Available online at www.sciencedirect.com

ScienceDirect

Journal of Catalysis 245 (2007) 184–190

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Continuous acylation of anisole by acetic anhydride in mesoporous solid acid catalysts: Reaction media effects on catalyst deactivation

VidyaSagar R. Sarsani [a,b], Christopher J. Lyon [b], Keith W. Hutchenson [c], Mark A. Harmer [c], Bala Subramaniam [a,b,*]

[a] *Department of Chemical & Petroleum Engineering, University of Kansas, Lawrence, KS 66045, USA*
[b] *Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, KS 66049, USA*
[c] *DuPont Central Research & Development, Wilmington, DE 19803, USA*

Received 30 August 2006; revised 2 October 2006; accepted 3 October 2006

Abstract

The acylation of anisole with acetic anhydride was carried out in a continuous slurry reactor over mesoporous supported Nafion® (SAC-13) and heteropolyacid (HPA) catalysts. At 70 °C, using an anisole-rich feed molar ratio of 5:1 and a space velocity of 1.6 $g_{\text{acetic anhydride}}\,g_{\text{cat.}}^{-1}\,h^{-1}$, acetic anhydride conversions of 40–50% with excellent selectivity (>95%) toward the primary product, *p*-methoxyacetophenone (*p*-MOAP), were observed at time on stream (TOS) of a few hours. However, all the catalysts deactivated completely during liquid-phase operation in less than 24 h. It was observed that the Keggin ions from the supported HPA-based catalyst (70% HPA/SiO_2) leached out into the solution, as confirmed by elemental analysis. The 50% $Cs_{2.5}$-HPA/SiO_2 catalyst, on the other hand, was more leach-resistant, yet deactivated rapidly during liquid-phase operation. SAC-13-type catalysts, which displayed the best combination of stability and leach resistance during liquid-phase operation, were evaluated in CO_2-expanded liquids (CXLs) to better enhance the transport properties and potentially mitigate deactivation. It is observed that the CXL media gave lower conversion and surprisingly, faster deactivation compared with liquid-phase operation, indicating that CO_2 had a detrimental effect despite the use of polar cosolvents like nitromethane. The spent catalysts were subjected to Soxhlet extraction with polar solvents like nitromethane. Such treatment did not restore catalyst activity. BET surface area, pore volume of the fresh and spent catalysts, GC/MS analysis of the Soxhlet extract, and IR analysis of the spent catalyst (before and after Soxhlet extraction) indicate that the deactivation could be caused by the primary product, *p*-MOAP and/or multiply acetylated products in the micropores of Nafion® catalyst aggregates. Treating the spent catalyst with boiling HNO_3 solution restored complete activity of the SAC-13-type catalysts. The high TON (∼400) achieved with these catalysts before deactivation and their ability to regain complete activity for acylation reactions indicate that Nafion® catalysts are promising alternatives to the conventional homogeneous Lewis acids like $AlCl_3$.

Keywords: Friedel–Crafts acylation; Anisole; Acetic anhydride; Dense carbon dioxide; CO_2-expanded liquid; Mesoporous catalyst; Heteropolyacids; Nafion® catalyst; SAC-13; Catalyst deactivation

1. Introduction

Friedel–Crafts acylation and the related Fries rearrangement of aromatic compounds are important methods for synthesizing aromatic ketones and key intermediates for the preparation of alkylated products used for fragrances, fine chemicals, and pharmaceuticals. Current industrial acylation processes use homogeneous Lewis acids (e.g., $AlCl_3$, BF_3, $FeCl_3$) or Brønsted acids (e.g., HF, polyphosphoric acid) as catalysts and acyl halides as acylating agents. The major drawback is the need to use stoichiometric quantities of Lewis acid because the products form stable complexes with the acid. The decomposition of these complexes is performed with water, leading to total destruction of the Lewis acid. The quantity, handling, corrosive nature, and associated disposal problems of the Lewis acids used and the hazardous nature of mineral acids have led to environmental concerns that have stimulated research aimed at

---

[*] Corresponding author. Fax: +1 785 864 6051.
E-mail address: bsubramaniam@ku.edu (B. Subramaniam).

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.10.001

developing safer and non-waste-producing alternatives based on solid acid catalysts. According to Clark and Macquarrie, “the successful substitution of traditional but dangerous and polluting acids like H_2SO_4, HF, and $AlCl_3$ is one of the most important goals of green chemistry” [1]. In addition, the use of carboxylic acids and/or anhydrides as acylating agents instead of conventional acid halides, which yield HCl as byproduct, is more attractive from an environmental standpoint. Despite extensive research efforts in academia and industry, the route to commercialization of solid acid catalysts for acylation reactions is still in its infancy, due primarily to the rapid deactivation of the catalysts by fouling, low catalyst activity for less active aromatic compounds, and, in some cases, poor selectivity to the desired product. The uses of solid acid catalysts for these reactions have been reviewed previously [2].

