

One-step conversion of *n*-butane to isobutene over H-beta supported Pt and Pt,M (M = Cu, In, Sn) catalysts: An investigation on the role of the second metal

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Abstract

The one-step transformation of *n*-butane to isobutene was studied over H-beta zeolite supported Pt and Pt,M (M = Cu, In, Sn) catalysts. Catalytic performance of monometallic Pt/H-beta samples resulted to be affected by the support acidity, a lower number of acid sites leading to higher *iso*- and *n*-butenes selectivities and lower by-products formation. Addition of Cu, In or Sn to Pt enhanced both isobutene and *n*-butenes selectivities, which were in the order: Pt,In > Pt,Sn ≫ Pt,Cu > Pt. All Pt,M samples exhibited also a higher stability than the corresponding monometallic Pt samples, the sequence of deactivation rates being: Pt > In,Pt > Cu,Pt ≈ Sn,Pt. On the basis of characterization results it was stated that the addition of Cu, In or Sn to Pt affects the *n*-butane dehydroisomerization modifying both the surface structure of Pt clusters and the support acidity. In particular the observed order of isobutene selectivity was related to the degree of Pt–M interaction leading to a dilution of Pt clusters, which inhibits hydrogenolysis reactions and enhances dehydrogenation processes. The decrease in the number of acid sites caused by addition of the second metal was instead accounted for the improved resistance to deactivation of Pt,M catalysts.

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1. Introduction

Isobutene, a key intermediate in the petrochemical industry, is currently produced starting from butanes using a twin reactor system where an isomerization step is followed by a dehydrogenation step or vice versa [1]. Since some years the direct one-step conversion of *n*-butane to isobutene, known as *n*-butane dehydroisomerization, has been reported as an interesting alternative [2–10], with two applicable technologies. The first one involves the use of a two-bed system with a dehydrogenation catalyst in combination with an isomerization catalyst [2,3]; the second approach uses a bifunctional system, usually a Pt/zeolite catalyst [4–10], where Pt provides the dehydrogenation activity while the zeolite supplies Bronsted acid sites, responsible for isomerization. In this context several Pt catalysts have been up to now exploited, e.g. Pt–MOR [4], Pt–ZSM5 [5,6], Pt–ZSM11 [7], Pt–MCM22 [8], Pt–FER [6], Pt–TON [6,9], Pt–FAU [10],

in order to maximize isobutene yield, at the same time minimizing undesired side reactions (cracking, hydrogenolysis and oligomerization), which can be detrimental to catalyst performances.

Bimetallic and multi-metallic catalysts have been extensively studied in recent years due to the fact that they may exhibit better catalytic performances compared to corresponding monometallic samples [11–13]. Pt-based bimetallic catalysts are among the most investigated bimetallics, their use being reported in several industrial processes, such as naphtha reforming and dehydrogenation of heavy and light paraffins [12,13]. Recently, Pt-based bimetallic systems were applied in the direct conversion of *n*-butane to isobutene [9,10]. Derouane-Abd Hamid et al. reported that addition of copper to Pt/H-TON has a positive effect for dehydroisomerization, reducing hydrogenolysis side reactions [9]. Scirè et al. found that Pt,Sn/H-Y catalysts exhibit enhanced isobutene selectivity and resistance to deactivation compared to the corresponding monometallic Pt/H-Y system [10]. The improved performance of Pt,Sn catalysts was accounted for a dilution effect of Pt ensembles and a decrease in the surface acidity of the system both induced by tin [10].

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Table 1
Code, properties and catalytic activity data of supported Pt and Pt-M catalysts

Code	Support	Second metal	H/Pt ratio	NH ₃ adsorbed (mmol g ⁻¹) ^a	V × 10 ⁵ (mol g _{cat} ⁻¹ s ⁻¹) ^b	Activity loss (%) ^c
Pt75	BEA75	–	0.31	0.85	3.6	40
CuPt75	BEA75	Cu	0.27	0.68	3.2	31
InPt75	BEA75	In	0.23	0.77	3.2	35
SnPt75	BEA75	Sn	0.21	0.67	2.9	30
Pt300	BEA300	–	0.24	0.30	2.9	29
CuPt300	BEA300	Cu	0.23	0.27	2.7	20
InPt300	BEA300	In	0.16	0.29	2.5	25
SnPt300	BEA300	Sn	0.11	0.26	2.4	18

^a Estimated by integrating the area of desorption peaks in NH₃-TPD experiments.

