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Enhanced activity and selectivity in *n*-octane isomerization using a bifunctional SCILL catalyst

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1. Introduction

Isomerization of alkanes is an important catalytic process in refineries to improve the Research Octane Number (RON) of the produced gasoline [1]. It is the state-of-the-art in industry to isomerize heterogeneously light naphtha streams with predominantly C₅/C₆ alkanes using bifunctional catalysts, such as e.g. platinum on chlorinated alumina, metal oxide, or zeolite. Carbon deposits on the catalyst can be reduced if these reactions are operated under hydrogen atmosphere. The chlorinated alumina-based catalysts are active below 473 K. A strictly dry and oxygen-free feed as well as a continuous addition of small amounts of organic chlorides are required to maintain the catalyst activity in this process. In an alternative system, metal oxide-based catalysts are applied for the isomerization of light naphtha applying temperatures between 453 and 483 K. These systems are not deactivated irreversibly by water or oxygen but are not as robust and tolerant to coordinating poisons in the feedstock compared to isomerization catalysts containing zeolites. However, the relevant processes using these robust zeolite catalysts are run at significantly higher reaction temperatures (523-643 K) [2].

It would be desirable to extend the isomerization reaction to heavier alkanes (larger than C_6) provided that high isomerization yields with minimum losses by hydrocracking could be achieved.

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ABSTRACT

Bifunctional *Solid Catalyst with Ionic Liquid Layer* (SCILL) systems are presented and applied in the skeleton isomerization of *n*-octane in a slurry-phase reaction mode. It is demonstrated that Pt on silica, coated with a thin film of acidic chloroaluminate ionic liquid exhibits remarkable catalytic performance under mild conditions in the presence of hydrogen. Interestingly, both selectivity and activity of *n*-octane isomerization increase in these systems as a function of hydrogen pressure. This does not only suggest a hydrogenation activity of the catalytic Pt-centers embedded in the strongly Lewis acidic ionic liquid but also a significant increase in the proton acidity in this system as a function of the hydrogen pressure. © 2012 Elsevier Inc. All rights reserved.

> As known from previous literature, the isomerization of C_{7+} alkanes is very different from the isomerization of light paraffins (e.g., $n-C_4-n-C_6$) as cracking becomes increasingly competitive to isomerization as the carbon chain length increases [3]. Moreover, it would be desirable to decrease the reaction temperature of the isomerization as the equilibria to the desired highly branched alkanes (leading to the highest RONs) become more favorable with lower temperature [4] and the tendency for coke formation is greatly reduced.

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Important examples of recent research achievements in the heterogeneously catalyzed hydroisomerization/hydrocracking are briefly presented in the following. The selected examples are grouped according to the different catalyst types applied and they deal with *n*-heptane and *n*-octane as model feedstock to allow direct comparison with our results.

The hydroisomerization of *n*-octane with the hierarchical mesoporous zeolite Pt/ZSM-22 yielded 70% monobranched isomers, 5% dibranched, and ca. 5% cracking products at 80% conversion (*T* = 573 K, *p* = 50 bar, *p*_{H2} = 5 bar, W/F = 14–90 kg s mol⁻¹) [5]. Liquid-phase *n*-octane hydroisomerization in a stirred semi-batch microautoclave was investigated over beta, USY, and mordenite zeolites loaded with 1 wt.% Pt. Best results regarding multibranched isomer selectivity (*S*_{multibranched} = 36.6 mol% and *S*_{monobranched} = 55.7 mol%) were achieved with PtMOR (*T* = 543 K, *p* = 90 bar, conversion = 77.4%, reaction time = 10.5 h, 7 g_{zeolite}/ mol_{*n*-C8}) [6]. Hydroisomerization of *n*-octane was studied kinetically by Chica and Corma using different zeolitic structures with



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large pore sizes (12 MR) [7]. It is evident that at temperatures at which zeolites show catalytic activity, the cracking of mono- and specially dibranched isomers is faster than the isomerization of mono- to dibranched products. With the experimental conditions of this study (T = 493-723 K, $p_{total} = 20$ bar, H_2/n -octane = 10, WHSV = 5.13 h^{-1} referred to *n*-octane), the thermodynamic equilibrium of monobranched products was obtained, but this was not the case for the dibranched products due to fast cracking. The rate of cracking of dibranched products equaled almost the isomerization of mono- to dibranched products. Consequently, high levels of di- or tribranched C₈ alkanes could only be reached by introducing a distillation and recycling unit or by using membrane reactors. Weitkamp et al. elucidated in model compound studies the possibility of isomerizing the C7 cut obtained from atmospheric distillation of crude oil as an alternative to its aromatization [8]. The zeolites 0.27 Pd/LaNaY-72, 0.27 Pd/HMCM-41, and 0.27 Pd/HBeta were used for the hydroisomerization of *n*-heptane $(p_{H2} = 10 \text{ bar}, p_{n-\text{heptane}} = 0.10 \text{ bar}, W/F_{n-\text{heptane}} = 400 \text{ g h mol}^{-1} \text{ with}$ W = dry mass of catalyst). Isomerization of *n*-heptane was found to be possible up to medium conversions without considerable hydrocracking. However, the RON of the resulting isomerization products was much too low (37-43).

Sulfated zirconia was tested in the *n*-octane hydroisomerization by Busto and coworkers [9]. This study aimed for a maximum liquid product yield (C_5-C_8), which was obtained at 18.5% conversion for the Pt/SZ catalyst (T = 573 K, p = 15 bar, WHSV = 4 h⁻¹, molar ratio H₂/*n*-C₈ = 6, time-on-stream = 30 min). Unfortunately, selectivities to mono- and multibranched alkane isomers within the liquid products were not reported in this publication.

