

Water promotion or inhibition effect on isopropanol decomposition catalyzed with a sol–gel MgO–Al₂O₃ catalyst

J.H. Zhang^a, X.L. Zhou^b, J.A. Wang^{c,*}

^a Chemistry and Chemical Engineering College, Xinyang Normal University, 464000 Xinyang, Henan, PR China

^b Petroleum Processing Research Center, East China University of Science and Technology, 200237 Shanghai, PR China

^c Laboratorio de Catálisis y Materiales, SEPI-ESIQIE, Instituto Politécnico Nacional, Av. Politécnico S/N, Col. Zacatenco, 07738 México D.F., Mexico

Received 6 October 2005; received in revised form 29 November 2005; accepted 30 November 2005

Available online 6 January 2006

Abstract

A magnesia-alumina mixed oxide containing both acid sites (3.9 sites/nm²) and base sites (3.0 sites/nm²) was synthesized via a sol–gel method. Catalytic evaluation of isopropanol decomposition catalyzed with the magnesia-alumina oxide catalyst showed that acetone and propene as major products were formed through dehydrogenation and dehydration pathways. When water stream was present the inlet feedstock, the catalytic activity for isopropanol decomposition was found to be promoted or inhibited that strongly depends upon the reaction temperature. The selectivity to acetone, however, was significantly enhanced after water addition either isopropanol conversion increasing at a reaction temperature below 300 °C or decreasing at a temperature above 300 °C. A new reaction pathway of hydroxyls-assisted dehydrogenation was postulated.

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Keywords: Al₂O₃–MgO; Sol–gel; Catalyst; Isopropanol; Basicity; Acidity

1. Introduction

Alcohols decomposition over a variety of metal single or binary oxides, such as ZnO₂, TiO₂, TiO₂–SiO₂ and TiO₂–ZrO₂, has been frequently used as an indicator of surface acidity and basicity of oxides, which is based on the postulation of alcohol dehydration to propene taking place on acid sites, and dehydrogenation to acetone catalyzed by basic sites [1–6]. The relative ratio of dehydration to dehydrogenation is therefore used to characterize the surface acidity and basicity of the solids. However, some researches show that isopropanol decomposition over oxides is to be a function of not only surface properties but also the experimental parameters [7–11]. It was reported that in the isopropanol decomposition catalyzed with TiO₂ catalyst, selectivity to acetone by dehydrogenation is significantly affected by the reaction stream composition [7,9]. Similar conclusion was obtained on a sol–gel MgO oxide [8]. Portillo et al. claimed that particle size of oxides should be also taken into account when one wants to establish a relationship between reaction selectivity

and surface acidity or basicity of the catalyst [10]. In a previous work, it is found that basicity of a sol–gel alumina catalyst indeed determines the acetone selectivity by dehydrogenation in the isopropanol decomposition, however, no evidence on the correlation between acidity and dehydration selectivity could be found [11]. Therefore, care must be taken when such a probe reaction is used as simple diagnostics of surface acid–base properties of oxides.

In this communication, dehydration and dehydrogenation of isopropanol catalyzed with a MgO–Al₂O₃ mixed oxide catalyst prepared by a sol–gel method was studied, with particular emphasis on the dependence of catalytic activity and selectivity upon the experimental variables of reaction temperature and water stream addition. A new hydroxyls-assisted reaction pathway concerning acetone formation is postulated.

2. Experimental

2.1. Sample preparation

21.3 ml of magnesium ethoxide (Aldrich, 99%) were dissolved into a given amount of absolute butanol to obtain a solution. The 1 g of oxalic acid (Baker, 99%) was used as a

* Corresponding author. Tel.: +52 55 57296000x55124; fax: +52 55 55862728.
E-mail address: jwang@ipn.mx (J.A. Wang).

hydrolysis catalyst to add into this solution where the pH value was maintained at approximately 5. The solution was then under reflux for 3 h at 70 °C with continuous stirring; afterwards, 6.5 ml of aluminum trisecbutoxide and 15 ml of water were slowly dropped into the above mixture until the gel was formed. Finally, the resultant material was dried at 70 °C and calcined at 600 °C for 4 h in static air.

