Catalysis Letters Vol. 83, No. 1–2, October 2002 (©2002)

Propionitrile hydrolysis over sulfonic resins

María Rosa Capeletti, Nora Fígoli, and Ulises Sedran *

Instituto de Investigaciones en Catálisis y Petroquímica (FIQ, UNL–CONICET),
Santiago del Estero 2654, (3000) Santa Fe, Argentina

Received 11 February 2002; accepted 26 May 2002

Mixtures of propionitrile, methanol and water were reacted during different times over a sulfonic acid resin at 15 kg cm^{-2} and temperatures from 30 to 93 °C. Propionitrile hydrolysis was followed by means of FTIR spectroscopy of the catalyst surfaces. In the spectra of used catalysts, different bands appeared that can be attributed to propanamide. The intensity of those bands increased with reaction time and temperature. These observations were consistent with a reaction scheme in which a methyl propionimidate ion is an intermediate species. MTBE synthesis as a test reaction showed that there is a direct relationship between the formation of propanamide and the loss of catalyst activity.

KEY WORDS: propionitrile; sulfonic resins; nitrile hydrolysis; amides.

1. Introduction

Ethers (MTBE or TAME) and alcohols are used as oxygenate additives in gasoline blending operations, following legislation about fuel composition. The most important oxygenate additive, MTBE, is produced at about 15–20 kg cm^{-2} and temperatures of approximately 80 °C by the selective reaction of methanol and isobutylene over sulfonic polystyrene–polydivinylbenzene resins as the standard catalysts, which are strongly acidic [1]. The hydrolysis of acetonitrile (a very low concentration byproduct in the C_4 cut from the process of catalytic cracking of hydrocarbons containing reactant isobutylene) was suggested as one of the most probable causes of catalyst deactivation in the synthesis of MTBE. Another cause is the interaction with metal ions or basic compounds [2].

It was shown in a previous work [3] that the hydrolysis of acetonitrile on macroreticular sulfonic resins is feasible under the conditions of MTBE commercial synthesis. In this way, acetamide is formed adsorbed on the catalyst surface, which can act as a catalyst poison, and eventually the reaction could proceed further to yield acetic acid and ammonia. A reaction mechanism can be envisaged based on a Pinner's synthesis route (the condensation of a nitrile and an alcohol, with the presence of hydrogen bromide or chloride).

It is the objective of this work to study the reaction of hydrolysis of propionitrile over commercial sulfonic resins with methanol and water under conditions similar to those of MTBE synthesis and to compare results with those of acetonitrile. The FTIR technique was applied to follow the development of surface species, and the catalyst activity decay was studied by means of the MTBE synthesis reaction as a test.

2. Experimental

The experiments on hydrolysis reaction were carried out with a reactant mixture of methanol (Carlo Erba, 99.9%), propionitrile (Merck, 99.55%) and demineralized water, the molar ratios being 3 : 2 : 1. The mixture was contacted in a batch, stirred tank reactor at 15 kg cm^{-2} with the Amberlyst-15 WET resin (Rohm & Haas) without previous treatments. Particles were approximately spherical, with diameters in the 0.35–1.20 mm range, and the water content was about 50%. The base temperature was 65 °C, but experiments were also performed at 30 and 93 °C. The reaction time was varied between 1 and 48 h. The mass of catalyst was always 6 g (on a dry basis) and the total volume of the reactant mixture was 105 cm^3.

The FTIR analyses of all catalyst samples were carried out at room temperature using Shimadzu 8101 M equipment. The dried resin particles were finely ground, sieved, diluted at 2% in KBr, and pressed to obtain wafers of about 108 mg cm^{-2}.

MTBE synthesis was used as the test reaction to determine the catalytic activity of samples that had been used in the hydrolysis reaction. A flow fixed-bed tubular reactor was used at atmospheric pressure and 100 °C, feeding 1.32 cm^3 min^{-1} of methanol and 13.1 cm^3 min^{-1} of isobutylene during 3 h over 1.4 g of catalyst.

In both cases (batch and flow reactors), the composition of reactor effluents was followed by gas chromatography using a thermal conductivity detector.

---

* To whom correspondence should be addressed.
E-mail: usedran@fiqus.unl.edu.ar

1011-372X/02/1000-0015/0

3. Results and discussion

The hydrolysis of low-molecular-weight nitriles over acidic sulfonic resins was shown to be feasible with the example of acetonitrile [3]. However, the reaction rate at 15 kg cm^{-2} and temperatures in the range 30–93 °C was very low with the usual nitrile concentrations of less than 500 ppm found in the C_4 cut in FCC effluents. Then, the eventual hydrolysis of propionitrile was studied with higher concentrations of the nitrile. It is to be mentioned, however, that in every experiment it was not possible to observe noticeable amounts of compounds other than reactants in the reactor's effluents.