Silica-supported tungsten zirconia catalysts were tested in the simultaneous hydroisomerization and hydrocracking of n-octane $(T = 573 \text{ K}, p = 1 \text{ bar}, \text{ WHSV} = 1 \text{ h}^{-1}, \text{ H}_2/n\text{-}C_8 = 6 \text{ mol mol}^{-1})$ for the production of C_4 - C_8 products with high octane number [10]. The catalysts applied in this study deactivated rapidly in the absence of Pt, which is required to hydrogenate coke precursors. $Pt(0,5\%)W^{7.5}Z^{1.0}Si$ performed best in *n*-octane isomerization with the following selectivities within the *iso*-octanes: $S_{\text{monobranched}} =$ 69.5%, $S_{\text{dibranched}}$ = 23.3%, and $S_{\text{tribranched}}$ = 7.2%. Multicomponent nanocomposite catalysts of the type $Pt/WO_3/M-ZrO_x$ were also tested in the *n*-heptane hydroisomerization (398-473 K) [11]. At 398 K under trickle bed conditions, 30% n-C7 was converted with an isomerization selectivity of more than 99% using a Pt/WO₃/ Al-ZrO_x catalyst (p = 8 bar, $H_2/n-C_7 = 1$, volume hour space velocity = 1 h⁻¹). Bifunctional Pt/WO_x-ZrO₂ (Pt/WZr, 12.7 wt.% W) and Pt/Beta (Si/Al = 12) catalysts were studied for the simultaneous *n*-alkane hydroisomerization and aromatic hydrogenation using a *n*-heptane/benzene feed mixture (25 wt.% benzene) at 30 bar, WHSV = 3.1 h^{-1} and H_2 /hydrocarbon = 10 mol mol⁻¹ by Arribas and coworkers [12]. The Pt/WO_x-ZrO₂ (0.6% Pt) yielded 51.7% iso-C7 at 493 K. The obtained heptane isomers contained 30.8% of di-and tri-branched and 69.2% of monobranched products. The experiments with Pt/Beta (1% Pt) resulted in a 49.9% iso-C7 yield at 533 K with selectivities of 27.5% for the multibranched heptanes and 72.5% for the monobranched heptanes.

In a quite different approach, Ohno et al. studied the catalytic properties of H₂-reduced H_xMoO₃ in alkane isomerization in comparison with those of H₂-reduced MoO₃ and 0.01 wt.% Pt/MoO₃ [13]. The latter had the highest activity in *n*-heptane hydroisomerization (96.7% isomerization selectivity at 57.2% conversion; 76.7% monobranched, 19.1% dibranched, and 4.2% tribranched heptanes) at 523 K (atmospheric pressure, molar ratio H₂/C₇ = 10, flow rate of C₇ 0.02 mol h⁻¹). *n*-octane hydroisomerization was also carried out using the metal–acid bifunctional catalyst MoO_{2-x}(OH)_y [14]. This system achieved 73.5% isomerization selectivity at 86.3% conversion, with 50.8% monobranched and 22.7% multibranched isooctanes (*T* = 623 K, p_{H2} = 5 bar, LHSV = 0.8 h⁻¹, H₂/*n*-C₈ = 30.2). The

product mixture included alkanes ranging from C_1-C_8 and small amounts of aromatics.

Another catalyst system for alkane isomerization to mention is the heteropolyacid $H_3PW_{12}O_{40}$ supported on ZrO_2 , SiO_2 , or carbon [15]. These catalyst systems were investigated in the hydrocracking and hydroisomerization of *n*-octane to gain fuel-grade gasoline (C_4-C_7) (T = 573 K, p = 1 bar, WHSV = 1 h⁻¹, $H_2/n-C_8 = 6$). The systems were positively influenced by the addition of Pt with regard to their activity and stability.

The interest in running the alkane isomerization reaction at very low temperatures has triggered attempts in the past to apply highly acidic chloroaluminate ionic liquids (IL) as catalysts for this reaction. Our group demonstrated that catalyst systems of the general type [cation]Cl/AlCl₃ ($x_{AlCl3} > 0.5$) + H₂SO₄ are very effective in *n*-octane isomerization at temperatures as low as room temperature [16]. Interestingly, these systems operate in a liquid–liquid biphasic reaction mode allowing for a straight forward catalyst separation and recycling. Joni and coworkers developed a *Supported Ionic Liquid Phase* (SILP) catalyst based on these acidic chloroaluminate ionic liquids. These authors showed the importance of support pretreatment if acidic chloroaluminate ionic liquids are to be immobilized on high-surface silica materials and the high level of acidity is to be maintained [17].

In the present work, we apply for the first time the *Solid Catalyst* with *Ionic Liquid Layer* (SCILL) catalyst concept to realize a bifunctional catalytic system for the alkane hydroisomerization reaction. In detail, we use Pt on silica (Pt/silica) coated with a highly acidic chloroaluminate ionic liquid ($[C_4C_1Im]Cl/AlCl_3 = 1/2$) for the isomerization of *n*-octane in the presence of hydrogen. The reaction is carried out under moderate temperature conditions ($T_{reaction} = 373-423$ K) and hydrogen pressures of up to 40 bar in a slurry-phase reaction mode (liquid organic phase and solid SCILL catalyst). The beneficial interaction of hydrogen, platinum, and acidic ionic liquid is highlighted by comparing the new bifunctional SCILL catalyst in the presence of hydrogen with the same catalyst in the absence of hydrogen pressure.

For monofunctional catalysts, the SCILL concept has been already successfully demonstrated in a number of studies, mostly for hydrogenation reactions [18–24]. In SCILL catalysis, a traditional heterogeneous catalyst is coated with a thin film of ionic liquid to modify the catalyst's activity and/or selectivity. In particular, significant effects on selectivity have been reported. These effects have been explained by either differential solubilities of the reactants in the ionic liquid layer leading to modified ratios of feedstock and product molecules at the catalytic center or by direct chemical interactions of the IL coating with the active sites of the catalyst. This latter option has been supported by surface science and model catalysis studies revealing distinct interactions of an imidazolium $[NTf_2]^-$ ionic liquid with different catalytic sites of Pd or Pt on alumina [25].

2. Experimental

All steps in the preparation of the catalysts were carried out under inert conditions in a Plexiglas[®] glovebox (GS GLOVEBOX Systemtechnik GmbH) using argon (Linde AG, 4.6) as inert gas.

2.1. Catalyst preparation

2.1.1. Preparation of the Lewis acidic chloroaluminate ionic liquid

The Lewis acidic chloroaluminate ionic liquid $[C_4C_1Im]Cl/$ AlCl₃ = 1/2 was prepared by mixing $[C_4C_1Im]Cl/AlCl_3 = 1/1$ (Sigma-Aldrich, 95%) with an equimolar amount of AlCl₃ (Merck, sublimed, 98%). The mixture was stirred until complete dissolution of the $AlCl_3$ was observed. This acidic chloroaluminate ionic liquid was directly used as monofunctional catalyst in the liquid–liquid biphasic *n*-octane isomerization experiments and for the preparation of the SILP and SCILL catalysts.

2.1.2. Preparation of the SILP and SCILL catalysts

Silica gel 100 (Merck, particle size 0.2–0.5 mm) was used as support for the preparation of the SILP catalyst. The silica gel was calcined prior to catalyst preparation (4 K min⁻¹ \rightarrow 423 K, 2 h isothermal at 423 K, 4 K min⁻¹ \rightarrow 873 K, 12 h isothermal at 873 K, under N₂). Platinum on silica (Pt/silica) (Sigma-Aldrich, 1 wt.% Pt) was used for the preparation of the SCILL catalyst. The Pt/silica was ground, sieved (particle size 125–400 µm), and dried at room temperature under high vacuum overnight prior to catalyst preparation.

