2O_3$ system [10]. Zeolite Na-Y does not exhibit Brønsted acidity, thus the samples containing boron resembled essentially the properties of pure B_2O_3 deposited onto the neutral Na-Y zeolite. Very low conversion of propane points to the following observations: (i) oxide boron species supported on zeolite Na-Y behave as an inert component, there is no interaction of B species with the support; (ii) in the temperature range of 400–550°C the radical dehydrogenation of propane is absent or negligible; (iii) no cracking activity confirms that Brønsted acid sites are not present in these samples.

The *extraframework* boron species can be also obtained by heating the zeolites containing initially the *tetrahedral* framework boron (MFI, BEA). The samples obtained in this way exhibit pronounced selectivity to propene at much higher conversion level [4,8]. The boron species in those samples were finely dispersed in the zeolite channels.

3.2. Ca- and Mg-containing faujasite

It is well known that Si/Al ratio is a primary factor which affects physicochemical and catalytic properties of zeolites. We have studied therefore the calcium and magnesium forms of the parent zeolite Y with low Si/Al ratio and also the stabilized form USY-ex with much higher Si/Al (Table 1).

The conversion of propane on the parent and stabilized forms of zeolite Y is shown in Fig. 3, while the selectivity pattern is depicted in Fig. 4. As seen, both solids gave much more pronounced conversion in comparison to samples modified with boron. Two features were found for these samples: (i) the calcium form is more active than the magnesium one and (ii) upon increasing the Si/Al ratio in the zeolitic support, the overall activity of the samples prepared from USY-ex zeolite decreases. The different activity of Mg^{2+} and Ca^{2+} in the zeolites studied may be ascribed to different polarising power of the cation.

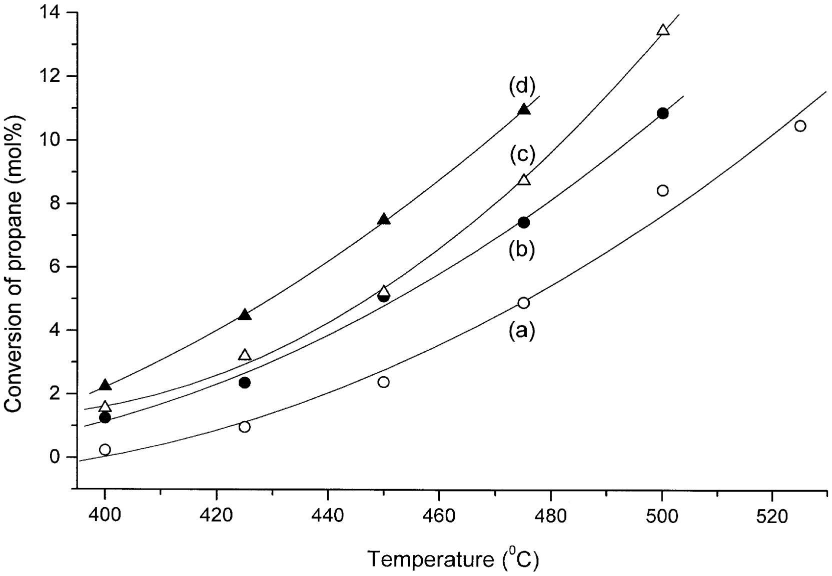

Fig. 3. Oxidative dehydrogenation of propane (OXD). The overall conversion of propane as a function of temperature for samples: (a) Mg-USY-ex, (b) Mg-Y, (c) Ca-USY-ex and (d) Ca-Y. Reaction conditions: 0.25 g of catalyst, propane:oxygen:helium=12:6:82 (by volume), W/F=9.204 $g_{catal.}$ h/gmol C_3.

Interestingly, the selectivity of propene formation, within experimental error, is not affected by the cations present in the standard form of zeolite Y. It is, however, increased considerably (by 20–25%) when the calcium and magnesium cations are ion-exchanged into the stabilized form of zeolite Y. This behaviour is observed for the whole range of propane conversion (Fig. 4c and d).

