



Liquid phase alkylation of benzene with dec-1-ene catalyzed on supported 12-tungstophosphoric acid

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ABSTRACT

The liquid phase alkylation of benzene with dec-1-ene was catalyzed by 12-tungstophosphoric acid (WP) supported on different solids (ZrO₂, SiO₂, activated carbon and boehmite-Al₂O₃). Catalysts prepared with 20 wt.% of WP were thermally treated at 300 °C and then the acidity was estimated by FT-IR pyridine adsorption spectroscopy. Additionally, the catalysts were characterized by X-ray diffraction, thermal gravimetric analysis, and N₂ adsorption measurements. Thermal stability of supported WP and changes in textural properties of the catalysts were analyzed. Of all the catalysts, 20WP on SiO₂ showed the highest acidity and was found to be the most active catalyst in alkylation of benzene with dec-1-ene at 80 °C, at dec-1-ene conversion of 70% and alkyl benzenes selectivity of nearly 40%.

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1. Introduction

The alkylation of aromatic hydrocarbons with olefins is applied on a large scale in the chemical industry. Alkylation of benzene with C_{10–14} linear alkenes is used for the synthesis of linear alkyl benzenes (LABs), which are the primary raw material for the production of LAB sulfonates, a surfactant detergent intermediate [1–3]. Currently, Alkylation of aromatics is carried out commercially using Friedel–Crafts catalysts such as AlCl₃, FeCl₃ and ZnCl₂ or a strong Brønsted acid such as HF. Nonetheless, these catalyst systems show many drawbacks as alkylating agents since they generate many problems such as pollution, handling, safety, corrosion and tedious work up. At present, considerable efforts are being made to find efficient, sustainable, recyclable, and eco-friendly catalysts that can successfully catalyze the above reaction [4,5]. Numerous materials have been evaluated as solid acids for this alkylation process. Among the materials evaluated are zeolites [6–9], clays [10], ionic liquids [11], and various metal oxides [12]. For example, strong solid acids based on supported transition metal oxides are potential replacements for liquid acids and halide containing solids [13,14].

Heteropolyacids (HPAs) constitute an alternative for alkylation reactions, as they are characterized by a strong acidity, fundamentally of the Brønsted type, comparable to that of HF and H₂SO₄

acids; some of the more interesting HPAs have the Keggin structure. The Keggin HPAs comprise heteropoly anions of the formula [XM₁₂O₄₀]ⁿ⁻ (α-isomer), where X is the heteroatom (P⁵⁺, Si⁴⁺, etc.) and M the addendum atom (Mo⁶⁺, W⁶⁺, etc.). The structure of the heteropoly anion is composed of a central tetrahedron XO₄ surrounded by 12 edge- and corner-sharing metal–oxygen octahedra MO₆ [15]. 12-Tungstophosphoric acid (WP) is the usual catalyst of choice because of its high acidic strength, relatively high thermal stability, and lower oxidation potential. A serious problem associated with the use of this type of materials as heterogeneous catalysts is their low surface area (~5–8 m²/g) [1]. The use of HPA in supported form is preferable because of its high surface area compared to the bulk material. Acidic or neutral solids, which interact weakly with HPAs such as silica, active carbon and acidic ion-exchange resin, have been reported to be suitable as HPA supports [16]. Zirconia-supported WP acts as an efficient catalyst for but-1-ene isomerization reaction [17,18]. The use of supported HPAs in alkylation reactions [19–21] and the production of linear alkyl benzenes [22–24] have been reported.

The essential feature of the alkylation reaction consists in the replacement of hydrogen atom of an aromatic compound by an alkyl group derived from an alkylating agent. When the replaced hydrogen is on the aromatic ring, the reaction is an electrophilic substitution and it proceeds in via an acid catalyst. On the other hand, when the hydrogen on the side chain of aromatic is replaced, base catalysts or radical conditions are required. The nature of the alkylations product thus depends on the acid–base properties of the selected catalyst.

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In this study, benzene alkylation with 1-decene in liquid phase was studied over four different catalysts. The effects of support and the generation of acid sites were examined. The catalysts were characterized by XRD, thermal analysis, N₂ adsorption, and FT-IR of pyridine adsorption. A correlation of the activity of these catalysts with their acidic properties was attempted.

2. Experimental

2.1. Catalyst preparation

All the Supports were impregnated with an ethanol solution containing the required amount of the WP, that is, 20 wt.% referred to the total weight of the dried WP + support. Ethanol was removed using a rotary evaporator. After impregnation, the catalysts were dried at 120 °C and calcined overnight at 300 °C. The supports included alumina (Bohemite HiQ-10, Alcoa-Kasei), silica gel (J. T. Baker), activated carbon (Aldrich) and the dried zirconium oxyhydroxide, which was obtained by the precipitation method reported elsewhere [17,25]. The prepared catalysts were denoted as xWP/y, where x is the loaded WP weight percent and y represents SiO₂, Carbon, Al₂O₃ and hydrated ZrO₂, respectively.

