Solid acid catalysts for alkylation of hydrocarbons

A. de Angelis [*], P. Ingallina, D. Berti, L. Montanari and M.G. Clerici

EniTecnologie, via Maritano 26, I-20097 San Donato Milanese, Italy
E-mail: adeangelis@enitecnologie.eni.it

Received 6 April 1999; accepted 8 June 1999

Solid acid catalysts based on heteropoly acids supported on different oxides catalyse the alkylation of isobutane with n-butenes to yield high-octane gasoline components. They are active for a short period of time on stream. Regeneration is easily made by thermal treatment under air. The catalysts have been characterised by NMR, EPR, XRD and TEM-EDS techniques.

Keywords: solid acids, alkylation of hydrocarbons, heteropoly acids

1. Introduction

The alkylation of isobutane with n-butenes to yield saturated–branched octanes is a reaction of great interest in the refining industry. The products have high octane number and are commonly used for gasoline blending. Current production is based on strong mineral acids, i.e., sulphuric and fluoridric acids, used in large amounts. For safety reasons, their substitution with non-corrosive and non-toxic solid catalysts could be highly desirable. To date, a number of solid acids have been investigated such as Y-zeolite [1], sulphated zirconia [2,3], SbF_5 [4], β-zeolite [5], MCM-22 [6] and supported trifluoromethanesulphonic acid [7–9]. After a high initial activity all these catalysts deactivate quite rapidly unless they are used in peculiar reactor apparatus [4,7].

Heteropoly acids are crystalline solids and possess strong acid properties both in solid state and in solution [10]. To our knowledge, they have never been used in the alkylation of isobutane except in one case. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was shown by Corma et al. [11] to be active in this reaction. Partially salified heteropoly acids are reported to have increased surface area and better acid properties [11,12]. Another useful way to increase their surface area is to support them on an appropriate material. We have found that an active catalyst is formed when the heteropoly acids are supported on amorphous oxides in the presence of a low amount of a mineral acid. In this paper, we will illustrate their preparation and the catalytic results in the alkylation of isobutane.

2. Experimental

$H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, H_2SO_4 (98%), HF (38%), HCl (36%), CF_3SO_3H (98%), $ZrOCl_2{\cdot}8H_2O$, $FeCl_2$, Mn$(NO_3)_2$, all from Fluka, Al_2O_3 (Harshaw AI3912), TiO_2 (P25 Degussa) were used as received.

2.1.1. Synthesis of ZrO_2

28% aqueous ammonia (170 ml) was added dropwise into a clear solution of $ZrOCl_2{\cdot}8H_2O$ in distilled water (500 ml). The white suspension (pH $\approx$ 10) was stirred for 2 h at room temperature, then filtered and washed with distilled water until chloride free. The solid was dried at 250 °C under air flow for 24 h, obtaining 45.5 g of pure and amorphous zirconia (SA 350 m^2/g)

2.1.2. Synthesis of $H_3PMo_{12}O_{40}/ZrO_2/SO_4$

Zirconia (20 g) was added into an aqueous solution of $H_3PMo_{12}O_{40}$ in 200 ml of 0.1 N solution of sulphuric acid. The slurry was stirred for 4 h, filtered and washed with distilled water to neutrality. The solid was dried under air flow at 350 °C for 12 h.

2.1.3. Synthesis of HPA/oxide/X

The procedure for $H_3PMo_{12}O_{40}/ZrO_2/SO_4$ was adopted. The heteropoly acid (HPA), the support oxide, the mineral acid (HX) and the composition of each catalyst are listed in table 1.

2.1.4. Reaction apparatus

The catalysts are tested in a fixed-bed reactor at the temperature of 70 °C and pressure of 20 bar. The catalysts are pressed, crushed and sieved (70–230 mesh). In each run, 10 ml (ca. 11 g) of catalyst is used. The reagents, pure isobutane and a mixture of isobutane/1-butene (10/1 ratio), are fed alternatively (20 and 10 s, respectively). Under the reaction conditions they are in the liquid phase. WHSV referred to 1-butene was 0.04 h^{-1}. Reaction samples are analysed on a poly(dimethylsiloxane) capillary column (SPB-1, Supelchem) and a Hewlett–Packard 5890 gas chromatograph.