^b Reaction rate (*n*-butane conversion) calculated at 550 °C.

^c After 8 h of run.

In this context, we here report a study on the dehydroisomerization of *n*-butane over a series of bimetallic Pt,M (where M=Cu, In, Sn) catalysts supported on H-beta zeolites, with the purpose to get a better insight on the effective role that the addition of the second metal has on activity, selectivity and stability of the catalytic system. Cu (Ib group), In (IIIa group) and Sn (IVa group) have been selected as second metal, choosing among those elements which are inactive towards the considered reaction and have been reported in the literature as affecting positively catalytic performance of Pt catalysts [11–18], being also representative of different periodic table groups. The effect of SiO₂/Al₂O₃ ratio of the zeolite used as support on the performance of catalysts was also investigated.

2. Experimental

Pt and Pt,M (M=Cu, In, Sn) catalysts were prepared by (co)impregnation of the support with aqueous solutions of precursors (Pt=0.5 wt%, M/Pt atomic ratio=0.5). H₂PtCl₆·6H₂O (Alfa Aesar), Cu(NO₃)₂·2.5H₂O (Riedel-de Haën), In(NO₃)₃·5H₂O (Aldrich) and SnCl₂·2H₂O (Fluka) were used as precursor salts. Two H-beta zeolites, provided by Zeolysts, with SiO₂/Al₂O₃ ratios of 75 (BEA75) and 300 (BEA300) were used as support. For comparison H-beta supported monometallic M (M=Cu, In, Sn) samples were also prepared, with a content of M equal to that of corresponding Pt,M samples.

Catalytic activity tests were carried out in a fixed bed reactor operating at atmospheric pressure and at 550 °C, using 50–200 mg of catalyst (80–140 mesh) mixed with 400 mg of quartz of the same grain size. The reactant mixture was 10% *n*-butane, 20% H₂ and 70% He. The total gas flow was varied from 15 to 60 ml min⁻¹ (WHSV ranging from 1.2 to 18.6 h⁻¹ for *n*-butane). Before catalytic tests all samples were reduced at 550 °C in H₂ for 1 h. Reaction products were analyzed with an online gas chromatograph equipped with FID detector. Under experimental conditions used isobutene, *n*-butenes, isobutane and C₁–C₃ hydrocarbons were major products formed. Small amounts of butadiene and pentenes were also detected. Preliminary runs carried out at different flow-rates showed the absence of external diffusional limitations. The absence of internal diffusion limita-

tions was verified by running experiments with crushed pellets at different grain size.

H₂ uptake was measured in a static system operating at room temperature. Before the measurements samples were reduced in H₂ at 550 °C for 1 h, evacuated at 550 °C for 1 h and then cooled at room temperature.

FT-IR spectra were recorded with a Perkin-Elmer System 2000 FT-IR spectrophotometer (resolution of 2 cm⁻¹) using self-supporting pressed discs of the pure catalyst powders (25 mg cm⁻²). The disc, placed in an IR cell, which allows thermal treatments in a controlled atmosphere, was reduced in pure H₂ at 550 °C for 1 h, evacuated at this temperature for 1 h and finally cooled at room temperature. CO (2 mbar) was then adsorbed at room temperature. Subsequent evacuations were then performed at room temperature. Data are reported as difference spectra obtained by subtracting the spectrum of the sample before the admission of CO and are normalized to the same amount of catalysts per cm².