2.2. Catalyst characterization

The specific surface area, pore volume and pore size distribution of the samples were measured in an automatic adsorption instrument (Quantachrome Autosorb 1C) using low-temperature N₂ adsorption–desorption isotherms. Prior to the measurements, the samples were evacuated in situ at 300 °C for 3 h under vacuum. The surface area was calculated from these isotherms using the multi-point Brunauer–Emmett–Teller (BET) method based on the adsorption data within the partial pressure P/P_0 range from 0.05 to 0.35. The pore size distribution was determined by BJH method from the desorption part of isotherm, the pore volume was determined from total volume of nitrogen adsorbed at $P/P_0 = 0.98–0.99$.

Thermogravimetric analyses were recorded in a PerkinElmer TG-7 apparatus. The samples were heated in flowing anhydrous air (20 mL/min) from ambient temperature to 800 °C, with a constant heating rate of 10 °C/min.

A Siemens D-5000 diffractometer coupled to a copper anode tube was used to obtain the X-ray diffraction (XRD) pattern, identify the crystalline compounds and estimate the dispersion of WP on the supports. The Cu K α ($\lambda = 0.15406$ nm) was selected with a diffracted beam monochromator.

The solids were characterized by FT-IR spectroscopy using a 170-SX Nicolet spectrometer. Self-supported wafers (14 mg) were mounted in a glass cell equipped with KBr windows, which allowed in situ thermal treatments. For the acidity determination, the sample was evacuated to 10⁻¹ Pa at 300 °C for 30 min. After that, the sample was cooling and followed by exposure (2.14 L h⁻¹)

to pyridine-saturated N₂ for 15 min, and then outgassed 1 h at room temperature (pressure 10⁻¹ Pa), and finally, linearly heated up to the desire temperature. The concentration of Brønsted and Lewis acid sites was obtained using a standard procedure based on the Lambert–Beer law. The absorbency (A_I) is determined as the integrated area under the curve as follows:

$$A_I = BC \int e_v d_v$$

where $\int e_v d_v$ is the extinction coefficient and it is proportional to 0.4343 (I_v). In agreement with Ref. [26], $I_v = 3.03$ or 3.26 cm μmol^{-1} for the bands at 1545 and 1450 cm⁻¹, respectively. B is related to weight (g)/area (cm⁻²) wafer ratio, and C the concentration of Brønsted or Lewis acid sites which can be calculated as:

$$C_{\text{Brnsted}} = \frac{A_I(\sim 1545 \text{ cm}^{-1})}{w(0.4343 \times 3.03/\text{area})}$$

$$C_{\text{Lewis}} = \frac{A_I(\sim 1450 \text{ cm}^{-1})}{w(0.4343 \times 3.26/\text{area})}$$

2.3. Catalytic activity experiments

The alkylation of benzene with dec-1-ene in the liquid phase was carried out at atmospheric pressure in a 100-mL glass batch reactor equipped with a magnetic stirrer and a reflux condenser. Prior to introduction into the reactor, the catalysts were activated in air for 4 h at 300 °C. The reaction temperature was 80 °C, using typically a 5 mol/mol ratio of benzene (Aldrich, 99.8%) to dec-1-ene (Aldrich, 94%) and a 20 mL/g ratio of dec-1-ene to catalyst. After 1 or 3 h, as indicated, the reaction was stopped and the catalyst separated. The filtrate was analyzed using a Varian CP-3600 gas chromatograph equipped with an HP-5 capillary column (cross-linked 5% ME silicone, 30 m \times 0.53 mm \times 1.5 μm film thickness), coupled with a Flame Ionization detector.

3. Results and discussion

3.1. Physico-chemical characterization

The textural properties of the different solids were studied by N₂ adsorption–desorption isotherms method. The related textural data of the catalysts are reported in Table 1 and the N₂ adsorption–desorption isotherms are shown in Fig. 1. The carbon support showed a high initial surface area of 788 m²/g and pore volume of 0.76 cm³/g, and when the support was impregnated with 20 wt.% of WP, the surface area decreased to 566 m²/g (loss of area of 30%). A Similar effect occurred on initial Al₂O₃ and 20WP/Al, which presented 263 and 172 cm²/g, respectively. A reasonable explanation of this event is that the heteropolyacid was located in the micro and mesoporous surface of the support, because of the

Table 1
Textural properties and acidity measurements of WP catalysts.

Catalysts	S_{BET} (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Average pore diameter (Å)	Total acidity ($\mu\text{mol py g}^{-1}$) ^a	B/L (I_{1536}/I_{1442}) ^a
SiO ₂	220	1.05	191	24	n.e. ^b
C	788	0.76	38	n.e. ^b	n.e. ^b
ZrO ₂	271	0.28	32	42	1.06
Al ₂ O ₃	263	0.33	50	n.e. ^b	n.e. ^b
20WP/Si	227	0.86	151	366	1.02
20WP/C	566	0.57	40	n.e. ^b	n.e. ^b
20WP/Zr	272	0.22	32	254	0.90
20WP/Al	172	0.20	46	233	0.76

^a Acidity values obtained from FTIR pyridine adsorption at 100 °C.

^b Not evaluated.

