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Isomerization and hydrocracking of *n*-decane over bimetallic Pt–Pd clusters supported on mesoporous MCM-41 catalysts

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n-Decane hydroconversion has been investigated on bifunctional catalysts comprising bimetallic Pt–Pd clusters supported on an AlMCM-41 ($n_{Si}/n_{Al} = 23$) mesoporous molecular sieve. The catalytic activity of the bimetallic Pt–Pd catalysts is higher than that of the monometallic Pt and Pd catalysts. The good balance between the two catalytic functions, namely acid sites and metal sites, also results in a higher isomer yield at a substantially lower reaction temperature. Moreover, cracking on the metal sites (hydrogenolysis) is largely suppressed over certain bimetallic catalysts.

KEY WORDS: *n*-decane; isomerization; bimetallic clusters; MCM-41; mesoporous molecular sieves.

1. Introduction

Bifunctional metal/acid zeolite catalysts are used in various industrial processes, such as isomerization of C_5/C_6 alkanes, hydrocracking, dewaxing, and isomerization of C_8 aromatics. The hydroconversion of *n*-alkanes is achieved over bifunctional catalysts containing fine dispersed noble metal clusters on a matrix which contains Brønsted acid sites. During the reaction, the noble metal catalyses hydrogen transfer reactions (hydrogenation–dehydrogenation), while isomerization and hydrocracking occur on the Brønsted acid sites [1]. For a catalyst where the metal function and the acid function are well balanced, isomerization and hydrocracking are consecutive reactions and the rate-limiting step is the skeletal rearrangement of the alkenes obtained *via* dehydrogenation over the metal sites, which takes place on the Brønsted acid sites [2].

Platinum- and palladium-containing zeolites are known to give high isomerization yields at medium conversion levels [3], whereas at high conversion level hydrocracking becomes dominant due to faster cracking of the branched isomers. The exact value of the isomerization maximum is expected to be independent of the balance between the two catalytic functions, namely the density and the strength of Brønsted acid sites and the nature, amount and dispersion of the metal. Only little attention has been paid to studying the influence of bimetallic clusters. Zeolite Beta and Y containing Pt–Pd clusters were used for the isomerization of *n*-heptane [4], while Meriaudeau *et al.* [5] investigated the isomerization of *n*-octane over Pt–Pd/SAPO-11 and Pt–Pd/SAPO-41 catalysts.

Since the discovery of the new class of mesoporous materials [6], much research work has been devoted to the evaluation of their catalytic potential. Because of their relatively mild acid sites and the possibility to vary the n_{Si}/n_{Al} ratio in a wide range (~ 10–∞) without significant changes in pore structure, these materials are very attractive model catalysts for the hydroconversion of normal paraffins. Del Rossi *et al.* [7] reported that the selectivity for *n*-hexane isomers is higher on Pt/MCM-41 as compared with amorphous silica–alumina. At equivalent conversion, the yield of cracked products is significantly lower on Pt/MCM-41. The hydroconversion of *n*-hexane was also studied over a series of aluminum-containing MCM-41 materials with different n_{Si}/n_{Al} ratios and varying platinum content by Chaudhari *et al.* [8]. High selectivities for feed isomers were reported for an optimized metal/acid-site ratio. Mokaya *et al.* [2] studied the hydroconversion of *n*-heptane over a series of platinum-containing mesoporous molecular sieves prepared with dodecylamine and found remarkable selectivities for aromatics at higher conversion levels especially when Pt/AlMCM-41 was used as a catalyst. Klemt *et al.* [9] reported recently that NiMo/AlMCM-41/ZSM-5 composite catalysts exhibit a higher activity in *n*-decane cracking and a higher selectivity for monobranched isomers than a NiMo/AlMCM-41 catalyst.

In the present study, Pt- and Pd-containing monometallic and bimetallic clusters supported on aluminium-containing mesoporous molecular sieves (AlMCM-41) were tested in the hydroconversion of *n*-decane. We show that these catalysts can achieve conversions and isomerization yields comparable with zeolites. It was found that catalysts containing both platinum and palladium lead to superior catalytic performances with respect to activity and isomerization yield.

