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**PILLARED MONTMORILLONITES DOPED WITH CATALYTICALLY
ACTIVE TRANSITION METAL IONS
PART 2. CATALYTIC PROPERTIES**

Abstract. Versatile catalytic properties of Cu- and V-doped Al-, Ti-, and Zr-pillared montmorillonite clays are presented and the results related to the physico-chemical properties of the resulting materials. Examples of catalytic reactions include conversion of isopropanol, ammoxidation of m-xylene, selective catalytic reduction of NO with ammonia, oxidative dehydrogenation of propane, hydroxylation of phenol, and oxidation of toluene and xylenes with hydrogen peroxide.

Key-words: pillared montmorillonites, catalysis by PILC

INTRODUCTION

Catalytic properties of clays are known since the 19th century, but their application as catalysts on industrial scale took place around 1930 when it was noted that acid activated montmorillonite clay were active in cracking oil to give high-octane petrol (Occelli, Rennard 1988). Only in the sixties were the acid activated clays replaced by zeolites as cracking catalysts. The oil crisis in the seventies and the rising prices of petrol renewed interest in catalytic properties of clays. The aim was to design catalysts capable of cracking large molecules of heavy fractions of oil. Synthetic zeolites known at the time had pores of dimensions less than 5 Å and could not be used to process bulky hydrocarbon molecules. The concept of pillaring, in which the smectite layers served as prefabricated elements for construction of porous solids with bidimensional zeolite-like channels, opened new field in catalyst design (Vaughan 1988). Initially, the main use of pillared clays was seen in acid catalysis, in particular in dehydration of alcohols, conversion of methanol to hydrocarbons, oligomerization, alkylation, oil cracking and production of fine chemicals (Burch,

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Warburton 1986; Vaughan 1988; Bartley 1988; Kikuchi, Matsuda 1988; Occelli, Rennard 1988; Ming et al. 1988; Jones 1988). However, successful incorporation of transition metal ions, either at the stage of pillar formation or in the post-pillaring treatment, extended the field of application of pillared clays also to processes of redox nature. Activity of such materials in syngas conversion, dehydrogenation of hydrocarbons, ammoxidation of toluene, removal of nitrogen oxides (denox), low temperature liquid phase hydroxylation and oxidation of aromatic compounds has been announced (Bartley, Burch 1986; Yamanaka, Hattori 1988; Bahranowski et al. 1995b; Chen et al. 1995; Yang, Li 1995; Bahranowski et al. 1997; Bahranowski et al. 1998; Barrault et al. 1998; Bahranowski et al, 1999).

In this part of the paper the results of investigations are presented in which pillared clays doped with copper or vanadium were tested as catalysts in reactions occurring according to the redox mechanism. Examples of the catalytic performance in the reaction of isopropanol conversion, ammoxidation of m-xylene (Bahranowski et al. 1995a), selective catalytic reduction of NO with ammonia (Bahranowski et al. 1997), oxidative dehydrogenation of propane (Bahranowski et al. 1995b; Bahranowski et al. in print^a; Bahranowski al. in print^b), hydroxylation of phenol (Bahranowski et al. 1998) and oxidation of toluene and xylenes with hydrogen peroxide (Bahranowski et al. 1999). The synthesis details and the nomenclature of pillared clay catalysts are described in Part 1.

CATALYTIC TESTS

Conversion of isopropanol

Conversion of isopropanol is a test reaction probing acid-base and redox properties of the catalysts (B. Grzybowska-Świerkosz 1987). The alcohol may be decomposed through two parallel routes: dehydration to propene on acid type centres and dehydrogenation to acetone on basic redox centres. The rate of the propene formation may be regarded as a measure of the catalyst acidity, whereas the acetone/propene ratio as a measure of catalyst basicity and redox properties. Since pillared clays are known as acid catalysts, it is interesting to check to what extent they are affected by introduction of the dopant possessing redox properties.

Table 1 shows the results of the isopropanol conversion in the presence of V-doped Al- and Ti-pillared montmorillonites. The data show that the acid-base properties of Ti-PILC and Al-PILC differ, the former being more acidic and less basic than the latter.

