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FTIR and Reaction Studies of Styrene and Toluene over Silica–Zirconia-Supported Heteropoly Acid Catalysts

B. Bachiller-Baeza[1] and J. A. Anderson

Surface Chemistry and Catalysis Group, Division of Physical and Inorganic Chemistry University of Dundee, Dundee, DD1 4HN, United Kingdom

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The interactions of styrene and toluene with a sol–gel-prepared SiO_2–ZrO_2 mixed oxide and with two supported heteropolytungstic acid samples have been studied by FTIR. The results of the IR study of styrene adsorption and toluene/styrene coadsorption indicate that the oligomerization of styrene, which proceeds through a carbenium intermediate, takes place over the support and the supported catalysts. The alkylation of toluene by styrene, which also proceeds via the formation of a carbenium ion from styrene, is only detected for the supported heteropoly acid catalysts. These spectroscopic observations, which are in good agreement with the product distribution obtained for reaction experiments conducted in the liquid phase, suggest that the reaction of the adsorbed, activated styrene with toluene or with a second molecule of styrene depends on the relative coverage of the two competing reagents. The incorporation of the HPA to the silica–zirconia support increased the density and strength of the acid sites favoring the retention of a higher fraction of toluene and consequently the production of higher yields of alkylated products. Differences between the two supported HPA catalysts could be ascribed to the nature of the supported heteropoly acid species and the modification of the acid characteristics due to the interaction with the silica–zirconia support. © 2002 Elsevier Science (USA)

Key Words: **FTIR; toluene alkylation; styrene; supported heteropoly acid; silica–zirconia.**

1. INTRODUCTION

Among the metal oxides, mixed oxides with two or more components are of significant scientific interest due to improved stability or modification of chemical properties with respect to the component oxides. For example, the incorporation of ZrO_2 into a SiO_2 matrix can improve the thermal stability and the chemical resistance to alkaline attack and leads to generation of surface acidic properties absent in the single-component oxides (1–4). These materials may have application in their own right as solid acids; however, additionally, it has been shown that by modifying the preparation parameters during the sol–gel synthesis of the materials, the acidic and textural properties can be modulated (5). This being the case, these SiO_2–ZrO_2 sol–gels might prove appropriate as support materials for anchoring different active phases, since the degree of interaction and distribution over the surface can be controlled to some extent by adapting the preparation methods and thereby altering, for example, the chemical and electronic properties of the support and the pore distribution.

Heteropolyoxometalates have attracted much attention in recent years because of their applicability in several acid-catalyzed reactions (esterification, acylation, isomerization) (6, 7). These compounds with a general formula for the Keggin structure, $XM_{12}O_{40}^{x-8}$, where X is the central atom (Si^{4+}, P^{5+}), x its oxidation state, and M the metal ion (Mo^{6+}, W^{6+}), possess characteristic acidic and redox properties which can be controlled by substitution of the metal atoms of the anion (central and addenda atoms) and the countercations and can be related to their catalytic activity (8). The thermally stable and strongest heteropolyacid in the Keggin series, the $H_3PW_{12}O_{40}$, has been the most widely studied. However, due to their low surface area most recent studies have focused on heteropoly acids (HPA) loaded on different supports which allow their use in heterogeneous reactions, replacing the more common solid acid catalysts such as HY and HX zeolites, SiO_2–Al_2O_3, H_3PO_4/SiO_2. Basic supports such as alumina or magnesia lead to the decomposition of the HPA (9), so SiO_2, mesoporous molecular sieves, or activated carbons are favored (10–12).

Recently, the use of heteropoly acids have been suggested as a possible means of supporting transition metals through the inclusion or attachment of organometallic complexes into the structure of the polyanion (13). By combining these with an appropriate support, these compounds could be considered a potential alternative to the typical homogeneous catalysts currently used in reactions such as hydrogenation, oxidation, or hydroformylation (14, 15). However, due to the high activity of the HPA, particularly in acid-catalyzed reactions, as described above, it is appropriate as a first step to study the supported heteropoly acid under the conditions of the reaction of interest. Additionally, it is well known that loss of the active metal and/or the

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[1] To whom correspondence should be addressed. Fax: +44 1382 345517. E-mail: b.bachillerbaeza@dundee.ac.uk.

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associated ligands to the liquid phase may occur during the hydroformylation reaction over supported metal catalysts with chiral modifiers (16). It is therefore appropriate, as a check for degradation of HPA-anchored reagents, that the products of direct HPA catalyzed reaction be known. Patents by the Exxon group for this reaction over zeolite HY indicate potential industrial importance of the alkylation of toluene by styrene (17). In the present investigation, two catalysts were prepared by supporting two different heteropoly acids, a Keggin type ($H_3PW_{12}O_{40}$) and a Dawson type ($H_6P_2W_{18}O_{62}$), on a sol–gel-synthesized SiO_2–ZrO_2 support. Results of an IR study of styrene adsorption and toluene/styrene coadsorption on the two prepared samples are reported, in addition to results of catalyst testing under standard conditions for the hydroformylation of styrene.