As interactions between the acidic IL and the basic surface sites of the silica support would result in a loss of acidity, the silica and Pt/silica materials, respectively, were pretreated according to a method developed by Joni et al. [17a]. In the pretreatment step, silica or Pt/silica, respectively, were impregnated with the acidic IL to eliminate any hydroxyl group or any basic site on the support surface. A defined amount of acidic IL was diluted in dichloromethane (Akzo Nobel, 99.9%, water <20 ppm, solvent purification system applied prior to use) and the silica or Pt/silica, respectively, was added. After stirring this suspension for at least 1 h at 450 rpm, the dichloromethane was removed by evaporation under vacuum. In the next step, the impregnated support was washed with dichloromethane to remove the excess of acidic IL that was not covalently bound to the basic surface sites on the silica support. The pretreated silica and pretreated Pt/silica were used for the preparation of the SILP and SCILL catalyst by impregnating it with a defined amount of acidic IL to reach the targeted IL loading ε (Eq. (1)). According to Eq. (1), the IL loading ε of the SILP and SCILL catalyst is defined as the ratio of the used mass of acidic IL m_{IL} and the total mass $m_{\text{cat,tot}}$ of the SILP and SCILL catalyst, respectively. The obtained catalyst was stored inside the glovebox until usage for the catalytic isomerization experiments.

$$\varepsilon = \frac{m_{\rm IL}}{m_{\rm cat.tot}} \tag{1}$$

2.2. Isomerization experiments

The *n*-octane isomerization experiments were carried out in a 300 ml Parr batch autoclave (see Supporting information for details, Fig. S1). The reactor was equipped with a gas entrainment stirrer and a glass liner. The desired amount of catalyst ([C₄C₁Im]Cl/AlCl₃, SILP, or SCILL catalyst) and n-octane (Merck, 99%) was filled into the glass liner within the glovebox. The defined amount of 1-chlorooctane (Merck, 98%)-if applied-was injected into the organic phase before reaction. The filled glass liner was placed inside the reactor and the reactor was flushed with argon. Prior to heating, the reactor was charged with helium (Linde AG, 4.6) or hydrogen pressure (Linde AG, 5.0) according to the desired reaction conditions ($p_{total} = p_{hvdro-}$ gen + p_{helium}). An external heating jacket and internal cooling coil were used for reactor heating, temperature control, and to ensure isothermal reaction conditions. Upon reaching the reaction temperature, the gas entrainment stirrer was set to 1000 rpm (slurry-phase experiments with SILP or SCILL catalyst) or 1200 rpm (liquid-liquid biphasic experiments), respectively. This moment was defined as reaction start ($t_{reaction} = 0$). Samples of the organic phase were taken during the experiment after 15, 30, 45, 60, 120, 180, and 240 min. The organic product was filled in the sample line under reaction pressure and valve V1 and V2 were closed. The sample line was cooled to T = 268 K to avoid evaporation of light boiling components while sampling. The organic product was released in excess solvent cyclohexane (BASF, 99.9%, water <20 ppm, solvent purification system prior to use) and the resulting mixture was analyzed via gas chromatography (GC).

In order to ensure reproducible data, reproducibility experiments were conducted and the results are shown in the Supporting information (Figs. S2–S7).

2.3. Analytics

2.3.1. Gas chromatography (GC) analysis

All organic product samples were analyzed using a Shimadzu 2010 Plus GC equipped with a CP Sil PONA CS capillary column (50 m × 0.21 mm × 0.5 µm) and a flame ionization detector. Conversion of *n*-octane ($X_{n-octane}$) and selectivity for component *i* (S_i) were calculated according to Eqs. (2), (3), or (4), respectively, with A_i = peak area of component *i*.

$$x_i = \frac{A_i}{\sum_j A_j} \tag{2}$$

$$X_{n-\text{octane}} = 1 - \frac{x_{n-\text{octane}}}{x_{n-\text{octane},0}}$$
(3)

$$S_i = \frac{X_i - X_{i,0}}{X_{n-\text{octane},0} - X_{n-\text{octane}}}$$
(4)

2.3.2. Gas chromatography-mass spectrometry (GC-MS)

To check the intactness of the IL layer of the SCILL catalyst after reaction, the IL layer was removed in a washing procedure with dichloromethane after the experiment. Ca. 50 ml distilled water and 50 ml cyclohexane were added to the removed IL, stirred for 16 h followed by 5 h without stirring for phase separation. The organic phase was analyzed using a Varian 450-GC equipped with a Varian VF-5 ms column (30 m \times 0.25 mm \times 0.25 µm) and Varian 220-MS (ion trap mass spectrometer) with electron ionization.

2.3.3. Electrospray ionization-mass spectrometry (ESI-MS)

ESI–MS measurements of the organic product mixture were taken on an esquire 6000 (Bruker Daltonics Inc.). The organic phase was dissolved in methanol prior to analysis. Scans ranging from 50 m/z to 1500 m/z were achieved with N₂ dry gas, 220 V at capillary exit, and 1562 µs accumulation time.

2.3.4. Inductively coupled plasma atom emission spectroscopy (ICP-AES)

The platinum and aluminum content in the organic product mixture were analyzed by ICP-AES to determine the degree of metal and IL catalyst leaching into the organic product. The acidic IL was analyzed for platinum to exclude dissolution of the platinum from the silica support into the acidic IL. For this analysis, the IL layer was washed off the SCILL catalyst (5 times) after use in catalysis using dichloromethane. The amount of silicon, platinum, and aluminum of the Pt on silica was analyzed as purchased, after pretreatment, after IL impregnation, after reaction, and after removing of the IL with dichloromethane. The analyses were carried out using a Ciros CCD (SPECTRO Analytical Instruments GmbH). The latter was calibrated prior to measurement using plasma standard solutions of platinum (1000 μ g ml⁻¹, Plasma emission standard (ICP) from VWR Prolabo), aluminum (1000 μ g ml⁻¹, Specpure[®] from Alfa Aesar) and silicon (1000 μ g ml⁻¹, Specpure[®] from Alfa Aesar).

2.3.5. H₂ chemisorption

Pulse H₂ chemisorption was performed on a Chembet 3000 (Quantachrome) at T = 273 K. Two independent investigations of the Pt/silica catalyst (1 wt.%) ($d_p = 125-400 \,\mu\text{m}$) were carried out, after drying with argon (Rießner Gase, 4.6, T = 423 K, 10 K min⁻¹,

1 h) and after reduction in hydrogen (10% H₂ in argon, H₂: Rießner Gase, 3.0, argon: Rießner Gase, 5.0; *T* = 473 K, *t* = 0.5 h; desorption under argon flow at *T* = 473 K for 0.75 h). For analysis, pulses of hydrogen in argon (10%) (V_{pulse} = 200 µl, Δt_{pulse} = 3.5 min) were injected.