These experiments clearly show that OXD of propane is catalysed by cationic forms of faujasite

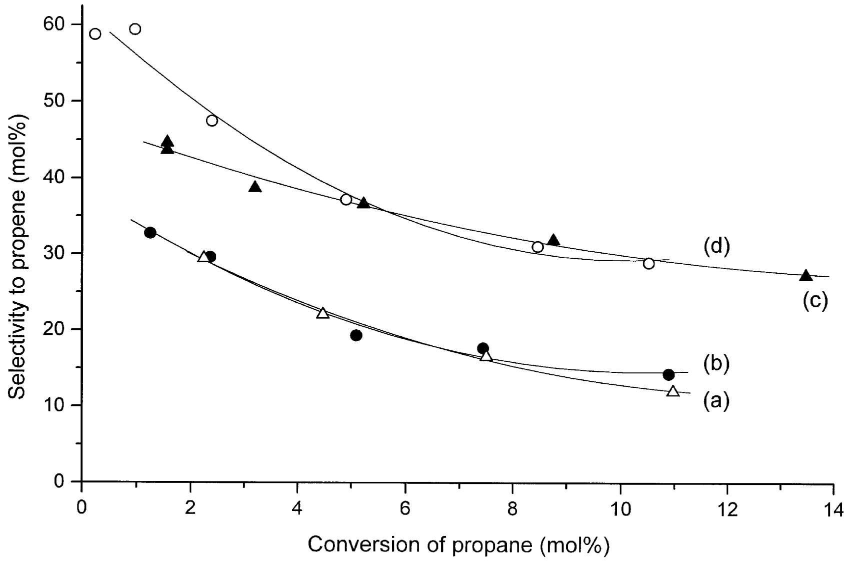

Fig. 4. The selectivity of propene formation for samples: (a) Ca-Y, (b) Mg-Y, (c) Ca-USY-ex and (d) Mg-USY-ex. Conditions as in Fig. 3.

(Ca-Y and Mg-Y). These samples contain therefore active sites needed for dehydrogenation of propane. It is known that pure Ca-Y and Mg-Y forms display medium Brønsted acidity which is due to dissociation of the water molecules on cations. Magnesium forms are also more acidic than calcium ones [11]. It is therefore clear than in the oxidative dehydrogenation of alkanes the acidity, while probably required to some extent, is not a decisive factor determining the overall conversion of propane. The active sites for dehydrogenation are presumably both cations of alkaline earth metals and OH groups situated in the faujasite supercages. As seen in Fig. 4, the selectivity to propene increases sharply from 13 to 15% on Ca-Y and Mg-Y, to about 30% for Ca-USY-ex and Mg-USY-ex (at the 10% conversion of propane). The stabilized form of zeolite Y should be preferentially used to obtain better olefin selectivity. The cations present in the solid have, on the other side, no influence upon experimentally observed selectivity of olefin formation (Fig. 4).

3.3. Sn- and Sb-USY-ex

Tin and antimony are frequent components of dehydrogenation catalysts (vanadium is another one; V-containing faujasites are however not stable thermally). It was therefore of interest to study the Sn- and Sb-forms of the USY-ex matrix. Attempts to insert tin and antimony by c.i.i.e. failed; despite the conditions used an inevitable loss of zeolite integrity was found after the calcination step. The cations were therefore ion-exchanged from the ethanol solutions. Introduction of Sb and Sn from the ethanol solutions prevents probably hydrolysis and formation of the oxide phases deposited inside the faujasite pore system. The XRD and BET measurements confirmed high crystallinity and phase purity of the zeolites (BET$_{Ar}$: 702 m^2/g for Sn-USY-ex and 571 m^2/g for Sb-USY-ex).

The two solids revealed very similar overall activity (6% conversion at 500°C, Fig. 5). It was lower than that found for the calcium Ca-USY-ex (14%) and Mg-USY-ex (9%) samples. Selectivity to propene at 10% conversion level is 28% (Fig. 6).