---

[*] To whom correspondence should be addressed.

Table 1
Synthesis of heteropoly acids supported on amorphous oxides (HPA/oxide/X). Reagents used.[a]

Catalyst number	Support	Heteropoly acid (metal content)	HX (anion content)
1	ZrO_2	$H_3PMo_{12}O_{40}$ (7.46% Mo)	H_2SO_4 (0.46% SO_4^{2-})
2	ZrO_2	$H_3PMo_{12}O_{40}$ (13.4% Mo)	HNO_3 (0% NO_3^-)
3	ZrO_2	$H_3PMo_{12}O_{40}$ (11.51% Mo)	CF_3SO_3H (0.47% $CF_3SO_3^-$)
4	ZrO_2	$H_3PMo_{12}O_{40}$ (12.12% Mo)	HCl (0.25% Cl^-)
5	ZrO_2	$H_3PMo_{12}O_{40}$ (10.44% Mo)	HF (0.3% F^-)
6	TiO_2	$H_3PMo_{12}O_{40}$ (7.8% Mo)	H_2SO_4 (0.45% SO_4^{2-})
7	Al_2O_3	$H_3PMo_{12}O_{40}$ (3.96% Mo)	H_2SO_4 (0.57% SO_4^{2-})
8	Fe_2O_3	$H_3PMo_{12}O_{40}$ (4.12% Mo)	H_2SO_4 (0.23% SO_4^{2-})
11	ZrO_2	$H_3PW_{12}O_{40}$ (18.6% W)	H_2SO_4 (0.11% SO_4^{2-})
12	ZrO_2	$H_6P_2W_{18}O_{62}$ (22.1% W)	H_2SO_4 (0.27% SO_4^{2-})

[a] In parentheses are reported the molybdenum, tungsten and anion weight contents in the catalysts.

2.1.5. Conversion and selectivity definition

Conversion and selectivity are defined in the following way:

$$\text{conversion:}\quad \frac{\text{moles of butene reacted}}{\text{initial moles of butenes}},$$

$$\text{selectivity:}\quad \frac{\text{moles of saturated octanes}}{\text{moles of butene reacted}},$$

$$\text{TMPs selectivity:}\quad \frac{\text{moles of trimethylpentanes}}{\text{moles of saturated octanes}}.$$

2.2. Characterisation techniques

2.2.1. ^{31}P-MAS-NMR

121.44 MHz ^{31}P-MAS-NMR spectra were measured at room temperature on a Bruker AMX-300 equipped with a double-bearing MAS device. 200 transient responses were collected with pulse duration of 3 μs (30° flip angle) and with repetition time of 16 s. Spinning rate was 5 kHz. Exponential multiplication of 20 Hz was applied prior to Fourier transformation. 1% H_3PO_4 in D_2O was used as an external reference.

2.2.2. EPR

EPR spectra were obtained with a Bruker ESP 300 E spectrometer working in X-band (9–10 GHz) equipped with a resonant cavity and a variable temperature device. A standard Bruker DPPH sample was used as a g-marker.

2.2.3. XRD (X-ray powder diffraction) analysis

The XRD data were collected under ambient conditions using a Philips equipment with monochromatic Cu Kα radiation ($\lambda = 1.5418$ Å). Qualitative phase analysis was carried out using the Siemens Diffrac AT package run on an IBM PC 330 P-75.

2.2.4. TEM-EDS (transmission electron microscopy and energy dispersive spectroscopy) and HRTEM (high-resolution transmission electron microscopy)

TEM experiments were done on a Philips 420T microscope (120 kV, max. resolution 5 Å) equipped with an EDAX PV9900 EDS apparatus; images were obtained at 100 kV.

HRTEM experiments were done on a Jeol JEM-3010 microscope (max. acceleration voltage 300 kV, max. resolution 1.6 Å) equipped with a Link Isis EDS apparatus; images were obtained at 300 kV.