The effect of doping with vanadium depends on the method of preparation and the nature of pillars. First portion of vanadium introduced into Al-PILC by means of cation exchange significantly increases the catalyst acidity (the rate of propene formation is 2.5 higher than for the undoped material).

Results of isopropanol conversion at 180°C

TABLE 1

Sample	Propene ($\times 10^{-6}$ mole/m ² /s)	Acetone ($\times 10^{-6}$ mole/m ² /s)	Acetone/propene
Al-PILC	0.45	0.10	0.22
V ₁ -(Al-PILC)	1.17	0.04	0.03
V ₂ -(Al-PILC)	1.18	0.00	0.00
(V-Al)-PILC	0.11	0.14	1.27
Ti-PILC	0.81	0.13	0.16
V ₁ -(Ti-PILC)	0.84	0.25	0.30
V ₂ -(Ti-PILC)	0.25	0.28	1.12
(V-Ti)-PILC	1.74	0.23	0.13

Simultaneously, the basicity measured as acetone/propene ratio drastically falls. The second portion of V dopant does not affect the rate of propene formation but completely suppresses the dehydrogenation pathway to acetone, destroying the remnants of basic properties. The co-pillared catalyst, which is the one with interlayer densely packed with Al pillars and containing significant amount of vanadium, shows completely different behaviour. Its acidity is low, while the basicity reaches maximum among all Al-pillared materials.

Addition of vanadium by means of cation exchange to Ti-PILC modifies the acid-base properties of the catalyst in a completely different manner than in the case of Al-pillared samples. First portion of vanadium inserted into the Ti-PILC matrix does not affect the acidic properties of the sample as the rate of the propene formation remains almost unchanged, but it doubles the acetone to propene ratio showing that in this case the presence of vanadium enhances basic (and redox) properties. The next portion of V reduces the acidity and strongly increases the basicity. It is interesting to compare the co-pillared (V-Ti)-PILC sample with the undoped Ti-PILC catalyst, both having microporous texture and a similar chemical composition (the amount of V dopant is only ca. 0.1 wt.% of V₂O₅). The co-pillaring results in the material being twice as much acidic as the Ti-PILC sample.

The results show that insertion of typical redox centres affects also the acid-base properties of the pillared clays.

Ammoxidation of m-xylene

In the presence of oxygen and ammonia the unsaturated and aromatic hydrocarbons can be catalytically converted to corresponding nitriles, important

substrates in chemical industry. The process is known as ammoxidation. The V-doped Al- and Ti-pillared montmorillonites have been tested for their ability to catalyse the ammoxidation of m-xylene (Bahranowski et al., 1995a). The reaction was carried out in a high-temperature IR cell and its progress was studied by monitoring of the appearance of the nitrile group band at 2240 cm^{-1} in the IR spectrum.

In the case of both Al-PILC and Ti-PILC supports, introduction of vanadium into the pillared structure strongly increased the amount of nitrile product. The catalytic activity depended on the method of V insertion. It was particularly high for (V-Ti)-PILC co-pillared sample, despite the low level of doping with vanadium. The effect was assigned to the unique character of the vanadyl species present in this catalyst, identified with ESR spectroscopy. The vanadyl centres in the (V-Ti)-PILC sample have been found to possess the highest degree of covalent bonding within V–O bonds perpendicular to the V=O vanadyl axis among all types of V species observed (Bahranowski, Serwicka 1993; Bahranowski et al. 1996a). It was argued that higher covalency facilitates electron transfer from the electron accepting to the electron donating sites at the catalyst surface and, thus, enhances the catalytic redox reaction occurring with participation of these centres.

Selective catalytic reduction of NO with ammonia

Selective catalytic reduction (SCR) by ammonia is the most common method used for the removal of nitrogen oxides (deNO_x) from industrial flue gases. The process is currently performed mainly with aid of titania-supported vanadia catalysts (Bosch, Janssen 1988). Thus, it seemed of interest to check the usefulness of the V-doped Ti-pillared clays for the SCR of NO with NH₃ and compare their performance with a classical vanadia-titania catalyst (Bahranowski et al. 1997).