2.2. X-ray diffraction (XRD) analysis

The XRD patterns of the samples packed in a glass holder were obtained at room temperature with Cu K α radiation in a Bruker Advanced D-8 diffractometer having a θ – θ configuration and a graphite secondary beam monochromator. Diffraction intensities were measured between 5° and 110°, with a step of 0.02° for 2.3 s per point.

2.3. Fourier transform infrared (FT-IR) characterization

The surface dehydroxylation and removal of the residual organic groups from the dried samples were characterized by the in situ FT-IR spectroscopic technique on a Nicolet Magna-IR 550 spectrometer. The sample wafer was placed in the IR cell, which was linked to vacuum and heating systems. The sample can be exposed to various gaseous environments at various pressures at a temperature not exceeding 500 °C. The in situ IR spectra reported herein were recorded at 25, 100, 200, 300, 400 and 500 °C, respectively.

2.4. Textural analysis

Textural properties including surface area and pore size distribution of the MgO–Al₂O₃ solid were analyzed by nitrogen adsorption–desorption isotherms method on an automatic ASAP 2000 analyzer.

2.5. Acidity and basicity measurement

The total basic and acidic sites of the solid were measured by temperature-programmed desorption (TPD) of CO₂ and NH₃ on an Altamira Automatized apparatus. Before adsorption, the sample was heated in a He stream at 300 °C for 1 h to remove any surface impurities. Then, it was saturated with ammonia (or carbon dioxide) for 30 min at 50 °C. After the excess adsorbant was eliminated by flowing dry He at the same temperature, the sample was heated in steps of 10 °C/min. A set of desorption signals were recorded through a thermal conductivity detector.

To evaluate and analyze the type and strength of acid sites, MgO–Al₂O₃ sample was characterized by adsorption of weaker base pyridine on a 170-SX FT-IR spectrometer in a temperature range between 25 and 400 °C. Before pyridine adsorption, the sample was thermally treated under vacuum condition up to 400 °C at a rate of 20 °C/min, and then it was cooled to room temperature. The sample was exposed to pyridine by breaking, in the IR spectrometer cell, a capillary tube containing about 100 μ l of pyridine. After adsorption for 30 min, the IR spec-

tra were recorded at the temperature of interest with outgassing treatment.

2.6. Catalytic evaluation

Catalytic measurements of the catalyst were performed on a flow microreactor-gas chromatography (MR-GC) system by using isopropanol decomposition as reaction probe. Isopropanol was put in an H-shape saturator, which was placed in a container where an ice–water mixture was contained to maintain the temperature of the saturator at approximately 14 °C. Nitrogen (99.9%) was used as carrier in all the tests. The partial pressure of isopropanol can be controlled by altering the temperature of the ice–water mixture. In the test reported herein, the partial pressure of isopropanol is 22.4 Torr. Fifty milligrams of catalyst sample were used in the catalytic activity measurements. The inlet rate into the reactor was 20 ml/min. After 15 min of reaction, the experimental data were recorded. In terms of the product distribution and total conversion, selectivity for different products was calculated. All the data used to calculate the conversion and selectivity were averaged on three measurements done under the same condition. The experimental error is 0.01%.

3. Results and discussion

Fig. 1 shows the XRD patterns of the sample calcined at different temperatures. The as-made sample (70 °C) chiefly consists of two phases: brucite (Mg(OH)₂) and hydrotalcite (Mg₆Al₂(OH)₁₈·4.5H₂O). When the calcination temperature increased to 200 °C, all the XRD peaks remained unchanged, indicating that decomposition of brucite and hydrotalcite did not occur yet. At 400 °C, however, intensities of the peaks corresponding to Mg(OH)₂ and Mg₆Al₂(OH)₁₈·4.5H₂O phases strongly reduced; simultaneously, very tense peaks corresponding to periclase (MgO) appeared. These changes reveal that brucite decomposed into periclase, and hydrotalcite was probably dehydrated. At 800 °C, the peaks corresponding to hydrotalcite completely disappeared, instead, some peaks located $2\theta = 32^\circ$, 45° and 65° were observed, showing the formation of γ -alumina phase. This result confirms that hydrotalcite was decomposed to γ -alumina and MgO phases.