One of the most widely studied model reactions is the acylation of anisole, because the presence of the methoxy group activates the electrophilic substitution reaction. This reaction has been reported on various catalysts, most widely on zeolites [3–7] and more recently on other solid acid catalysts like S-ZrO_2 [8], heteropolyacid-based catalysts [9–12], supported Nafion® catalysts [13], and other cation-exchange resins like Amberlyst-36 [14]. Although most studies have focused on the activity and selectivity in batch reactions, a few studies have tested solid acid catalysts in the continuous mode to assess the extent of catalyst stability or deactivation with time on stream. In one of the first studies on the origin of deactivation of solid acid catalysts, Rohan et al. [3] claimed that the multiple acylated products entrapped in the micropores and the primary product retained in the zeolite mesopores caused deactivation, whereas Derouane et al. [4] attributed deactivation to strong, yet reversible adsorption of the primary product. Guidotti et al. [6] investigated the acylation of various substrates with acetic anhydride and concluded that deactivation was due mainly to the inhibiting effect of the products of acetic anhydride transformation, more pronounced in the case of deactivated substrates like fluorobenzene. To date, although improved activity has been achieved with modifications in both the catalysts and operating conditions, the exact cause of deactivation is not known, and stable activity remains elusive. Although Rhodia recently commercialized a process for acylating anisole and veratrol using zeolites [15], catalyst deactivation remains the primary roadblock to widespread application of solid acid catalysts for Friedel–Crafts synthesis.

The aim of the present study is to investigate the stability of mesoporous catalysts, like HPA/SiO_2, $Cs_{2.5}$-HPA/SiO_2, and supported Nafion® catalyst, during continuous operation in a slurry reactor. In an attempt to reduce catalyst deactivation, CO_2-expanded liquids (CXLs) [16,17] were used as reaction media. Such media were recently studied for solid acid-catalyzed alkylation of isobutane by supported Nafion® catalysts [18] and also by heteropolyacid catalysts [19]. With CXLs, unique combinations of fluid properties, such as liquid-like densities to solubilize the foulant precursors and gas-like transport properties to transport them out of the pores, may be achieved at relatively mild pressures. We report here the first work on acylation reactions in a continuous-mode slurry operation and first demonstration of a continuously operated CXL process.

Table 1
Characteristics of various solid acid catalysts

Catalyst	BET surface area (m^2/g)	Pore volume (cc/g)	Avg. pore diameter (Å)
SAC-13 B catalyst	56	0.11	95
SAC-13 D catalyst	127	0.39	110
SAC-13 E catalyst	20.3	0.05	115
SAC-13 F catalyst	86	0.26	131
SAC-13 N catalyst	129	0.51	162
70% HPA/SiO_2	92	1.5	646
$Cs_{2.5}$-HPA/SiO_2	85	3.1	1449

2. Experimental

2.1. Catalysts

Table 1 summarizes the characteristics of the various solid acid catalysts investigated. The heteropolyacid catalysts were synthesized at Pacific Northwest National Laboratory as reported previously [19]. In brief, 70% HPA/SiO_2 was prepared by impregnating HPA on Davison 645 silica using methanol as a solvent. $Cs_{2.5}$-HPA catalyst was prepared by adding the Cs_2CO_3 solution dropwise to the HPA solution while stirring. The HPA solution was prepared using the Keggin-type $H_3PW_{12}O_{40}\cdot nH_2O$ (Aldrich). The resulting precipitate was dried at 110 °C overnight in vacuum and calcined at 300 °C for 2 h.

SiO_2-supported Nafion® catalyst (SAC-13) was supplied by Engelhard (now BASF Catalysts). Other variations of SAC-13-type catalysts (SAC-13 B, D, E, and F) were synthesized at DuPont. For all of these supported Nafion® catalysts, acid site density (ASD) was determined by ion exchange with NaCl followed with titration by NaOH in accordance with the procedure specified by Engelhard. BET surface area and BJH pore volume measurements for all catalysts were done using a Micromeretics Gemini II 2370 surface area analyzer, using nitrogen physisorption.

The 70% HPA/SiO_2 catalyst was pretreated in situ under flowing nitrogen at 175 °C for 1 h, and 50% $Cs_{2.5}$-HPA/SiO_2 was pretreated ex situ in a degasser (Micromeritics) under flowing nitrogen at 300 °C for 1 h and then quickly transferred into the reactor. Silica-supported Nafion® catalyst extrudates were crushed and sieved to a particle size range of 62–212 µm. These catalysts were pretreated in situ under flowing nitrogen at 150 °C for 3 h.

2.2. Chemicals

The chemicals anisole (An; reagent plus grade with 99% purity, Sigma), acetic anhydride (AcAn; reagent grade with 98% purity, Sigma), and *para*-methoxyacetophenone (*p*-MAOP; 98% purity, Acros Organics) were procured and used as received. Nitromethane and nitrobenzene of reagent plus grade (99% purity, Aldrich) were used. Acetic acid, glacial (99.7%) and methylene chloride (99.9%) were procured from Fisher Scientific. CO_2 of 99.995% purity (Airgas) was used.

2.3. Phase behavior and activity studies

The phase behavior studies with high-pressure CO_2 were performed in a 50-mL Jerguson cell (Clark Reliance Co.) rated to 400 bar at 100 °C as described previously [16]. In a simple modification to the previous method, the CO_2 was bubbled through a fine porous (5 µm) cylindrical SS frit (Mott Corp), forming minute bubbles through the organic solvent. This improved the mass transfer rate significantly, allowing faster attainment of the VLE equilibrium, while avoiding such phenomena as viscous fingering or channeling through the organic liquid. As reported previously for the gas antisolvent recrystallization process, bubbling aeration of the liquid phase by CO_2 has an order of magnitude greater vapor liquid mass transfer rate than surface aeration [20]. The experimental procedure is as follows. First, the organic solvent is loaded in the Jerguson view cell. While the temperature is maintained constant by an external bath, the volume of the expanded liquid phase is measured after equilibrium is achieved as CO_2 is introduced into the cell. The increase in volume of the liquid phase relative to the volume of the organic liquid loaded initially is thus plotted with pressure. These expansion data are collected for various mixture compositions and temperatures of relevance to the reaction studies to gain insight into the phase behavior of the polar reaction mixtures in the presence of CO_2.

