

Alkylation of benzene catalysed by supported heteropolyacids

Alberto de Angelis, Stefano Amarilli, Donatella Berti, Luciano Montanari,
Carlo Perego *

EniTecnologie, via F. Maritano 26, 20097 S. Donato Milanese, MI, Italy

Abstract

A new kind of solid acid based on heteropolyacids has been proved to be a useful catalyst in alkylation of benzene with propylene to obtain cumene. The new catalysts are based on a heteropolyacid supported on zirconia treated with very low contents of sulphate anions. Two different heteropolyacids have been studied, both with Keggin structure, ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$), and both produced active catalysts. The zirconia was used either pure or doped with few percent of iron oxide. The catalysts have been characterised through XRD, ^{31}P NMR and HREM. These catalysts are very active in alkylation reaction even at mild temperature. Their two outstanding features are the low *n*-propylbenzene production and the possibility to regenerate it at moderate temperature (350°C). The best catalyst is based on $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on zirconia doped with iron and treated with sulphate ions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Alkylation; Benzene; Heteropolyacids

1. Introduction

The alkylation of benzene with propylene gives cumene, a very important petrochemical commodity used for the production of phenol and acetone [1]. More than 90% of the world's phenol demand is derived from cumene. Hence, the growth rate of cumene is closely associated with that of phenol. Cumene demand is expected to grow about 3.5% a year over the next 5 years [2]. The cumene capacity in the world is about 8 million tons/year distributed over about 40 plants. The most widespread process is the UOP. The catalyst for such a process is phos-

phoric acid, supported on kieselguhr (SKPA), patented by Ipatieff [3]. Only few plants are based on the Monsanto technology, which uses aluminum trichloride (AlCl_3) as catalyst. Both processes have problems of corrosion, waste treatment (AlCl_3) and exhaust catalyst disposal (SKPA). This accounts for the efforts devoted to the research of new more efficient, safe and environment-friendly catalysts.

Different kinds of solid acids have been extensively tested for alkylation of aromatics such as: heteropolyacids, pillared clays, silica alumina and acidic zeolites. Acidic zeolites have been thoroughly evaluated for benzene alkylation with propylene since 1965 [4], but their use in commercial plants has been announced only recently by Dow, Mobil, CDTech, UOP and Enichem [5]. During the search for new cata-

* Corresponding author. Fax: +39-2-5205-6364; E-mail: cperego@enitecnologie.eni.it

lysts, which led to the development of the Enichem process based on zeolite beta [6,7], we performed a wide screening considering solid acids other than zeolites, such as pillared clays, mesoporous silica–alumina (MSA) and heteropolyacids.

In this paper, we shall describe a new kind of catalyst based on a heteropolyacid supported on zirconia treated with very low content of sulphate anion [8]. Such catalyst shows pretty high activity and a very low formation of *n*-propylbenzene (NPB). Furthermore, the catalyst can be easily reactivated at relatively low temperature without significant loss of activity or change in its crystalline structure also after some reaction cycles.

2. Experimental

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, H_2SO_4 , (98%) ZrOCl_2 , $\text{Fe}(\text{NO}_3)_3$, all analytically pure and from Fluka are used as received.

2.1. Synthesis of ZrO_2

The oxide is prepared by hydrolysing in aqueous solution an opportune precursor such as ZrOCl_2 with ammonia till the pH value of the suspension reaches 10, filtering, washing it carefully with plenty of water, then drying it at 250°C for 24 h.

2.2. Synthesis of ZrO_2 doped with iron

The mixed oxide is prepared treating an aqueous solution of ZrOCl_2 and $\text{Fe}(\text{NO}_3)_3$ (0.5% weight as Fe) with ammonia till the pH value of the suspension reaches the value of 10, filtering, washing it thoroughly with distilled water and finally drying it at 250°C for 24 h.

2.3. Catalysts preparation

The catalyst is prepared by suspending the preformed oxide in aqueous solution of the

heteropolyacid and the free inorganic acid. The aqueous solution is made of 200 cc of 0.1 N solution of sulphuric acid in which 20 g of the heteropolyacid is dissolved. In such solution 20 g of the preformed oxide is suspended, stirred for about 4 h then filtered and washed with distilled water till neutrality of the mother water. The sample is then dried under air flow at temperature between 200°C and 350°C for a period of 12 h. The choice of the temperature depends on the thermal stability of the heteropolyacid [9,10].