The existence of different species on the catalyst surface was analyzed by FTIR spectroscopy of the catalysts after each hydrolysis run, the spectra being collected at room temperature without additional treatments of the samples. The spectra collected are presented in figures 1 to 4, in which comparisons can be established between used and fresh samples. Some changes in the spectra of the used catalysts can be observed to develop as a function of the reaction parameters, like temperature and reaction time.

The overall spectra (wavenumbers from 2500 to 4000 cm^{-1}) at various reaction times are presented in figure 1 for the reaction temperature of 93 °C, in which the following band assignations can be considered [4,5]. The broad bands at 3000–3600 cm^{-1} might include the bands due to both symmetric and asymmetric stretchings of the OH groups belonging to alcohols, acids and sulfonic groups (note that methanol and sulfonic groups on the resin surface are initially present in the reacting system). Also, propionic acid can be produced, as will be discussed later. A broad band at approximately 3150 cm^{-1}, that was not present in the spectrum of the fresh catalyst, appears in the spent catalyst samples, and its intensity becomes stronger as a function of reaction time. In that sense, it has to be considered that the stretching of the N–H bond corresponding to a primary amide produces a pair of bands located at 3450 and 3150 cm^{-1} [5]; both bands can be observed in the spent catalysts, and their intensity increases as a function of reaction time. Indeed, the band at 3450 cm^{-1}, which was already present in the fresh catalysts, could now be including this new band.

The range of wavenumbers between 1350 and 1750 cm^{-1} is shown in figure 2. New bands at about 1630 cm^{-1} can be seen in the spent catalyst samples, with intensities that increase as a function of reaction time; these bands can be assigned to the stretching of the C=O carbonyl groups [4,5]. Indeed, since different compounds with carbonyl groups can be present on the

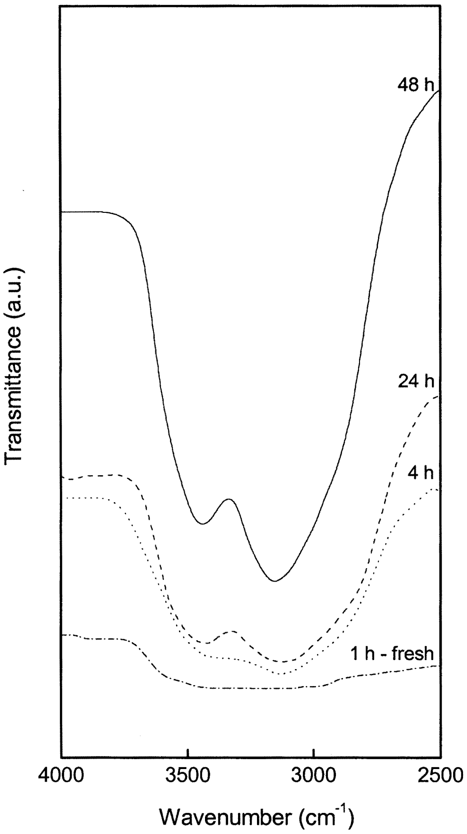

Figure 1. Effect of reaction time on propionitrile hydrolysis reaction at 93 °C and 15 kg cm^{-2}. The 2500–4000 cm^{-1} wavenumber region of the FTIR spectra.

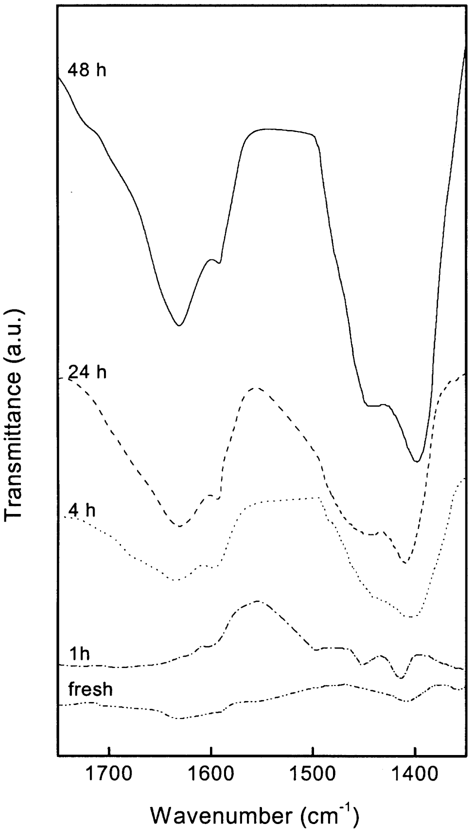

Figure 2. Effect of reaction time on propionitrile hydrolysis reaction at 93 °C and 15 kg cm^{-2}. The 1350–1750 cm^{-1} wavenumber region of the FTIR spectra.