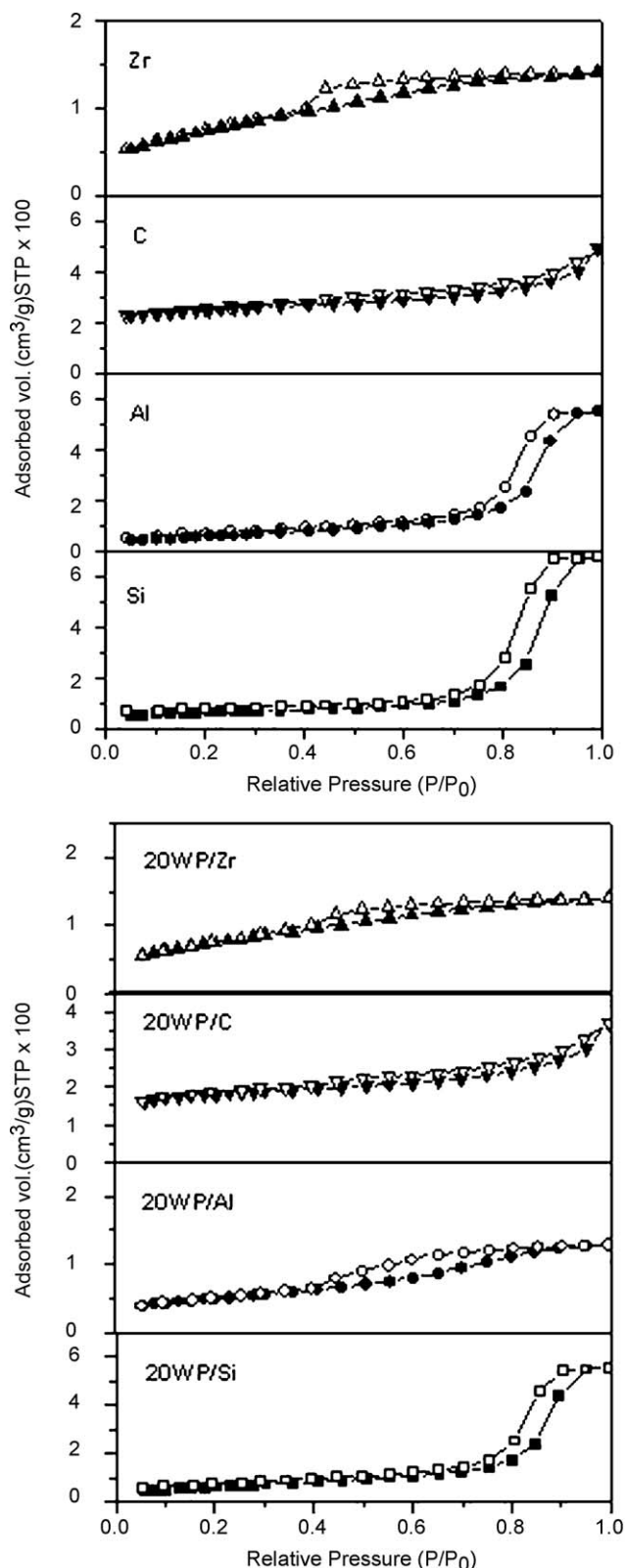


Fig. 1. N_2 adsorption–desorption isotherms of WP catalysts.

diameter of the WP molecule (approx. 12 Å) [27] is smaller than that of the average mesopore size (32–191 Å) of the catalysts, which usually leads to a decrease of the pore diameter. However, 20WP/Si and 20WP/Zr maintained the surface area and the size of pore of the pure supports.

Typical isotherms of the N_2 gas adsorption–desorption are shown in Fig. 1. All samples exhibited type IV isotherms according to IUPAC classification, which are characteristic of mesoporous materials [28]. The supports presented distinct hysteresis loops, for instance, SiO_2 and Al_2O_3 exhibit type H1, ZrO_2 presents a type H2 hysteresis loop while carbon show type H4. It is known that hysteresis is associated with the filling and emptying of the mesopores by capillary condensation and the exact shape of the hysteresis loop varies from one material to another. Type H1 loops are given by adsorbents with a narrow distribution of uniform pores. Many inorganic oxide gels give the more common type H2 loops, as in the case of the ZrO_2 obtained by precipitation and stabilized at 300 °C. While type H4 hysteresis loops are given by slit-shaped pores as in many activated carbons, but in this case the pore size distribution is mainly in the micropore range. When WP is impregnated on the supports, the hysteresis loops types are maintained with the exception of 20WP/Al; this solid transforms from type H1 to H2, due probably to the influence of the pH of the WP solution in the impregnation stage, with a likely peptization and partial dissolution of the support.

The thermal evolution of the catalysts was examined by thermogravimetry; typical TGA and derivative thermal gravimetry (DTG) profiles of 20WP/C, 20WP/Zr, 20WP/Al and 20WP/Si (initially dried at 120 °C) are shown in Fig. 2. The DTG analysis of pure WP hydrate ($H_3PW_{12}O_{40} \cdot xH_2O$) shows three weight loss stages [29]. In all samples, the first weight loss occurred from room temperature to 125 °C because of the loss of physisorbed water and it corresponds to a weight loss of 5–10%. After this event, a gradual weight loss from 150 to 800 °C in 20WP/C, 20WP/Zr and 20WP/Si was observed. In the case of 20WP/C and 20WP/Al, a small event at ~200–250 °C was assigned to the dehydration and dehydroxylation of the supports as well as to crystallization water removal from the WP. Additionally, 20WP/Al presented another stage at 457 °C from the structural change of the support (e.g. boehmite to γ -alumina). The solids, 20WP/Al, 20WP/C, 20WP/Zr, and 20WP/Si, presented a total weight loss of 27, 23, 17 and 13%, respectively.