Temperature programmed desorption of ammonia (NH₃-TPD) was carried out in a quartz reactor in a flow of He with a constant heating rate of 10 °C min⁻¹. The desorbed products were detected by a quadrupole mass spectrometer (Sensorlab VG Quadrupoles). Before TPD samples were reduced in flowing H₂ for 1 h at 550 °C, maintained at 550 °C for 1 h in flowing He and then cooled at 30 °C always in a flow of He.

Code of all samples together with measured properties (H/Pt ratio and total amount of NH₃ adsorbed) and main catalytic activity data are reported in Table 1.

3. Results and discussion

The performance of Pt and Pt,M catalysts supported on H-beta zeolites for *n*-butane dehydroisomerization was evaluated at atmospheric pressure and 550 °C. This temperature was chosen on the basis of thermodynamic considerations. Effectively, the top thermodynamic limit of isobutene yield (ca 27%) is reachable at 620 °C, however at this temperature large amounts of butadiene (up to 10%), which is known to rapidly deactivate acid catalysts [5], can be formed. At 550 °C, instead, the yield to butadiene is strongly limited by thermodynamics to less than 2%, whereas achievable yields to isobutene are still of practical interest (ca 20%). It is important to remind that on Pt-free H-beta

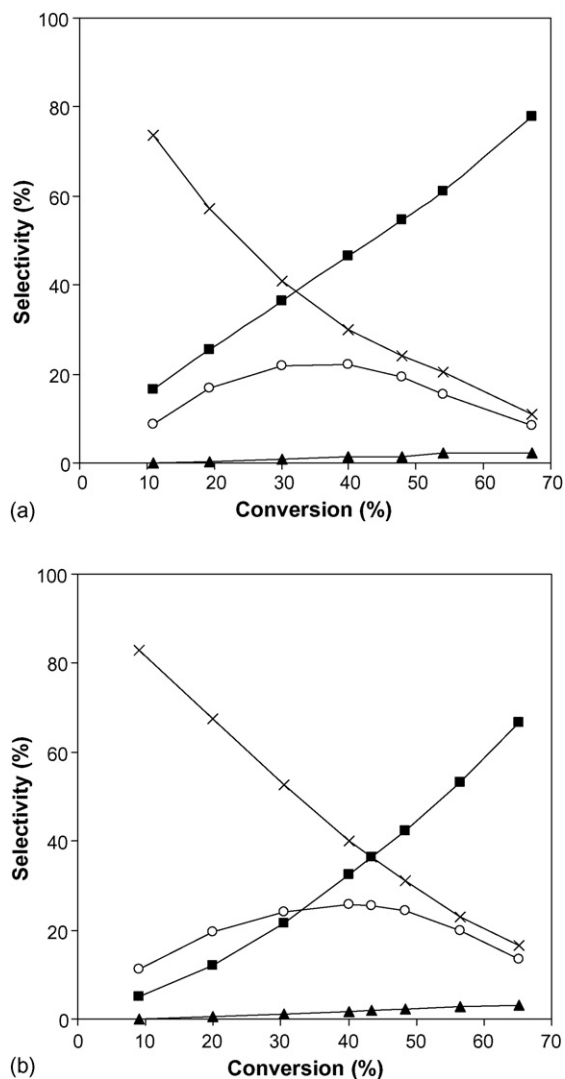


Fig. 1. Selectivities to the major reaction products as a function of *n*-butane conversion levels over monometallic Pt samples: (a) Pt75; (b) Pt300. Selectivity to (○) isobutene; (■) C₁-C₃ hydrocarbons; (▲) isobutane; (×) *n*-butenes.

samples no significant *n*-butane conversion was observed under experimental conditions of this study.