3.4. Ga-USY-ex and In-USY-ex

Zeolitic matrix USY-ex was loaded with Ga and In by using the c.i.i.e. method. Ga-loaded zeolites were previously studied by different groups (for a review cf. [2]), and were shown to be efficient catalysts both for alkanes dehydrogenation followed by aromatization,

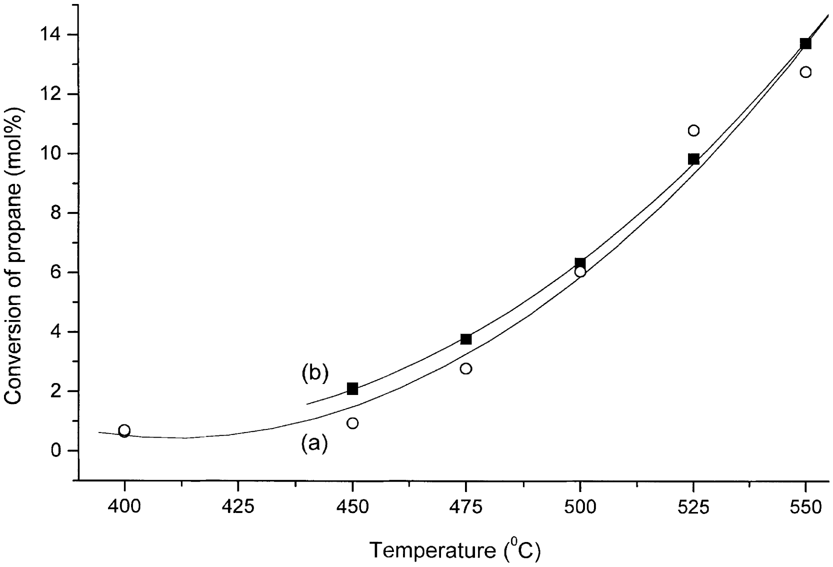

Fig. 5. The overall conversion of propane in OXD for samples: (a) Sb-USY-ex and (b) Sn-USY-ex. Conditions as in Fig. 3.

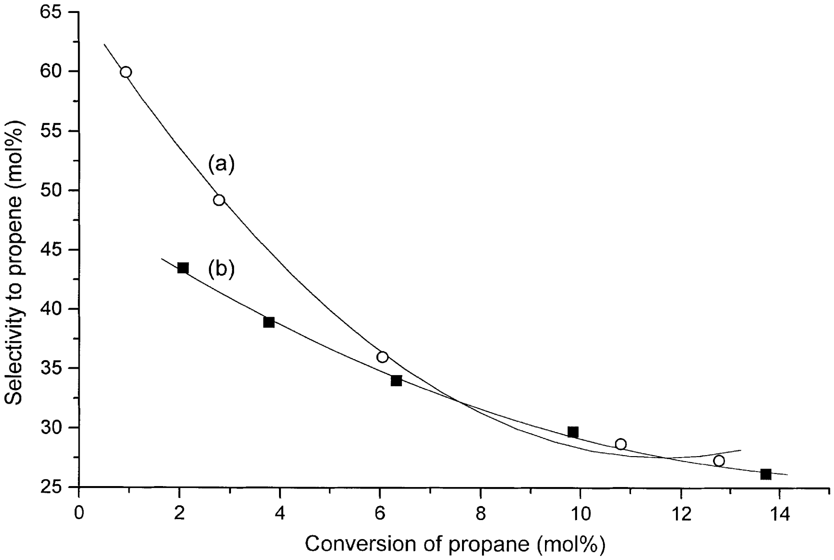

Fig. 6. The selectivity of propene formation for samples: (a) Sb-USY-ex and (b) Sn-USY-ex. Conditions as in Fig. 3.

and also by oxidative dehydrogenation [3,4]. Scarce information on the properties of In-loaded zeolites is available [12,13]. The Ga/Al and In/Al ratio was kept at the same molar ratio of 0.495. The activity of two solids is compared in Fig. 7. As seen, the activity follows essentially the same pattern, the gallium-loaded sample being more active at the higher temperatures. However, the selectivity towards olefin differs significantly (Fig. 8b and e). At 5% propane conversion the selectivity to propene is 35% for Ga1-USY-ex and