2.3.6. N_2 adsorption

Specific surface area and pore volume of porous catalyst samples were determined by physisorption of nitrogen using a QUADRA-SORB SI (Quantachrome). Before nitrogen adsorption was carried out at 77 K, the samples were heated under vacuum (Pt/silica and pretreated Pt/silica: 423 K, 4 h). The specific surface area was calculated according to Barrett–Joyner–Halenda (BJH) method and the pore volume with the help of the isotherm at p p0-1 nearby 1.

3. Results and discussion

3.1. Bifunctional SCILL material and its characterization

The hydrogen uptake and dispersion of platinum on the porous silica were determined by H_2 chemisorption of the dried Pt/silica and the reduced one (see Supporting information for details, Table S1). The dispersion of the platinum was found to be in a similar range for both, the dried and reduced Pt/silica. We concluded from this result that the commercial Pt/silica was already in its reduced form. Therefore, the material was applied without further reduction step prior to SCILL preparation.

The bifunctional SCILL catalyst was prepared by taking the commercial Pt/silica material and modifying it with the acidic IL $[C_4C_1Im]Cl/AlCl_3 = 1/2$ after silica pretreatment to neutralize basic surface groups of the silica [17]. The ICP-AES analysis (Pt and Si) of the Pt/silica resulted in a mean Pt value of 0.566 wt.%, which was used for all further calculations (see Supporting information for details, Table S2).

As expected, both the specific surface area A_{BJH} , as determined with BJH method (desorption), and the pore volume V_{pore} decrease if the Pt/silica is pretreated according to the method described by Joni et al. [17] (Table S3, Figs. S8–S10).

The so obtained pretreated Pt/silica was coated with a defined amount of the Lewis acidic ionic liquid $[C_4C_1Im]Cl/AlCl_3 = 1/2$. The applied amount of IL was chosen to obtain a catalyst material with defined IL pore filling degree α (Eq. (5)) and catalyst loading ε (Eq. (1)). The α -value calculation is based on the volume of Lewis acidic IL $[C_4C_1Im]Cl/AlCl_3 = 1/2$ and the pore volume of the pretreated Pt/silica as calculated from the nitrogen adsorption isotherm nearby p p0-1 = 1.0.

$$\alpha = \frac{V_{\rm IL}}{V_{\rm pore}} \tag{5}$$

For the evaluation of all catalytic experiments, a modified reaction time $t_{\text{mod.}}$ (Eq. (6)) was applied, which includes the reaction time t_{reaction} , mass of *n*-octane $m_{n\text{-octane}}$, and the mass of catalytically active Lewis acidic IL [C₄C₁Im]Cl/AlCl₃ = 1/2 m_{IL} (mass of IL used in liquid–liquid biphasic experiments or used for the impregnation of the SILP and SCILL catalyst).

$$t_{\rm mod} = t_{\rm reaction} \cdot \frac{m_{\rm IL}}{m_{n-\rm octane}} \tag{6}$$

3.2. Catalytic experiments with monofunctional, Lewis acidic IL in liquid–liquid biphasic reaction mode under various hydrogen pressures

The first set of catalytic experiments applied a monofunctional, Lewis acidic IL catalyst in liquid–liquid biphasic reaction mode for



Fig. 1. Influence of hydrogen partial pressure on *n*-octane conversion for the monofunctional, Lewis acidic IL catalyst using different amounts of the promoter 1-chlorooctane; conditions: $[C_4C_1Im]Cl/AlCl_3 = 1/2$, $T_{reaction} = 393$ K.

n-octane isomerization. No metal catalyst and porous support were applied in these experiments. Fig. 1 indicates the influence of hydrogen partial pressure ($p_{hydrogen} = 0-40$ bar) on *n*-octane conversion at 393 K for two different amounts of the promoter 1-chlorooctane ($n_{Cl-octane}/n_{AlCI3} = 0.036$ and 0.36). From the results, it is evident that the presence of hydrogen and the level of hydrogen pressure do not result in significantly higher catalytic activity. The higher conversions obtained for the higher level of the 1-chlorooctane promoter (compare results with $n_{Cl-octane}/n_{AlCI3} = 0.36$ vs. $n_{Cl-octane}/n_{AlCI3} = 0.036$ in Fig. 1) can be rationalized by the higher concentration of carbenium ions in the system.

The carbenium ions are generated directly by the reaction of 1chlorooctane with the Lewis acidic IL $[C_4C_1Im]Cl/AlCl_3 = 1/2$ and represent the active species in the isomerization/cracking reaction sequence. The promoting effect of chloroalkanes in acidic chloroaluminate ionic liquids observed here was already demonstrated by our group in a previous publication [26] (see also Supporting information for details, Fig. S11) and was first described by the group of Jess for the alkylation of isobutane and 2-butene [27].

Selectivity to *iso*-octanes was found to be a function of *n*-octane conversion but independent on the hydrogen partial pressure for this monofunctional, Lewis acidic IL catalyst (Fig. 2). Thus, hydrogen does not act as cracking inhibitor in the case of the monofunctional Lewis acidic IL catalyst. According to Weitkamp [3], the rate of β -scission of carbenium ions is drastically increased if the number of C atoms in the respective alkane is ≥ 8 . This conclusion derived from hydroisomerization studies using zeolite catalysts



Fig. 2. Influence of hydrogen partial pressure and *n*-octane conversion on selectivity to *iso*-octanes for the monofunctional Lewis acidic IL catalyst using different amounts of the promoter 1-chlorooctane; conditions: $[C_4C_1Im]Cl/AlCl_3 = 1/2$, $T_{\text{reaction}} = 393$ K.

seems also to be valid for the highly acidic IL and is indicative for an ionic mechanism of cleavage. Once the carbenium ions are generated, consecutive cracking reactions of mono- and dibranched octane isomers are faster than hydride transfer from molecular hydrogen to generate the branched high-octane products. The decrease of selectivity to branched octanes with increasing *n*-octane conversion is in excellent agreement with this mechanistic interpretation.

3.3. Pt/silica catalyst for n-octane isomerization

As expected, the untreated and uncoated Pt/silica catalysts ($\varepsilon = 0$, $\alpha = 0$) show no catalytic activity for *n*-octane conversion under hydrogen atmosphere ($T_{\text{reaction}} = 393$ K, $p_{\text{hydrogen}} = 40$ bar, $m_{\text{Pt/silica}} = 10.4$ g, $n_{\text{Cl-octane}}/n_{\text{AlCl3}} = 0.36$, $t_{\text{reaction}} = 4$ h). Due to the lack of any sufficiently acidic site in this system, no carbenium ions are generated and no alkane isomerization is observed.