Conversion and selectivity measurements were performed in a 50-mL stirred Autoclave reactor made of Hastalloy C 276. A schematic of the experimental unit is available elsewhere [18,19]. All of the materials in the setup, including seals and *o*-rings, were chosen so as to be compatible with the chemicals used. Only Hastalloy C 276, Teflon, and Inconel 600 are wetted materials in the heated reaction zone, with SS 316 lines used in the rest of the experimental unit. A BPR-50 back-pressure regulator with compatible materials (TEMCO) was used to maintain the pressure in the reactor. Catalyst particles were suspended in the reaction mixture by an impeller operating at 800 rpm. All heated zones were controlled and monitored with a Camile 2500 data acquisition system. After catalyst pretreatment, the reactant mixture, premixed to the desired An/AcAn ratio, was pumped through the catalyst slurry, and the samples collected at various times on stream were analyzed by GC/FID.

For experiments using CO_2, the run was started by establishing the operating temperature and pressure with dense CO_2 (unless mentioned otherwise), followed by injection of the premixed feed along with flow of dense CO_2. In these runs, the ratio of the volumetric flow rate of CO_2 relative to that of the organic feed was chosen to ensure that the resulting CXL phase in the stirred reactor (at a composition dictated by the conversion) was maintained within the reactor volume based on the equilibrium volumetric expansion ratio (at the reactor temperature and pressure) measured in the Jerguson cell.

The catalyst was suspended as slurry, and a small disc-shaped porous frit that fits inside the exit dip tube was used to prevent the catalyst from leaving the reactor. During initial experiments, pressure was seen to build up across the frit in about 4–5 h. After eliminating all mechanical means of particle size reduction leading to blockage of the frit, we attribute this phenomenon to the interaction of acetic anhydride with the catalyst support, causing the disintegration of particles and thus clogging of the frit (with pore sizes 0.5, 5, and 20 µm). This was confirmed by controlled experiments in which the pressure build-up (and hence blocking the frit) occurred sooner when an acetic anhydride-rich mixture was fed into the reactor. This pressure buildup was observed with both HPA/SiO_2 and supported Nafion® catalysts. The problem can be averted (at least for the duration of the runs lasting up to 24 h) by fitting a hollow cylindrical frit with a large surface area onto the exit dip tube.

The product mixture was trapped in a sample loop between two valves at high pressure and depressurized by bubbling through a solvent in ice-cooled condenser. The sample loop was rinsed with dense CO_2 to ensure that all the organics from the sample loop are collected. Products were analyzed off-line by gas chromatography with an HP 5890 II GC, equipped with an FID and a DB-5ms column (J&W Scientific) operated in a split mode (split ratio = 30).

Elemental analysis of fresh and spent catalysts and of the reactant mixtures was performed by Desert Analytics, Tucson, AZ. The FTIR spectra of fresh and spent catalysts were obtained using a Nicolet Protégé 460 FTIR instrument in diffuse reflectance mode. GC/MS of the product mixtures and of the Soxhlet extracts were performed using an Agilent 6890 N equipped with a mass selective ion detector.

3. Results and discussion

3.1. Studies on heteropolyacid catalysts

Fig. 1 shows the temporal conversion and selectivity profiles on 70% HPA/SiO_2 in a CSTR at 70 °C for An/AcAn ratios of 1:1 and 5:1. The anisole-rich mixture showed relatively slower deactivation rates, as was reported by Rohan et al. [3] on zeolites. Elemental analysis of spent catalysts showed ~80% leaching of the Keggin ions into the reaction mixture for 70% HPA/SiO_2, as reported in Table 2. These results stand in sharp contrast to those reported by Cardoso et al. [10], who did not observe leaching of the Keggin ions. The differences could be due to the solvent used (i.e., dichloromethane as opposed to

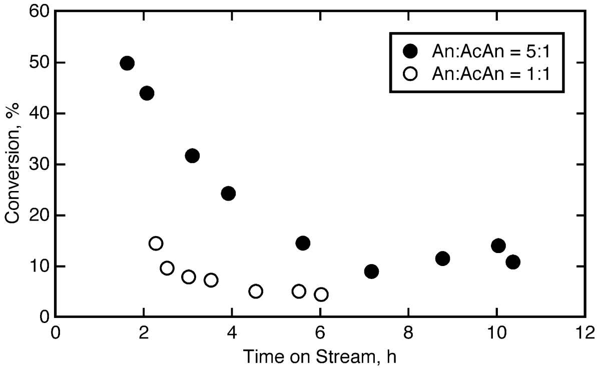

Fig. 1. Temporal conversion profiles on 70% HPA/SiO_2 (liquid phase, $T = 70\,^{\circ}C$, WHSV = 1.6 $g_{AcAn}\,g_{cat.}^{-1}\,h^{-1}$ for An:AcAn = 5:1 and 5.0 $g_{AcAn}\,g_{cat.}^{-1}\,h^{-1}$ for An:AcAn = 1:1).

