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New bifunctional catalyst based on Pt containing layered silicate Na-ilerite

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Abstract

Silica-supported Pt nanoparticles were prepared by intercalation of $[Pt(NH_3)_4]^{2+}$ ions into layered silicate Na-ilerite. This material, with a high amount of Pt (20 wt.%), was used as a metal support in mechanical mixtures with the acidic zeolite, H-erionite, and tested for the conversion of *n*-hexane. The activity of these mechanical mixtures is comparable to those of the classical bifunctional systems consisting of Pt/H-erionite. The synergistic effect is explained in terms of the spillover of activated hydrogen.

Keywords: Activated hydrogen; Layered silicates; Bifunctional catalysts; Spillover

1. Introduction

Metal supported bifunctional catalysts play an important role in heterogeneous catalysis. For the first time Mills et al. [1] and Weisz and Swegler [2] have proposed a model to understand the mechanism of bifunctionally catalyzed hydroconversion of hydrocarbons. Recently, an extended model taking into account the surface mobility of hydrogen was suggested [3]. Surface mobility of reactants and intermediates, especially of activated (spilt-over) hydrogen, is a well-known phenomenon in heterogeneous catalysis [4]. The corresponding mobile species are formed at surface sites which are distinct from sites where the reaction takes place, whereas the latter cannot form the active species. In some cases activation and reaction sites of the catalyst system are separated and active hydrogen formed on one surface site can diffuse to another surface site without loss of activity.

Hydrogen from the gas phase is activated on noble metals like Pt. The diatomic molecule adsorbs on the metal and dissociates into two hydrogen atoms [5]. The activated hydrogen migrates onto the support where it is involved in special reaction pathways, e.g. hydroisomerization [3]. Moreover, this activated hydrogen can influence the reaction pathway and thus the product distribution. On the other hand, in the absence of Pt and/or in the presence of nitrogen no hydroisomerization was observed [6].

Another approach is given by Sachtler and coworkers who suggest the migration of platinum as an alternative to hydrogen spillover. They performed temperature-programmed reduction on mixtures of Pt/Na-mordernite with Fe_2O_3 and showed the abundance of hydrogen spillover on iron oxide and the absence of hydrogen spillover from Pt^0 particles along the walls of the zeolite. The presence of Pt clusters on Fe_2O_3 particles after an oxidative treatment was shown by TEM and EDX analysis [7]. The same results were obtained using Pd, Rh, Co and Ni on Na-mordernite and Na-ZSM-5, respectively [8].

Taking into account the investigation on hydrogen spillover by Roessner et al. [9] an influence of Pt migration on the catalytic activity can be excluded. They compared a bifunctional Pt/H-erionite with an H-erionite which was activated in the presence of Pt/Al_2O_3. The Pt containing compound was removed before the reaction was carried out in hydrogen atmosphere. Only products of acid cracking were observed but no products typical for the bifunctional

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pathway. Therefore, it was concluded that no appreciable amounts of Pt migrated onto the zeolite during the activation procedure.

Bianchi et al. [10] studied the hydrogenation of ethylene on alumina. After activation of alumina in the presence of a nickel on alumina catalyst in hydrogen the metal catalyst was removed. On the alumina which has been in contact with the nickel on alumina only 20 ppm of Ni (not necessarily metallic) were detected by atomic absorption spectroscopy. The Ni content was nearly the same as in the initial alumina (33 ppm). Furthermore, with ESR no metallic nickel was detected on the sample which has been in contact with the nickel on alumina. Therefore, it was concluded that the catalytic activity cannot be explained by Ni migration.