2. EXPERIMENTAL

2.1. Preparation of the Support

A silica–zirconia mixed oxide (33% mol Zr) was prepared via the sol–gel technique following a procedure described previously (4, 5). Tetraethylorthosilicate (TEOS) was added to a solution of propanol, water, and nitric acid and stirred for 2 h under N_2. The zirconium tetrapropoxide and propanol were then combined, and water was finally added after 1 h of stirring. The gel obtained was redispersed in boiling ethyl acetate and refluxed for 5 h. The resultant material was then transferred to a critical-point drying apparatus, where it was dried under supercritical CO_2 for 2 days, with the CO_2 replaced every 3 h. Finally, the solid was calcined at 873 K for 5 h under flowing air. The S_{BET} of the support was 252 $m^2\ g^{-1}$, the average pore diameter was in the range 25–75 nm, and the solid was stable to hydrothermal treatment at 873 K. Equivalent samples gave acid site densities of 0.161 and 0.217 nm^{-2}, for Lewis and Brønsted sites, respectively, as determined by the amount of pyridine retained by the samples after evacuation at 423 K (4).

2.2. Preparation of HPA-Supported Samples

Two types of heteropoly acids were used. The Keggin type or 12-tungstonophosphoric acid ($H_3PW_{12}O_4 \cdot 9H_2O$) was obtained commercially (Aldrich). The Dawson structure ($H_6P_2W_{18}O_{62} \cdot 2H_2O$) was synthesized from its ammonium salt according to a procedure reported in the literature (18). A mixture of $Na_2WO_4 \cdot 2H_2O$ (Aldrich) and H_3PO_4 in water was refluxed for 8 h. After cooling, the ammonium salt was precipitated by adding solid NH_4Cl. The precipitate was filtered, dissolved in warm water, and recrystallized. The acid was obtained as an addition compound with ether from an aqueous solution of the ammonium salt treated with ether and concentrated HCl. The ether was then evaporated and the acid crystallized in water. The identity and purity of the acid was confirmed by ^{31}P NMR and thermogravimetric analysis (TGA).

The supported HPA samples (10 wt%) were prepared by impregnating the support with an aqueous solution of the heteropoly acid previously dispersed in water. The dispersion was stirred for 2 h and then evaporated to dryness. The solids were dried overnight at 343 K and will be referred to as HPA(K)/SiZr for the Keggin precursor and HPA(D)/SiZr for the Dawson structure.

2.3. FTIR Characterization

The samples pressed into 25-mm-diameter self-supported wafers were placed in a quartz cell connected to a conventional vacuum-line apparatus and evacuated at room temperature for 30 min. With this pretreatment, an amount of adsorbed water was retained by the samples. However, as reaction studies were also conducted using samples without pretreatment, removal of all water for spectroscopically examined samples would have made any observations less relevant. Infrared spectra for styrene and toluene/styrene at increasing vapor pressures were recorded on a Perkin–Elmer 1710 FTIR spectrometer at 4-cm^{-1} resolution and an average of 25 scans.

Thin-film liquid-phase spectra of styrene and toluene were obtained using a cell fitted with CaF_2 windows. A spectrum of a reference polystyrene film was also obtained.

2.4. Activity Measurements

The reaction was carried out under high pressure in a 270-cm^3 steel autoclave fitted with an internal glass vessel, a magnetically coupling stirred head, inlet/outlet ports, and a pressure measuring gauge. The catalysts (150–200 mg) were transferred to the reactor flask containing a solution of styrene (17.3 mmol, Aldrich, 99%) in toluene (18 ml, Aldrich, 99.8%, HPLC grade) previously dried with a 5-Å molecular sieve. The autoclave was purged in N_2, pressurized to 80 bar with the reaction mixture CO/H_2 (1 : 1) and then heated in an oil bath to 333 K. After the reaction had been carried out for 4.5 h and cooled to room temperature, the gases were vented off and the composition of the solution was analyzed by gas chromatography using a 10% SP 2330 on a SUPELCOPORT column and a FID detector. A GC–MS (HP-6890, MSD HP-5973) fitted with a HP-5MS column was used to identify the reaction products.

3. RESULTS

3.1. Reaction Results

The results of the test reaction are summarized in Table 1. Both supported heteropoly acids were highly active, leading to styrene conversions of up to 94% after 4 h, while the pure SiO_2–ZrO_2 support was almost inactive, with only 8% conversion after the safe reaction time. The Dawson

TABLE 1

Data of Reaction of Styrene in Toluene at 333 K under H_2/CO (1 : 1)

Catalysts	Conversion (%)	Activity ($\mathrm{mmol \cdot g_{cat}^{-1} \cdot h^{-1}}$)	Composition (%) 2 + 3	4	5	6
SiZr	8	1.7	25.2	4.6	56.2	7.5
HPA(K)	7	1.8	9.2	1.7	77.9	11.2
HPA(K)/SiZr	47	6.3	15.7	10.2	55.6	18.5
HPA(K)/SiZr[a]	48	11.1	17.1	8.9	56.2	17.8
HPA(D)/SiZr	94	17.7	10.2	16.5	46.1	27.2
HPA(D)/SiZr[a]	84	19.6	11.3	16.8	46.2	25.7
HPA(D)/SiZr[b]	71	54.2	14.6	15.6	46.8	23.0

[a] Experiment carried out under N_2 atmosphere.