3. Results and discussion

3.1. Catalyst synthesis and reactivity

Phosphomolybdic acid on zirconia prepared in the presence of sulphuric acid (table 1) catalyses the alkylation of isobutane with 1-butene at 70 °C to yield a mixture of saturated octanes and other products. After 1 h of time on stream, butene conversion is nearly 80%, with an almost total selectivity to saturated octanes. The trimethylpentanes content in the octane fraction is 30%, with the balance being predominantly dimethylhexanes. No methylheptanes are detected. Small amounts of C_4–C_7 and C_{9+} hydrocarbons are also present. As the time on stream increases, catalyst deactivation manifests itself with a decrease of conversion and selectivity. After 3 h, the molar conversion of 1-butene is high (76%), while the selectivity to saturated octanes is only 26%. After 19 h, conversion is still 56%, but selectivity drops to negligible values.

All the three components of the catalytic system (i.e., the heteropoly acid, a low amount of an additional strong acid and the oxide support) are necessary in order to obtain an active catalyst. Phosphomolybdic acid on zirconia prepared in the absence of any strong acid HX (table 2) catalyses only the oligomerization of the olefin. The role of HX or of its anion X^- adsorbed on the catalyst is not clear. However, its presence is necessary and must be stable to thermal treatments. When nitric acid is used, of which the anion is lost at high temperature, the oligomerization of 1-butene is the only catalysed reaction. When the catalytic system is made only of heteropoly acid dispersed on zirconia, without HX, a very poor selectivity to saturated octanes is obtained (butene conversion 54%, selectivity to saturated octanes 4% at TOS = 3 h) [9]. If heteropoly acid is used without having been supported on an amorphous oxide, no significant butene conversion is obtained.

Active catalysts are produced not only by sulphuric acid but also by other strong acids, such as fluoridric, chloridric and trifluoromethanesulphonic acid (table 2). However, while these are able to convert comparable or even

Table 2
Alkylation of isobutane catalysed by $H_3PMo_{12}O_{40}/ZrO_2/HX$. Effect of anion X^-.[a]

Anion	Butene molar conversion (%)	Selectivity to saturated octanes (%)	TMPs selectivity in octanes fraction (%)
None	70	0.2	0
Sulphate	79	97	30
$CF_3SO_3^-$	78	37	36
Chloride	93	28	28
Fluoride	95	22	18

[a] $P = 20$ bar, WHSV = 0.04 h^{-1}, TOS = 1 h.

Table 3
Alkylation of isobutane catalysed by $H_3PWo_{12}O_{40}/ZrO_2/SO_4$. Regeneration cycles.[a]

Reaction cycle	Butene molar conversion (%)	Selectivity to saturated octanes (%)	TMPs selectivity in octanes fraction (%)
Fresh catalyst	93	95	76
First	92	55	69
Second	95	40	62
Third	91	91	70
Eleventh	83	78	84

[a] $P = 20$ bar, WHSV = 0.04 h^{-1}, TOS = 1 h.

higher amounts of butene than $H_3PMo_{12}O_{40}/ZrO_2/SO_4$, the selectivity to saturated octanes is relatively low and decreases in the order $CF_3SO_3H > HCl > HF$.

Less effective materials are also produced by supporting $H_3PMo_{12}O_{40}$ and H_2SO_4 on TiO_2, Fe_2O_3 and Al_2O_3. Although the conversion of butene ranges from 99 to 66%, the selectivity to saturated products is never higher than 25%.

Active catalysts are also prepared using heteropoly acids with different compositions and structures. A most effective catalyst is obtained by substituting phosphomolybdic with phosphotungstic acid (table 3). $H_3PW_{12}O_{40}/ZrO_2/SO_4$ not only shows higher values of butene conversion (95 vs. 79%), comparable selectivity to saturated octane (95 vs. 97%) and higher selectivity to TMPs (76 vs. 30%) than the corresponding Mo catalyst, but also a longer catalytic life (3.5 h instead of 2). It is known from the literature that the acid strength of phosphotungstic acid is higher than that of phosphomolybdic acid [14], and this is a possible reason for the different behaviour. The analogous catalyst prepared using $H_6P_2W_{18}O_{62}$, with Dawson structure [15] (table 1, entry 12) shows a much lower selectivity to saturated octanes (20%) at an almost complete 1-butene conversion.