3.4. SCILL catalyst ($[C_4C_1Im]Cl/AlCl_3$ on Pt/silica) for n-octane isomerization

3.4.1. Influence of hydrogen partial pressure on activity and selectivity of the bifunctional SCILL catalyst

In the next set of experiments, the influence of hydrogen partial pressure ($p_{hydrogen} = 0$, 15, and 40 bar) on activity and selectivity of the bifunctional SCILL catalyst was investigated in the hydroisomerization of *n*-octane (*T* = 393 K and $n_{\text{Cl-octane}}/n_{\text{AlCl3}}$ = 0.036). The results are depicted in Fig. 3. They reveal a remarkable dependence of the catalyst's activity on the hydrogen partial pressure. Obviously, higher hydrogen partial pressures result in a significant increase in *n*-octane conversion and *iso*-octane selectivity. At a hydrogen partial pressure of 40 bar, the *n*-octane conversion was 73.7% after 4 h reaction time, while in the absence of hydrogen, the conversion was less than 20% under otherwise identical conditions. Comparing these results with the outcome of the reactions with the same acidic ionic liquid in liquid-liquid biphasic mode (see Fig. 1, n_{Cl-octane}/ n_{AICI3} = 0.036), it is evident that the bifunctional SCILL system provides a much more active and selective catalyst system. A rise in total pressure from 15 to 40 bar helium in the absence of hydrogen shows no significant effect on *n*-octane conversion.

Apart from the strongly enhanced activity, the almost parallel shift of the *iso*-octane selectivity in the $S_{iso-octane}/X_{n-octane}$ -plot with rising hydrogen partial pressures is highly remarkable (Fig. 4). At the same level of *n*-octane conversion, a hydrogen partial pressure of 15 bar increases the selectivity toward *iso*-octanes by an absolute value of 10% compared to the reaction in the absence of hydrogen. Comparing the reaction at a hydrogen partial pressure



Fig. 3. Influence of the hydrogen partial pressure on *n*-octane conversion over modified reaction time; conditions: $m_{SCILL} = 20$ g, $[C_4C_1Im]CI/AlCI_3 = 1/2$, $\varepsilon = 0.5$, $\alpha = 0.85$, $T_{reaction} = 393$ K, $n_{Cl-octane}/n_{AlCI_3} = 0.036$.



Fig. 4. Influence of the hydrogen partial pressure on the selectivity to *iso*-octanes over *n*-octane conversion; conditions: $m_{SCILL} = 20$ g, $[C_4C_1Im]Cl/AlCl_3 = 1/2$, $\varepsilon = 0.5$, $\alpha = 0.85$, $T_{reaction} = 393$ K, $n_{Cl-octane}/n_{AlCl_3} = 0.036$.

of 40 bar with the hydrogen-free system, this difference increases to an absolute value of up to 15%. Like in the case of *n*-octane conversion, the effect of total pressure on the selectivity has been checked by pressurizing the system to the same values with helium (15 and 40 bar) but in this case, the selectivity effect was negligible.

3.4.2. Influence of the reaction temperature on activity and selectivity of the SCILL catalyst

To investigate the influence of the reaction temperature on the activity and the selectivity of the SCILL catalyst, hydroisomerization experiments were carried out between 373 K and 423 K. Fig. 5 shows the conversion of *n*-octane as a function of the modified reaction time. As expected from the Arrhenius law, the reaction rate of the SCILL-catalyzed reaction and thus the conversion of *n*-octane over time increases with higher reaction temperature. Remarkably, the selectivity toward *iso*-octanes was found to be nearly identical for all three temperatures at comparable *n*-octane conversions (see Fig. 6). This indicates that, at least within the considered temperature range, the selectivity toward *iso*-octanes is independent on the applied reaction temperature.

3.4.3. Comparison of bifunctional SCILL and monofunctional SILP catalysis in n-octane isomerization

To further elucidate the remarkable performance of the bifunctional SCILL catalyst under hydrogen pressure and to underline the necessity of all three essential components of the catalytic



Fig. 5. Influence of reaction temperature on *n*-octane conversion over modified reaction time; conditions: $m_{SCILL} = 20$ g, $[C_4C_1Im]CI/AICI_3 = 1/2$, $\varepsilon = 0.5$, $\alpha = 0.85$, $p_{hydrogen} = 40$ bar, $n_{CI-octane}/n_{AICI_3} = 0.036$.



Fig. 6. Influence of reaction temperature on selectivity to *iso*-octanes over *n*-octane conversion conditions: $m_{\text{SCILL}} = 20 \text{ g}$, $[C_4C_1\text{Im}]\text{Cl}/\text{AlCl}_3 = 1/2$, $\varepsilon = 0.5$, $\alpha = 0.85$, $p_{\text{hydrogen}} = 40 \text{ bar}$, $n_{\text{Cl-octane}}/n_{\text{AlCl}_3} = 0.036$.

system—platinum, Lewis acidic chloroaluminate IL, and hydrogen—comparison experiments with a Pt-free, monofunctional, solid supported system (SILP catalyst) were carried out. All experiments were conducted at 373 K. For both the bifunctional SCILL system and the monofunctional SILP system, the effect of hydrogen vs. helium pressure was investigated (Figs. 7 and 8). The SILP and



Fig. 7. Comparison of *n*-octane conversion over modified reaction time for the SILP catalyst under hydrogen atmosphere ($p_{hydrogen} = 40$ bar) vs. the SCILL catalysts under helium ($p_{helium} = 40$ bar) and hydrogen atmosphere ($p_{hydrogen} = 40$ bar); conditions: [C₄C₁Im]Cl/AlCl₃ = 1/2, $T_{reaction} = 373$ K; SILP: $m_{SILP} = 23$ g, $\varepsilon = 0.4$, $\alpha = 0.85$; SCILL: $m_{SCILL} = 20$ g, $\varepsilon = 0.5$, $\alpha = 0.85$.



Fig. 8. Comparison of selectivity to *iso*-octanes as function of *n*-octane conversion for the SILP catalyst under hydrogen atmosphere ($p_{hydrogen} = 40$ bar) vs. the SCILL catalysts under helium ($p_{helium} = 40$ bar) and hydrogen atmosphere ($p_{hydrogen} = 40$ bar); conditions: [C_4C_1 Im]CI/AICI₃ = 1/2, $T_{reaction} = 373$ K; SILP: $m_{SILP} = 23$ g, $\varepsilon = 0.4$, $\alpha = 0.85$; SCILL: $m_{SCILL} = 20$ g, $\varepsilon = 0.5$, $\alpha = 0.85$.

SCILL catalysts under investigation were loaded with the same mass of Lewis acidic IL after the support pretreatment [17] and exhibited the same pore filling degree α . (For details of the silica support characterization, see Supporting information, Table S4, Fig. S12–S14.)