2.4. Reaction apparatus

The catalysts have been tested in a fixed bed reactor, at temperature of 100–150°C and pressure of 4 MPa; under this condition the feed is liquid. The reactor was charged with 3 g of catalyst, crushed from 5 tons/cm² pelletised wafers and sieved to 20–40 mesh particles. The catalyst was then flushed in slowly flowing dry nitrogen while heating up to 150°C for 3 h.

The benzene/propylene molar ratio is 7 and the reagents are fed separately with two different pumps. Total WHSV (weight hourly space velocity) is in the range 1–20 h⁻¹. Benzene was a C.Erba reagent, > 99% pure. Propylene was supplied by SIAD, > 99.9% pure. All these reagents were used as supplied.

The analysis of gases is performed on a GC (Hewlett Packard 5890) connected on-line with the plant. Liquid reaction samples are taken by cooling the effluents at 10°C and analysed through GC (Hewlett Packard 5890) using a capillary column PONA (50 m long and 0.21 mm O.D., coated with a 0.5 mm thick film of stationary phase). Compounds from C₃ to C₁₅ have been detected.

2.5. Catalyst characterisation

The catalysts have been characterised through HREM-EDS and XRD.

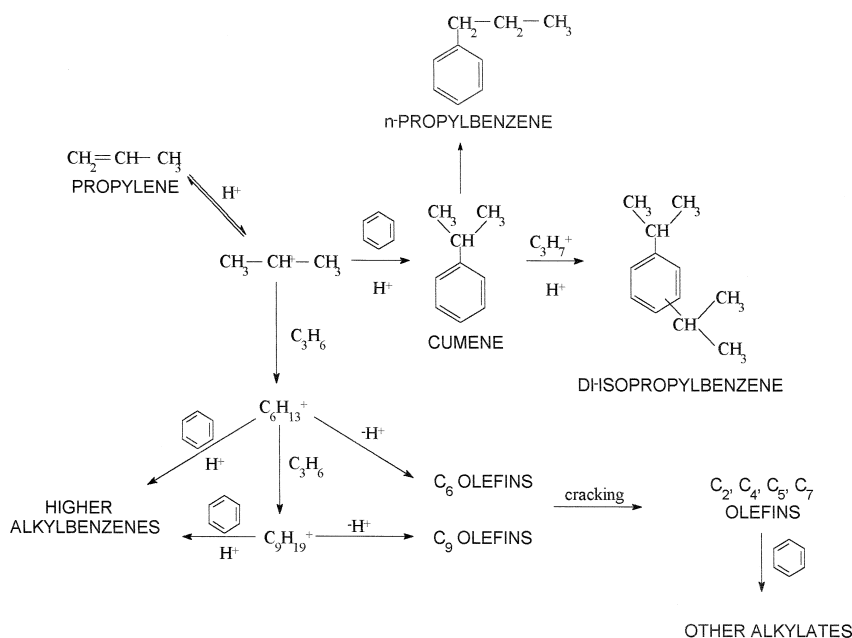


Fig. 1. Reaction scheme of alkylation of benzene with propylene.

2.5.1. X-ray diffraction (XRD) analysis

The XRD data were collected using a Philips equipment with monochromatic Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The spectra were taken at ambient conditions in step-scanning mode, in the range $5^\circ < 2\theta < 70^\circ$ (step 0.03° , time 10 s/step). Qualitative phase analysis was carried out using the Siemens Diffrac AT package run on a IBM PC 330 P-75.

Crystal sizes were calculated from diffraction line broadening applying the Scherrer equation.

2.5.2. High-resolution transmission electron microscopy (HREM) and energy dispersive spectroscopy (EDS) analysis

HREM experiments were done on a Jeol JEM-3010 microscope (max. acceleration voltage: 300 kV, max. resolution: 1.6 \AA) equipped with a Link Isis EDS apparatus.

The catalyst powder was embedded in epoxy resin and then microtomed with a diamond knife to obtain sections $\sim 400 \div 700 \text{ \AA}$ thick. Images were obtained at 300 kV.