XRD patterns for 2θ between 4° and 70° are shown in Fig. 3 for the following solids: 20WP/Al, 20WP/Si, 20WP/Zr and 20WP/C. It has been reported that the distinct diffractions peaks associated to the Keggin structure of WP appear at $2\theta = 10.2^\circ$, 20.6° , 25.3° , 29.4° and 34.6° [25,30]. By comparing the XRD patterns of the four samples with that of WP, it can be noted that neither of the catalysts showed peaks that can be assigned to this active phase, which indicates that the supported WP is well dispersed on the surface of the supports. Also, we observed that the supports have low crystallinity when they are calcined at 300 °C, except in the case of alumina which shows the typical XRD of boehmite. This good dispersion can be related to the mean pore diameter of the supports, which is about 30 Å (see Table 1) while the diameter of the HPA is about 12 Å [27]. This difference in the pore diameter allows a more uniform distribution of WP on the support's surface, minimizing the possibility of agglomerations of WP which could induce crystallization and pore plug.

IR spectroscopy of adsorbed pyridine was used to examine the different acid sites in the 1700–1400 cm^{-1} region. The FTIR pyridine adsorption spectra of the supports (as a comparison) and those of supported WP are shown in Fig. 4. The catalysts showed Brönsted (B) and Lewis (L) acidity at 1536 and 1442 cm^{-1} , respectively, and the B/L ratios calculated from the IR absorbance intensities [31] are given in Table 1. Firstly, one observes that the supports at 100 °C presented little or null pyridine adsorption. Notwithstanding, when the WP was deposited in the surface of the different supports an important quantity of acid sites was generated and an increase in the amount of pyridine adsorption was observed (total acidity). These acid sites are strong enough to keep pyridine adsorption at temperatures above 300 °C. The

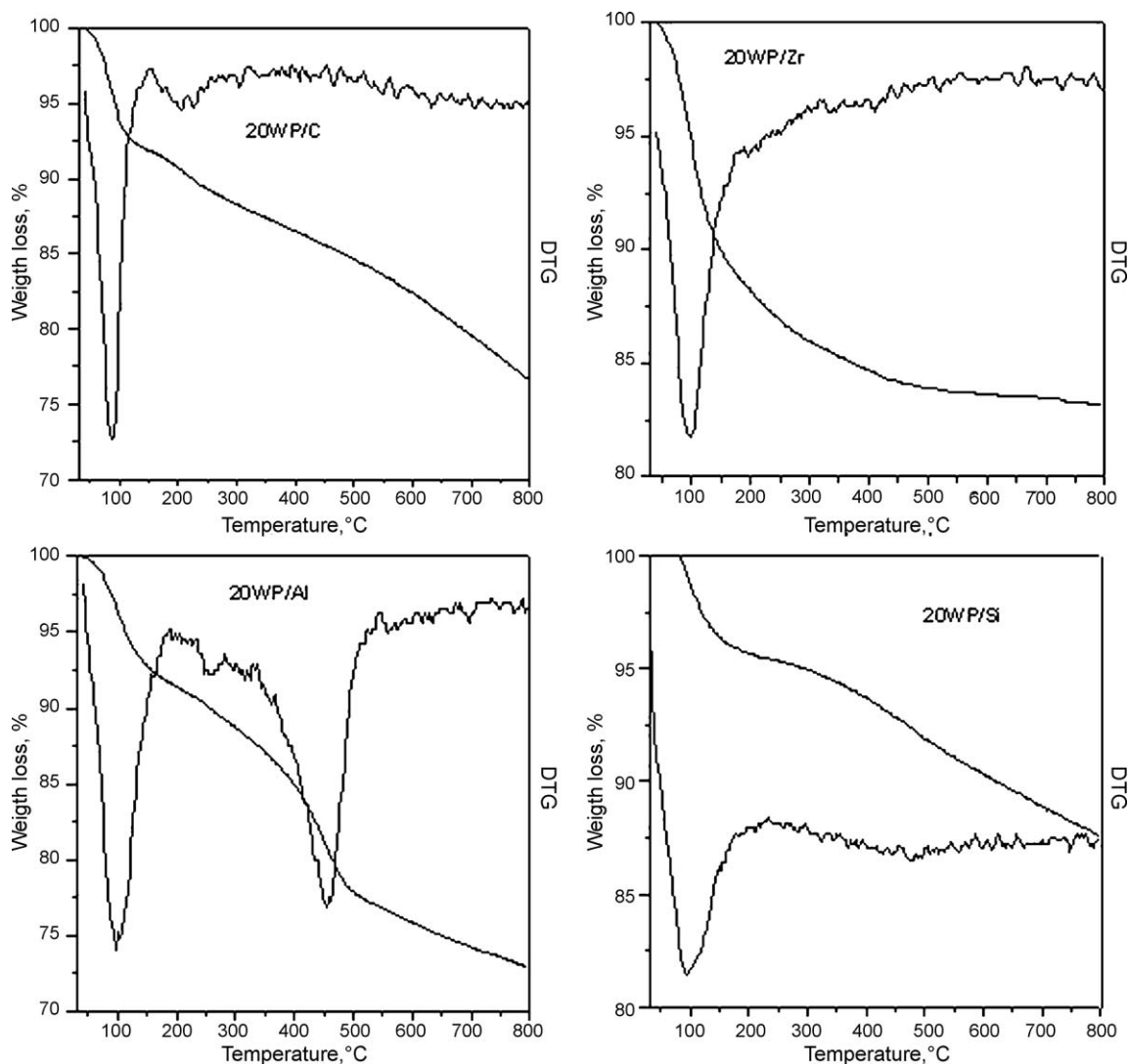


Fig. 2. TGA and DTG profiles of the WP catalysts.