Interestingly, the catalytic results showed very similar results for the SILP catalyst under hydrogen atmosphere as for the SCILL catalyst under helium. This behavior suggests that the bifunctional SCILL catalyst—with platinum as differentiating factor—acts like the monofunctional SILP catalyst in the absence of hydrogen. Thus, the presence of Pt becomes only relevant if the reaction is carried out under hydrogen pressure and only the presence of hydrogen, platinum on support, and acidic ionic liquid leads to a significant increase in catalytic activity.

The fact that the SCILL system shows significantly higher *n*octane conversion and selectivity to iso-octanes in the presence of hydrogen in comparison with the SCILL catalyst under helium atmosphere further confirms the importance of hydrogen activation by the catalytic Pt-center for the observed reactivity. According to the mechanism of isomerization, the *n*-octane molecule is converted first to an unbranched octanyl cation by hydride abstraction through a highly acidic proton or by another carbenium ion. The octanyl cation undergoes isomerization to form a branched octanyl cation. The latter can react via hydride transfer with any alkane of the reaction mixture to yield the corresponding branched octane isomer and a new carbenium ion. However, besides the desired hydride transfer, the branched octanyl cation can also undergo undesired side reactions. These include cracking reactions via βscission or alkylation reactions of carbenium ions with certain amounts of olefins that are formed e.g. by deprotonation of carbenium ions (Scheme 1) [28] or cracking [3]. Both reactions decrease the selectivity to branched iso-octanes significantly.

In the presence of hydrogen, Lewis acidic ionic liquid, and active platinum centers, most of the olefin formed by deprotonation is likely to be hydrogenated prior to the undesired alkylation reaction. This hydrogenation activity explains the higher selectivity to *iso*-octanes. The role of hydrogenation reactions in the bifunctional SCILL system can also be recognized by monitoring the total reactor pressure during the different isomerization experiments (Fig. 9). The hydrogen pressure of the experiment conducted with



Scheme 1. Equilibrium reaction of carbenium ion and olefin in acidic media [28].



Fig. 9. Reactor pressure over modified reaction time for SILP ($p_{hydrogen} = 40$ bar) and SCILL catalysts under hydrogen and helium atmosphere ($p_{hydrogen} = 40$ bar and $p_{helium} = 40$ bar); conditions: [C₄C₁Im]Cl/AlCl₃ = 1/2, $T_{reaction} = 373$ K; SILP: $m_{SILP} = 23$ g, $\varepsilon = 0.4$, $\alpha = 0.85$; SCILL: $m_{SCILL} = 20$ g, $\varepsilon = 0.5$, $\alpha = 0.85$.

the SCILL catalyst showed a notable continuous decrease, while the pressure in the two comparison runs—monofunctional SILP under hydrogen and bifunctional SCILL under helium—remained almost constant (the little jags in the graphs are due to reactor sampling). Only in the presence of Pt and hydrogen, the hydrogenation of ole-fins that are formed via β -scission of carbenium ions or by carbenium ion deprotonation takes place and results in steady hydrogen consumption throughout the reaction time. Note that no net hydrogen consumption should be observed if olefins are hydrogenated that are formed by deprotonation of a carbenium ion, as the released acidic proton will typically react with an alkane to yield a new carbenium ion and hydrogen molecule (see Supporting information for details, Scheme S1).

While the hydrogenation activity gives a good explanation for the improved selectivity of the bifunctional SCILL system, it does not explain vet its much higher activity. The fact that the catalytic activity correlates also strongly to the level of hydrogen partial pressure (see Fig. 3) suggests that the concentration of acidic protons and thus the acidity of the catalytic system increases if hydrogen dissolved in the Lewis acidic ionic liquid is in contact with the active platinum center. It is known that hydrogen can homolytically split on platinum [29]. The catalytic result is in line with the interpretation that in the strongly Lewis acidic environment of the chloroaluminate melt, electron transfer may lead to the formation of Pt-hydride and additional protons in the IL. This interpretation is supported by the fact that 1-chlorooctane added to the bifunctional SCILL system causes no additional enhancement of the catalytic activity (see Supporting information for details, Figs. S15 and S16). Obviously, the amount of carbenium ions formed from hydrogen at the catalytic Pt-center is dominating the catalytic activity of the system.

3.5. Comparison of the product distributions for the bifunctional SCILL catalyst vs. liquid–liquid biphasic catalysis

Fig. 10 represents the composition of the octane isomers as a function of *n*-octane conversion for the slurry-phase experiment using the bifunctional SCILL catalyst and the liquid–liquid biphasic experiment using the monofunctional Lewis acidic IL alone ($p_{hydrogen} = 40$ bar, T = 393 K). Both catalyst systems yield only monobranched and dibranched octane isomers in very similar distributions. The absence of even higher branched octane isomers is due to their high cracking rate.

When comparing the composition of the alkane products with carbon chain length other than C_8 , differences between the



Fig. 10. Composition of the formed branched octane isomers as a function of *n*-octane conversion for the monofunctional IL catalyst and for the bifunctional SCILL catalyst; conditions: $[C_4C_1Im]CI/AICI_3 = 1/2$, $T_{reaction} = 393$ K, $p_{hydrogen} = 40$ bar; SCILL catalyst: $m_{SCILL} = 20$ g, $\varepsilon = 0.5$, $\alpha = 0.85$, $n_{CI-octane}/n_{AICI_3} = 0.036$; IL catalyst: $m_{IL} = 10$ g, $n_{CI-octane}/n_{AICI_3} = 0.36$.



Fig. 11. Composition of by-products (carbon fraction in the respective by-product fraction) as a function of *n*-octane conversion for the monofunctional IL and the bifunctional SCILL catalyst. The fractions contain *n*- and *iso*-alkanes. The sum of all fractions adds up to 100%; conditions: $[C_4C_1Im]CI/AICI_3 = 1/2$, $T_{reaction} = 393$ K, $p_{hydrogen} = 40$ bar; SCILL catalyst: $m_{SCILL} = 20$ g, $\varepsilon = 0.5$, $\alpha = 0.85$, $n_{CI-octane}/n_{AICI3} = 0.036$; IL catalyst: $m_{IL} = 10$ g, $n_{CI-octane}/n_{AICI3} = 0.36$.

bifunctional SCILL catalyst and the liquid-liquid catalysis with the acidic IL can be observed. In Fig. 11, the selectivities for products of different chain lengths are given as their fractions in total carbon. For the SCILL catalyst, the fraction of propane and butanes within the by-products increases, while the fraction of pentanes, hexanes, and heptanes decreases compared to the monofunctional Lewis acidic IL catalyst. The fraction of the by-products with a chain length higher than C₈ is unaffected. The differences in the distributions of the by-products can again be explained by the hydrogenation activity of the Pt-containing catalyst. While the shorter chain by-products (C_3-C_4) are mainly formed by β -scission, the formation of by-products with a higher chain length requires a combination of alkylation and cracking reactions. The alkylation reactions are dependent on the existence of olefines, which are formed by cracking reactions via B-scission or by deprotonation of carbenium ions. In the presence of platinum and hydrogen, a significant part of the olefins is hydrogenated. With decreasing concentration of olefins, the alkylation rate decreases leading to a lower fraction of C_5-C_7 products. For both the monofunctional and the bifunctional catalyst, the formed by-products consist mainly of branched alkanes (around 90% iso-alkanes and 10% n-alkanes).