A synergistic effect of metal and acidic support is observed for many hydroconversion reactions [6,11,12]. Besides the acidity, the noble metal strongly influences the activity. In order to develop an advanced catalytic system it is necessary to improve the metal dispersion and its stabilization. This is possible by physically separating the two functions of the catalyst during their preparation. The metallic component is supported on an oxidic, catalytically inactive material by ion exchange or impregnation followed by calcination and reduction [13–16]. Admixing an acidic component results in mechanical mixture which is expected to have bifunctional properties [3]. Recently, it was demonstrated that zeolites as well as silica are suitable supports for metals. Layered silicates remained unregarded as supporting materials for the metal. Now they are attracting much attention because of their exceptional adsorption, ion exchange and intercalation properties [17,18]. Silica highly loaded (20 wt.%) with Pt nanoparticles (2–5 nm) has recently been prepared by intercalating Na-ilerite with $[Pt(NH_3)_4]^{2+}$ ions at room temperature followed by calcination at 380 °C in air for 5 h [19].

In the present paper the well understood system, the conversion of *n*-hexane on Pt/H-erionite, was chosen as test reaction to study the mono- and bifunctionality of catalytic systems [9]. The exceptional shape selectivity of erionite allows to distinguish between acidic and bifunctional reaction pathways [9]. Fig. 1 shows the dependence of product distributions and conversions on the catalyst properties (monofunctional/bifunctional) and on the carrier gas used (H_2/N_2) for the conversion of *n*-hexane.

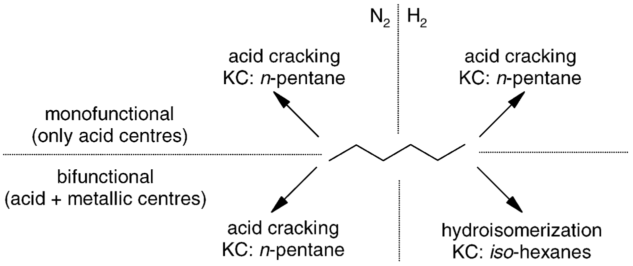

Fig. 1. Reactions of *n*-hexane in dependence on carrier gas and used catalysts, KC: key component (according to Roessner et al. [6]).

The aim of this work is to demonstrate the ability of Pt supported layered silicate Na-ilerite to be used as the metal containing part of a bifunctional catalyst.

2. Experimental section

Na-ilerite was synthesized according to a previously published procedure [20] using colloidal silica (Chemiewerk Köstritz, Germany) as the source of silica. The chemical composition of the Na-ilerite was $8SiO_2{:}1.1Na_2O{:}8.8H_2O$ as determined by chemical and thermogravimetric analysis.

Intercalation of $[Pt(NH_3)_4]^{2+}$ ions into Na-ilerite was typically performed as follows: 500 mg of Na-ilerite was mixed with 25 mL of deionized water and sonicated for 30 min. Then the required amount of aqueous solution of $[Pt(NH_3)_4]Cl_2$ was added to the above mixture. The final mixture was then stirred at room temperature for 48 h. The molar ratio of Na ions present in the host matrix Na-ilerite to Pt was 1:1. The resulting intercalated product, $[Pt(NH_3)_4]^{2+}$-ilerite, was filtered and dried at room temperature for 24 h.

The as-synthesized Pt/Na-ilerite was intensively mechanically mixed in a small ball mill for 2 h with the acidic H-erionite (Chemiewerke Bitterfeld, Germany). Pt/H-erionite with 0.5 wt.% Pt (Chemiewerke Bitterfeld, Germany) was synthesized by wet impregnation with aqueous $H_2[PtCl_6]$ solution. In all experiments the amount of Pt was adjusted to 0.5 wt.% in the mechanical mixture by varying the ratio of both components. The mixture was pressed, grinded and sieved to a grain fraction of 200–315 μm particle size. The catalysts were activated in situ in synthetic air for 3 h at 430 °C, cooled down to 150 °C in nitrogen for 3 h and reduced in hydrogen for 3 h at 430 °C. The flow rate was 50 mL/min for all gases.