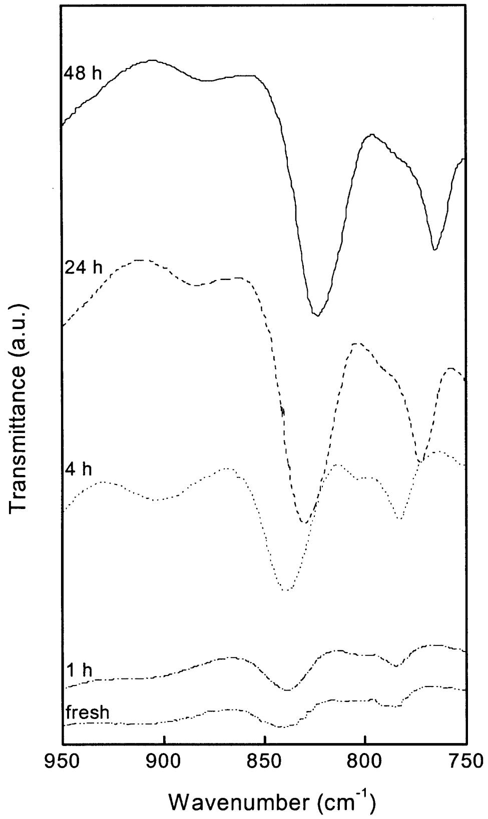

Figure 3. Effect of reaction time on propionitrile hydrolysis reaction at 93 °C and 15 kg cm^{-2}. The 750–950 cm^{-1} wavenumber region of the FTIR spectra.

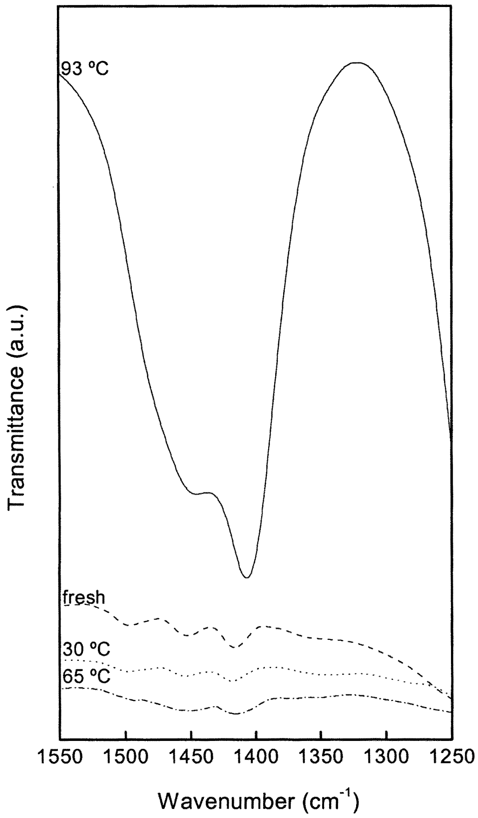

Figure 4. Effect of temperature on propionitrile hydrolysis reaction for 24 h at 15 kg cm^{-2}. The 1300–1500 cm^{-1} wavenumber region of the FTIR spectra.

catalyst surface, the band could be composed of their individual contributions. However, the important band broadening observed suggests that the bands examined are those corresponding to band I (carbonyl group stretching) and band II (N–H bond bending) in amides. Even the contribution from propionic acid carbonyl groups, which would shift to lower wavenumbers, could be considered.

The C–N asymmetric stretching in the group O=C–N that could be represented by the band at approximately 1400–1415 cm^{-1}, on the spent samples (refer to figure 2) also increases as a function of reaction time, with a shift to lower wavenumbers. The bending of the bond N–H out of the plane of an amide molecule [5], yielding a band at about 830 cm^{-1}, also increases as a function of reaction time and temperature (see figure 3 as an example).

The evidence gathered in figures 1–3 points to the existence of a primary amide adsorbed on the catalyst surface, which should be propanamide (see a description of the reaction mechanism in the following paragraph). The comparison of all the spectra with that of pure propanamide [6] (not shown), in which all the mentioned bands were observed, allowed one to confirm the assignations, indicating that propanamide is formed on the catalyst surface as a consequence of the reaction of propionitrile.

The formation of propanamide can be explained by means of the extension of a Pinner's synthesis mechanism [7] occurring on the catalyst surface. This reaction can proceed at low temperatures in homogeneous systems and, in this particular case of propionitrile, water and methanol reactants, it could proceed through the protonation of the nitrile by the sulfonic sites of the resin, followed by the slow addition of methanol to the surface ion to generate a methyl propionimidate ion; finally, the reaction with water may yield methyl propionate and ammonium ion. The intermediate methyl propionimidate ion could be subjected to decomposition to propanamide if the temperature is high enough. The kinetic scheme for the analogous case of acetamide formation has been presented elsewhere [3].