20WP/Si catalyst presented the formation of both Brönsted and Lewis acidity, the other catalysts showed mainly Lewis-type acidity. 20WP/Si, 20WP/Zr and 20WP/Al showed a total acidity of 366, 254 and 233 $\mu\text{mol py g}^{-1}$, respectively. In the case of the activated carbon samples, it was not possible to determine the acidity type because the solids adsorb all energy emitted in the 1700–1400 cm^{-1} spectral region.

3.2. Activity and selectivity of benzene alkylation

The results of the alkylation of benzene with dec-1-ene over various catalysts activated at 300 °C for 4 h are presented in the Table 2. The supports used in this study did not present any activity in the benzene-alkylation reaction at 80 °C during 1.5 h of reaction. When WP was deposited on the supports a considerable increment in activity was observed, which depended on the interaction of the WP with the supports and the generation of acid sites, as indicated in the IR section. The 20WP/Zr catalyst showed a 6% dec-1-ene initial conversion and that of 20WP/Si was 62.4%. The selectivity for alkylated product (BA) depended on the acid site type generated by WP on the supports. Clearly, the high activity of 20WP/Si catalyst is due to the formation of Brönsted acidity. The 20WP/Al catalyst did not present any activity, probably because a higher reaction temperature is necessary in this case. In this preliminary evaluation of the catalysts we observed that the main

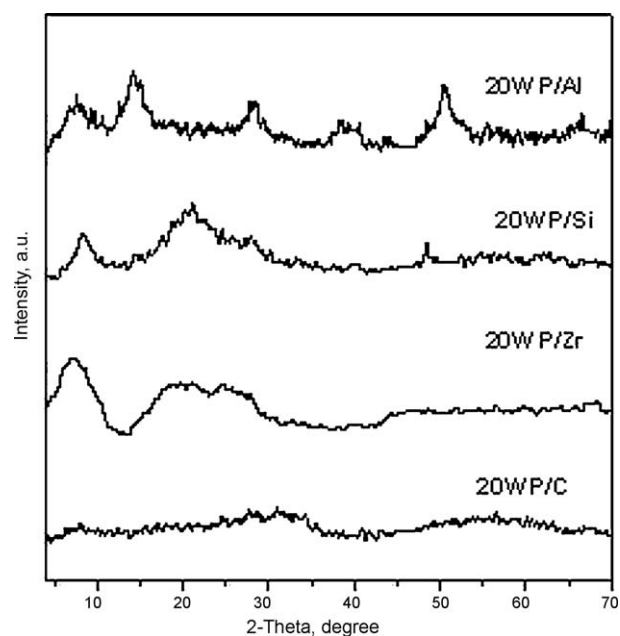


Fig. 3. XRD patterns of supported 20 wt.% WP on Al_2O_3 , SiO_2 , ZrO_2 and activated carbon.