2.5.3. ^{31}P -MAS-NMR analysis

^{31}P -MAS-NMR spectra (121.44 MHz) were measured at room temperature on a Bruker AMX-300 equipped with a Double Bearing MAS device. Two hundred transient responses were collected with pulse duration of 3 ms (30° flip angle) and with repetition time of 16 s. Spinning rate was 5 kHz. Exponential multipli-

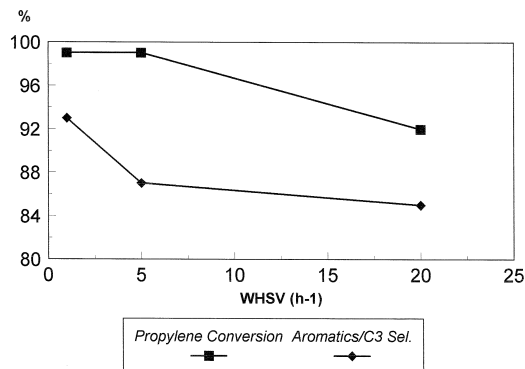


Fig. 2. Catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on $\text{ZrO}_2-\text{SO}_4^-$ at different WHSV ($T = 100^\circ\text{C}$, t.o.s. 15 h).

Table 1
Catalytic test results of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2\text{-SO}_4^-$

Reaction temperature (°C)	Propylene molar conversion, %	Aromatics/ C_3 selectivity, %	NPB (ppm/cumene)
100	99	93	96
150	99	96	184

Influence of reaction temperature.

$P = 4$ MPa.

WHSV = 1 h^{-1} .

t.o.s. = 15 h.

cation of 20 Hz was applied prior to Fourier Transformation. 1% H_3PO_4 in D_2O was used as an external reference.

3. Cumene chemistry

The most important reactions involved in the alkylation of benzene with propylene are shown in Fig. 1. Cumene is obtained according to the classical carbenium ion mechanism in which propylene gives the propyl cation which attacks a benzene molecule. Then, through transfer of a proton, the propylbenzenium cation rearranges to cumene. However, it can be subsequently alkylated to give diisopropylbenzenes (DIPB) (ortho, meta and para). The *m*-DIPB is the most favoured isomer according to the thermodynamic distribution in the range 100–150°C. Nevertheless, from the DIPB, it is possible to recover cumene through the transalkylation reaction carried out on an acid catalyst in presence of benzene. There are also several reactions that lead to unwanted by-products. For example propylene form $\text{C}_6\text{-C}_9$ oligomers

which can alkylate benzene or crack to lighter products (olefins and paraffins). But the most unwanted impurity is NPB. In fact, it is not possible to separate this component from the cumene by distillation and than its formation should be prevented. A thermodynamic equilibrium exists between cumene and NPB; the latter is favoured at increasing temperatures.

4. Results and discussion

4.1. Catalytic activity and selectivity

Fig. 2 reports the catalytic activity for the catalyst based on $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPA) on zirconia treated with sulphated anion. The sulphur content in this sample is very low (0.11% wt.), while the tungsten is 18.6% (wt.). The results of the test have been reported as propylene conversion, selectivity to useful aromatics (cumene and DIPB) and NPB (measured as ppm/cumene).

This catalyst is very active. In fact the propylene conversion is higher than 90% also when

Table 2
Catalytic test results of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2\text{-SO}_4^-$ vs. $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{ZrO}_2\text{-SO}_4^-$

Catalyst	Propylene molar conversion, %	Aromatics/ C_3 selectivity, %	NPB (ppm/cumene)
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	99	93	96
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	71	95	50

$T = 100^\circ\text{C}$.

$P = 4$ MPa.

WHSV = 1 h^{-1} .

t.o.s. = 15 h.

Table 3
Catalytic test results of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2\text{-SO}_4^-$

Catalyst	Support	Propylene molar conversion, %	Aromatics/ C_3 selectivity, %	NPB (ppm/cumene)
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	$\text{ZrO}_2\text{-SO}_4$	99	93	96
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	$\text{ZrO}_2\text{-Fe}_2\text{O}_3\text{-SO}_4$	99	92	< 10

Influence of the dopant.

$T = 100^\circ\text{C}$.

$P = 4 \text{ MPa}$.

WHSV = 1 h^{-1} .

t.o.s. = 15 h.

the WHSV reaches the value of 20 h^{-1} (Fig. 2). The selectivity to useful aromatics lowers increasing the WHSV; this is due to an increase of oligomers production. The production of NPB is much lower (96–97 ppm/cumene at WHSV = 1) than the one reported for SKPA (200 ppm) [6]. This lower value of NPB is due to the milder temperature (100°C) required by $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2\text{-SO}_4^-$ with respect to the SKPA (200°C).