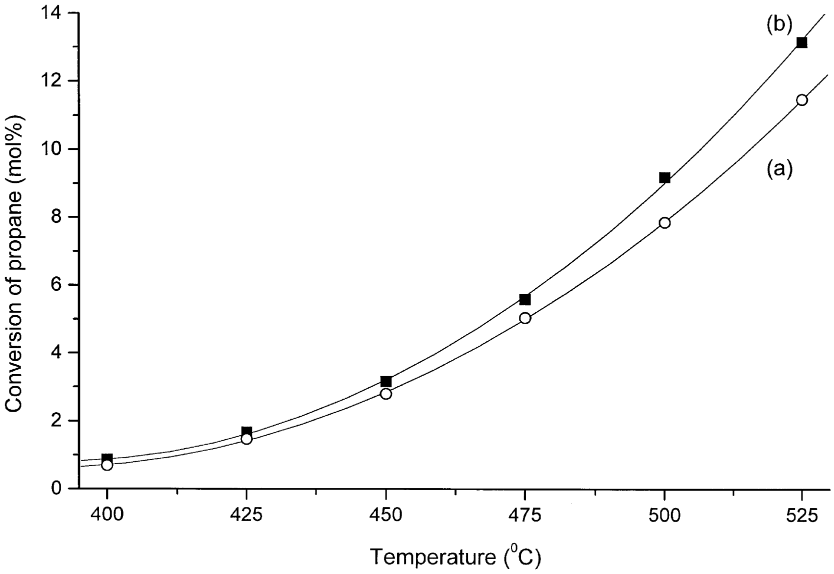

Fig. 7. The overall conversion of propane in OXD for samples: (a) In-USY-ex and (b) Ga1-USY-ex. Conditions as in Fig. 3.

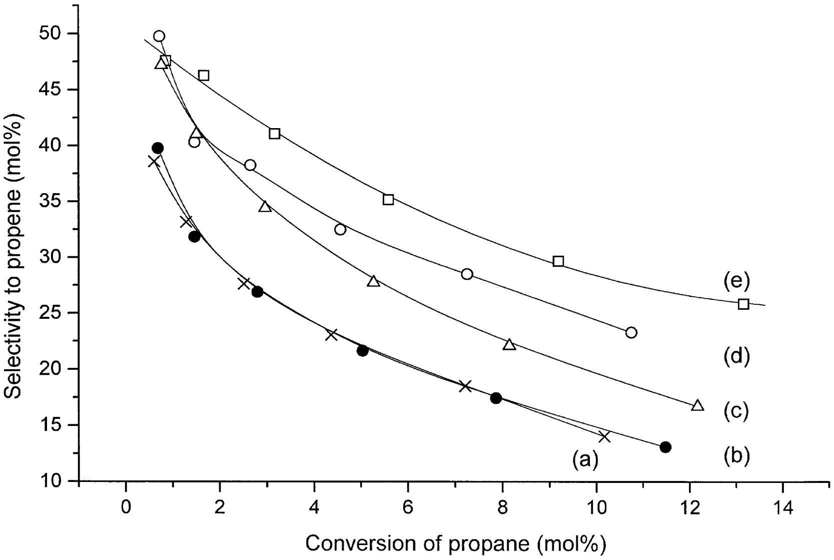

Fig. 8. The selectivity of propene formation for samples: (a) In3Ga-USY-ex, In/Ga=0.495; (b) In-USY-ex; (c) In2Ga-USY-ex, In/Ga=0.328; (d) In3Ga-USY-ex, In/Ga=0.164; and (e) Ga1-USY-ex. Conditions as in Fig. 3.

23% for In-USY-ex. Introduction of indium to faujasite decreases considerably the selectivity. Under the conditions used in this work we did not observe any aromatization activity of the catalysts (as found for Ga-ZSM-5 [12]).

3.5. Ga, In-USY-ex

In a series of experiments we compared the activity and selectivity of In- and Ga-FAU with three catalysts modified *simultaneously* with indium and gallium oxides. As already known from other reactions, a synergetic effect between the cations modifying simultaneously zeolites can be sometimes observed [13,14]. After preparation no other phases were detected in the samples by XRD. As during the preparation of such hybrid catalysts the possibility of blocking pore mouth by clogging with an oxide cannot be excluded, their sorption properties were studied in details using a larger molecule than propane, i.e. isobutane. The adsorption isotherms (calculated in mmol/g of catalyst, not shown), revealed excellent sorption properties. Blocking of zeolitic pore system was therefore not observed. The activity of all the three solids was comparable, while the selectivity patterns were different (Fig. 8a, c and d). For 5% propane conversion it decreased from 33 to 22% upon increasing the indium content in the sample. Thus, in the Ga, In-USY-ex system no evidence of any type of synergism between the gallium and indium species was found. We conclude that the presence of In^{3+} cations, which can be easily reduced to In^{+} and theoretically should form a good redox system, is not beneficial for the reaction studied (at least for faujasite).