The results showed that introduction of vanadium was essential for good catalytic activity of pillared samples. The best catalyst, converting 90–100% NO in the temperature range 250–350°C, was obtained by a single exchange of Ti-PILC with vanadyl ions (Fig. 1). Its good performance was attributed to the presence of well dispersed V centres and to the lack of polymeric V species. The latter, appearing in the catalyst doped by multiple exchange, were responsible for poorer performance of this sample, despite the higher total V content. Interestingly, the maximum NO conversion observed on the reference vanadia-titania catalyst was only 85%, which points to the superior properties of V-doped Ti-pillared material.

Oxidative dehydrogenation of propane

Oxidative dehydrogenation of propane to propene represents a great challenge, because it converts a cheap, saturated hydrocarbon into an important substrate for many industrial processes.

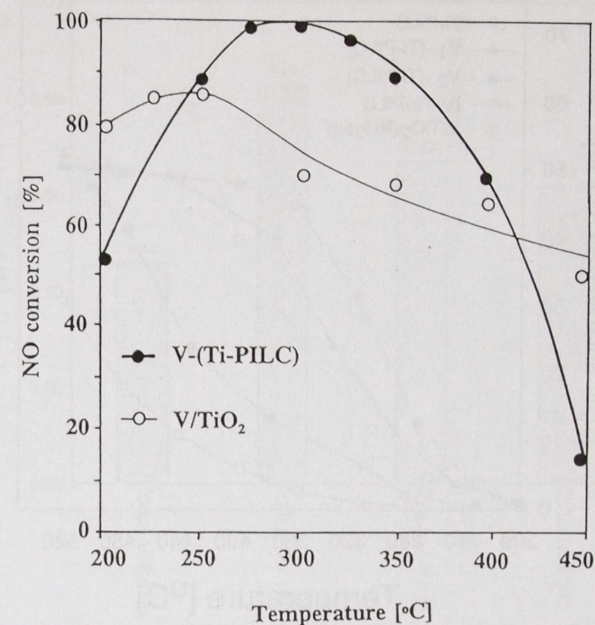


Fig. 1. Temperature dependence of NO conversion over V-doped Ti-pillared clays

V-doped Ti- and Zr-pillared samples were tested in this reaction (Bahranowski et al. 1995b; Bahranowski et al. in print^a; Bahranowski et al. in print^b). The performance of the catalysts depended on the nature of pillar and on the method of vanadium incorporation. Generally, the Ti-pillared catalysts were more active (i.e. converted more propane) but less selective (i.e. less propene was formed) than the Zr-PILC samples. In both cases addition of vanadium by means of cation exchange improved the catalytic activity, measured as a percentage of converted propane, indicating that V redox centres were beneficial for the reaction. Also, in both cases the co-pillared samples showed the highest selectivity to propene. This is shown on the example of V-doped Ti-PILC catalysts (Fig. 2 a, b). Similarly as in the case of ammoxidation of m-xylene, the effect of the improved selectivity was attributed to the unique electronic properties, inferred from the ESR spectra, of V species present in the co-pillared samples.

Hydroxylation of phenol

Hydroxylation of phenol consists in attachment of the second OH group to the aromatic ring. The products are dihydroxybenzenes (DHBs) which may appear as two isomers: catechol and hydroquinone. Both compounds are important reagents in the production of the so-called fine chemicals. The reaction is carried out in the liquid phase, at a temperature below 100°C, in the presence