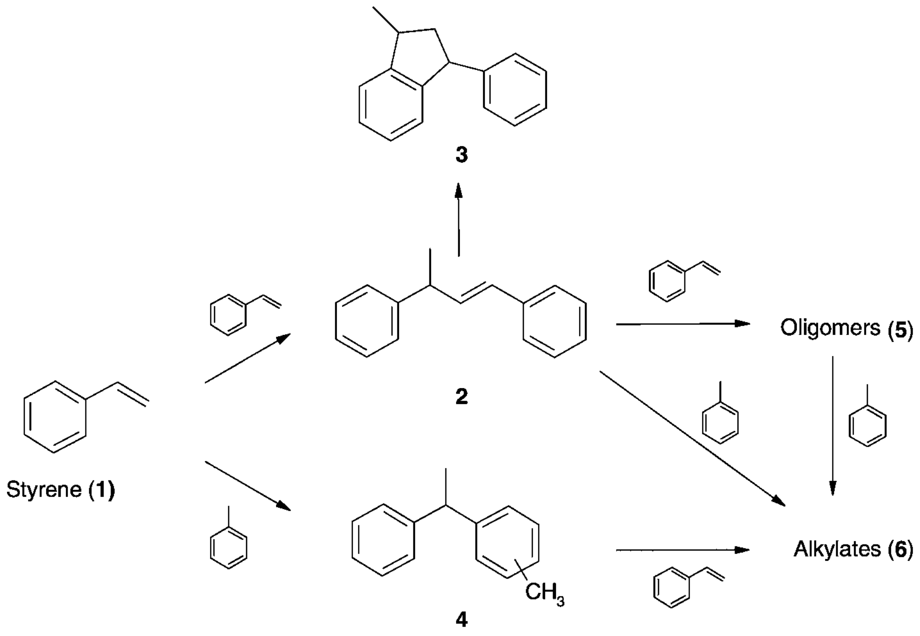
[b] Experiment carried out for 1.5 h.

catalyst showed higher activity than the supported Keggin. Additionally, the former sample exhibited a color change from white to slightly blue after removal from the reaction vessel, suggesting the formation of the heteropoly blues by reduction of the Dawson units.

No carbonylation products resulting from the hydroformylation of styrene were obtained. The products obtained resulted from the dimerization and oligomerization of the olefin, and from the mono- (and poly-) alkylation of toluene by styrene and these were detected by GC and identified by MS–GC. Scheme 1 shows the possible reaction pathways. Note that catalysts as prepared would be expected to contain a few percentage water. The role of this water has been shown to be critical, both in terms of modifying catalysts behavior by suppressing oligomerization reactions (19) and by maintaining an active solid–acid catalyst which is resistant to deactivation by coking (19, 20). It is expected that catalysts which had been pretreated at elevated temperatures to remove water would have exhibited significantly different results, in terms of both activities and selectivities. The catalysts differ not only in activity, as reflected in the levels of conversion after equivalent reaction times, but also in the product distribution. The SiZr support exhibited low activity and the products **2** and **3**, both derived from the oligomerization of styrene, present much greater levels than the alkylation product **4**. The greatest yield of the monoalkylated product **4** was obtained using the HPA(D)/SiZr. In addition, this catalyst showed a slightly higher amount of higher molecular weight alkylates, **6**, than the supported Keggin catalyst.

An unsupported Keggin acid (HPA(K)) was also tested in the reaction and its activity was very low, in fact somewhat similar to that obtained for the SiO_2–ZrO_2 support. This is probably a consequence of the low surface area that the bulk compound shows and the subsequently lower accessibility of the acid sites. This sample exhibited a lower selectivity to the alkylated products than the corresponding supported Keggin heteropoly acid.

Experiments carried out by replacing the CO/H_2 by N_2 for both the HPA(D)/SiZr and HPA(K)/SiZr gave slightly dissimilar results in terms of the measured activities (Table 1); however, the product distributions were not affected by the change of conditions. The color change that was observed under the CO/H_2 mixture for the supported Dawson catalyst was not detected when the reaction was performed under N_2. When the HPA(D)/SiZr was tested for shorter reaction times, the conversion was reduced