Fig. 1 shows the selectivity to main reaction products (*n*-butenes, isobutene, isobutane and C₁-C₃ hydrocarbons) over Pt75 (Fig. 1a) and Pt300 (Fig. 1b) samples as a function of conversion levels. It can be seen that on both Pt samples at low conversions *n*-butenes are the predominant products (90–100% selectivity can be extrapolated at zero conversion), selectivities to isobutene and C₁-C₃ hydrocarbons are rather low, isobutane selectivity is close to zero. When conversion increases, C₁-C₃ hydrocarbons undergo a rapid and continuous rise, isobutene selectivity increases moderately reaching a maximum at 30–50% conversion then decreasing continuously, isobutane becomes detectable only at ca 30% conversion, remaining always very low (<3%) even at high conversions. These activity data are consistent with the reaction mechanism reported in the literature over H-ZSM5 [5] and H-Y [10] supported Pt catalysts. According to this mechanism, dehydrogenation of *n*-butane to *n*-butenes is a primary reaction step occurring

on Pt metal sites. *n*-Butenes are then isomerized to isobutenes or oligomerized/cracked to form other by-products (mainly C₁-C₃ hydrocarbons) over acid sites of the zeolite. Hydrogenolysis (over Pt sites) and protolytic cracking (over support acid sites) of *n*-butane to C₁-C₃ hydrocarbons are also primary parallel reactions competing with dehydrogenation. Specifically, cracking leads to olefins (or mixture of olefins and alkanes) whereas hydrogenolysis gives alkanes exclusively. Finally the formation of isobutane presumably occurs as a consequence of the rehydrogenation of isobutene over Pt sites. The above mechanism agrees well with the observed difference in product selectivities of Pt75 and Pt300 samples (Fig. 1). A comparison between product selectivities, reported at the same conversion level (Fig. 2), points out, in fact, that a lower amount of C₁-C₃ hydrocarbons is produced on Pt300 with respect to Pt75, with a corresponding higher formation of *n*-butenes and isobutene on the Pt300 sample. It is also noteworthy that the ratio of isobutene to the sum

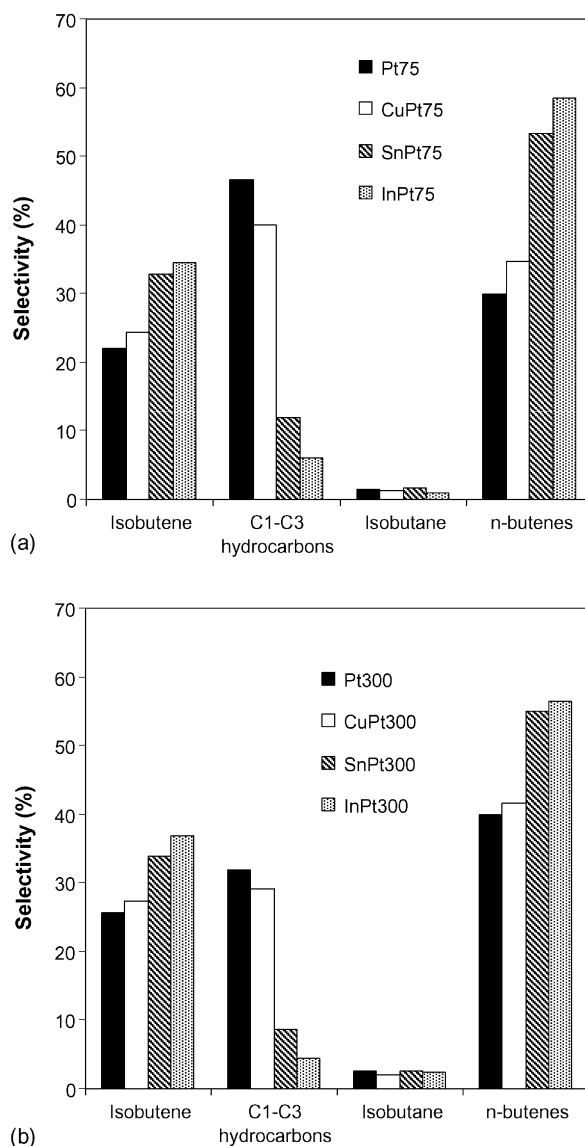


Fig. 2. Comparison among products selectivities at the same conversion level (40%) over: (a) BEA75 and (b) BEA300 supported Pt and Pt,M samples.