Experiments performed at different thermal levels confirmed a similar landscape, again denoting the formation of the amide. For example, as can be seen in figure 4 for the reaction time of 24 h, the band assigned to the asymmetric stretching of the bond C–N in the group O=C–N, located at approximately 1400–1415 cm^{-1}, increases significantly when the reaction temperature is 93 °C. However, it is observed that the reaction rate is very low at the lowest temperature of 30 °C, since the spectra of the fresh and spent catalysts do not differ. The same observations apply to the other bands belonging to the amide.

In analogy to the case of acetonitrile, the stretching of the C−N bond at about 1400–1415 $\mathrm{cm^{-1}}$ in all adsorbed intermediate compounds in the various steps may be masked by the band from carbonyl groups. A similar situation applies to other possible products from the reaction of methyl propionimidate ion, like methyl propionate, because its signals may be hindered by those of alcohols and amide molecules. This route would also be favored at higher temperatures [7].

Propionic acid and ammonia could also be formed directly from propanamide but, as mentioned previously, no evidence of compounds other than the reactants was found among the reactor's effluents.

Catalyst deactivation is expected as a consequence of the formation and adsorption of propanamide on the catalyst surface, since proton acid sites would be lost. Since these resin catalysts are very active for the reaction of MTBE synthesis [2], it was chosen as a test to assess catalyst activity, with experiments performed on various samples for at least 3 h, and the results were compared with those of a fresh, fully active sample. The commercial process is stable over an extended period of time and the same was observed under these particular laboratory conditions [3]. Results presented in table 1 clearly show that catalyst deactivation, as shown by the decrease in isobutylene conversion with constant reaction selectivity, is very significant, and that it increases along with the yield of propanamide. The areas of the FTIR bands observed at 830 $\mathrm{cm^{-1}}$, considered as representative of propanamide formation, were assessed for the particular case of 93 °C reaction temperature, where signals were more noticeable, at various reaction times and compared with isobutylene conversion, results showing the direct relationship between hydrolysis reaction extent and catalyst deactivation (see table 1).

Table 1
Catalyst activity for the synthesis of MTBE from methanol and isobutylene at 100 °C. Catalyst samples used in the reaction of propionitrile hydrolysis under different experimental conditions.

Propionitrile hydrolysis reaction				MTBE synthesis
Temperature (°C)	Reaction time (h)	Propanamide yield (830 $\mathrm{cm^{-1}}$ FTIR band intensity and areas, fresh catalyts: 1)		Isobutylene conversion (a.u.)
		Intensity	Area	
No reaction	–	–	*	100.0
30	1	–	*	100.0
30	4	+ +	*	84.3
30	24	+ +	*	79.9
65	1	+	*	76.9
65	4	+ +	*	72.0
65	24	+ + +	*	64.0
93	1	+	1.24	72.0
93	4	+ + +	3.42	59.3
93	24	+ + + +	5.68	53.1

* Not measured.

4. Conclusions

The hydrolysis of propionitrile under mild conditions is feasible on commercial sulfonic resins. The evidence of the reaction, leading to the formation of propanamide on the catalyst surface, was observed through the FTIR spectra of the spent catalysts. Results were consistent with a Pinner's-synthesis-type mechanism, and the higher the temperature and the longer the reaction time, the more extensive the reaction. As a consequence of the loss of acid sites, the reaction products induce catalyst deactivation for the conversion of isobutylene and methanol to MTBE, in direct proportion to the extension of propanamide formation.

Acknowledgments

This work was performed with the financial assistance of the National University of Litoral, Secretary of Science and Technology (Santa Fe, Argentina), project 12/H163, and the ANPCYT.

References

[1] G.J. Hutchings, C.P. Nicolaides and M.S. Scurrell, Catal. Today 15 (1992) 23.

[2] E. Schwarz, K. Rock, J. Byeseda and R. Pehler, presented at AICHE 1992 Annual Meeting, November 1992, Miami (Florida).

[3] M. Quiroga, M.R. Capeletti, N. Fígoli and U. Sedran, Appl. Catal. A: General 177 (1998) 37.

[4] M. Avram and Gh. Mateescu, *Infrared Spectroscopy* (Wiley, New York, 1972).

[5] E. Pretsch, T. Clerc, J. Seibl and W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, 3rd edition (Springer, Berlin, 1989).

[6] Ch. Pouchet, *The Aldrich Library of Infrared Spectra* (Aldrich Chemical, Wisconsin, 1981).

[7] R. Roger and D. Neilson, Chem. Rev. 61 (1961) 173.