Table 2
Elemental analysis of fresh and spent heteropolyacid catalysts

Sample	% Tungsten
70% HPA/SiO_2-spent	6.0
70% HPA/SiO_2-fresh	30.8
50% $Cs_{2.5}$-HPA/SiO_2-spent	16.4
50% $Cs_{2.5}$-HPA/SiO_2-fresh	20.8

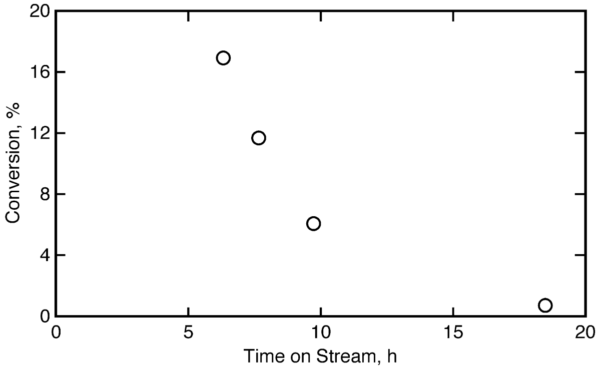

Fig. 2. Temporal conversion profile on 50% $Cs_{2.5}$-HPA/SiO_2 (liquid phase, $T = 70\,^{\circ}\mathrm{C}$, WHSV $= 1.7\ g_{\mathrm{AcAn}}\ g_{\mathrm{cat.}}^{-1}\ h^{-1}$, An:AcAn = 5:1).

no solvent in this study), the composition, the time exposed to the reaction mixture, the differences in synthetic procedures in supporting the active catalyst (i.e., aqueous solution rather than methanol during impregnation), and the nature of silica. Bachiller-Baeza and Anderson [11] investigated the reaction on HPA/SiO_2 catalyst and do not report any leaching of the Keggin ions.

$Cs_{2.5}$-HPA/SiO_2, on the other hand, is known to be insoluble and leach-resistant. Kaur and Kozhevnikov [12] reported the acylation of anisole with carboxylic acids on $Cs_{2.5}$-HPA as a highly efficient and reusable catalyst. Fig. 2 shows the temporal profile of the run with 50% $Cs_{2.5}$-HPA/SiO_2, which also displays a deactivating trend similar to that of HPA/SiO_2. Elemental analysis of fresh and spent catalysts reveals that $Cs_{2.5}$-HPA/SiO_2 is more leach-resistant than HPA/SiO_2 (see Table 2).

3.2. Studies on supported Nafion® catalysts

Initial batch screening studies were conducted to obtain a window of operating conditions (e.g., temperature, particle size, reaction time) for the experiments in the continuous mode. These studies were conducted on single batch of SAC-13, labeled SAC-13 N. Fig. 3 shows the temporal conversion profiles for experiments in liquid phase with a molar An/AcAn ratio of 5 and a space velocity of 1.6 $g_{\text{acetic anhydride}}\ g_{\mathrm{cat.}}^{-1}\ h^{-1}$ at various temperatures. Higher initial activity and faster deactivation were observed at higher temperatures. Studying the effect of using polar solvents (with the excess anisole essentially replaced by the solvents like nitrobenzene and nitromethane) at 70 °C reveals lower conversions and faster deactivation compared with those obtained in anisole-rich media (Fig. 4). Further, experiments with different SAC-13-type catalysts (SAC-13 B, D, E, F as shown in Table 1) were tested in the liquid phase. As shown in Table 1, catalysts SAC-13 B, D, E, and F had average pore diameters essentially in the same range, with surface areas ranging from 55.5 to 205 m^2/g and pore volumes ranging from 0.11 to 0.72 cc/g. The catalysts with high surface area and pore volume had higher initial conversions but subsequently deactivated with time, as shown in Fig. 5, indicating that diffusion limitations play a limited role, similar to the conclusion reached by Guidotti et al. [6] in their study on various substrates. These results led us to examine the postreaction analysis in more detail, as discussed later.

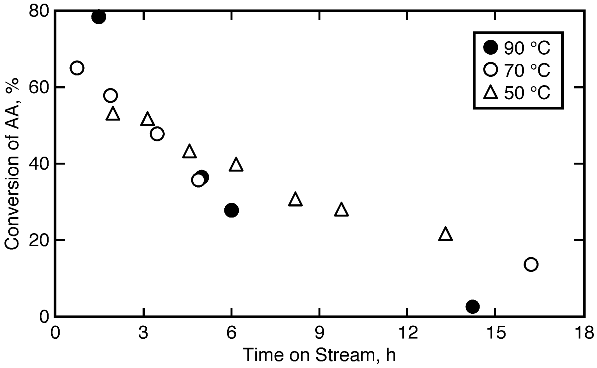

Fig. 3. Effect of temperature on the conversion profiles on SAC-13 N catalyst (other conditions are the same as noted in Fig. 2 caption).