Catalyst life is an important issue when dealing with solid alkylation catalysts. In most cases deactivation is relatively fast and both $H_3PMo_{12}O_{40}/ZrO_2/SO_4$ and $H_3PW_{12}O_{40}/ZrO_2/SO_4$ are no exceptions. These show fair activity and selectivity for a few hours TOS, 2 and 3.5 h, respectively, then the production of saturated octanes and trimethylpentanes drops to very low levels. Catalyst deactivation is likely due both to catalyst fouling and to the reduction of Mo^{VI} to a lower oxidation state. More detail will be provided when discussing their characterisation. After treating the deactivated catalysts $H_3PMo_{12}O_4$ and $H_3PW_{12}O_{40}$ under air flow for 2 h, at 250 and 350 °C, respectively, the catalytic activities return to initial levels. It is remarkable that higher regeneration temperatures at which the Keggin structure is known to be unstable ($T > 450\,°C$) [16,17] are not necessary, a prerequisite for repeated reaction–regeneration cycles. However, the catalytic system based on phosphomolybdic acid shows quite soon a progressive degradation of catalytic properties. Even though butene conversion still remains high for further several cycles, octanes selectivity decreases quickly from 97% of fresh catalyst to 22% after two reaction–regeneration cycles. In contrast, the system based on phosphotungstic acid is stable for at least 11 cycles (table 3). The differences in selectivity to saturated octanes shown in table 3 can be attributed to the choice of using different temperatures for the regeneration. A temperature of 200 °C (first two cycles) is clearly less satisfactory than 350 °C (third cycle).

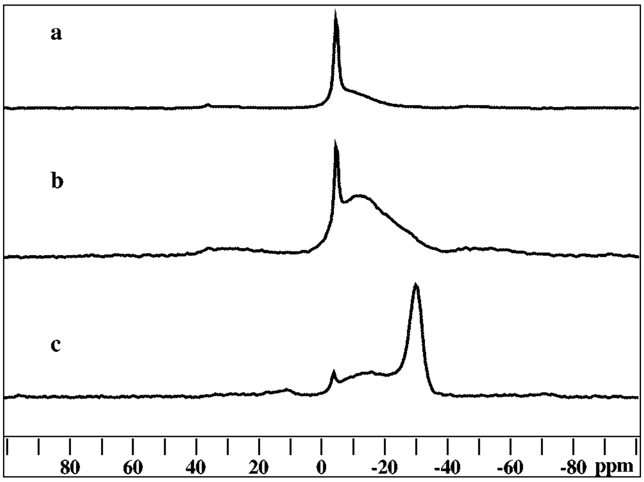
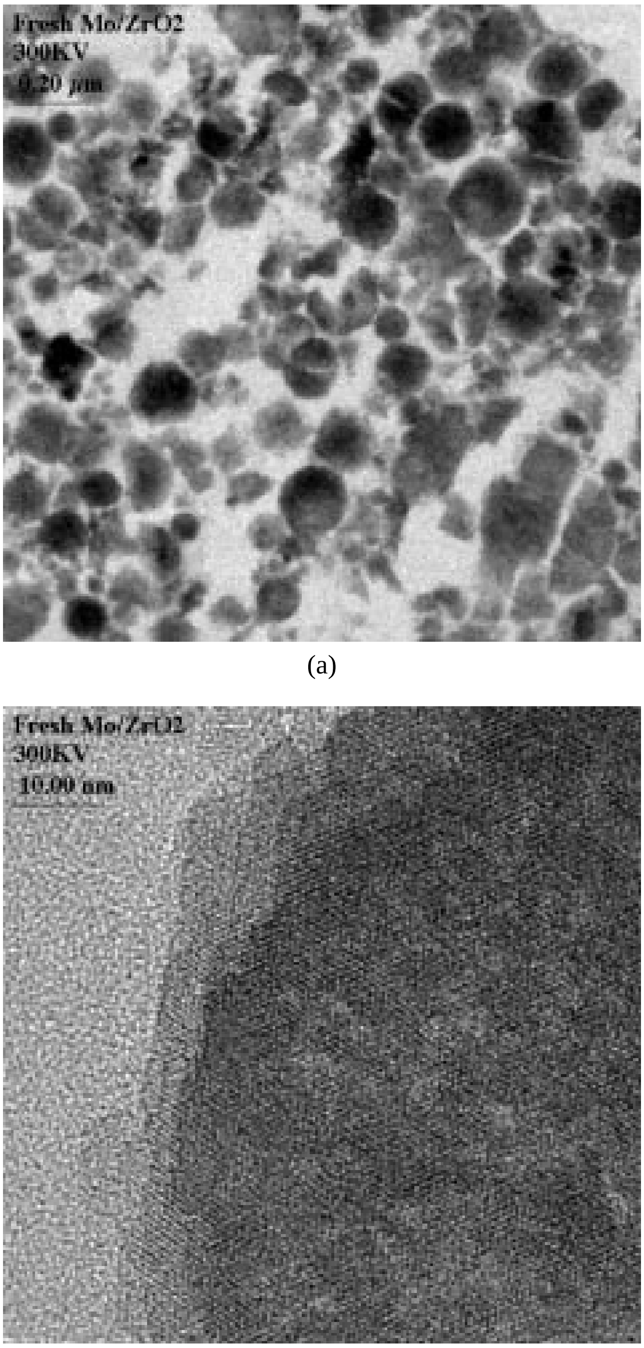