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2. Experimental

AlMCM-41 ($n_{Si}/n_{Al} = 23$) was synthesized using tetradecyltrimethylammoniumbromide (C_{14}TMABr), sodium water glass, sodium aluminate and diluted sulfuric acid according to reference [10]. After synthesis, the sample was calcined at 540 °C for 10 h. The sample was repeatedly ion-exchanged with ammonium nitrate at 40 °C. The metal incorporation was carried out by ion exchange with $Pt(NH_3)_4Cl_2$ and $Pd(NH_3)_4Cl_2$, respectively. To obtain catalysts with similar molar metal loadings, the molecular sieve was loaded with 0.27 wt% Pd, 0.5 wt% Pt and different mixtures of the two metals. The metal precursor was diluted in 50 ml of distilled water and the solution was added dropwise to 1.5 g of the molecular sieve slurried in 50 ml of distilled water. After stirring the solution for 6 h at 40 °C the water was removed in a rotary evaporator at 70 °C under vacuum. Thereafter the samples were dried at 110 °C for 12 h. The resulting materials were pressed without binder at moderate pelletizing pressure, crushed and sieved to obtain catalyst particles with a diameter of 0.25 to 0.355 mm.

The catalytic experiments were carried out in a fixed-bed flow-type apparatus with on-line gas chromatographic analysis of the reaction products. The experiments were conducted at a hydrogen pressure of 1 MPa (10 bar) and the pressure of *n*-decane was adjusted to 10 kPa to obtain a $n_{H_2}/n_{n\text{-decane}}$ ratio of 100. The dry mass of the catalysts and the hydrogen gas flow were adjusted to achieve a modified residence time $W_{cat}/F_{n\text{-decane}} = 400\,\mathrm{g\,h\,mol^{-1}}$. The conversion of *n*-decane was varied by varying the reaction temperature. Prior to the catalytic experiments, the catalysts were dehydrated at 260 °C for 2 h in a flow of argon, activated in oxygen at 310 °C for 4 h and flushed with argon at 410 °C for 4 h. Finally the metal clusters were obtained by hydrogen reduction at 310 °C for 4 h.

3. Results and discussion

The specific surface area ($A_{BET} = 1100\,\mathrm{m^2/g}$), specific pore volume ($V_{pore} = 0.67\,\mathrm{cm^3/g}$) and the pore diameter ($d_{pore} = 2.4$ nm) of the AlMCM-41(23) material used in this investigation correspond well to those data reported in the literature [10]. ^{27}Al MAS NMR spectra (not shown) reveal that aluminum is exclusively tetrahedrally coordinated in the AlMCM-41(23) material. No changes in the Al spectra were observed after ion-exchange, activation of the catalyst and use of the catalyst in the isomerization reaction, respectively.

In figure 1, the results of *n*-decane conversion over bimetallic Pt–Pd catalysts with different n_{Pt}/n_{Pd} ratios are depicted in comparison with the monometallic catalysts. Conversion of *n*-decane over the monometallic catalysts 0.27 Pd/HAlMCM-41 and 0.5 Pt/AlMCM-41 starts at reaction temperatures around 250 °C (figure 1 (left)). For conversions up to 30%, isomerization is the sole reaction. With increasing conversion, hydrocracking of C_{10} isomers occurs as a consecutive reaction. The yield of feed isomers passes through a maximum around 55% and then declines again (figure 1 (right)). These results are in complete agreement with the well-known reaction mechanism for isomerization and hydrocracking of alkanes. It is noteworthy that due to the high reaction