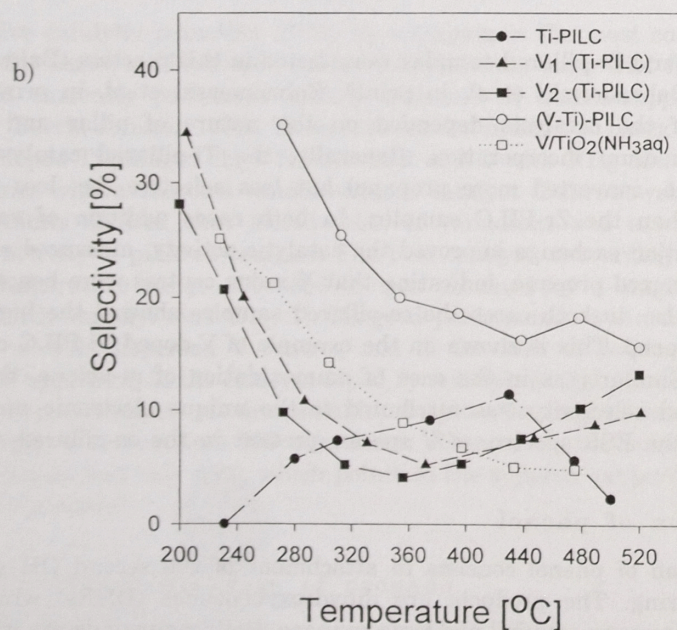
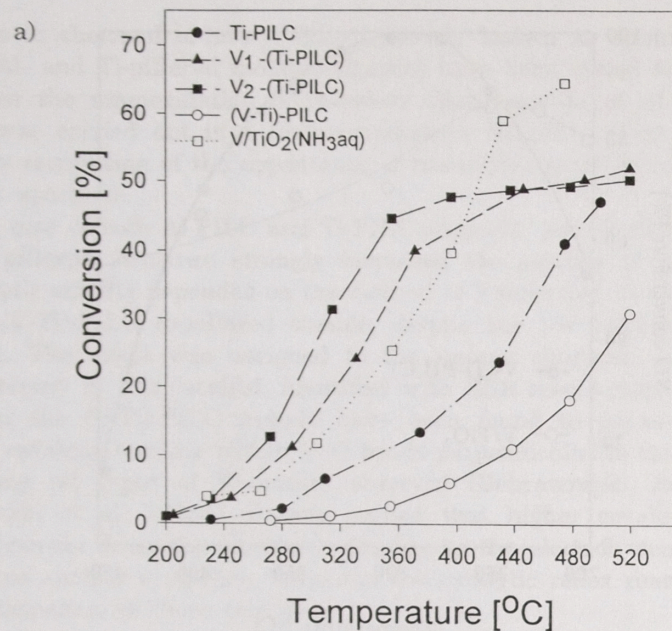


Fig. 2. Temperature dependence of
a) propane conversion, b) selectivity to propene over V-doped Ti-pillared clays

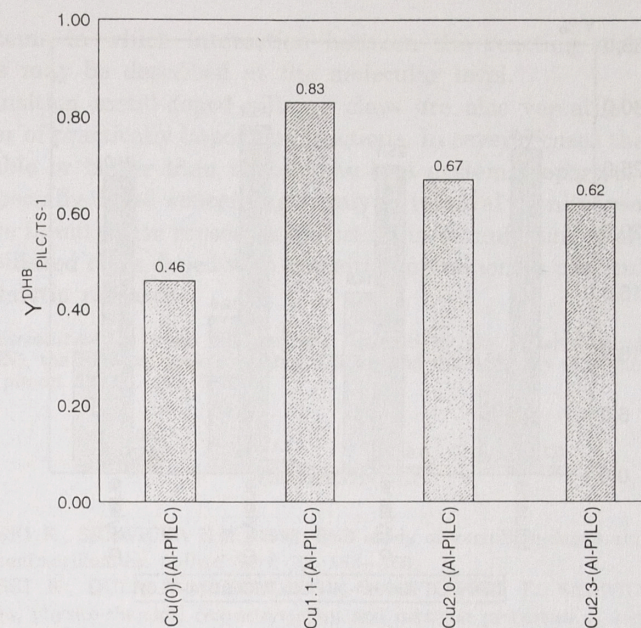


Fig. 3. Yield of dihydroxybenzenes over Cu-doped Al-pillared catalysts relative to the performance of TS-1 catalyst

of H₂O₂ which is an environmentally friendly oxidant. The recently developed industrial process uses a titanium-containing zeolite known as TS-1 as a catalyst and gives the best reported DHB yields (Notari 1988). Nevertheless, there is a constant search for cheaper systems capable of catalysing this reaction.

A series of Cu-doped Al-pillared montmorillonite samples, with dopant introduced by means of consecutive exchange/calcination treatments, were tested in the phenol hydroxylation (Bahranowski et al. 1996b, c; Bahranowski et al. 1998). The experiments have shown that all Cu-doped clays are very active in this process, the sample obtained by single exchange giving the best results, comparable to the performance of the reference TS-1 catalyst (Fig. 3). On the basis of ESR data it was argued that the clustered copper ions, whose contribution increases with the number of exchange treatments, are not active in the reaction. Bearing in mind the relative simplicity of preparation of PILC materials in comparison to the synthesis of TS-1 catalyst, the results have shown that Cu-doped Al-pillared montmorillonite can be considered an interesting alternative as catalyst in the process of phenol hydroxylation.