SCHEME 1

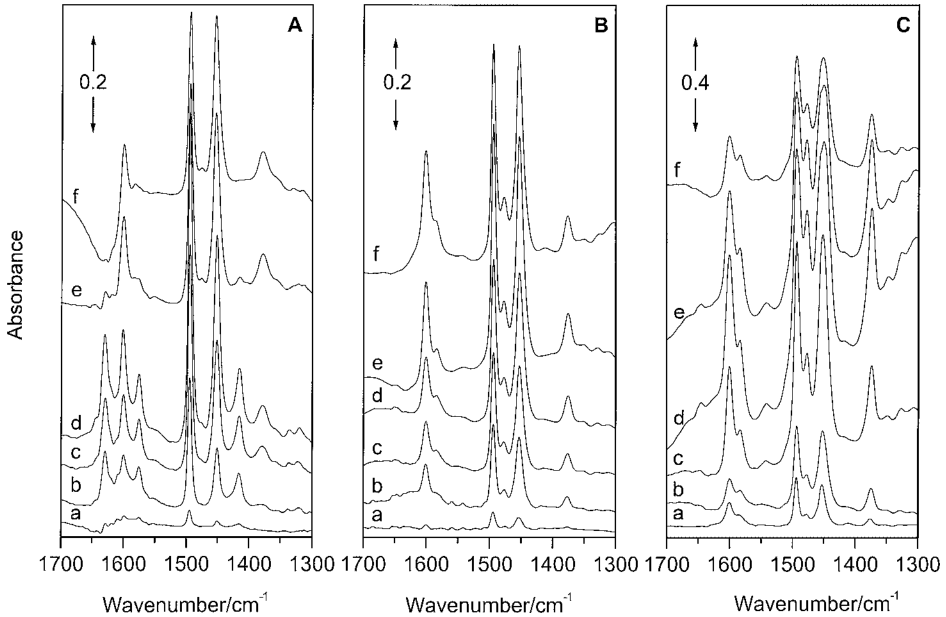


FIG. 1 Infrared spectra of (A) SiZr, (B) HPA(K)/SiZr, and (C) HPA(D)/SiZr after (a–d) exposure to increasing pressures of styrene and (e) evacuation at 298 K (10 min) and (f) 353 K (15 min).

(Table 1) but the product distribution was very similar, indicating that selectivity was effectively independent of conversion.

3.2. Adsorption of Styrene

The interaction of styrene with the supported HPA samples and the bulk support was studied by the adsorption of styrene from the vapor phase. Figures 1A–1C compare the spectra for SiZr, HPA(K)/SiZr, and HPA(D)/SiZr catalysts exposed to styrene vapor at increasing pressures. Bands in the region 1700–1300 cm^{-1} confirm the presence of adsorbed species at lower coverage for the SiZr sample, with the most intense features, at 1450, 1494, 1576, and 1601 cm^{-1}, assigned to the stretching vibrations of the phenyl ring, and which are consistent with the features observed in the spectrum of liquid styrene (Fig. 2a). The bands at 1630 and 1416 cm^{-1} are attributed to the, $\nu_{C=C}$ and $\delta_{=C\text{–}H}$ vibrations of the vinyl group, respectively. However, the relative intensity of the band at 1630 cm^{-1} with respect to the 1601-cm^{-1} peak was lower than for the liquid styrene, suggesting that either an interaction existed between the double bond of the molecule and the support surface, or that only a fraction of the detected species was present as adsorbed styrene and the remainder was present as the cyclization product **3** of the dimer or as oligomeric species **5**. As the coverage was increased, additional bands, at 1478 and 1378 cm^{-1}, were observed. After brief outgassing of the sample at room temperature the band assigned to $\nu_{C=C}$ disappeared and only the bands at 1600, 1584 (sh), 1494, 1478, 1450, and 1378 cm^{-1} remained (Fig. 1A). These bands correspond well with those observed in the IR spectrum of a reference polystyrene film (Fig. 2b), although bands at 1478 and 1378 cm^{-1}, attributed to vibrations of CH_3 end groups of short-chain polymers with few repeating units (21), were absent for the latter.

A band at 3735 cm^{-1} (not shown) due to the stretching vibration of isolated terminal hydroxyl groups of the silica component of the mixed oxide (5) was observed for the support prior to exposure to styrene. This band intensity was significantly reduced after the adsorption of styrene, consistent with expectation for an interaction of the double bond of the molecule with the surface hydroxyl group of

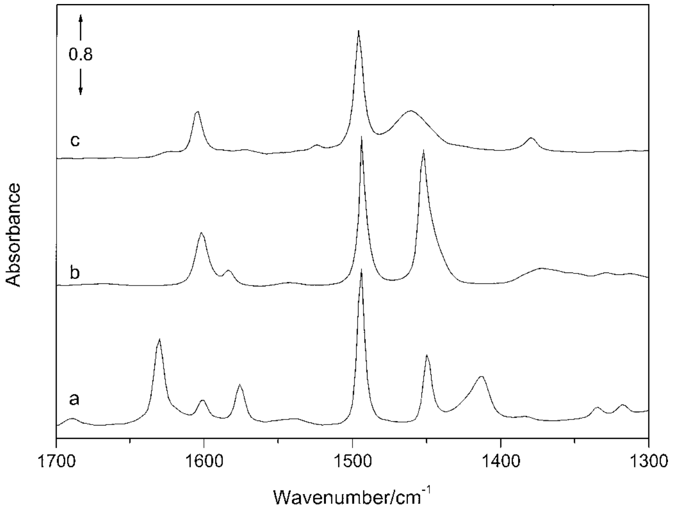


FIG. 2 Infrared spectra of (a) liquid styrene, (b) solid polystyrene film, and (c) liquid toluene.

the support. The intensity of the band due to the isolated silanol group was fully recovered following evacuation of the adsorbate.

Both SiZr-supported heteropoly acids showed similar spectra following exposure to styrene (Figs. 1B and 1C) but which differ from that of the pure support. The dominant species present on the surface did not show any apparent coverage dependence and the peaks at 1601, 1585, 1494, 1478, 1450, and 1378 cm^{-1} that correspond to the polymeric species were detected even at the lowest coverage. Unlike the spectra for the SiZr support, the characteristic bands of the vinyl group at 1630 and 1416 cm^{-1} were absent at low coverage for the supported heteropoly acids. Examination of the spectra at higher coverages showed that the intensities of the bands at 1478 and 1378 cm^{-1} were relatively higher for the Dawson-type heteropoly acid than for the Keggin type, possibly reflecting the higher activity (Table 1) of the former. However, as the first pulses of styrene underwent complete conversion over both supported heteropoly acids, as indicated by the absence of the characteristic vinyl bands at 1630 and 1416 cm^{-1}, the greater activity of the HPA(D) (Table 1) would not explain the differences observed in the 1478- and 1378-cm^{-1} band intensities and thus indicates inherent differences in the selectivities of the two catalysts. Differences could be interpreted in terms of the formation of oligomers with shorter chain length or a higher proportion of CH_3 end groups over the supported Dawson. Davanzo *et al.* (21) reported that the polymer chain length for styrene reacted over sulfated titania showed a dependence on the sulfate density (and hence acid site density/strength) with sulfate-rich samples favoring shorter chains. Evacuation of the samples at RT caused no variation in the intensity of the bands although evacuation at higher temperature (353 K) caused slight loss in intensity, especially in the case of the supported Dawson sample.