3.6. H- and Ga, H-ZSM-5

For MFI system the performance of standard hydrogen form was compared with Ga-containing material. The latter sample was more active, and the selectivity to propene was higher, especially at the higher conversion.

Protolytic dehydrogenation of low molecular weight alkanes on zeolites proceeds probably, according to recent quantum chemical calculations [15], by attack of (acidic) proton from zeolite onto the C–H bond of the alkane. The structure of an activated complex resembles rather a polarized hydrogen molecule placed between the carbenium ion and the negatively charged cluster modelling the zeolite. There is also convincing evidence that protolytic dehydrogenation is not a concerted reaction [15]. Analysis of our experimental

Table 2
Selectivity and apparent activation energy for modified zeolites. Reaction conditions: 0.25 g of catalyst, propane:oxygen:helium=12:6:82 (by volume), $W/F=9.204\ \mathrm{g_{catal.}}$ h/gmol C_3

Sample	Selectivity (%) to propene for 10 mol% propane conversion	Apparent energy of activation (kcal/mol)
Ga-H-ZSM-5	40.4	24.6±0.1
Ca-USY-ex	30.8	22.3
Sb-USY-ex	29.7	24.4
Sn-USY-ex	29.5	22.6
Mg-USY-ex	29.5	24.7
Ga1-USY-ex	28.7	23.6
In1Ga-USY-ex	24.3	23.0
In2Ga-USY-ex	19.9	23.8
In3Ga-USY-ex	14.3	24.2
In-USY-ex	14.8	24.1
Mg-Y	14.7	22.7±0.2
Ca-Y	13.3	21.1±0.2

results showed that the primary parameter, which affects significantly the selectivity towards olefin, is the Si/Al ratio of the zeolite matrix used and its type. In Table 2, the selectivity of propene formation for 10% propane conversion is compared for all the samples. It is readily seen that the selectivity on Ca-Y, Mg-Y and In-USY-ex is the lowest. The selectivity is increased to 29–31% for the stabilized zeolite Y and comparable for the samples modified with Ca, Mg, Sb, Sn and Ga. The influence of indium is detrimental for selectivity, and decreases with the amount of indium introduced in the Ga, In-USY-ex samples.

The active sites for oxidative dehydrogenation of propane on zeolites are presumably cations and oxide species located at the *extraframework* positions in zeolites and OH acidic groups. The reaction mechanism is probably similar on all the samples studied here. Note that the apparent activation energies are very close (Table 2). What is even more interesting is the oxidative dehydrogenation of propane proceeding on zeolites which are modified either with reducible (Ga, In, Sb, Sn) or not reducible cations (Ca, Mg).

4. Conclusions

Zeolite Na-Y containing boron species has very low activity in the OXD of propane. Oxide boron species behave as an inert component not interacting with the zeolitic support. The selectivity of propene formation obtained for 10% conversion of propane are increasing in the following order (when not given, the support is USY-ex):

$$\text{Ca-Y} \sim \text{Mg-Y} < \text{In} < \text{In, Ga} < \text{Ga} \sim \text{Mg} \sim \text{Sn} \sim \text{Sb} \sim \text{Ca} < \text{Ga-H-ZSM-5}$$

The effect of cations upon selectivity to olefin in the stabilized zeolite Y is not significant. The only exception is indium, which decreases olefin selectivity to a large extent. The presence of both In and Ga oxide species is not beneficial for the reaction selectivity. Finally, there is no marked difference in the OXD of propane on the stabilized zeolite Y modified with reducible (Ga, In, Sb, Sn) and not reducible (Ca, Mg) cations.

We have found that a decisive role is played by the zeolitic support, used for the preparation of catalysts for oxidative dehydrogenation of propane, and its Si/Al ratio. The selectivity towards propene is increased in the following order when the amount of framework aluminium in zeolitic matrix is decreased:

$$\text{zeolite Y} < \text{stabilized zeolite USY-ex} < \text{ZSM-5}$$

The apparent activation energies of propane OXD on the zeolite catalysts are from 21.1 to 24.7 kcal/mol.

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