Surface variations of the solid at different temperatures were characterized with FT-IR spectroscopy. A set of in situ FT-IR spectra of the as-made MgO–Al₂O₃ mixed oxide recorded at various temperatures are shown in Fig. 2. At 25 °C, a very tense and sharp band at 3695 cm^{–1} and a broad band centered at about 3464 cm^{–1} were observed. The former is assigned to OH stretching vibration absorption, and the latter is due to adsorbed water on the sample's surface. In the region of 1700–1500 cm^{–1}, there is a very sharp band at 1639 cm^{–1}, which corresponds to flexion vibration of hydroxyl groups in the oxide. The double bands at 1495 and 1386 cm^{–1} resulted from the vibration of bending mode of the C–H bonds in the residual organic groups due to the synthesis precursors [12]. In the low energy range below 1100 cm^{–1}, several peaks, 1082, 972 and 592 cm^{–1}, were observed, these are assigned to the vibration of symmetric and

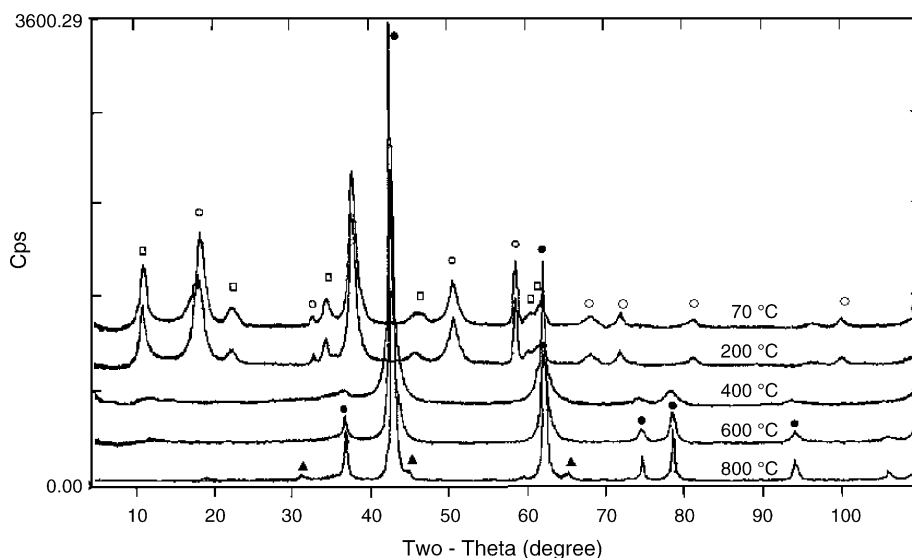


Fig. 1. XRD patterns of the sample calcined at various temperatures. (□) $\text{Mg}_6\text{Al}_2(\text{OH})_{18}\cdot 4.5\text{H}_2\text{O}$; (○) $\text{Mg}(\text{OH})_2$; (●) MgO ; (▲) γ -alumina.

asymmetric flexion of Mg–O, Al–O and Mg–O–Al bonds. As temperature increased from 25 to 500 °C, adsorbed water in the oxide was mostly desorbed, and the bands related to hydroxyl groups and organic groups entirely disappeared. It is noteworthy that a tense band around 1400 cm^{-1} was formed above 300 °C, it characterizes the formation of carbonaceous species resulted from the combustion of residual organic compounds [13]. Because the IR cell can only be work at a temperature not exceeding 500 °C, in situ characterization at higher temperature was not performed. However, IR characterization of the sample annealed at 600 °C shows that all the adsorbed water and the retained hydroxyls can be removed leaving only trace carbonaceous species on the sample.