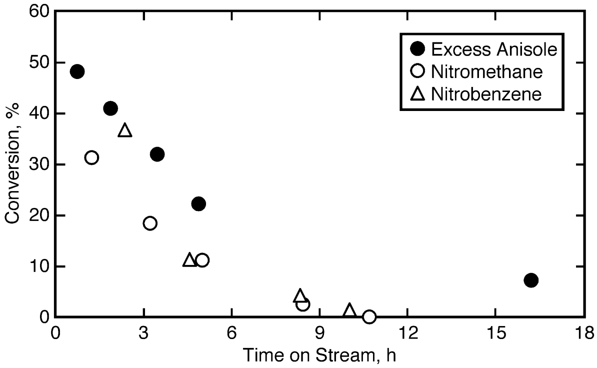

Fig. 4. Effect of replacing the excess anisole with various polar solvents on SAC-13 N catalyst (other conditions are the same as noted in Fig. 2 caption).

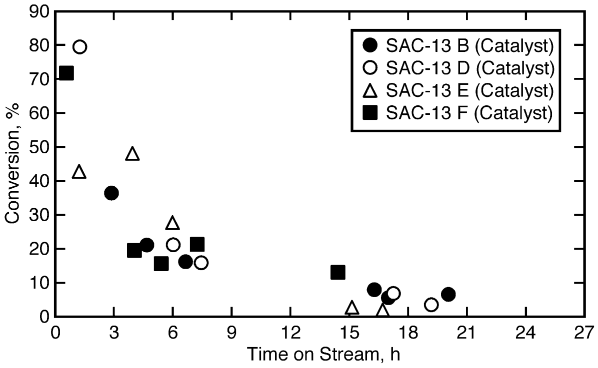

Fig. 5. Temporal conversion profiles on various SAC-13-type catalysts (other conditions are the same as noted in Fig. 2 caption).

3.3. Phase behavior studies and experiments in CXLs

It was reported previously that the reactants anisole and acetic anhydride showed complete miscibility in CO_2, whereas

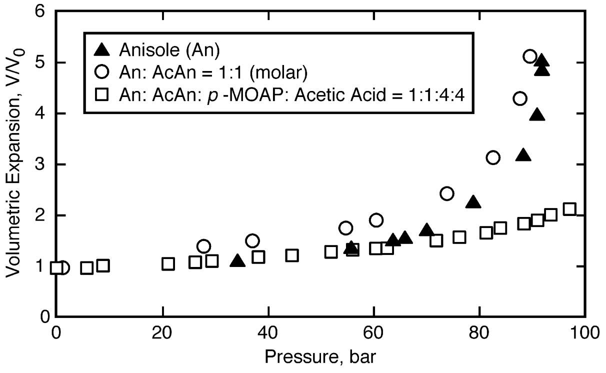

Fig. 6. Volumetric expansion of various reactant/product mixtures at 50 °C upon CO_2 addition into a Jerguson view-cell.

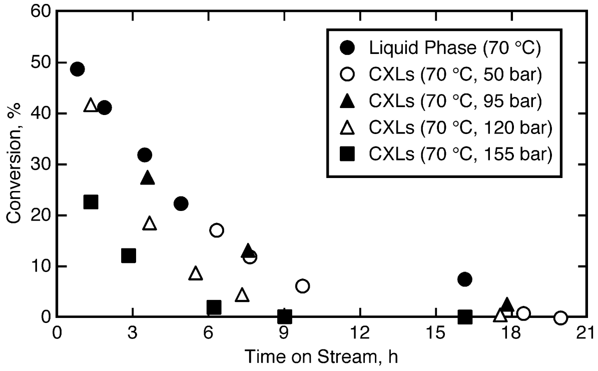

Fig. 8. Effect of pressure (CO_2 fraction) on conversion profiles (other conditions are the same as in Fig. 2 caption).

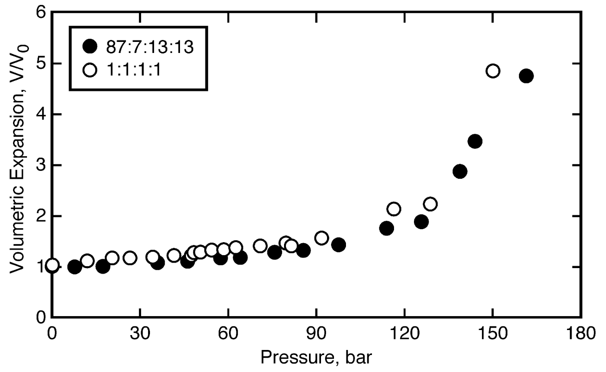

Fig. 7. Comparison of volumetric expansion of reactant/product mixture at 70 °C by CO_2 (at two molar ratios of An, AcAn, p-MOAP, and acetic acid of 1:1:1:1 and 87:7:13:13).

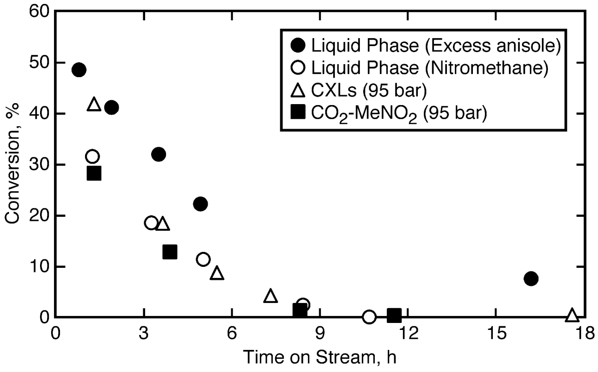

Fig. 9. Cosolvent effects on conversion profiles (other conditions are the same as in Fig. 2 caption).