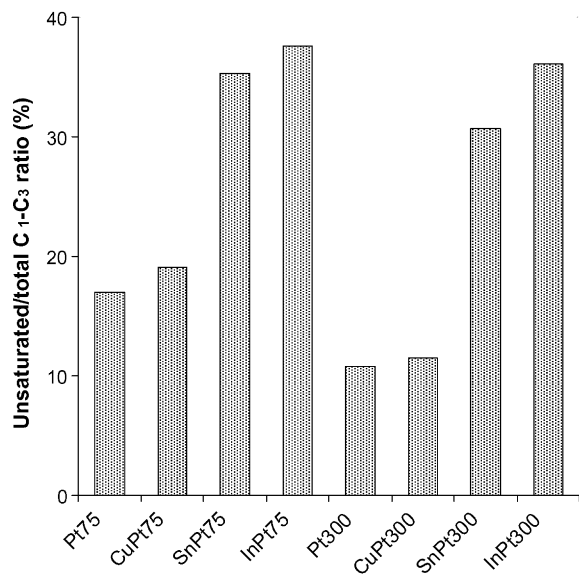


Fig. 3. Comparison among the unsaturated C₁-C₃ fractions (i.e. the unsaturated/total C₁-C₃ percent ratio) over Pt and Pt,M catalysts (all samples are compared at 40% conversion).

of all butenes is higher on the sample supported on the zeolite with lower SiO₂/Al₂O₃ ratio. This behaviour can be rationalized on the basis of the different acidity of the two monometallic Pt samples (see data of NH₃ adsorbed in Table 1), which is a result of the different SiO₂/Al₂O₃ ratio of the supporting zeolite. A higher number of acid sites (Pt75 sample) should promote, in fact, isomerization of butenes, leading to higher iso/normal butenes ratio, but also cracking reactions, resulting in a higher amount of C₁-C₃ by-products. A further confirm to this suggestion derives from the fact that the unsaturated/total C₁-C₃ ratio (Fig. 3) was lower on the Pt sample supported on the zeolite with higher SiO₂/Al₂O₃ ratio (Pt300). Considering that olefins should be formed exclusively through cracking reactions, the above behaviour shows, in fact, that a minor extent of cracking occurs on the less acid monometallic Pt sample. It must be also reminded that Pt dispersion was found to have a role in directing the product selectivity in *n*-butane dehydroisomerization [9,10], larger Pt particles favouring C₁-C₃ hydrocarbons formation. However, in our case, dispersions of the two monometallic Pt samples are close (see H/Pt ratio in Table 1), the small variations not matching the expected effect (the less disperse sample exhibits in fact lower C₁-C₃ production). Therefore this factor cannot be claimed to justify the different product selectivities of Pt75 and Pt300.

With concern to the deactivation behaviour of monometallic Pt samples must be noted that Pt300 exhibits a lower deactivation rate compared to Pt75 (see activity loss in Table 1). The lower stability of the monometallic Pt sample supported on the more acidic zeolite (BEA75) fits also well the reaction mechanism, being accounted for the fact that a higher acidity favours oligomerization reactions which lead to carbonaceous residues, considered responsible of catalyst deactivation [5,9].

Catalytic activity data, expressed in terms of reaction rates of *n*-butane conversion at 550 °C (Table 1) show that addition

of a second metal (copper, indium or tin) to platinum results in a slight decrease (<20%) in the activity of H-beta supported Pt catalysts. Correspondingly, on Pt,M samples a lower H₂ uptake was measured (Table 1), indicating a lower number of Pt active sites exposed on the catalytic surface of doped Pt catalysts. It is important to remind that H-beta supported Cu, In or Sn samples, in the absence of Pt, were unable to promote the dehydroisomerization reaction under experimental conditions used in this work.