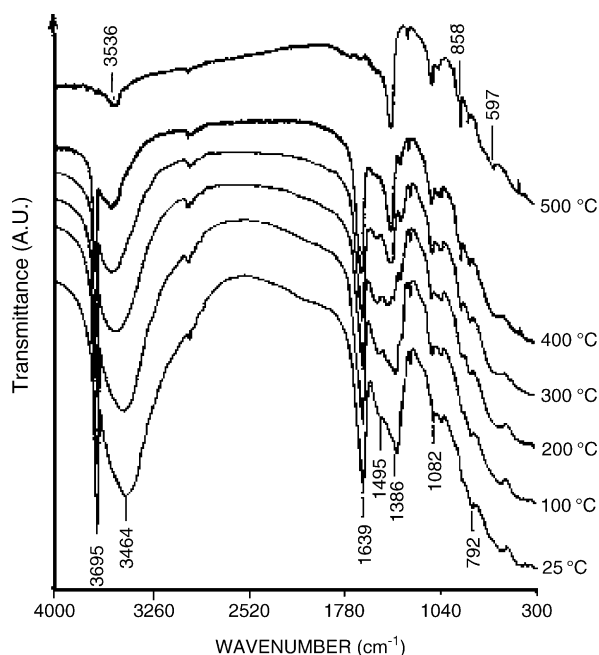


Fig. 2. A set of in situ FT-IR spectra of the $\text{MgO-Al}_2\text{O}_3$ solid recorded at various temperatures in the IR cell.

Table 1 shows the textural properties of $\text{MgO-Al}_2\text{O}_3$ solid measured by BET method and its surface acidity and basicity determined by TPD- NH_3 and TPD- CO_2 techniques. The solid annealed at 600 °C had a surface area $237\text{ m}^2/\text{g}$ with an average of pore diameter 9.8 nm. On the solid surface, both acid and basic sites are formed. The total acidity and basicity are $1545.1\text{ }\mu\text{mol/g NH}_3$ and $1200.4\text{ }\mu\text{mol/g CO}_2$, which correspond to 3.9 acid sites and 3.0 basic sites per spare nanometer, respectively. Both the number of acid sites and basic sites on the $\text{MgO-Al}_2\text{O}_3$ are superior to that shown in sol-gel MgO or Al_2O_3 solid [8,11].

In order to determine the types and strength of the acid sites, FT-IR characterization of pyridine adsorption on the catalyst surface was performed (Fig. 3). Several absorption bands were observed: the strong bands round 1448 and 1593 cm^{-1} are assigned to the different vibration modes of pyridine adsorbed on Lewis acid sites (coordinatively unsaturated or electron-pair acceptors); the other one around 1490 cm^{-1} is attributed to pyridine associated with both neighbored Lewis and Brønsted acid sites [14]. No evidence of the formation of isolated Brønsted acid sites on the catalyst was found because no band around 1540 cm^{-1} was observed in the FT-IR spectra. Intensities of all the bands gradually decreased when the heating temperature was increased. Even after 500 °C of thermal treatment, the band at 1490 cm^{-1} still observable, that indicates high strength of the Lewis acidity on the catalyst.

Table 1
Textural data and surface acid and basic properties of the sample annealed at 600 °C

Surface area (m^2/g)	237.0
Average pore diameter (nm)	9.8
Pore volume (cm^3/g)	0.618
Total acidity ($\text{NH}_3\text{ }\mu\text{mol/g}$)	1545.1
Number of acid sites (nm^{-2})	3.9
Total basicity ($\text{CO}_2\text{ }\mu\text{mol/g}$)	1200.4
Number of basic sites (nm^{-2})	3.0

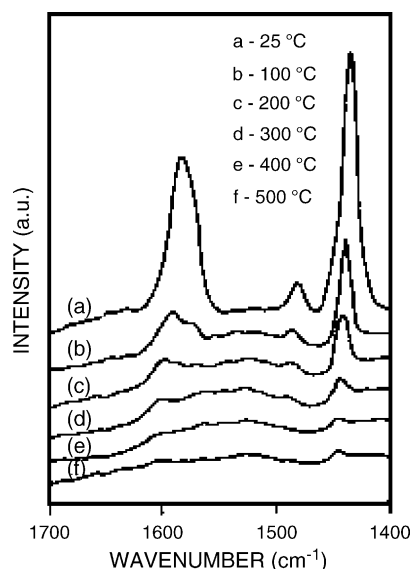


Fig. 3. (a–f) A set of FT-IR spectra of pyridine adsorption on the MgO-Al₂O₃ solid. The spectra were recorded at different temperatures in the IR cell.