Also for $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2\text{-SO}_4^-$ increasing the reaction temperature of 50°C (from 100 to 150°C) the value of NPB is nearly twice (from 96 to 184 ppm/cumene) (Table 1). The selectivity to aromatics instead increases from 93 to 96% owing to the lower formation of oligomers at higher temperatures.

This catalytic system is still active using a different metal in the Keggin structure: molybdenum, for example, can be substituted for tungsten in $\text{H}_3\text{PMe}_{12}\text{O}_{40}$ (Table 2). This change implies a decrease of the acid strength of the heteropolyacid [11]; as a consequence, there is a great loss of propylene conversion while the selectivity to aromatics is nearly the same. This is an obvious consequence of the minor activity of the catalyst.

Doping the zirconia with a low content of iron oxide this catalytic system becomes much more selective, lowering the content of NPB (Table 3), the amount of which is less than the detectable threshold (10 ppm). Propylene conversion and the aromatics selectivity are nearly the same as those obtained using pure zirconia as support. It is well known from literature that

doping sulphated zirconia with few percent of iron oxide increases the strength of the acid sites [12]. Compared to those of pure zirconia, such modified acid sites probably increase the relative stability of secondary carbenium ion with respect to the primary carbenium ion. As the latter is responsible for NPB formation [13], this could account for better selectivity of the catalyst doped with iron.

4.2. Catalyst deactivation and regeneration

The catalyst based on $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on sulphated zirconia has been subjected to a life test, feeding the propylene and benzene mixture (molar ratio = 7) for the first 18 h at WHSV = 1 h^{-1} and then at WHSV = 5 h^{-1} . This catalyst deactivates after more than 90 h when the propylene conversion is 70% less (Fig. 3).

A common method to regenerate a catalyst is to treat it at a temperature around 550°C under

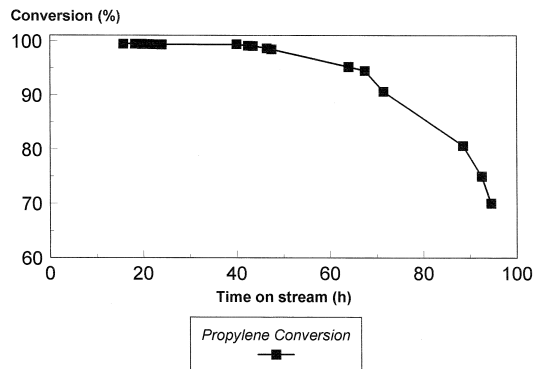


Fig. 3. Life test of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on $\text{ZrO}_2\text{-SO}_4^-$.

Table 4

Catalytic test results of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2\text{-SO}_4^-$

Catalyst	Propylene molar conversion, %	Aromatics/ C_3 selectivity, %	NPB (ppm/cumene)
$\text{H}_3\text{PW}_{12}\text{O}_{40}$ fresh	99	93	96
$\text{H}_3\text{PW}_{12}\text{O}_{40}$ 1st cycle	98	93	81
$\text{H}_3\text{PW}_{12}\text{O}_{40}$ 2nd cycle	97	94	54

Regeneration of the catalyst.

 $T = 100^\circ\text{C}$. $P = 4 \text{ MPa}$.WHSV = 1 h^{-1} .

t.o.s. = 15 h).

air flow. This results in the combustion of the carbonaceous residues, responsible for deactivation. This method cannot be applied to this kind of catalyst because it is well known from the literature [9] that the thermal stability of heteropolyacids, as free acids, does not exceed 450°C . We have found that it is possible to perform the regeneration of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on $\text{ZrO}_2\text{-SO}_4^-$ under air flow at temperature lower than 350°C for 2 h. Under these conditions there is an almost negligible lowering of propylene conversion and of selectivity to useful aromatics after each reaction-regeneration cycle while there is a continuous reduction of NPB formation (Table 4).

The possibility of regenerating this catalyst at mild temperature could exist probably due to the good redox properties of the heteropolyacids which allow the combustion of carbonaceous residues at lower temperature.