3.3. Coadsorption of Toluene/Styrene

Figure 3A shows the spectra of SiZr which was firstly exposed to toluene at 298 K and briefly evacuated, followed by exposure of styrene. The spectrum of adsorbed toluene contained the expected bands, in accordance with those observed for liquid toluene (Fig. 2c): peaks at 1603 and 1496 due to the aromatic C–C stretching modes, and bands at 1460 and 1384 cm^{-1} due to CH_3 deformation vibration (Fig. 3A, spectrum a). However, in the 2000- to 1600-cm^{-1} region, which corresponds to the overtones involving the out-of-plane C–H deformation modes, a shift of 15 cm^{-1} to higher frequencies with respect to the liquid-phase spectrum was observed. This may result from some kind of interaction of the π-type electrons of the benzene ring with the support, implying that the ring was lying parallel to the surface. In the presence of styrene, the characteristic C=C stretching vibrations of the group at 1630 and 1416 cm^{-1} were apparent (Fig. 3A, spectra b and c). With increasing styrene pressure, the band at 1384 cm^{-1} disappeared, indicating the displacement of the more weakly adsorbed toluene molecules. Evacuation of the sample at room temperature led to a decrease in intensity of the 1600-, 1495-, and 1450-cm^{-1} bands, while bands, assigned to the vinyl group disappeared, suggesting the desorption of the molecularly adsorbed styrene. This was accompanied by an enhancement in the bands at 1478 and 1378 cm^{-1}, as observed for the experiment involving styrene adsorption alone.

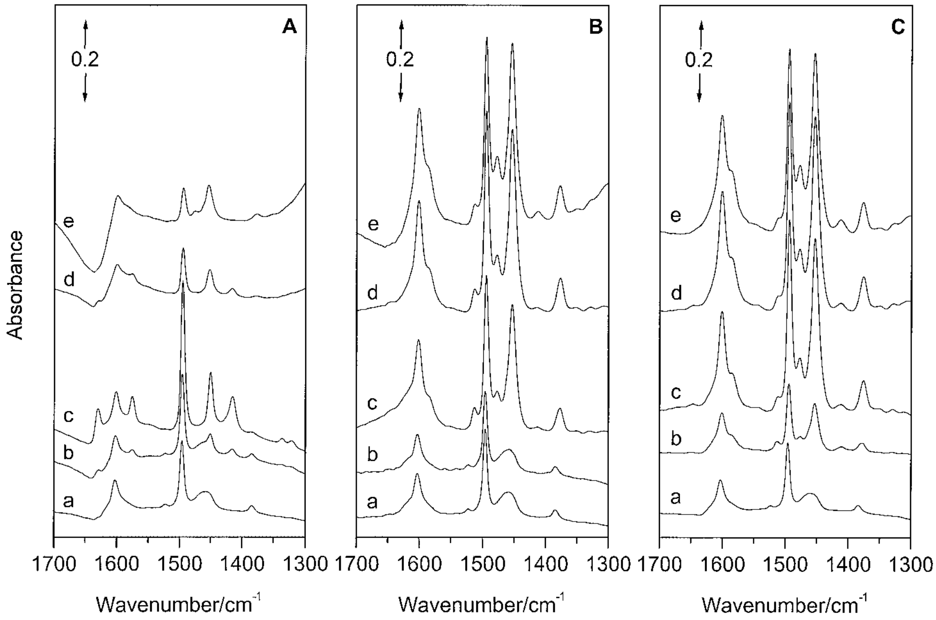


FIG. 3 Infrared spectra of (A) SiZr, (B) HPA(K)/SiZr, and (C) HPA(D)/SiZr after (a) exposure to toluene and brief evacuation at 298 K, (b, c) addition of increasing pressures of styrene, and (d) evacuation at 298 K and (e) 353 K.

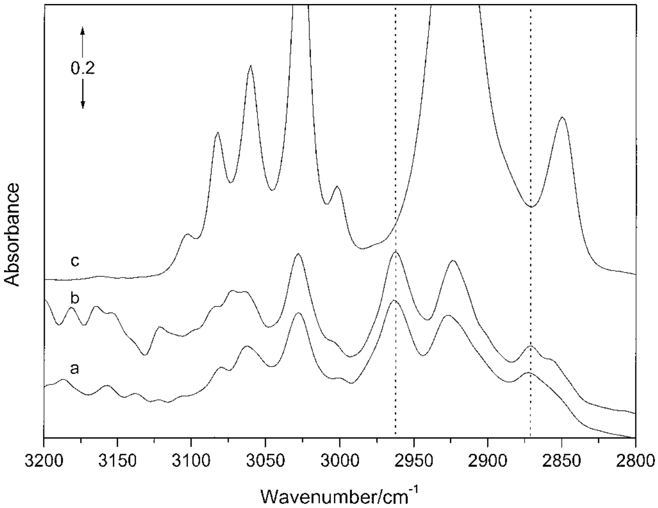


FIG. 4 Infrared spectra of (a) coadsorption of toluene/styrene for HPA(D)/SiZr, (b) adsorption of styrene on HPA(K)/SiZr, and (c) thin film of polystyrene.