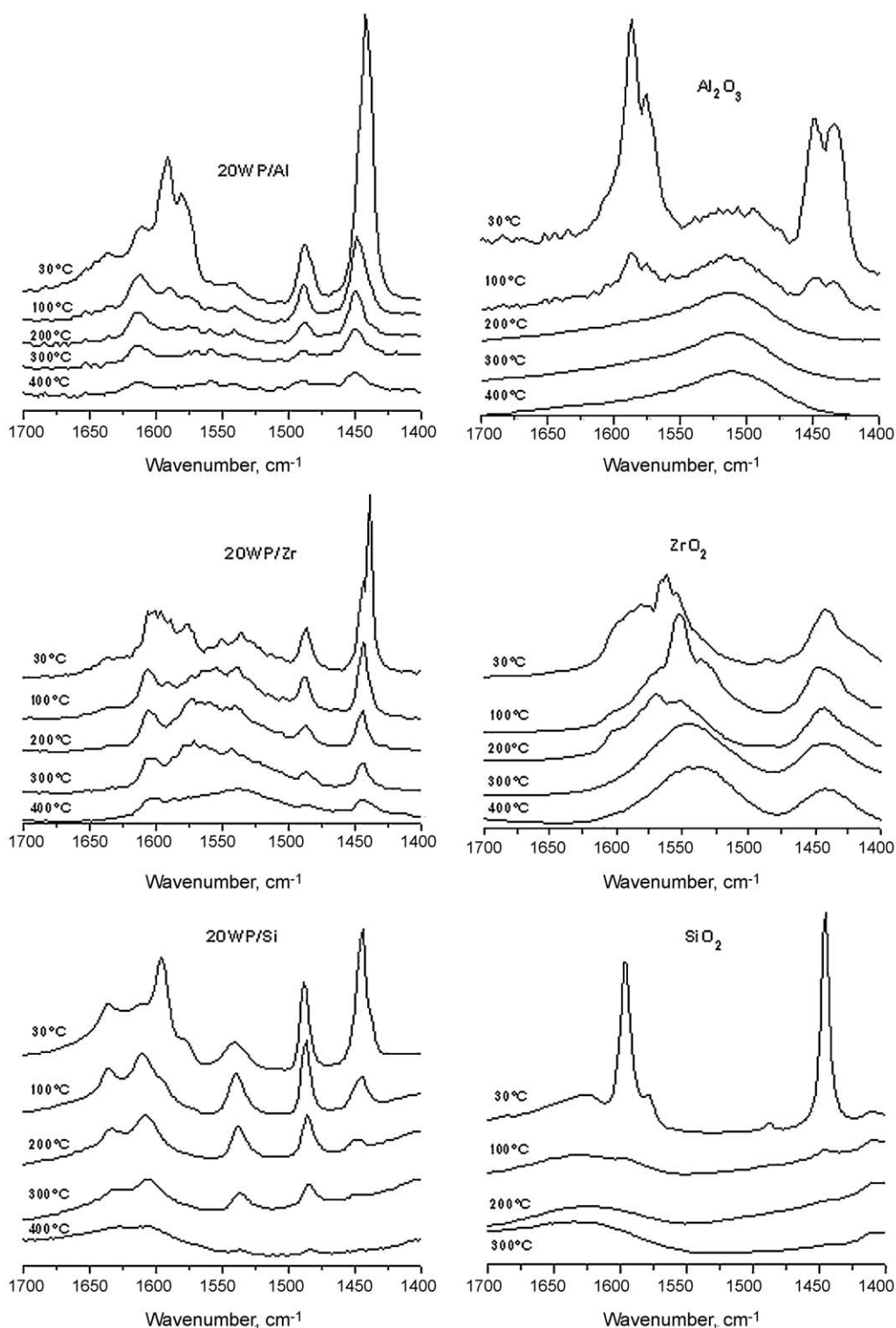


Fig. 4. Adsorbed pyridine FTIR spectra of pure supports and supported WP (20 wt.%).

reactions were alkene double-bond shift isomerization (ISO) and benzene alkylation (BA). The catalysts of WP supported on C and Si presented selectivity toward BA and ISO products and 20WP/Zr generates only isomerization products.

As a second activity test, the effect of the reaction time in the selectivity of the products was examined and the results are shown in Table 3. In these conditions, it was clear that 20WP/Al was inactive, while 20WP/Si and 20WP/C showed a considerable activity in the conversion of dec-1-ene, generating both isomeri-

zation and benzene-alkylation products. It has been reported that under these reaction conditions the pure WP presents a 21% conversion of dec-1-ene [24]; our catalysts exhibited approximately 3 times more activity than pure WP. Given the very low stability of 1-decyl primary carbonium anion [32], 1-decyl (benzene) was not detected in the reaction products.

The alkylation of benzene with olefins goes through a carbonium ion mechanism which involves two steps. In the first step, the alkene interacts with the acid site to form an

Table 2
Benzene alkylation with dec-1-ene on various catalysts.

Catalyst	X _{1D} ^a (mol%)	ISO ^a (mol%)	BA ^a (mol%)
Al ₂ O ₃	0.0	–	–
C	0.0	–	–
SiO ₂	0.0	–	–
ZrO ₂	0.0	–	–
20WP/Al	0.0	–	–
20WP/C	55.0	56	44
20WP/Si	62.4	64	36
20WP/Zr	6.0	100	0

^a Dec-1-ene conversion, (BA) selectivity to benzene alkylation, (ISO) isomerization products at 80 °C. Reaction time 1.5 h.

Table 3
Alkylation of benzene with dec-1-ene and products distribution on catalysts calcined at 300 °C.

Catalyst	t _{rxn} (h)	X _{1D} (mol%)	Selectivity (mol%)				
			ISOs	1BHB	1PHB	1EOB	1MNB
20WP/Si	1	73.0	63.5	0	4.2	8.5	23.8
	3	73.7	42.9	4.2	5.9	12.1	34.8
20WP/C	1	54.8	54.7	5.1	6.0	11.2	23.0
	3	52.8	58.5	5.9	7.0	9.4	19.2
20WP/Z	1	5.3	100.0	0	0	0	0
20WP/Al	1	0	0	0	0	0	0

T_{rxn} = 80 °C; ISOs = decen-*x*-ene, *x* = 2, 3, 4, 5; 1BHB = (1-butylhexyl)benzene; 1PHB = (1-propylheptyl)benzene; 1EOB = (1-ethyloctyl)benzene; and 1MNB = (1-methylnonyl)benzene.

alkylcarbenium ion. This intermediary can isomerize to other olefins by hydrogen transfer, for example, dec-1-ene isomerizes to internal decenes (dec-*x*-ene, *x* = 2, 3, 4, and 5). The second step is the attack of benzene ring by alkylcarbenium to form phenyldecanes, which can also isomerize to form other phenyldecane isomers (see Fig. 5). In the case of dec-1-ene, five carbonium ions are possible. The relative stabilities of carbonium ions increase as the C-number increase, for example, the least stable being the primary ion (e.g. 1-decene). In fact, due to its very low stability, the 1-phenyl isomer was undetected in the product. On the basis of the relative stabilities of the other carbonium ions (all secondary), it is expected that the isomer content will increase with the carbon number (toward the center of the alkyl-chain). The double-bond migrations in olefins proceeds by interaction with Brønsted acid

Table 4
Alkylation of benzene with dec-1-ene and products distribution on catalysts calcined at 400 °C.