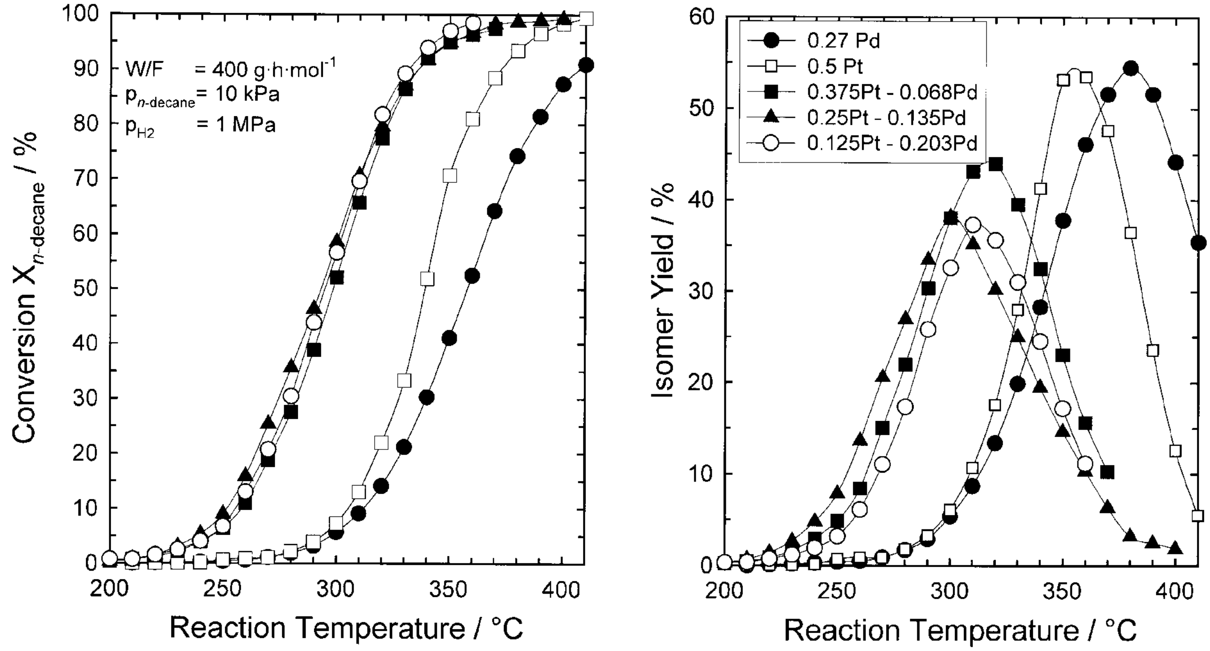

Figure 1. Conversion of *n*-decane (left) and isomer yields (right) as a function of the reaction temperature over Pt–Pd/AlMCM-41 catalysts with different n_{Pt}/n_{Pd} ratios.

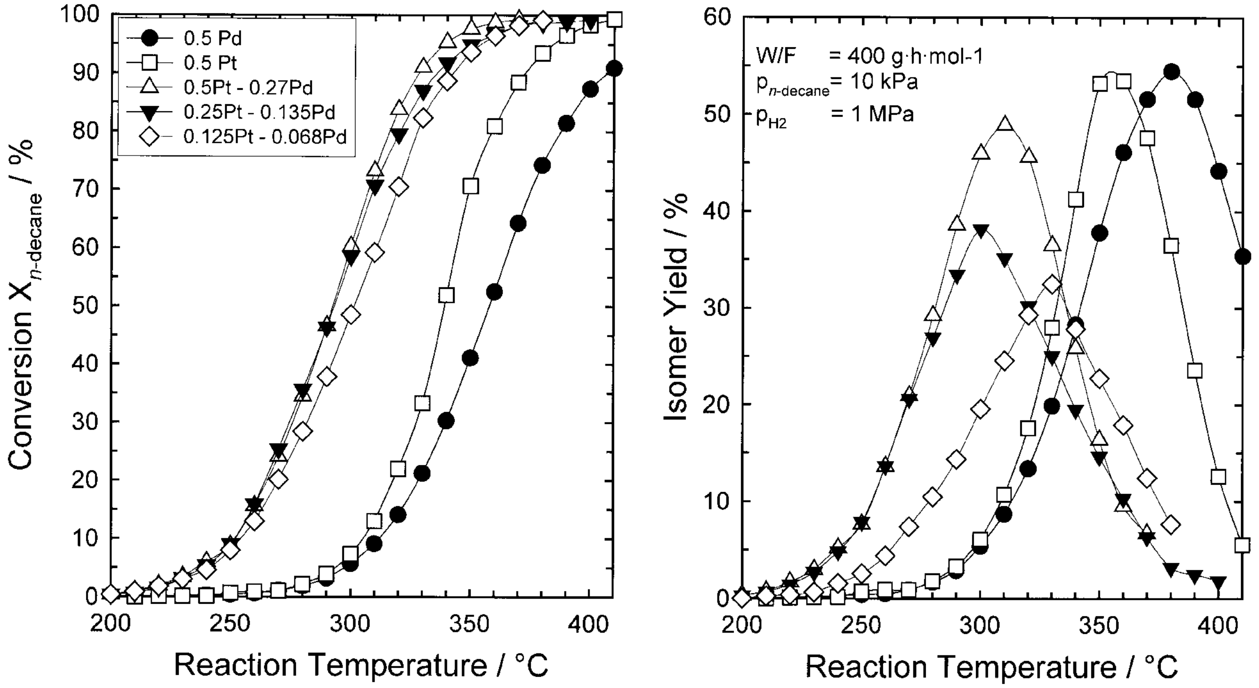

Figure 2. Conversion of n-decane (left) and isomer yields (right) as a function of the reaction temperature over Pt–Pd/AlMCM-41 catalysts with different metal content at a fixed n_{Pt}/n_{Pd} ratio.