Figure 1. ^{31}P-MAS-NMR spectra of catalyst 1 (Mo-based): (a) fresh; (b) after 2 h of catalytic test; (c) after 11 reaction–regeneration cycles.

3.2. Physical–chemical characterisation

3.2.1. $H_3PMo_{12}O_{40}/ZrO_2/SO_4$

The catalyst, obtained supporting phosphomolybdic acid on zirconia in the presence of sulphuric acid (table 1, entry 1), is analysed by ^{31}P-MAS-NMR, EPR, XRD and TEM-EDS. In the ^{31}P-MAS-NMR spectrum of the fresh catalyst there are two resonance lines (figure 1(a)). The first one at -3 ppm is sharp and is due to the phosphomolybdic acid with Keggin structure [18]. The second one at -9 ppm is much broader and is not completely assigned in the literature [18–20]. Fresh catalyst shows no EPR signal, indicating that all Mo present is Mo^{VI} as in the starting heteropoly acid. XRD spectra confirm the presence of phosphomolybdic acid with Keggin structure, having orthorhombic symmetry ($a = 2.081$ nm, $b = 1.304$ nm, $c = 1.893$ nm), on an amorphous support. From TEM-EDS analysis, the heteropoly acid is well dispersed on the amorphous zirconia matrix and forms spongy aggregates



(a)

(b)

Figure 2. HRTEM micrographies of fresh Mo-based catalyst: (a) HPA on zirconia; (b) HPA structure.

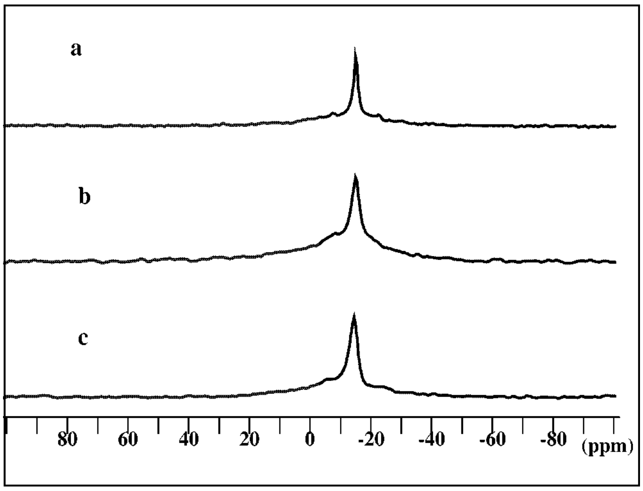


Figure 3. ^{31}P-MAS-NMR spectra of $H_3PW_{12}O_{40}$ catalyst: (a) fresh; (b) after one reaction–regeneration cycle; (c) after eleven reaction–regeneration cycles.

(figure 2), of which the size is between 100 and 500 nm. The aggregates are formed by crystallites of 10–20 nm, made by hexagonal packing of Keggin units.