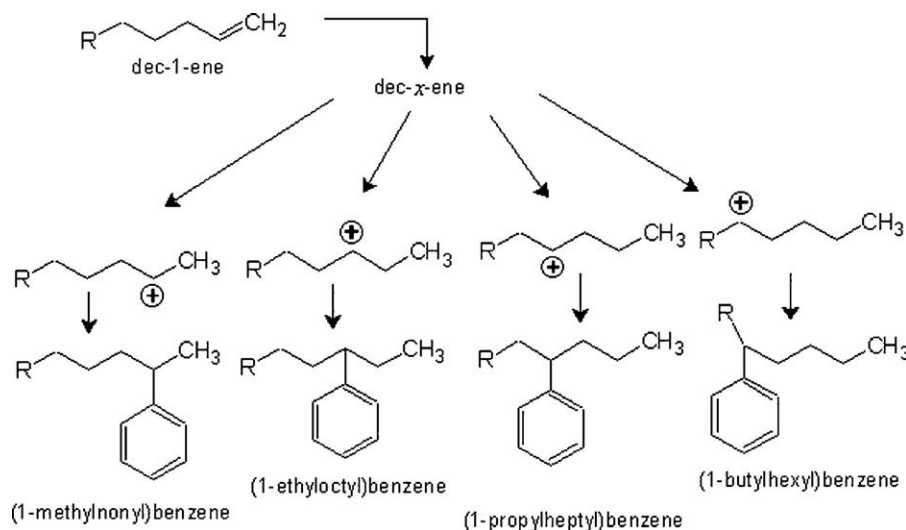
Catalyst	t _{rxn} (h)	X _{1D} (mol%)	Selectivity (mol%)				
			ISOs	1BHB	1PHB	1EOB	1MNB
20WP/Si	1	70.4	60.9	3.3	3.9	8.9	22.9
	3	68.3	41.9	4.0	5.5	13.7	34.9
20WP/C	1	5.6	72.0	5.0	3.0	6.0	14.0
	3	29.3	53.9	4.6	5.8	10.8	24.8
20WP/Z	1	8.3	100.0	0	0	0	0
	3	15.4	100.0	0	0	0	0
20WP/Al	1	0	0	0	0	0	0

T_{rxn} = 80 °C; ISOs = decen-*x*-ene, *x* = 2, 3, 4, 5; 1BHB = (1-butylhexyl)benzene; 1PHB = (1-propylheptyl)benzene; 1EOB = (1-ethyloctyl)benzene; and 1MNB = (1-methylnonyl)benzene.

sites (e.g. those in WP) generating activated species forming a more or less tight ion pair, having a considerable covalent bonding degree between the carbocation and the anion. As a result, the nature of anions has a considerable influence on the reactivity and selectivity of the alkylating agent.

The solids that have Brønsted acidity were 20WP/Si and 20WP/C, favoring the alkylbenzenes production. Among all the supports evaluated, only activated carbon lacks surface hydroxyl groups, which are considered the main cause of loosing acid H⁺ Brønsted in WP when supported on hydroxylated metal oxides (e.g. alumina, zirconia and silica). Thus 20WP/C is able to keep its Brønsted acidity and that is why it is so selective in comparison with the other supports. This selectivity to alkylbenzenes is not observed in 20WP/Al and 20WP/Zr due to the absence of this acidity type.

When the catalysts were calcined at 400 °C, attempting to generate more active sites, these solids presented the catalytic behavior shown in Table 4. Noteworthy, the generation of new acid sites, in the case of the 20WP/Zr, favors the catalytic activity. After 3 h of reaction the conversion of dec-1-ene was of 15.4% with a total selectivity toward isomerization products. The loss of Brønsted acidity on WP/Z, which occurs upon the transformation of ZrO₂ when heat treated, may likely be responsible of this behavior [25]. 20WP/Al was inactive in this reaction. Accordingly, it has been reported that WP presents a great catalytic activity when supported on SiO₂ and activated carbon, however, the Keggin structure of WP is destroyed when deposited on Al₂O₃ [33]. The results of Table 4 point out that calcination temperature has a

**Fig. 5.** Scheme of the products formed in the alkylation of benzene with dec-1-ene (where R = C₅H₁₁ and *x* = 2, 3, 4 and 5).

crucial effect on the structure of the supports, with a possible partial destruction of WP; this can generate new acid sites that affect either the alkylation of benzene and/or the isomerization of dec-1-ene.

4. Conclusions

20WP/Si and 20WP/C act as efficient solid acid catalysts for the synthesis of linear alkyl benzenes. In contrast, 20 wt.% WP on zirconia was active mainly for the double-bond migration (e.g. isomerization of dec-1-ene) while alumina was inactive in either alkylation or isomerization at the conditions of this study. Thus, the activity of the catalyst in the alkylation of benzene with dec-1-ene depends on the support type and the thermal treatment temperature. Under the reaction conditions of 80 °C, benzene/dec-1-ene molar ratio of 5 (after 3 h reaction time), the most active catalyst, 20 wt.% WP on SiO₂, gives more than 50% dec-1-ene conversion, and ~40% selectivity to isomerization products, and ~60% selectivity to alkylbenzenes. The type of acid sites affects the selectivity of the reaction, for instance Lewis-type acidity favors isomerization products (e.g. 20WP/Z) and the coexistence of both Brønsted and Lewis acid sites favors the selectivity toward alkylbenzenes (20WP/Si and 20WP/C).