3.6. Catalyst stability

An important aspect for the further development of these bifunctional SCILL systems toward technical applications is the stability of the catalyst. ICP-AES analyses of the product proved that no platinum and aluminum leach into the organic phase (Table 1). As no aluminum leaching is observed, we conclude that no Lewis acidic IL is lost to the product phase during reaction. This indicates that the very unpolar feedstock/product phase is not able to dissolve the ionic liquid off the support. Moreover, the results indicate that the ionic liquid physical adsorption on the support is strong enough to avoid removal of ionic liquid droplets from the support.

In addition, the platinum leaching into the immobilized acidic IL was analyzed. The question whether the Pt stays on the support

Table 1ICP-AES (Pt and AI) results of the organic and removed IL phase.

Element	Analyzed phase	Leaching (wt.%) (referred to total Pt, Al)	Detection limit (wt.%) (referred to total Pt, Al)
Pt	Organic	-	0.03
Al	Organic	-	0.03
Pt	Ionic liquid	0.21	0.03

Table 2

ICP-AES (Pt, Si, and Al) results of the applied Pt on silica material, SCILL catalyst before reaction (ε = 0.5, α = 0.85), SCILL catalysts after reaction, and removal of acidic IL.

Entry	Sample	Pt/Si ratio (mol mol ⁻¹)
1	Pt/silica (mean value)	1.76×10^{-3}
	Standard deviation (for mean value calculation)	1.03×10^{-3}
2	SCILL catalyst, before reaction	$1.36 imes 10^{-3}$
3	SCILL catalyst, IL washed off	$1.52 imes 10^{-3}$

(the bifunctional SCILL concept) or dissolves in the acidic ionic liquid during reaction (leading to a bifunctional SILP concept) is of conceptual importance. In the SCILL case, the support material is of direct relevance for the nature of the catalytic Pt-center, while in the SILP case, only the embedding ionic liquid defines the reactivity of the dissolved Pt-complexes. The platinum leaching into the ionic liquid layer was checked in two independent ways: (a) the acidic IL was removed after reaction from the support by a washing procedure with dichloromethane and the washing solution was checked for its Pt-content by ICP-AES; (b) the Pt/Si ratio of the applied Pt on silica catalyst was determined by ICP-AES prior to the IL coating and after catalytic reaction and removal of the ionic liquid. The results are given in Table 2. The deviation of the Pt/ Si ratio of SCILL catalyst and Pt/silica (entry 1, 2 and entry 1, 3, respectively) is higher than the standard deviation of the Pt/silica mean value calculation (Table 2). This fact indicates small amount of platinum leaching from the silica into the Lewis acidic IL, which is proved by the ICP-AES results (0.21 wt.% of the total Pt) of the washed-off acidic IL. The Pt leaching can take place during pretreatment or during catalysis. However, it is important to note that by far the largest part of the platinum remains on support, making the whole catalyst a true bifunctional SCILL system.

To exclude the theoretical possibility of chlorine insertion from the chloroaluminate IL into the organic products, the organic phase (experiments without 1-chlorooctane addition) was analyzed by ESI–MS. The chlorine concentration was found to be clearly below the detection limit as no characteristic chlorine peaks $(m_1/z + 2 = m_2/z)$ were found in the mass spectrum (see Supporting information for details, Fig. S17).

Typical heterogeneous, state-of-the-art isomerization/cracking catalysts operate at much higher temperatures than the here presented SCILL systems. Therefore, the deposition of heavy products on the catalytic surface and coking is a major deactivation path in these high temperature systems. To demonstrate the advantage of the SCILL systems operating at mild temperatures in this respect, the ionic liquid was tested after reaction for any accumulation of high boiling, unsaturated, or cyclic by-products. The removed IL from the SCILL catalyst (washing procedure with dichloromethane) was contacted with an excess water to hydrolyze the IL anion. The resulting aqueous solution was extracted with cyclohexane, and the organic extraction phase was investigated for all organic products accumulated in the IL phase during reaction. The highest m/z ratio found in the mass spectrum in this analysis was 164, which might originate from cyclic unsaturated hydrocarbons. However, this mass and the respective size of the molecule are still small enough to expect this species to be in extraction equilibrium with the organic product phase. Thus, accumulation of carbon-rich species in the SCILL system or coke formation can be excluded under the conditions applied in this study. Catalyst stability including coke formation under extended operation or in a continuous reaction mode has not been investigated up to now.

3.7. Catalyst recycling

The recycling of the catalyst is an issue of practical relevance. The results discussed in chapter 3.6 already demonstrate the



Fig. 12. Comparison of *n*-octane conversion over modified reaction time for three catalytic runs with the same SCILL catalyst; conditions: $m_{SCILL} = 12$ g, $[C_4C_1\text{Im}]Cl/AlCl_3 = 1/2$, $\varepsilon = 0.5$, $\alpha = 0.85$, $T_{\text{reaction}} = 373$ K, $p_{\text{hydrogen}} = 40$ bar.



Fig. 13. Comparison of selectivity to *iso*-octanes as function of *n*-octane conversion for three catalytic runs with the same SCILL catalyst; conditions: $m_{SCILL} = 12$ g, $[C_4C_1Im]CI/AICI_3 = 1/2$, $\varepsilon = 0.5$, $\alpha = 0.85$, $T_{reaction} = 373$ K, $p_{hydrogen} = 40$ bar.

stability of SCILL catalysts as no Al and Pt can be detected in the organic product phase after reaction. Consequently, the recyclability of the SCILL catalysts under hydrogen atmosphere was tested in two recycling runs (see Figs. 12 and 13). For the recycling experiments, most of the organic phase was drawn off with a syringe from the SCILL catalyst after settling time at ambient reaction conditions and replaced with new *n*-octane. A small amount of organic matter left in the glass liner acted as protective liquid layer for the SCILL catalyst during loading of *n*-octane. It was unavoidable that some amount of the solid SCILL catalyst sticking to the stirrer and cooling coil were shortly exposed to air while the organic phase was changed in the glass liner.