An important change in the distribution of reaction products was instead determined by adding a second metal (Cu, In or Sn) to platinum. Fig. 2 shows, in fact, that both on BEA75 (Fig. 2a) and BEA300 (Fig. 2b) supported catalysts selectivities to isobutene and *n*-butenes of Pt,M samples were higher than those observed on the parent monometallic Pt sample, while the formation of C₁-C₃ products was sensibly reduced. The enhancement in the formation of unsaturated C₄ and the corresponding drop in the C₁-C₃ hydrocarbons production was strong in the case of Sn- and In-doped Pt systems whereas was moderate on Cu-doped Pt-samples. In particular, on both series of BEA supported samples isobutene yields were in the order: Pt,In > Pt,Sn >> Pt,Cu > Pt. It is noteworthy that the isobutene yield obtained on the most selective sample (InPt300) was about 15%, value which is sensibly higher than that of monometallic Pt samples (10% maximum) and which can be considered quite satisfactory from a practical point of view, taking into account that the thermodynamic limit under experimental conditions of this work is ca 20%. It is also remarkable that the highest values of isobutene yields up to now reported in the literature for this reaction range from 12 to 14% [5,8,10].

With regard to the deactivation behaviour of bimetallic Pt-M catalysts, the values of activity loss after 8 h of runs, reported in Table 1, clearly show that all bimetallic samples are more resistant to deactivation compared to the corresponding monometallic Pt samples, deactivation rates being in the order: Pt > In, Pt > Cu, Pt ≈ Sn, Pt. It is interesting to note that the above order fits well with that of catalyst acidity, in terms of number of acid sites (see amounts of NH₃ adsorbed in Table 1). This is quite reasonable considering that, as before discussed, acid sites are the main responsible for the formation of carbonaceous residues, which deactivate catalysts [5,9].

In order to comprehend the role of the second metal in affecting the catalytic performance of Pt/BEA system it is necessary to recall the reaction mechanism above discussed. According to this mechanism, in fact, the overall selectivities towards reaction products can depend both on the support acidity and the status of platinum. In our case, data of amounts of NH₃ adsorbed (Table 1) show that addition of Cu, In or Sn to Pt causes a decrease in the total number of acid sites of the system, the resulting order of acidity being on both series of catalysts Pt > In, Pt > Cu, Pt ≈ Sn, Pt. A decrease in the amount of acid sites by tin or indium addition has been reported in the literature in the case of alumina [19] or ZSM5 [10] supported Pt catalysts. Therefore it cannot be ruled out that the lower acidity of Pt,M catalysts can contribute to the minor C₁-C₃ formation over these systems. However it must be stressed that the above order of acidity does not agree with that of selectivity to C₁-C₃ products, which

is instead $\text{Pt} > \text{Cu}, \text{Pt} \gg \text{Sn}, \text{Pt} > \text{In}, \text{Pt}$. Moreover the effect of the second metal on the acidity is moderate in the BEA75 series and really very small in the BEA300 series, being on both cases sensibly lower than that produced by a different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite used as support (compare amounts of NH_3 adsorbed in Table 1). On the contrary the products selectivity is influenced by the addition of the second metal much more than by a change in the acidity of the supporting zeolite. It is also interesting to point out that the internal distribution of $\text{C}_1\text{--C}_3$ products is strongly modified in the presence of the second metal. This is well evidenced in Fig. 3, where the unsaturated/total $\text{C}_1\text{--C}_3$ percent ratio over Pt and Pt,M catalysts is reported (all samples are compared at 40% conversion). From this figure it can be seen that on Pt,M samples, unsaturated $\text{C}_1\text{--C}_3$ fraction is higher than that of the corresponding monometallic Pt sample. This indicates that in the presence of the second metal (Sn and In have the highest effect) the formation of saturated $\text{C}_1\text{--C}_3$ hydrocarbons (due to hydrogenolysis) is preferentially suppressed with respect to that of unsaturated products (due to protolytic cracking). On the basis of this observation it seems reasonable to suggest that the improved isobutene selectivity of Pt,M catalysts in the *n*-butane dehydroisomerization is essentially related to an inhibition of hydrogenolysis reaction, which is known to occur on platinum sites, and therefore is presumably associated with the Pt surface status.