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References

- [1] J.A. Kocal, B.V. Vora, T. Imai, *Appl. Catal. A: Gen.* 221 (2001) 295.
- [2] P.R. Pujado, *Linear Alkylbenzene Manufacture: Handbook of Petroleum Refining Processes*, 1997, p. 1.53.
- [3] X. Dai, J. Suo, X. Duan, Z. Bai, L. Zhang, *J. Surfact. Deterg.* (2008), doi:10.1007/s11743-008-1061-y.
- [4] A. Corma, *Chem. Rev.* 95 (1995) 559.
- [5] L.R. Pizzio, P.G. Vazquez, C.V. Caceres, M.N. Blanco, *Appl. Catal. A: Gen.* 256 (2003) 125.
- [6] B. Wang, C.W. Lee, T. Cai, S. Park, *Bull. Korean Chem. Soc.* 22 (9) (2001) 1056.
- [7] I. Craciun, M. Reyniers, G.B. Marin, *J. Mol. Catal. A: Chem.* 277 (2007) 1.
- [8] I. Iliuta, G. Bozga, M. Lupascu, *Chem. Eng. Technol.* 24 (9) (2001) 933.
- [9] A. Nociar, P. Hudec, T. Jakubik, A. Smieskova, Z. Zidek, *Petroleum Coal* 45 (3–4) (2003) 184.
- [10] S.R. Guerra, L.M.O.C. Merat, R.A.S. San Gil, L.C. Dieguez, *Catal. Today* 133–135 (2008) 223.
- [11] H. Xin, Q. Wu, M. Han, D. Wang, Y. Jin, *Appl. Catal. A: Gen.* 292 (2005) 354.
- [12] B.M. Devassy, F. Lefebvre, W. Böhringer, J. Fletcher, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 236 (2005) 162.
- [13] M. Misono, T. Okuhara, *Chemtech* 23 (11) (1993) 23.
- [14] J.M. Thomas, *Sci. Am.* 112 (1992) 2664.
- [15] M.T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983.
- [16] Y. Wu, X. Ye, X. Yang, X. Wang, W. Chu, Y. Hu, *Ind. Eng. Chem. Res.* 35 (1996) 2546.
- [17] E. López-Salinas, J.G. Hernández-Cortez, M.A. Cortes-Jacome, J. Navarrete, M.E. Llanos, A. Vazquez, H. Armendariz, T. López, *Appl. Catal. A: Gen.* 175 (1998) 43.
- [18] W. Kuang, A. Rives, M. Fournier, R. Hubaut, *Appl. Catal. A: Gen.* 250 (2003) 221.
- [19] B.M. Devassy, G.V. Shanbhag, F. Lefebvre, W. Böhringer, J. Fletcher, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 230 (2005) 113.
- [20] B.M. Devassy, G.V. Shanbhag, F. Lefebvre, S.B. Halligudi, *J. Mol. Catal. A: Chem.* 210 (2004) 130.
- [21] T. Blasco, A. Corma, A. Martínez, P. Martínez-Escolano, *J. Catal.* 177 (1998) 306.
- [22] B.M. Devassy, F. Lefebvre, S.B. Halligudi, *J. Catal.* 231 (2005) 1.
- [23] R.T. Sebulsky, A.M. Henke, *Ind. Eng. Chem. Process Des. Dev.* 10 (2) (1971) 272.
- [24] H. Zhu, X. Ren, J. Wang, *React. Kinet. Catal. Lett.* 83 (1) (2004) 19.
- [25] E. López-Salinas, J.G. Hernández-Cortez, I. Schifter, E. Torres-García, A. Gutiérrez-Carrillo, T. López, P.P. Lottici, D. Bersani, *Appl. Catal. A: Gen.* 193 (2000) 225.
- [26] T.R. Hughes, H.M. White, *J. Phys. Chem. Rev.* 71 (1967) 7.
- [27] I.V. Kozhevnikov, *Catal. Rev. Sci. Eng.* 37 (1995) 311.
- [28] F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by Powders & Porous Solids*, Academic Press, 1999, pp. 18 and 204.
- [29] I.V. Kozhevnikov, *Catalysis for Fine Synthesis polyoxometalates*, vol. 2, Wiley, New York, 2002, p. 15.
- [30] Y. Izumi, K. Urabe, M. Onaka, *Zeolite, Clay and Heteropoly Acid in Organic Reactions*, Kodansha/VCH, Tokyo, 1992, p. 99.
- [31] B.H. Davis, R.A. Keogh, S. Alerasool, D.J. Zalewski, D.E. Day, P.K. Doolin, *J. Catal.* 183 (1999) 45.
- [32] S. Sivasanker, A. Thangaraj, *J. Catal.* 138 (1992) 386.
- [33] K. Mohana Rao, R. Gobetto, A. Iannibello, A. Zecchina, *J. Catal.* 119 (1989) 512.