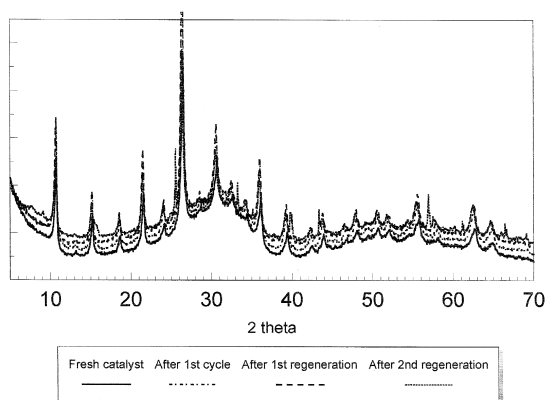
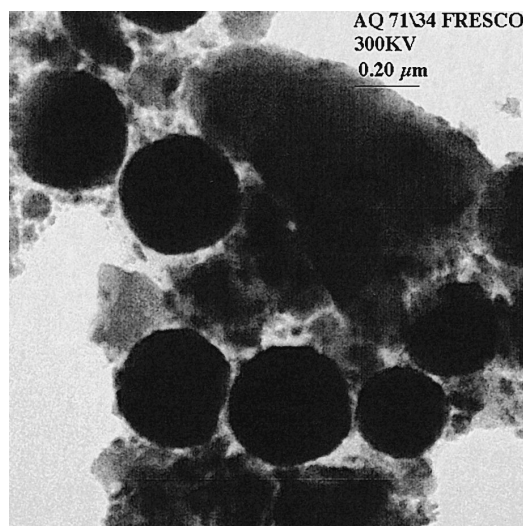


Fig. 4. XRD spectrum of catalyst (fresh, after 1st cycle, after 1st regeneration, after 2nd regeneration).

4.3. Chemical–physical characterisation

The feature that the catalyst shows no significant differences after each reaction cycle is in agreement with the fact that there are no significant differences between the crystalline structure of the fresh catalyst and that of the one regenerated after two reaction cycles.

From XRD analysis, the only crystalline phase present in the fresh catalyst (Fig. 4) is the Keggin acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$. After one activity-regeneration cycle (Fig. 4) there are no significant differences in the spectra: no change in the crystallinity of the Keggin acid is detected and no crystallisation of the amorphous support occurs. The conclusion is the same also after the second activity-regeneration cycle (Fig. 4).

Fig. 5. HREM Analysis of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on $\text{ZrO}_2\text{-SO}_4^-$.

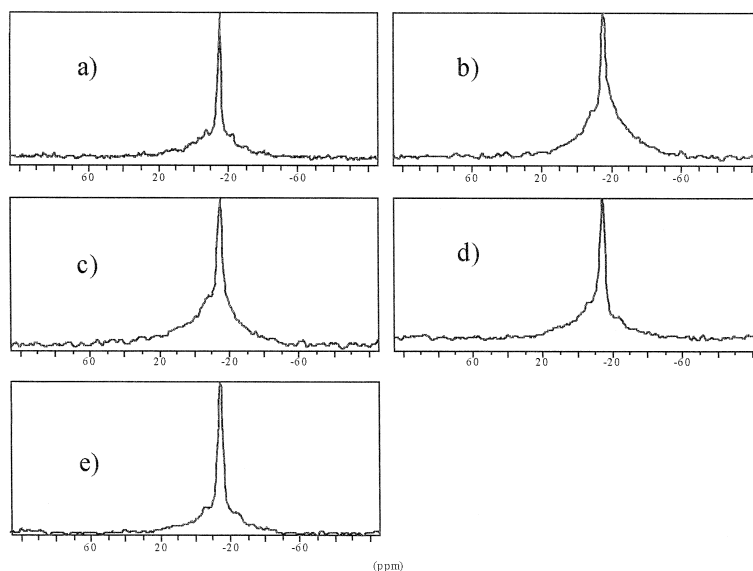


Fig. 6. ^{31}P -MAS-NMR spectra of (a) fresh catalyst, (b) catalyst after 1 cycle, (c) catalyst after 1st regeneration, (d) catalyst after 2nd cycle and (e) after 2nd regeneration.

From HREM analysis of the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ fresh catalysts, HPA is well dispersed on the amorphous zirconia matrix and forms spongy aggregates (Fig. 5) whose size is between 100 and 500 nm. The aggregates are formed by crystallites of 10–20 nm, made by hexagonal packing of about 1 nm units (the Keggin unit). After two activity-regeneration cycles the Keggin structure of the heteropolyacid is preserved: no changes are observed in the morphology and the aggregates are still crystalline.