Conversion of *n*-octane decreases slightly with every catalyst recycling from 9.6% (recycling run 0) to 8.4% (recycling run 1) and finally 6.6% (recycling run 2) after 2 h reaction time. In contrast, the curve of *iso*-octanes selectivity over *n*-octane conversion is almost identical for all three catalytic runs (Fig. 13). These results indicate the recyclability of the SCILL catalyst. Losses in catalytic activity can be ascribed to the deactivation of SCILL catalyst that came in contact with air during the recharging procedure.

4. Conclusion

Bifunctional Solid Catalyst with Ionic Liquid Layer (SCILL) systems composed of Pt on porous silica coated with a thin layer of acidic chloroaluminate ionic liquid exhibit surprising catalytic performance in the isomerization of *n*-octane in the presence of hydrogen at moderate reaction conditions. Our investigations reveal that all components, the platinum on the solid support. the Lewis acid ionic liquid coating, and the hydrogen pressure in the system are critical to realize the observed enhancements in catalytic activity and iso-octane selectivity. While the selectivity effect is understandable from the fact that the Pt-centers in the system act as hydrogenation catalysts to decrease the concentration level of olefinic intermediates in the system (thus reducing consecutive alkylation steps), the increasing catalytic activity with increasing hydrogen partial pressure is very remarkable. Based on the known fact that catalytic activity in skeleton isomerization of alkanes is primarily a function of acidity, it is reasonable to assume that the special combination of the immobilized Pt nanocrystals embedded in the highly acidic ionic liquid may lead to a heterolytic cleavage of dissolved hydrogen forming surface bound Pt-hydride and additional protons during reaction. At least, the obtained catalytic results indicate a gradual increase of the systems acidity with increasing hydrogen pressure. This observation alone may open new and interesting research perspectives for the near future. In addition, the general industrial interest in efficient and durable alkane isomerization catalysts working at moderate reaction conditions for the upgrading of fuels makes the here reported bifunctional SCILL catalysts a highly attractive object for further research and development.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.05.008.

References

- [1] (a) H. Weyda, E. Köhler, Catal. Today 81 (2003) 51-55;
- (b) R.P. Silvy, Appl. Catal. A 261 (2004) 247-252.
- [2] N.A. Cusher, in: R.A. Meyer (Ed.), Handbook of Petroleum Refining Processes, third ed., McGraw-Hill, 2003. 9.29–9.39, 9.41–9.45.
- [3] J. Weitkamp, P.A. Jacobs, J.A. Martens, Appl. Catal. 8 (1983) 123-141.
- [4] R. Glaeser, J. Weitkamp, Springer Series, in: Chemical Physics, Springer-Verlag, Heidelberg, 2004, pp. 161–212.
- [5] D. Verboekend, K. Thomas, M. Milina, S. Mitchell, J. Pérez-Ramírez, J.-P. Gilson, Catal. Sci. Technol. (2011) 1, 1331–1335.
- [6] A. Fúnez, J.W. Thybaut, G.B. Marin, P. Sánchez, A. De Lucas, J.L. Valverde, Appl. Catal. A 349 (2008) 29–39.
- [7] A. Chica, A. Corma, Chem. Ing. Tech. 79 (6) (2007) 857-870.
- [8] S. Ernst, C. Bischof, M. Hartmann, J. Weitkamp, in: Proc. of the 16th World Petroleum Congress, vol. 3, 2000, p. 27.
- [9] M. Busto, K. Shimizu, C.R. Vera, J.M. Grau, C.L. Pieck, M.A. DAmato, M.T. Causa, M. Tovar, Appl. Catal. A 348 (2008) 173–182.
- [10] M. Busto, M.E. Lovato, C.R. Vera, K. Shimizu, J.M. Grau, Appl. Catal. A 355 (2009) 123-131.
- [11] J. Xu, J.Y. Ying, Angew. Chem. Int. Ed. 45 (2006) 6700-6704.
- [12] M.A. Arribas, F. Márquez, A. Martínez, J. Catal. 190 (2000) 309–319.
- [13] T. Ohno, Z. Li, N. Sakai, H. Sakagami, N. Takahashi, T. Matsuda, Appl. Catal. A 389 (2010) 52–59.
- [14] H. Al-Kandari, F. Al-Kharafi, A. Katrib, Appl. Catal. A 383 (2010) 141-148.
- [15] J.C. Yori, J.M. Grau, V.M. Benítez, J. Sepúlveda, Appl. Catal. A 286 (2005) 71– 78.
- [16] C. Meyer, P. Wasserscheid, Chem. Commun. 46 (2010) 7625-7627.
- [17] (a) J. Joni, M. Haumann, P. Wasserscheid, Adv. Synth. Catal. 351 (2009) 423– 431;
- (b) J. Joni, M. Haumann, P. Wasserscheid, Appl. Catal. A 372 (1) (2010) 8–15.
 [18] U. Kernchen, B. Etzold, W. Korth, A. Jess, Chem. Eng. Technol. 30 (8) (2007) 985–994
- [19] N. Wörz, J. Arras, P. Claus, Appl. Catal. A 391 (2011) 319–324.
- [20] J. Arras, E. Paki, C. Roth, J. Radnik, M. Lucas, P. Claus, J. Phys. Chem. C 114 (2010) 10520–10526.
- [21] J. Arras, D. Ruppert, P. Claus, Appl. Catal. A 371 (2009) 73-77.
- [22] J. Arras, M. Steffan, Y. Shayeghi, D. Ruppert, P. Claus, Green Chem. 11 (2009) 716-723.
- [23] R. Knapp, A. Jentys, J.A. Lercher, Green Chem. 11 (2009) 656-661.
- [24] Y. Gu, C. Ogawa, J. Kobayashi, Y. Mori, S. Kobayashi, Angew. Chem. Int. Ed. 45 (2006) 7217–7220.
- [25] H.-P. Steinrück, J. Libuda, P. Wasserscheid, T. Cremer, C. Kolbeck, M. Laurin, F. Maier, M. Sobota, P.S. Schulz, M. Stark, Adv. Mater. 23 (2011) 2571–2587.
- [26] C. Meyer, V. Hager, M. Haumann, P. Wasserscheid, in: Presentation at International DGMK Conference, Catalysis – Innovative Applications in Petrochemistry and Refining, Dresden, 2011.
- [27] S. Aschauer, L. Schilder, W. Korth, S. Fritschi, A. Jess, Catal. Lett. 141 (2011) 1405-1419.
- [28] H. Pines, N.E. Hoffman, Isomerization of Saturated Hydrocarbons, in: G.A. Olah (Ed.), Friedel Crafts and Related Reactions, vol. 2, Interscience Publishers, New York, 1964, pp. 1211–1217.
- [29] K. Christmann, G. Ertl, T. Pignet, Surf. Sci. 54 (1976) 365-392.