temperature needed to achieve full conversion for the monometallic clusters containing catalysts, aromatization also occurs to a significant extent. The yield for substituted benzene isomers (1-ethyl-3,5-dimethyl benzene, 1-ethyl-2,4-dimethyl benzene, 1,2,3,4-tetramethyl benzene and 1,2,4,5-tetramethylbenzene) at a reaction temperature of 410 °C amounts to 8.3% over 0.27 Pd/HAlMCM-41 ($X_{n\text{-De}} = 91\%$) and to 14% over 0.5 Pt/HAlMCM-41 ($X_{n\text{-De}} = 99\%$). Aromatization (on the metal function) is favoured at high reaction temperatures and competes with hydrocracking (on the acid sites).

The bimetallic systems are significantly more active compared with the monometallic catalysts. n-Decane conversion already starts at 200 °C and the maximum yield of feed isomers is already reached at reaction temperatures around 300 °C, which is 50–80 °C below the maximum for the monometallic systems. However, the maximum isomer yield reaches only 45% for the 0.375 Pt–0.068 Pd/AlMCM-41 catalyst and 38% for 0.25 Pt–0.135 Pd/AlMCM-41 (figure 1 (right)). In figure 2, variation of the n-decane conversion (left) and the isomer yield (right) with the reaction temperature as a function of the metal content for the bimetallic Pt–Pd systems is depicted. The activity and the isomer yield increases in the order 0.125 Pt–0.068 Pd/AlMCM-41 < 0.125 Pd–0.135 Pt/AlMCM-41 < 0.5 Pt–0.27 Pd/AlMCM-41.

In table 1, the isomerization, hydrocracking and aromatization yields at the temperature of maximum isomerization yield are compared. A lower temperature at maximum isomerization indicates higher activity. For all catalysts containing bimetallic clusters, the catalytic activity is increased in comparison with the monometallic catalyst. In particular, the catalyst 0.25 Pt–0.135 Pd/AlMCM-41 exhibits superior activity, while the isomerization selectivity is still high. The higher catalytic activity of the bimetallic systems has to be rationalized on the basis of the conventional reaction

Table 1

Yields of isomers ($Y_{iso.}$), cracked products ($Y_{cr.}$) and aromatization products ($Y_{arom.}$) at maximum isomer yield

Metal compound	T_{max}	Conversion (%)	$Y_{iso.}$ (%)	$Y_{cr.}$ (%)	$Y_{arom.}$ (%)	$S_{iso.}$ (%)
0.5 wt% Pt	355	81.0	53.5	24.6	2.9	66.0
0.27 wt% Pd	380	74.3	54.5	17.1	1.4	73.4
0.375 Pt–0.068 Pd	320	77.4	44.0	33.4	0.0	56.8
0.25 Pt–0.135 Pd	300	58.6	38.2	20.4	0.0	65.2
0.125 Pt–0.203 Pd	310	69.6	37.3	32.3	0.0	53.6
0.125 Pt–0.068 Pd	330	82.4	32.4	49.9	0.1	39.3
0.5 Pt–0.27 Pd	310	73.3	48.9	24.4	0.0	66.7
0.5 Pt : 0.27 Pd (50 : 50)	310	76.5	37.7	38.7	0.1	49.3

Table 2
Distribution of the cracked products at a cracking yield $Y_{Cr.}$ of 15%

Metal	0.5 Pt	0.27 Pd	0.375 Pt–0.068 Pd	0.25 Pt–0.135 Pd	0.125 Pt–0.203 Pd	0.125Pt–0.068 Pd	0.5 Pt–0.27 Pd	0.5 Pt–0.27 Pd (50 : 50)
Number of moles/100 moles cracked								
C1	37	7	10	1	9	10	5	11
C2	9	2	8	0.5	8	10	5	9
C3 + C7	45	37	50	26	69	63	43	68
C4 + C6	80	105	95	103	80	73	96	81
C5	43	60	48	71	45	39	53	46
C8	6	0	5	0	6	8	3	6
C9	7	0	4	3	4	5	1	4
Total	227	211	220	204.5	221	208	206	225
% iso in								
C4	42.3	55.48	40.0	68.9	24.0	12.6	55.0	33.0
C5	48.5	57.30	45.0	70.5	30.3	15.8	60.0	39.0