As shown in Figs. 3B and 3C, adsorption of toluene on HPA(K)/SiZr and on HPA(D)/SiZr gave similar spectra, as observed for adsorption on the support alone. Bands due to the out-of-plane C–H deformation modes were again shifted by 20 cm^{-1} to higher frequencies, which again indicates a strong interaction of the aromatic ring with some electron-withdrawing centers, pulling the molecule flat down on the surface. Increased pressures of styrene progressively displaced the adsorbed toluene, resulting in a typical spectrum of polymeric species on the catalysts, with maxima at 1601, 1583, 1494, 1478, 1450, and 1378 cm^{-1}. However, an additional band, at 1512 cm^{-1}, was detected for both catalysts that was absent for the support alone. This additional band may be assigned to a reaction product with an aromatic ring with substitution in the *p* position (22), implying that C–C bond formation had taken place at 298 K. The samples subjected to evacuation at this temperature showed no variation in the position or intensity of the bands mentioned, and even after the evacuation temperature was increased to 353 K, the spectrum remained largely unchanged.

Additional information regarding the nature of the species formed during the coadsorption experiment over supported HPA was obtained by comparing spectra (Fig. 4) in the C–H stretching region (3200–2800 cm^{-1}). When compared with the spectrum of polystyrene (Fig. 4c), although bands at 3082, 3060, 3025, 3002, 2925, and 2850 cm^{-1} were common to both sets of spectra, additional bands, at 2962 and 2869 cm^{-1}, were present (Fig. 4b) which were also observed for styrene adsorption alone. These bands are ascribed to the asymmetric and symmetric stretching vibrations, respectively, of CH_3 groups, which can be associated with the formation of oligomers or polymers of short chain length with terminal methyl groups (21).

3.4. *FTIR of Postreaction Solution*

In order to complete the spectroscopic investigation, IR spectra were recorded of samples extracted from the solutions after reaction. Drops of the toluene solution were spread between CaF_2 plates and the solvent allowed to evaporate. Figures 5A and 5B show spectra of postreaction

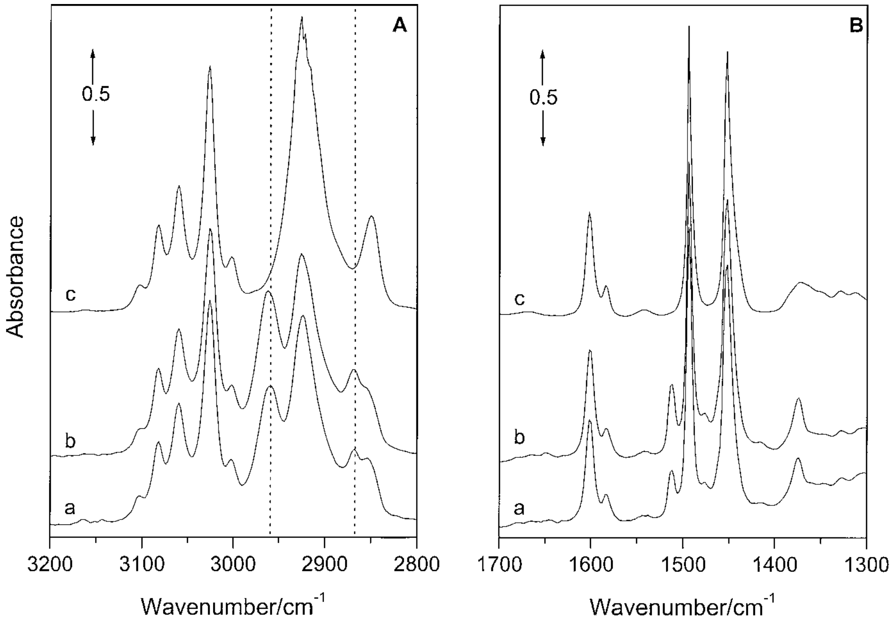


FIG. 5 Infrared spectra in the 3200- to 2800-cm^{-1} and 1700- to 1300-cm^{-1} regions of the solutions postreaction for (a) HPA(K)/SiZr, (b) HPA(D)/SiZr, and (c) a thin film of polystyrene.