Oxidation of toluene and xylenes with hydrogen peroxide

Oxidation of complex aromatic molecules, frequently unstable at higher temperatures, is one of the constant challenges in the manufacture of fine

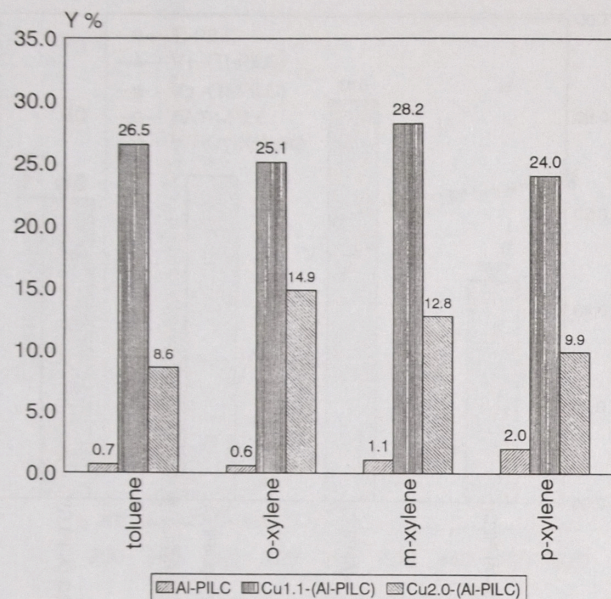


Fig. 4. Yield of oxidation products over Cu-doped Al-pillared catalysts

chemicals. A low-temperature liquid phase oxidation in the presence of a suitable catalyst offers an interesting possibility of obtaining the desired products.

The Cu-doped Al-pillared montmorillonites have been tested in the reaction of liquid phase oxidation of toluene, meta-, ortho-, and p-xylene below 100°C (Bahranowski et al. 1999). The results showed that the clay samples can be regarded as potential catalysts in these reactions. They possess significant activity for both the oxidation of methyl groups to aldehydes and hydroxylation of aromatic ring to give various phenols. As in the case of phenol hydroxylation, the sample doped by single exchange/calcination procedure was the most active (Fig. 4). The loss of activity of the catalyst containing more copper was attributed to the formation of catalytically inert clustered copper ions. Comparison with the literature data shows that the Cu-doped pillared clay catalysts give the best reported conversions of aromatic substrates.

CONCLUSIONS

From the point of view of catalysis, the transition metal-doped pillared clays represent materials interesting both theoretically and practically.

They possess both the acid-base and the redox type of centers, whose concentration and properties can be modified by an appropriate preparation. The existence of dispersed active centres allows to regard these catalysts as

model systems in which interaction between the reacting molecules and the active sites may be described at the molecular level.

The transition metal-doped pillared clays are also versatile catalysts active in a number of practically important reactions. In several cases their performance is comparable or better than that of the best systems reported. The presented results, especially those concerning catalytic removal of nitrogen oxides or low temperature liquid phase processes important in manufacturing of fine chemicals, make the pillared clays doped with transition metal ions a particularly promising field of catalytic research.

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PODPIERANE MONTMORILLONITY DOTOWANE KATALITYCZNIE AKTYWNYMI METALAMI PRZEJŚCIOWYMI CZĘŚĆ 2. WŁAŚCIWOŚCI KATALITYCZNE

Streszczenie

Praca przedstawia różnorodne właściwości katalityczne montmorillonitów podpieranych Al, Ti i Zr oraz dotowanych miedzią lub wanadem. Wyniki testów katalitycznych odniesione są do właściwości fizykochemicznych otrzymanych katalizatorów. Przykłady reakcji katalitycznych obejmują konwersję izopropanolu, utleniającą amoniak m-ksylenu, selektywną katalityczną redukcję NO amoniakiem, utleniające odwodornienie propanu, hydroksylację fenolu oraz utlenianie toluenu i ksylenów nadtlaniem wodoru.