In this context, FT-IR of adsorbed CO is a useful technique to obtain information on surface Pt clusters [20,21]. The FT-IR spectra after CO admission and subsequent outgassing at RT on BEA300 supported Pt and Pt,M samples are compared in Fig. 4. In the same figure it is also reported the spectrum after CO admission and subsequent outgassing at RT on the monometallic Cu/BEA300 sample. It must be reminded that the corresponding spectra of monometallic Sn/BEA300 and In/BEA300 samples are not shown, in so as they do not present CO adsorption bands.

On the monometallic Pt sample (spectrum a) two main bands can be observed, respectively centered at 2075 cm^{-1} (HF band) and 1840 cm^{-1} (LF band). In accordance to the literature the HF band is assigned to CO linearly adsorbed on Pt° , whereas the weaker LF band can be ascribed to bridged CO species on Pt° [22,23].

In the case of Pt,Sn and Pt,In samples (Fig. 4, respectively spectra b and c) the HF band is slightly less intense and ca 5 cm^{-1} downshifted compared to the monometallic Pt sample, whereas the LF band sensibly reduced in intensity (Pt,Sn) or even absent (Pt,In) is absent. This behaviour can be rationalized considering the occurrence of an ensemble effect on Pt,Sn and Pt,In samples, the dilution of surface Pt atoms by not CO-adsorbing atoms (Sn or In) accounting for the preferential suppression of bridged CO species for which the presence of adjacent Pt atoms is required [24,25]. The dilution of Pt by a second metal has been widely reported in the literature [12]. The concomitance of a ligand effect induced by Sn or In cannot be completely ruled out, but appears not consistent with FT-IR results above reported, in so as an electronic Pt–M interaction should mainly affect the HF rather than the LF band [26]. The predominance of an ensemble over a ligand effect agrees with results reported in the literature

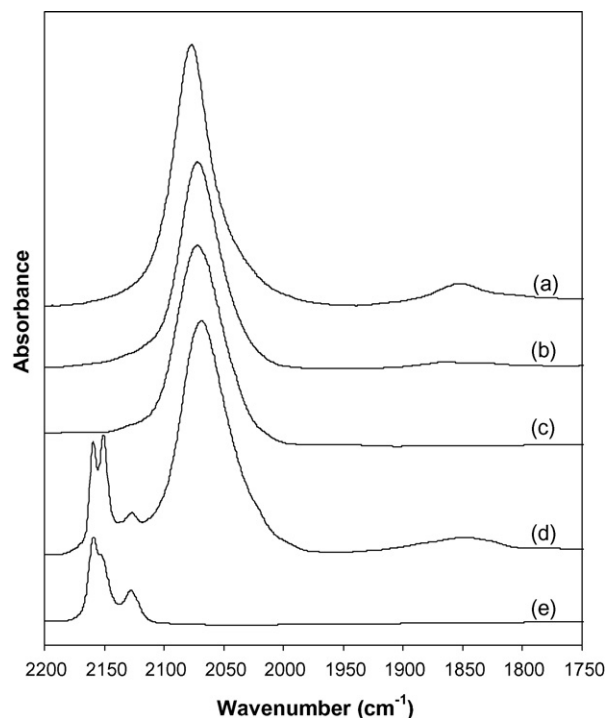


Fig. 4. FT-IR spectra of CO adsorbed on BEA300 supported Pt, Pt,M and Cu catalysts (compared after 10 min outgassing at RT). (a) Pt300; (b) SnPt300; (c) InPt300; (d) CuPt300; (e) Cu/BEA300.

by Meriadeau et al. in the case of Pt,In/NaY catalysts [27]. They found, in fact, that Pt and In form Pt,In bimetallic particles but there was no experimental evidence for a change in the electronic properties of platinum [27].