According to a recent publication [6] dealing with the conversion of *n*-hexane on H-erionite and Pt/H-erionite, respectively, the reaction of *n*-hexane was studied in a plug flow quartz glass reactor with 10 mm inner diameter at 300 °C. An amount of 0.8 g/h *n*-hexane was passed over 0.4 g catalyst. Hydrogen or nitrogen with a flow of 50 mL/min, respectively, were used as carrier gas. The products were analyzed on-line with a gaschromatograph HP GC 6390 equipped with MSD 5973. Prior to utilization, nitrogen (purity 99.999%) was passed over activated Ni/Al_2O_3 to remove oxygen and, consecutively, dried over molecular sieve 4A. Hydrogen (purity 99.999%) was passed over Pt/Al_2O_3. Formed water was adsorbed on molecular sieve 4A.

3. Results and discussion

The dependence of conversion of *n*-hexane on time on stream on modified erionites in hydrogen and nitrogen is shown in Fig. 2. The initial yields of products after 3 min time on stream are presented in Fig. 3. As depicted in Fig. 2, the parent Na,K-erionite does not show any activity due to

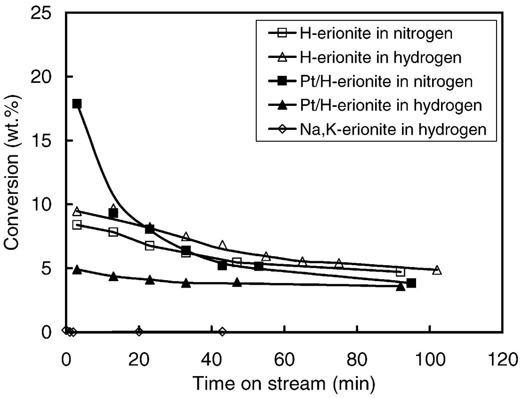

Fig. 2. Conversion of *n*-hexane vs. time on stream on H-erionite and Pt/H-erionite.

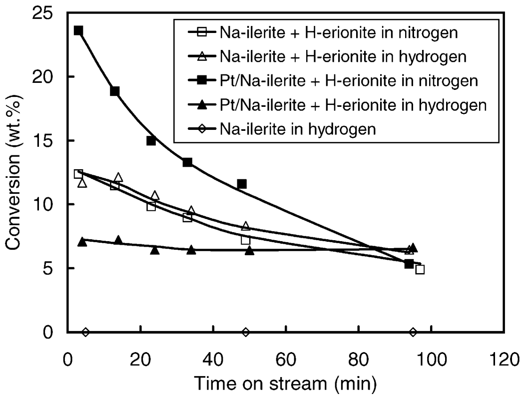

Fig. 4. Conversion of *n*-hexane vs. time on stream of mechanical mixtures of Pt/Na-ilerite + H-erionite and Na-ilerite + H-erionite.

the absence of acidic centers. In the presence of acidic centers, like in H-erionite, typical acid cracking was observed. Propane and *n*-butane were the predominant products (Fig. 3). Using hydrogen instead of nitrogen influences neither the conversion nor the product distribution (Figs. 2 and 3). Surprisingly, in a nitrogen atmosphere and in the presence of both acidic and metallic centers (Pt/H-erionite) the product distribution typical for acid cracking was observed (Fig. 3). Although, the conversion is significantly higher (Fig. 2) as on H-erionite. This effect can be explained by dehydrogenation of hexane on Pt. The formed hexene is then adsorbed on acidic sites increasing the concentration of C_6-carbenium ions on the surface. Therefore, the cracking activity is increased. When hydrogen is applied as the carrier gas, conversion of *n*-hexane on Pt/H-erionite as well as product distribution changes significantly. Hydroisomerization towards *iso*-hexanes (2- and 3-methylpentane) becomes the dominating reaction path (Fig. 3). The conversion of *n*-hexane is lower than in all other three experiments described above (Fig. 2). The difference in the catalytical behaviour is also obvious taking into account the catalyst deactivation. In hydrogen no catalyst deactivation was observed whereas in nitrogen the catalyst deactivates much faster. After 100 min time on stream in hydrogen Pt/H-erionite and H-erionite showed the same activity. The colour of the catalyst after the reaction also reflects different degrees of deactivation because the catalyst used in hydrogen was bright grey whereas the other one was dark green at the end of the reaction.