p-MOAP had 1% (wt.) solubility in liquid CO_2 [21]. Phase equilibrium studies involving CO_2 and reaction mixtures provide guidance for determining the operating conditions (P, T, and CO_2 mole fraction) for activity studies, by giving the expansion ratio at the operating pressure while ensuring no precipitation of p-MOAP at these conditions. Fig. 6 shows the expansion data for An and An + AcAn mixture at a molar ratio of 1:1 and An, AcAn, p-MOAP, and acetic acid mixture at a molar ratio of 1:1:4:4 at 50 °C. It can be seen that the reactant/product mixture was expanded twofold at 95 bar. Fig. 7 shows the expansion data at 70 °C of molar ratios of 1:1:1:1 and 87:7:13:13 for An, AcAn, p-MOAP, and acetic acid, corresponding to reaction mixtures of 50 and 65% conversion starting with An:AcAn ratios of 1:1 and 5:1, respectively. The product was fully miscible in the reaction mixture with CO_2 at these conditions; that is, no product precipitation or a separate phase was observed.

Fig. 8 compares the conversion profiles in the organic liquid phase (without CO_2 addition) with that of CXL runs with various expansion ratios (corresponding to different pressures of CO_2) at 70 °C. At higher pressures, the conversions were lower (as expected due to dilution of the reaction mixture by CO_2) and, contrary to expectations, deactivation was faster compared with liquid-phase operation. To eliminate any detrimental effects arising from the nonpolar nature of CO_2, tuning the polarity and diffusion properties was studied using a mixture of CO_2 and nitromethane. In addition, at the startup of the run, the reactor was pressurized with argon instead of CO_2. In these experiments, the excess anisole was essentially replaced by equimolar quantities of CO_2 and nitromethane in a typical run at 70 °C and compared with runs with pure solvents, as shown in Fig. 9. In all of the runs, deactivation was faster than that of a solvent-free, anisole-rich mixture run. These results indicate that CO_2 has a detrimental effect for this class of reactions. These results led us to examine the spent catalysts in detail.

3.4. Understanding the deactivation mechanism: Postreaction analysis and treatments

To analyze the nature of deposits on the spent catalysts, Soxhlet extraction with methylene chloride as the solvent was performed for about 8 h. The extract when analyzed by GC/MS contained anisole and the primary product, p-MOAP. When the Soxhlet-extracted catalyst was tested for acylation activity in a batch reaction, it was found to be inactive. This indicates that compounds responsible for deactivation, including p-MOAP, were not fully extracted. To ascertain the influence of a different solvent with different polarity, the Soxhlet extraction was done with Me-NO_2 for long periods (∼200 h); the catalyst was inactive when tested for acylation activity. This is in contrast to the findings of Rohan et al. [3], who reported increased activity for anisole acylation after Soxhlet extraction with methylene chloride was performed on HBEA zeolite catalyst. The fresh and

Table 3
BET surface area and pore volume of spent catalysts

SAC-13 N catalyst, spent after experiment at	BET surface area (m^2/g)	Pore volume (cc/g)	Avg. pore diameter (Å)
70 °C, 120 bar, A*	137	0.48	137
70 °C, 120 bar, B*	123	0.50	145
70 °C, liquid phase, B*	105	0.48	149
90 °C, liquid phase, B*	116	0.44	139
70 °C, liquid phase with Me-NO_2, B*	105	0.28	103
50 °C, liquid phase, B*	70	0.35	163
70 °C, 155 bar, B*	48.5	0.25	176
70 °C, 155 bar, A*	122	0.44	139

Note. A*: after Soxhlet extraction; B*: before Soxhlet extraction.

Table 4
Acid site density (ASD) of fresh and spent catalysts

Catalyst	H^+ concentration (mmol/g)
SAC-13 N catalyst, spent (70 °C, 120 bar)	0.18
SAC-13 N catalyst, spent (70 °C, 152 bar)	0.61
SAC-13 N catalyst, spent (70 °C, liquid phase)	0.34
SAC-13 N catalyst, fresh	0.13

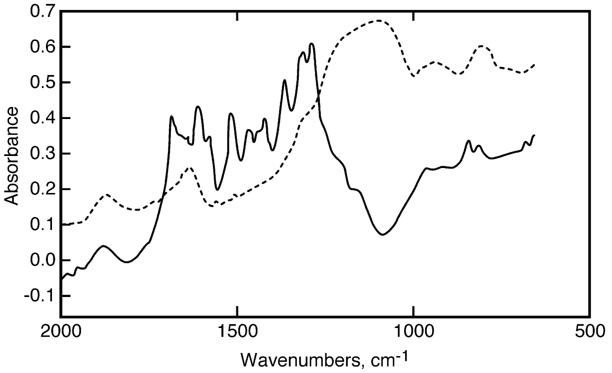

Fig. 10. Comparison of IR spectra of fresh (dotted line) and spent (solid line) SAC-13 N catalyst (liquid phase, 70 °C).

spent catalysts showed comparable BET surface areas and pore volumes in most runs except the high-pressure run (155 bar, 70 °C), which regained its surface area only after Soxhlet extraction (see Table 3). These results indicate that the deposits responsible for deactivation are in the micropores of Nafion® catalyst aggregates (at least in a liquid-phase operation), not in the mesopores, contrary to literature reports [3]. Further, as shown in Table 4, the titrations done to measure acid site densities of spent catalysts showed surprisingly larger values than those for fresh catalyst, which is attributed to the formation of acetate species as reported previously [11].