mechanism for the isomerization and hydrocracking of *n*-alkanes as developed by Coonradt and Garwood [1] and Weitkamp [3]. The metal phase dehydrogenates the alkanes to alkenes which are protonated at the Brønsted acid sites yielding alkylcarbenium ions. After rearrangement and/or scissions, these alkylcarbenium ions desorb from the acid sites as alkenes and are hydrogenated at the metal sites to yield saturated alkanes. Consequently, the stability and selectivity of bifunctional catalysts in *n*-decane transformation depend significantly on the balance between metal sites and acid sites. The higher activity of the bimetallic systems (on the same support) is, therefore, tentatively attributed to higher hydrogenation/dehydrogenation activity of the bimetallic Pt–Pd clusters and, hence, a higher concentration of alkenes, which are the intermediates in the hydroconversion of alkanes [3].

The variations of the monobranched and dibranched isomers with the conversion are the same irrespective of the sample considered and are in close agreement with our data on the monometallic catalysts [11]. This illustrates the consecutive nature of the transformation of the monobranched into dibranched and tribranched isomers which is favoured at high temperature. The formation of tribranched isomers is detected only at high temperature and to a small extent. Moreover cracking of dibranched and tribranched isomers is fast compared with cracking of monobranched isomers. Therefore, the selectivity for monobranched isomers is high over the whole conversion range.

Detailed analysis of the cracked products (table 2) shows that methane and ethane formation is significantly reduced for all catalysts containing bimetallic Pt–Pd clusters compared with 0.5 Pt/AlMCM-41. Therefore, hydrogenolysis (cracking on the metal function) does contribute to a smaller extent to the yield of the cracked products, which is probably a consequence of the increased activity at lower reaction temperatures. 0.25 Pt–0.135 Pd/AlMCM-41 and 0.5 Pt–027 Pd/AlMCM-41 exhibit product distributions which are characteristic for ideal hydrocracking, which is further supported by the high selectivity for the iso-isomers in the C_4 and C_5 fraction. It is assumed that these catalysts possess a better balance between the two catalytic functions. Furthermore aromatization is almost completely suppressed, which is a consequence of the reduced reaction temperature and, hence, the improved balance between the acid and metal sites.

The important question whether or not the prepared clusters are truly bimetallic or merely monometallic clusters in sufficiently close neighbourhood is addressed by the experiments shown in figure 3. In this figure, the activity and selectivity of the bimetallic catalysts 0.5 Pt–0.27 Pd/AlMCM-41 are compared with a 50 : 50 mixture of 0.5 Pt/AlMCM-41 with 0.27 Pd/AlMCM-41. While the conversion of *n*-decane is virtually identical for both catalysts, the maximum isomer yield at 310 °C is about 12% higher for the bimetallic system. Detailed inspection of the cracked products (figure 3 (right)) reveals that hydrogenolysis as evident by methane and ethane formation is significantly reduced over the 0.5 Pt–0.27 Pd/AlMCM-41 catalyst. It is therefore clear that the bimetallic catalyst exhibits distinctly different properties compared with the mixture of the monometallic catalysts. Similar results were obtained for Pt–Pd clusters supported on LaNaY [12] and on H-Beta [4]. In the latter case, it was found that substitution of a fraction of the platinum metal with palladium improves the catalytic activity and the isomerization selectivity of *n*-heptane [4]. In the bimetallic catalyst, the dispersion of bimetallic catalysts is significantly higher compared with the monometallic systems, which leads to a better proximity of the metal and acid sites and, hence, a better balance between the metal and acid catalytic function. The improved balance could account for the observed decreased hydrolysis activity and, hence, for the higher isomer yield found. It is generally accepted that a good "balance" between the activity of the acid sites and the activity of the metal sites is important for a high activity of the catalyst and