Summarizing the experiments on H- and Pt/H-erionite, one can conclude that it is possible to decide if there is active metal present on the catalyst by testing the catalyst in different carrier gases. This concept was applied to the results of the experiments with mechanical mixtures of Na-ilerite (pure of with Pt) with H-erionite which are described below.

As expected Na-ilerite is inactive in the conversion of *n*-hexane due to the absence of acidic hydroxyl groups (Fig. 4). Admixing H-erionite, typical acid cracking was observed (Fig. 5). Again, the conversion as well as the product distribution were independent of the carrier gas used.

In order to test the ability of Pt/Na-ilerite to act as the metallic component of a bifunctional catalyst, mechanical mixtures were prepared as described above and their activity for the conversion of *n*-hexane was tested. The conversion of *n*-hexane as a function of time on stream is shown in Fig. 4. The results show that the procedure used produces active bifunctional catalysts. The conversion observed for the mechanical mixtures (Fig. 4) is in the same range compared

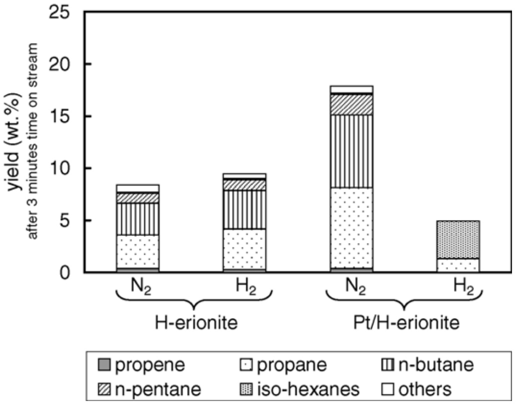

Fig. 3. Yields for the conversion of *n*-hexane on H-erionite and Pt/H-erionite.

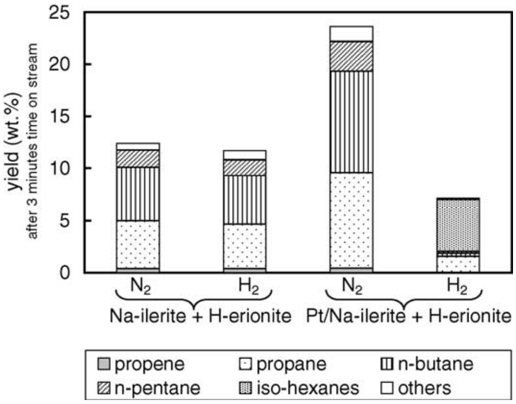

Fig. 5. Yields for the conversion of mechanical mixtures of Pt/Na-ilerite + H-erionite and Na-ilerite + H-erionite.

to the one observed for Pt/H-erionite (Fig. 2). As expected from the theory and from the results with Pt/H-erionite, the carrier gas influences the product distribution. Surprisingly, in all four experiments a higher conversion was observed compared to H-erionite and Pt/H-erionite, respectively. The product distributions obtained with the mechanical mixtures (Fig. 5) are very similar to the ones obtained with H-erionite and Pt/H-erionite.

The higher conversion for the Pt containing catalysts can be explained by taking into account the particle size distribution with average sizes of 2–5 nm [19] of Pt in the Pt/Na-ilerite. Therefore, more active metal centers are present in the catalysts. Consequently, the supply of activated hydrogen, which spills over from ilerite to erionite, is increased resulting in a higher hydroisomerization activity of the composite system. Despite the circumstance that the crystallinity of Pt/Na-ilerite was lost during the thermal treatment at 380 °C [19], platinum clusters are still accessable for hydrogen, which is activated there. Those hydrogen species spillover onto the support and to the acidic component (H-erionite) where they are involved in hydrocarbon conversion according to the model proposed in the literature [3].

4. Conclusion

The results clearly indicate that layered silicates can be used as supports for metals. Applying the concept of hydrogen spillover, a composite system was developed where Pt supported layered silicates are used as metallic component in mechanical mixtures with H-erionite to obtain bifunctional composites.

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