The same catalyst after 2 h of catalytic testing shows quite different features. In ^{31}P-MAS-NMR spectrum (figure 1(b)) there are again two signals, but in this case the broader one is much more intense and shifts from -9 ppm to -14 ppm, indicating a modification in the structure of the heteropoly acid. In the EPR spectrum there is a signal with $g_{\perp} = 1.953$ and $g_{\|} = 1.893$ which are typical values of Mo^{V} in octahedral symmetry. The ^{13}C-MAS-NMR shows the signals of organic matter prevalently aromatic, a possible reason for activity losses.

After the first regeneration, the XRD spectra of the catalyst show that the phosphomolybdic acid is still present with Keggin structure, but its quantity is reduced. From TEM-EDS analysis, the HPA aggregates begin to compact. ^{13}C-NMR signals are no longer present and also Mo^{V} appears to have been oxidised to Mo^{VI}, according to the EPR spectrum.

After many reaction–regeneration cycles, the catalyst suffers deep changes in its structural features. From ^{31}P-MAS-NMR spectrum (figure 1(c)), only a very small part of the starting heteropoly acid remains in the Keggin structure (small signal at -3 ppm), while the distorted form originated from the acid is still present (broad signal at -17 ppm). A new signal appears at -30 ppm, due to the P of ZrP_2O_7. XRD spectra confirm the structural changes both in the support and in the heteropoly acid structure. In fact, the latter is destroyed with formation of a new crystalline phase (ZrP_2O_7) while the support changes from amorphous to crystalline (cubic). According to EPR spectrum, a new Mo^{V} species with $g_{\perp} = 1.953$ and $g_{\|} = 1.872$, different from that present after the first reaction cycle, is formed.

3.2.2. $H_3PW_{12}O_{40}/ZrO_2/SO_4$

We have shown that the behaviour of the catalyst based on phosphotungstic acid is different from that based on phosphomolybdic acid, and this is in accord with characterisation results.

For the fresh W catalyst, the ^{31}P-MAS-NMR spectrum (figure 3) shows two signals: a sharp one at -15 ppm, due to the acid with Keggin structure, and a broad one at -10 ppm, which could be due to a lacunary form of the heteropoly acid or to a species interacting with the supporting material. The XRD spectrum (figure 4) is typi-

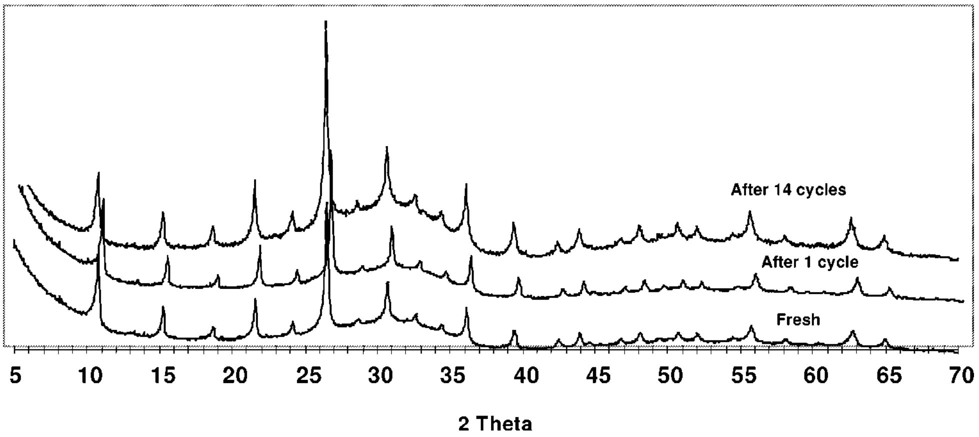


Figure 4. XRD spectra of W-based catalysts.

cal of phosphotungstic acid with Keggin structure on an amorphous support. TEM-EDS analysis is very similar to the one of Mo-based catalyst, showing a good dispersion and heteropoly acid aggregates between 100 and 500 nm, formed by crystallites of 10–20 nm.

After the reaction–regeneration cycles, Mo- and W-based catalysts are completely different: the W catalyst, even after eleven cycles, does not show significant changes in comparison with the fresh catalyst. No major differences are detectable in the ^{31}P-MAS-NMR and XRD patterns (figures 3 and 4). In TEM-EDS analysis, the Keggin structure of the heteropoly acid is preserved: no changes are observed in the morphology and the aggregates are still crystalline, while the zirconia is still amorphous. No EPR signal due to W^V was observed for this catalyst.