As shown in Fig. 10, the IR spectra of the spent catalyst from a liquid-phase run at 70 °C has many additional peaks, corresponding to IR active species retained in the catalyst, compared with those of a fresh batch of pretreated catalyst. Figs. 11 and 12 compare the IR spectrum of the spent catalyst with that of fresh catalysts exposed to the primary product, *p*-MOAP, in solutions with acetic anhydride and anisole, respectively. Comparing the IR spectra of a spent catalyst with that of the same catalyst after Soxhlet extraction (see Fig. 13) shows that the relative absorption corresponding to C=O (about 1700 cm^{-1}) was reduced after Soxhlet extraction, indicative of removal (at least in part) of *p*-MOAP. These results, along with the inactivity of the Soxhlet-extracted catalyst, indicate that the catalyst deactivation could be attributed to the primary product, *p*-MOAP and/or multiply acetylated compounds. Also of interest is the fact that the IR spectra of spent catalysts from all the CO_2-based runs showed an additional peak at ~2300 cm^{-1} corresponding to the C=O stretch, indicating strong adsorption of CO_2 to the

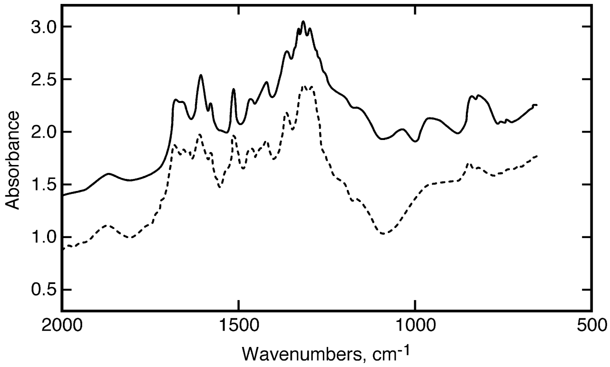

Fig. 11. Comparison of IR spectra of spent (dotted line) SAC-13 N catalyst (liquid phase, 70 °C) with that exposed to AcAn + *p*-MOAP (solid line).

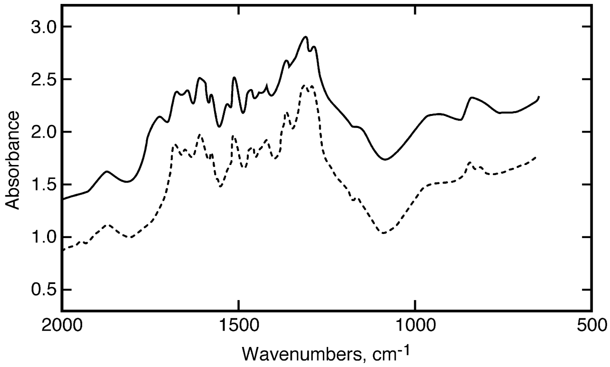

Fig. 12. Comparison of IR spectrum of spent (dotted line) SAC-13 N catalyst (liquid phase, 70 °C) with that exposed to An + *p*-MOAP (solid line).

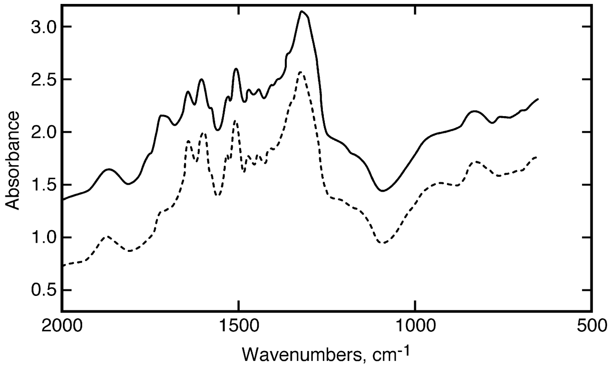

Fig. 13. Comparison of IR spectra of spent SAC-13 N catalyst (liquid phase, 90 °C) before (solid line) and after (dotted line) Soxhlet extraction.

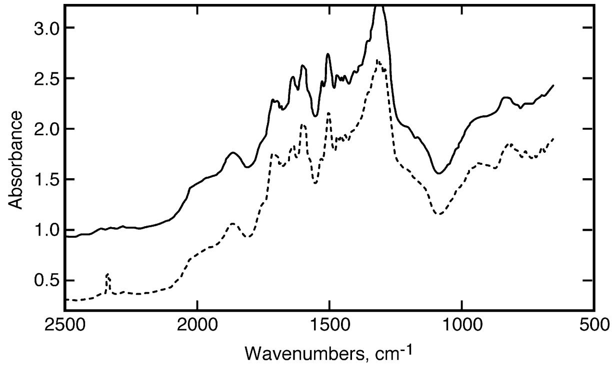

Fig. 14. Comparison of IR spectra of spent SAC-13 N catalyst from CXL run at 155 bar and 70 °C (dotted line) with that of spent SAC-13 N catalyst from liquid phase run at 70 °C (solid line).

catalytic sites (see Fig. 14). This demonstrates the detrimental nature of CO_2 on the solid acid catalysts (at least for acylation reactions).