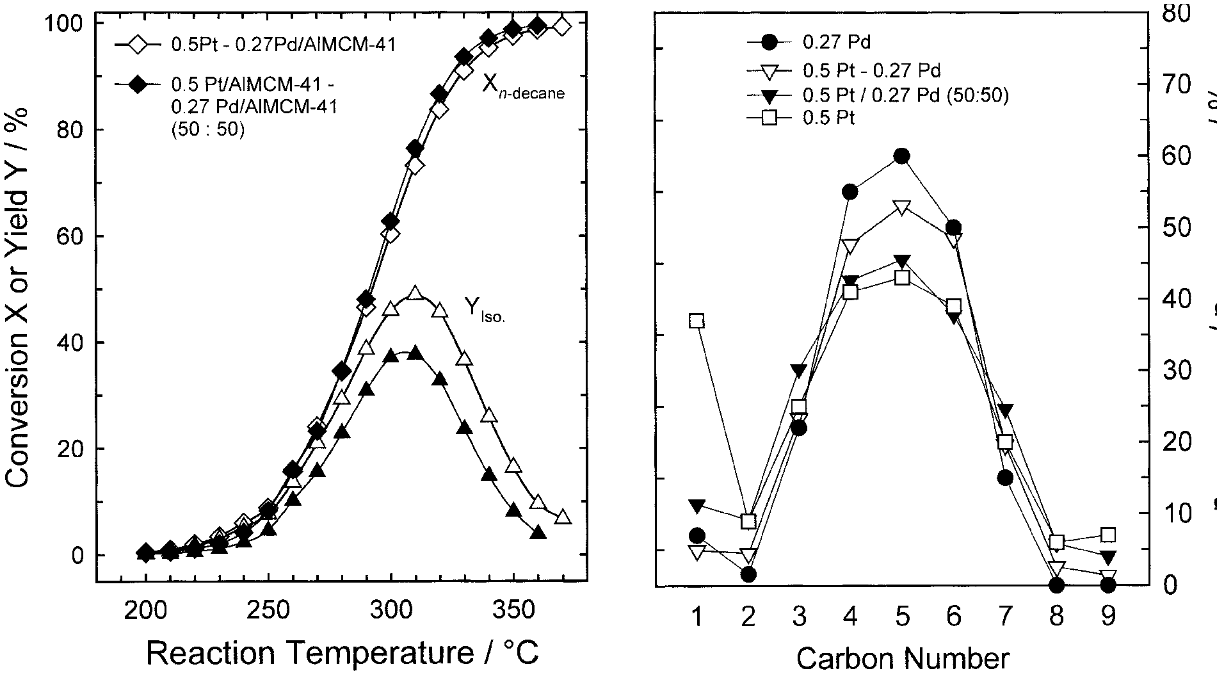

Figure 3. Conversion of *n*-decane (left) and cracked products distribution (right) as a function of the reaction temperature over 0.5 Pt–0.27 Pd/AlMCM-41 and 0.5 Pt/AlMCM-41 : 0.27 Pd/AlMCM-41 (50 : 50) mixture.

a high isomerization yield. Besides the metal dispersion also the distribution of both metals within the bimetallic catalyst is of paramount importance. Fiermans *et al.* [13] have found evidence for palladium segregation to the surface of bimetallic Pt–Pd clusters supported on zeolite Beta. The formation of a platinum core structure was also found for a bimetallic Pt–Pd cluster in zeolite NaY [14]. The observed higher catalytic activity and isomerization selectivity for our Pt–Pd/AlMCM-41 catalysts is presumably a consequence of higher dispersion of both platinum and palladium due to smaller bimetallic clusters. Spectroscopic studies aiming at a clarification of this point are currently underway.

The catalytic activity of the bimetallic systems is comparable irrespective of the composition of the bimetallic clusters and the overall metal content. These results can also be understood on the basis of the conventional bifunctional reaction mechanism. Provided that the reaction is not limited by alkene transport (sufficiently short distances between the two catalytic functions [15]) and the hydrogenation–dehydrogenation activity of the metal function is sufficient to balance the acidity, the rearrangements of the alkylcarbenium ions are the rate-limiting step. Therefore, only minor differences in activity are expected for different bimetallic clusters on the same support.

4. Conclusions

In comparison with monometallic Pd/AlMCM-41 and Pt/AlMCM-41 catalysts, bimetallic Pt–Pd/AlMCM-41 materials are superior bifunctional catalysts for *n*-decane isomerization. The use of bimetallic Pt–Pd clusters results in higher catalytic activity and a higher yield of C_{10} isomers at a substantially lower reaction temperature. This improvement is due to a better balance between the two catalytic functions. Compared with palladium, platinum is a more active hydrogenation/dehydrogenation function, but the realization of sufficient dispersions with current catalyst preparation techniques is difficult. Large platinum clusters catalyse *n*-decane hydrogenolysis, which is significantly reduced for the bimetallic clusters. The reasons for the observed behaviour are currently under investigation.

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