solutions for the two supported HPA catalysts in the 3200- to 2800-cm^{-1} and 1700- to 1300-cm^{-1} regions. Absorption bands show good correlation with the results for spectra presented for toluene–styrene coadsorption: strong bands at 2962, 2869, 1478, and 1378 cm^{-1} attributed to the presence of methyl groups in the polymeric species and a band at 1512 cm^{-1} resulting from the *p*-substituted aromatic ring. Moreover, the intensity of the bands at 1583 and 1478 cm^{-1} were less significant for the solution-phase spectra. This could indicate that polymerization at the solid–liquid interface led to products with longer chain and consequently the number of terminal CH_3 groups was lower. However, it is also possible that these species, once formed, remained on the surface of the catalysts in FTIR experiments performed by vapor adsorption onto pressed powder disks and thus appear concentrated, whereas the solubility of the polymer in toluene led to transfer from the solid surface to the liquid phase for experiments conducted in the reactor vessel. The intensity ratio between the bands at 2962 and 2925 cm^{-1} and those at 1512 and 1378 cm^{-1} provided further evidence for the difference in behavior between the two supported HPAs in reaction. The ratio between the peaks assigned to $\nu_{as}CH_3$ (2962) and $\nu_{as}CH_2$ (2925) is 0.82 for the Dawson-type heteropoly acid but only 0.65 for the Keggin type. The band characteristic of the *para*-substituted alkylation product (**4**) at 1512 cm^{-1} was more intense than the band at 1378 cm^{-1} for the Dawson-supported catalyst (ratio, 1.5 : 1), while for the supported Keggin heteropoly acid the ratio was 1.1 : 1.

4. DISCUSSION

The reaction test results indicate that under the conditions employed in this study, all the samples were active, leading to products of oligomerization of styrene and alkylation of toluene by styrene. Moreover, it is clear that both HPA-supported samples show significantly higher reactivity compared with the pure heteropoly acid phase or the SiZr support. This observation, coupled with the enhanced selectivity to the alkylated compounds, for the supported HPA catalysts suggests that the accessibility of acid sites has been increased by incorporation of the heteropoly acid onto the support and that the acidity that these catalysts present is stronger than the sites on the original support material. Since compounds of low polarity, such as styrene and toluene, have weak affinity for the heteropoly acid and cannot diffuse inside the solid, where most of the acid sites are located for the bulk HPA, reactants are limited to the interaction with surface protons of the HPA crystallites, in contrast to the pseudo-liquid catalysis proposed for polar molecules, where the majority of the protons may participate in the catalytic reaction (9, 23). Thus the dispersion of the HPA phases over a support increases the former's activity in surface-catalyzed reactions.

The interaction of styrene with the SiO_2–ZrO_2 and with two supported heteropoly acid samples has been evidenced by the FTIR study. In the case of the support alone, this initial interaction was indicated by a decrease in the SiO–H band intensity either involving the double bond of the styrene or via the π electrons of the aromatic ring. Although the sample as presented would have water associated with both the HPA and the support surface, perturbation of the SiO–H by the adsorbate provides evidence that the initial stages of adsorption on the support were not hindered by the presence of the water. Although the location of water molecules within the structure and their importance in activation of alkanes and alkenes is well known in the case of bulk heteropoly acids (20), the specific interaction between adsorbed water and supported isolated HPA units is less clear, as is the role of water in creating active Brønsted acid sites. However, as a typical acid-catalyzed reaction, the oligomerization process is expected to take place via a carbenium-type mechanism, in which the initial slow step is the protonation of the double bond by a Brønsted acid site of the catalyst to generate a secondary carbocation (7). An alternative mechanism, involving a surface-adsorbed carbene-type complex, has been proposed for sulfated titania where the Brønsted acid sites apparently play no role (21), although this mechanism has been refuted (24). Adsorption of toluene is thought to involve hydrogen bonding interactions of the acidic OH sites with the π-electrons of the aromatic ring (25, 26), although studies of the alkylation of benzene and related aromatics with olefins are thought (7) to follow an Eley–Rideal-type mechanism, with the carbenium ion being attacked by the free or weakly adsorbed aromatic. Although Corma (7) argues the case that any molecule within a zeolite pore is subject to interactions such that it must be viewed as an adsorbed state, the toluene molecule on samples employed here is assumed to undergo alkylation reaction without the prerequisite that it be in any adsorbed or activated state. The SiZr support and the two HPA-supported samples displayed different behavior when styrene was introduced onto a toluene-covered surface. In the case of the support alone, the styrene seemed to be in direct competition with the toluene for the same adsorption sites, as suggested by displacement of the latter by the styrene. Once the styrene is activated, it reacts with itself to form the corresponding oligomer (**2**) as the dominant reaction (Table 1). The incorporation of the HPA modifies the acidic properties of the samples, and even though oligomerization of styrene is observed, an additional band, at 1512 cm^{-1}, attributed to the *p*-substituted alkylation product, is also detected. The alkylation reaction also proceeds via a mechanism which involves the initial formation of a carbenium ion of the alkylating agent; i.e., both the alkylation and oligomerization reactions proceed via a common intermediate which is formed in a rate-determining step involving protonation of styrene. Although some of the adsorbed toluene molecules are displaced by the more strongly interacting styrene in the consecutive adsorption experiment (Fig. 3), alkylation selectivity is enhanced over the supported HPAs with respect to the support alone due to the ability of the latter to retain a significant fraction of the toluene, as confirmed by the FTIR results (Fig. 3). As all active catalysts must be considered to contain sites which have a Brønsted acid character strong enough to protonate styrene (although present at differing densities), the subsequent reaction with either styrene or toluene will depend on the relative concentration of the two competing reagents in the vicinity of the carbocation. In the reaction between benzene and propene over HZSM-5, the polymerization of propene only competes seriously with the alkylation reaction forming isopropylbenzene when the total pressure is significantly increased (27). As toluene is employed as solvent in the study, its large concentration relative to styrene would favor alkylation over oligomerization should the reaction proceed via a mechanism involving a nonadsorbed state of styrene/toluene. The only manner in which current results can be rationalized is where the reagent reacting with the carbocation is in the adsorbed state and thus selectivity becomes dependent on the relative surface concentration of the styrene/toluene. In addition to possessing few sites capable of activating styrene (Table 1), the support alone does not possess sites which are of sufficient strength to maintain a high local coverage of toluene and thus the oligomerization/polymerization reaction is favored. At high styrene conversion, the surface coverage of the monoalkylation product over the supported HPA also begins to reach significant levels, such that selectivity to polyalkylated products (**6**) increases relative to the oligomerization reaction (Table 1). The site which is responsible for maintaining the localized high concentrations of the competing styrene and toluene molecules (and at higher conversions, the monoalkylation product) most likely involve exposed Lewis acid sites, which interact with the π electrons of the ring in the case of toluene, leading to the observed 15-cm^{-1} shift of bands due to the out-of plane C–H modes (Fig. 3) or via the π electrons of the vinyl group of the styrene (Fig. 2). The relatively weak nature of exposed Lewis sites in the silica–zirconia support (5) relative to the supported HPAs would be consistent with this scheme; however, IR spectra (Fig. 2) also provide evidence for interaction between π electrons of the vinyl group of the styrene and silanol groups of the support, thus providing an alternative manner in which adsorbate molecules might be held in the vicinity of the carbocation intermediate.