The FT-IR spectrum of the Pt,Cu sample (Fig. 4, spectrum d) shows the presence of both HF and LF bands related to the adsorption of CO on Pt sites, together with three new bands at 2126 , 2151 and 2159 cm^{-1} . According to the literature [21,28,29], these bands are due to the adsorption of CO on copper sites, as also confirmed by the spectrum of the monometallic Cu/BEA300 sample (Fig. 4, spectrum e), exhibiting the same features with comparable intensities. In particular the 2126 cm^{-1} band can be assigned to the adsorption of CO on partially oxidized copper ($\text{Cu}^{\delta+}$ sites) [21,28], whereas both the 2159 and 2151 cm^{-1} bands can be assigned to CO adsorbed irreversibly on Cu^{1+} species on the ion-exchanging sites of the zeolite, respectively coordinated to two (2159 cm^{-1}) and three (2151 cm^{-1}) lattice oxygen atoms [29]. With regard to the bands of CO adsorbed on Pt sites, it is noteworthy that the HF band shows the same intensity compared to the monometallic Pt sample being ca 10 cm^{-1} downshifted. The LF band is a bit less intense than that observed in the monometallic Pt sample, being however sensibly more evident than on Sn- and In-doped Pt samples. The above FT-IR results point out that on the Pt,Cu sample the dilution of Pt aggregates occurs at a lower extent with respect to Pt,Sn and above all to Pt,In samples. This behaviour can be rationalized if we keep in mind that the extent of formation of bimetallic alloys has been reported to be inversely related to the degree of metal–support interaction [30–32], which there-

fore in our case should be Cu–BEA > Sn–BEA > In–BEA. This order appears to be reasonable considering that copper tends easily to exchange the protons of the zeolite [33], therefore being not more available to form Pt,Cu bimetallic clusters. This is in accordance with FT-IR results of Fig. 4, which point to the presence, both on monometallic Cu and bimetallic Pt,Cu samples, of Cu¹⁺ species on the ion-exchanging sites of the zeolite, with very small amount of Cu⁰ (observable as Cu^{δ+} species). This observation agrees with results reported in the literature for ZSM5 supported Pt,Cu samples, on which platinum and copper species have been found to exist independently in the form of metal Pt particles and CuO [34], due to a strong Cu–support interaction which does not allow the reduction to metallic copper. It must be reminded that FT-IR of CO does not allow to detect Cu²⁺ species, which are not able to irreversibly adsorb CO at RT [35]. Also in the case of zeolite supported Pt,Sn catalysts some degree of interaction between tin and the zeolite has been reported in the literature [10,16,36]. In particular, on Pt,Sn/K-L zeolite, by means of Mossbauer experiments, Cortright and Dumesic found that only a small part of the tin interacts with platinum to form Pt,Sn alloys, while the remainder is present as Sn²⁺ in the L-zeolite [16]. This agrees well with our FT-IR spectra, explaining that the LF band on the Pt,Sn/H-beta catalyst is sensibly less intense compared to the monometallic Pt sample, but it does not completely disappear, as instead it happens over Pt,In/H-beta. In this latter system the highest extent of Pt,M alloy formation observed among all three investigated bimetallic systems is consistent with a very low interaction degree of indium with the zeolite, trivalent ions (as In³⁺) being, in fact, highly hindered from exchanging the zeolite protons [37] and therefore more available to be reduced to the metal form and to alloy with platinum.

4. Conclusions

On the basis of the results reported in this paper it is possible to state that the addition of a second metal (Cu, In or Sn) to Pt/H-beta affects the reaction of *n*-butane dehydroisomerization modifying both the surface structure of Pt clusters and the support acidity. In particular the distribution of reaction products, and therefore the yield to isobutene, is strongly dependent on the extent of the Pt–second metal interaction degree occurring on M-doped Pt samples. When strong dilution effects of Pt clusters induced by the second metal occur (as in the case of Pt,Sn and Pt,In systems), the probability that adjacent Pt atoms can be found on the catalyst surface is strongly reduced. This preferentially inhibits hydrogenolysis reactions, which are structure sensitive and require several contiguous Pt sites [9,10,38], thus enhancing the selectivity for the dehydrogenation reaction that can instead proceed over smaller metal ensembles [4]. The decrease in the number of acid sites caused by addition of the second metal has instead a minor influence on the selectivity of Pt,M samples but appears as the main responsible of the improved resistance to the deactivation of Pt,M catalysts.

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