4. Conclusions

The catalysts produced by heteropoly acids supported on metal oxides in the presence of sulphuric and other strong acids are able to catalyse the alkylation of isobutane with n-butenes to yield a mixture of products, in which saturated octanes are the most important fraction. Trimethylpentanes in some cases constitute the major part of such octane fraction. Catalysts can be obtained using different heteropoly acids, both with Keggin and Dawson structure, different anions (sulphate, chloride, fluoride, triflate) supported on different oxides (ZrO_2, TiO_2, Al_2O_3, Fe_2O_3).

The catalyst composed by phosphotungstic acid supported on zirconia in the presence of sulphuric acid shows the best catalytic results, both as to 1-butene conversion and selectivity to trimethylpentanes. This catalyst undergoes reversible deactivation probably because of the deposition of heavy organics, which can be easily removed by *in situ* heating, under air flow, at temperatures between 250 and 350 °C. This process regenerates completely the catalyst, which can be reused for at least eleven reaction cycles without any significant change in its catalytic or structural properties.

The case of the catalyst based on phosphomolybdic acid is different, because deactivation is not only the result of active sites poisoning by organic matter but also of heteropoly acid degradation and the crystallisation of the zirconia support.

Acknowledgement

We thank EniTecnologie for its kind permission to publish this paper. We also want to thank Mr. R. Vanazzi for his work in performing the alkylation tests.

References

[1] A. Corma, A. Martinez and C. Martinez, J. Catal. 146 (1994) 185.
[2] A. Corma, A. Martinez and C. Martinez, J. Catal. 149 (1994) 52.
[3] C.-H. Liang, Alkylation of isobutane with n-butenes over solid catalysts, Dissertation N 9411297, UMI (1994).
[4] C.S. Crossland, A. Johnson and E.G. Pitt, US Patent 5,157,196 (1992).
[5] A. Corma, V. Gomez and A. Martinez, Appl. Catal. 119 (1994) 83.
[6] A. Corma, A. Martinez and C. Martinez, Catal. Lett. 28 (1994) 187.
[7] S.I. Hommeloft and H.F.A. Topsøe, US Patent 5,245,100 (1993).
[8] M.G. Clerici, C. Perego, A. de Angelis and L. Montanari, US Patent 5,571,762 (1993).
[9] M.G. Clerici, A. de Angelis and P. Ingallina, It. Patent 1,272,926 (1995).
[10] M. Misono, *Advances in Catalysis*, Vol. 41 (Academic Press, San Diego, CA, 1996).
[11] A. Corma, A. Martinez and C. Martinez, J. Catal. 164 (1996) 422.
[12] T. Okuhara, M. Yamashita, K. Na and M. Misono, Chem. Lett. (1994) 1451.
[13] T.K. Cheung, J.L. d'Itri and B.C. Gates, J. Catal. 151 (1995) 139.
[14] I.V. Kozhevnikov, Russ. Chem. Rev. 56 (1987) 811.
[15] B. Gruttner and G. Jander, in: *Handbook of Preparative Inorganic Chemistry*, Vol. 2, ed. G. Brauer (Academic Press, New York, 1965).
[16] L. Malaparade, in: *Nouveau Traité de Chimie Minerale*, ed. P. Pascal (Masson, Paris, 1959).
[17] C. Rocchiccioli-Deltcheff, A. Aouissi, M.M. Beetahar, S. Launay and M. Fournier, J. Catal. 164 (1996) 16.
[18] T. Chang, J. Chem. Soc. Faraday Trans. 91 (1995) 375.
[19] I.V. Kozhevnikov, A. Sinnema, R.J.J. Jansen, K. Pamin and H. van Bekkum, Catal. Lett. 30 (1995) 241.
[20] V.M. Mastikhin, S.M. Kulikov, A.V. Nosov, I.V. Kozhevnikov, I.L. Mudrakovsky and M.N. Timofeeva, J. Mol. Catal. 60 (1990) 65.