These data are fully confirmed by XRD and ^{31}P NMR. ^{31}P -MAS-NMR is the most revealing method for examining the state of phosphorous heteropolycompound [14]. Fig. 6 shows the ^{31}P -MAS-NMR spectra of the catalyst as fresh (a), after 1(b) and 2(d) activity cycles, and after the respective regeneration states (c, e) (Fig. 6).

All spectra are very similar and consist of a sharp signal centred at -15.2 ppm, attributed to the P of the Keggin structure [14], and of a much broader one centred at -12.8 ppm which can be due to a lacunary heteropolyanion [14] or to Keggin anion strongly interacting with the ZrO_2 support [15]. From the deconvolution of

the NMR spectra, we found that the sharp signal (Keggin structure) is 20% of all phosphorous while the broad one is 80%.

The attribution of the broad signal to Keggin ion strongly interacting with the support should be more correct because the lacunary heteropolyanions are not very stable, while the catalyst, as seen above, is stable under reaction conditions.

5. Conclusions

The catalytic system based on a Keggin heteropolyacid supported on zirconia treated with sulphate anion shows a good activity in the alkylation of benzene with propylene to cumene. It is possible to have an active catalytic system using different heteropolyacids with very low content of sulphate anion, and as support zirconia either pure or doped with few percent iron oxide. Choosing a suitable composition of the catalyst and reaction conditions, it is possible to lower the formation of NPB up to almost negligible values. Besides, this catalyst can be easily

regenerated at mild conditions, maintaining unchanged its crystalline structure and its catalytic properties.

Acknowledgements

We thank EniTecnologie for permission to publish this paper. We also thank Mr. Signoroni Secondo (EniTecnologie) for his helpful work.

References

- [1] P.R. Pujado, J.R. Salazar, C.V. Berger, *Hydrocarbon Process* 55 (1976) 91.
- [2] W.P. Kleinloh, Proc. 1997 World Petrochemical Conference (CMAI), Houston, TX.
- [3] V.N. Ipatieff, US Patent 2,382,318 (1945).
- [4] Kr.M. Minachev, Ya.I. Isakov, V.I. Garanin, L.I. Piguzova, V.I. Bogomolov, A.S. Vitukina, *Neftekhimiya* 5 (1965) 676.
- [5] G.R. Meima, M.J.M. van der Aalst, M.S.U. Samson, J.M. Garces, J.G. Lee, in: J. Weitkamp, B. Lücke (Eds.), *Proceedings of the DGMK-Conference, Catalysis on Solid Acids and Bases*, March 14–15, 1996, Berlin, Germany, 1996, p. 125.
- [6] G. Bellussi, G. Pazzuconi, C. Perego, G. Girotti, G. Terzoni, *J. Catal.* 157 (1995) 227.
- [7] C. Perego, S. Amarilli, R. Millini, G. Bellussi, G. Girotti, G. Terzoni, *Microporous Materials* 6 (1996) 395.
- [8] A. de Angelis, S. Amarilli, C. Perego, G. Girotti, Italian Patent MI95/A 001730 (1995).
- [9] L. Malaparade, in: P. Pascal, *Nouveau Traité de Chimie Minerale*, Vol. 14, Masson Editeurs, Paris, 1959, p. 902.
- [10] C. Rocchiccioli-Deltcheff, A. Aouissi, M.M. Bettahar, S. Launay, M. Fournier, *J. Catal.* 164 (1996) 16–27.
- [11] T. Okuhara, N. Mizuno, M. Misono, *Advanced in Catalysis*, Vol. 41, Academic Press, San Diego, CA, 1996, pp. 139–145.
- [12] T.K. Cheung, J.L. D'itri, B.C. Gates, *J. Catal.* 151 (1995) 139–145.
- [13] M.F. Benthams, G.J. Gajda, R.H. Jensen, H.A. Zinnen, in: J. Weitkamp, B. Lücke, *Proceedings of the DGMK-Conference, Catalysis on Solid Acids and Bases*, Berlin, Germany, March 14–15, 1996, 1996, p. 155.
- [14] I.V. Kozhevnikov, *Catal. Lett.* 30 (1995) 241–252.
- [15] T.-H. Chang, *J. Chem. Soc. Faraday Trans.* 91 (2) (1995) 375–379.