However, when the spent catalysts were treated with boiling HNO_3 (40% solution) followed by reuse, they regained their activity, comparable to that of the fresh catalysts. The high TON (∼400) achieved with these catalysts before deactivation and their ability to regain complete activity for acylation reactions indicate that SiO_2-supported Nafion® catalysts are promising alternatives for the conventional homogeneous Lewis acids like $AlCl_3$.

4. Conclusion

Acylation of anisole with acetic anhydride was performed on various mesoporous supported solid acid catalysts, like HPA/SiO_2, $Cs_{2.5}$-HPA/SiO_2, and supported Nafion® catalyst, in a continuous-mode slurry reactor. All of the catalysts deactivated almost completely in about 24 h at 70 °C and a space velocity of 1.6 $g_{\text{acetic anhydride}}\,g_{\text{cat.}}^{-1}\,h^{-1}$, with an anisole-rich feed molar ratio of 5:1. Elemental analysis confirmed that the Keggin ions from the supported HPA-based catalysts, 70% HPA/SiO_2 and 50% $Cs_{2.5}$-HPA/SiO_2, leached out into the solution. Experiments with different SAC-13-type catalysts with variations in surface area and pore volume indicated that diffusion plays a limited role in the deactivation process. The use of dense CO_2-based reaction mixtures (to enhance the transport properties and hence reduce deactivation) on SAC-13-type catalysts was found to be detrimental for acylation reactions, despite the use of polar solvents like nitromethane as a cosolvent. Among the catalysts tested, a TON of about 400 was achieved during a continuous run with SAC-13 (in a typical run at 70 °C) before complete deactivation. Soxhlet extraction of spent catalyst did not restore catalytic activity. Postreaction analyses, including BET surface area, pore volume, and IR spectra of spent catalysts, indicated that the deactivation was caused by the primary product, *p*-MOAP, and/or multiply acetylated products in the micropores of Nafion® catalyst aggregates. The ability of SAC-13 catalysts to completely regenerate with HNO_3 treatment demonstrates that these supported Nafion® catalysts are promising alternatives for the traditional homogeneous Lewis acid catalysts like $AlCl_3$.

Acknowledgments

This study was supported by the National Science Foundation (Grant NSF 0310689). The authors thank Engelhard (now BASF Catalysts) Corporation, Beechwood, Ohio for supplying the SAC-13 catalyst samples and Dr. Yong Wang, Pacific Northwest National Laboratory for providing the heteropolyacid-based catalyst samples.

References

[1] J. Clark, D. Macquarrie (Eds.), Hand Book of Green Chemistry and Technology, Blackwell, UK, 2002, p. xviii.
[2] P. Metivier, in: R.A. Sheldon, H. Van Bekkum (Eds.), Fine Chemicals through Heterogeneous Catalysis, Wiley–VCH, Weinheim, 2001, p. 161.
[3] D. Rohan, C. Canaff, E. Fromentin, M. Guisnet, J. Catal. 177 (1998) 296.
[4] E. Derouane, C. Dillon, D. Bethell, S. Derouane-Abd Hamid, J. Catal. 187 (1999) 209.
[5] P. Botella, A. Corma, F. Rey, S. Valencia, Stud. Surf. Sci. Catal. A 142 (2002) 651.
[6] M. Guidotti, C. Canaff, J. Coustard, P. Magnoux, M. Guisnet, J. Catal. 230 (2005) 375.
[7] E.G. Derouane, I. Schmidt, H. Lachas, C.J.H. Christensen, Catal. Lett. 95 (2004) 13.
[8] J. Deutsch, V. Quaschning, E. Kemnitz, A. Auroux, H. Ehwald, H. Lieske, Top. Catal. 13 (2000) 281.
[9] J. Kaur, K. Griffin, B. Harrison, I.V. Kozhevnikov, J. Catal. 208 (2002) 448.
[10] L.A.M. Cardoso, W. Alves Jr., A.R.E. Gonzaga, L.M.G. Aguiar, H.M.C. Andrade, J. Mol. Catal. A 209 (2004) 189.
[11] B. Bachiller-Baeza, J.A. Anderson, J. Catal. 228 (2004) 225.
[12] J. Kaur, I.V. Kozhevnikov, Chem. Commun. 21 (2002) 2508.
[13] A. Heidekum, M.A. Harmer, W.F. Hoelderich, J. Catal. 188 (1999) 230.
[14] G.D. Yadav, M.S.M. Mujeebur Rahuman, Org. Proc. Res. Dev. 6 (2002) 706.
[15] M. Spagnol, L. Gilbert, E. Benazzi, C. Marcilly, US Patent 6,013,840 (2000), to Rhodia Chimie.
[16] M. Wei, G.T. Musie, D.H. Busch, B. Subramaniam, J. Am. Chem. Soc. 124 (2002) 2513.
[17] H. Jin, B. Subramaniam, Chem. Eng. Sci. 59 (2004) 4887.
[18] C.J. Lyon, V.R. Sarsani, B. Subramaniam, Ind. Eng. Chem. Res. 43 (2004) 4809.
[19] V.R. Sarsani, Y. Wang, B. Subramaniam, Ind. Eng. Chem. Res. 44 (2005) 6491.
[20] C. Lin, G. Muhrer, M. Mazzotti, B. Subramaniam, Ind. Eng. Chem. Res. 42 (2003) 2171.
[21] A.W. Francis, J. Am. Chem. Soc. 58 (1954) 1099.