The alkylation of alkylaromatics generally favor *p*-/*o*-substitution due to the electron-donating effect of the alkyl group (28). The lack of production of the *o*-isomer with the catalysts employed results from the large steric hindrance effect of styrene as the alkylating agent, leading to the dominance of *p*-substitution. Subsequent isomerization of the *p*-isomer leads to the formation of the *m*-isomer (29).

It is well known that the presence of Zr in SiO_2–ZrO_2 mixed oxides leads to the generation of Brønsted acid sites which are otherwise absent in the single-component oxides (1, 2, 4, 5). However, the detection in the IR spectra of adsorbed styrene molecules and the absence of the band at 1512 cm^{-1} attributed to the alkylated product combined with the low conversions obtained in reaction suggest either that there is a low density of surface sites of sufficiently strong acid character or that these sites are blocked by coke precursors produced from the adsorbed oligomer species that inhibit activation of further styrene molecules. Studies of but-1-ene isomerization over a sulfated form of the SiO_2–ZrO_2 support show that a good correlation exists between activity and the density of Brønsted acid sites, as determined by pyridine adsorption (4, 30). However, an overestimation of sites was apparent for the nonsulfated SiO_2–ZrO_2, indicating that although all sites were of sufficient strength to protonate the pyridine molecule, only a small proportion of sites were of sufficient strength to protonate but-1-ene at 423 K. It can be envisaged that these same small number of sites on the SiO_2–ZrO_2 support which protonate but-1-ene are also effective in activating the vinyl group of the styrene molecule.

The addition of heteropoly acids to the SiO_2–ZrO_2 support resulted in an increase in the number of sites which were available for the activation and subsequent reactions involving styrene, as confirmed by the increased activity in catalytic tests and in the FTIR study. The HPA are compounds that present very strong, predominantly Brønsted acid sites (31), which act as the active sites for the oligomerization and alkylation reactions. It has been claimed that depending on the HPA loading, partial decomposition of the structure may be observed on supports such as ZrO_2, SiO_2, or MCM-41 and that in general a reduction in the acid strength of the HPA is detected when it is supported (20, 32, 33). HPA supported on hydrated ZrO_2 modified the distribution of acid sites on the support through the formation of $(\equiv\mathrm{Zr{-}OH_2})_n^+[\mathrm{H}_{3-n}\mathrm{W}_{12}\mathrm{PO}_{40}]^{n-3}$ or $(\equiv\mathrm{Zr{-}O})_n{-}[\mathrm{H}_{3-n}\mathrm{W}_{12}\mathrm{PO}_{40-n}]$ distorted Keggin units (32). Similar species have been described for the interaction of the HPA with SiO_2. Under conditions employed here for the HPA(K)/SiZr catalysts, the presence of lacunary species such as $\mathrm{PW}_{11}\mathrm{O}_{39}^{7-}$ or unsaturated dimeric species ($H_6P_2W_{18}O_{62}$, $H_6P_2W_{21}O_{71}$) is most likely due to the method of preparation, the use of a precalcined support with an aqueous solution at $\mathrm{pH} > 2$, and the low HPA content (10 wt%) (11, 34). These species show a higher activity in dealkylation of alkylphenols than the intact Keggin structure, as their acid strength is diminished to a lesser extent following interaction with the support. The presence of some amounts of the intact Keggin species in the HPA(K)/SiZr catalyst could account for its lower activity when compared with the Dawson-type supported catalyst, where the pure structure is expected (35). On the other hand, the HPA can modify (and enhance) the acidity of the support resulting from the established interaction with the hydroxyl groups of the latter, thereby leading to increased numbers of available acid centers when the HPA is present in the supported form.

The absence of compounds **2**–**6** during the hydroformylation reaction following the anchoring (14) of chiral phosphine complexes to the supported heteropoly acids can be regarded as an indication of the successful attachment of the chiral complex to the polyanion (36).

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