Catalytic activity and selectivity of isopropanol decomposition over the magnesia-alumina oxide annealed at 600 °C are reported in Table 2. In the outlet stream, 2-propanol, propene, acetone and isopropylether were identified. These results clearly show that dehydrogenation, dehydration and bimolecular polymerization take place during the reaction. At a reaction temperature below 100 °C, the main product was acetone; however, above 200 °C, propene was of dominant. At a temperature between 200 and 350 °C, less than 8% of isopropylether compound was produced. The isopropanol conversion linearly increased with increasing of the reaction temperature.

When water was added into the reaction mixture, in comparison with the results obtained in the case of water absence from the inlet mixture, both the catalytic activity and selectivity were remarkably altered. From the data of $\Delta C_a/C_a$ and $\Delta S/S_a$, the increased times of the acetone concentration or selectivity in the case of water presence relative to that obtained in the case of water absence can be clearly seen. It is better to use $\Delta C_a/C_a$ and $\Delta S/S_a$ than ΔC_a and ΔS_a to show water influences on catalytic behaviours because $\Delta C_a/C_a$ and $\Delta S/S_a$ are more sensitive to condition changing. From the results reported in Table 3, some conclusions can be drawn: (i) isopropanol conversion increased

Table 2
Total conversion and product selectivity after 30 min of reaction

Temperature (°C)	Conversion (%)	Product selectivity (%)		
		Propene	Acetone	Isopropylether
400	99.69	99.43	0.57	
350	98.14	99.49	0.43	0.08
300	32.51	96.13	1.06	0.81
250	5.08	87.19	5.29	7.52
200	0.42	73.01	20.48	6.51
150	0.16	54.72	38.94	
100	0.09	48.38	51.62	
50	0.05	35.22	64.78	

Table 3

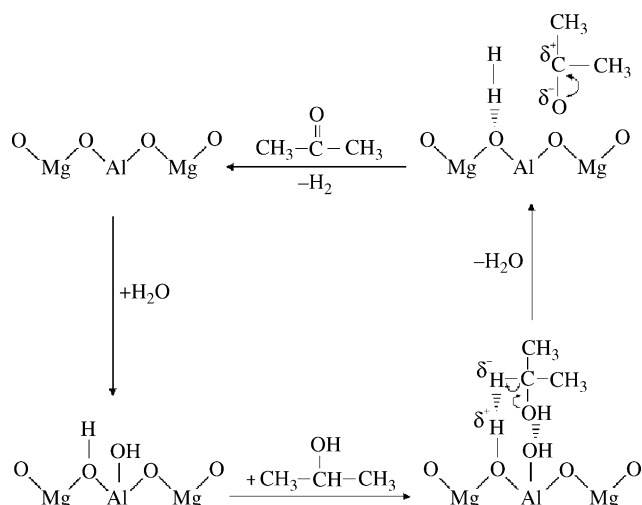
Acetone concentration differences between the cases of water presence and absence in the stream

Temperature (°C)	ΔC_t	ΔC_a	$\Delta C_a/C_a$	ΔS	$\Delta S/S_a$
400	-19.78	5.01	8.94	6.41	11.39
350	-19.41	7.24	17.25	9.30	21.60
300	40.92	13.03	37.54	17.53	10.50
250	23.98	16.50	61.32	52.40	9.91
200	6.40	5.50	64.75	61.55	3.01
150	0.84	0.92	12.79	53.72	1.18
100	0.48	0.48	5.29	51.59	1.05

$\Delta C_t = C_{tw} - C_t$, in %, difference of isopropanol total conversion in the case of water presence (C_{tw}) and absence (C_t) in the inlet stream; $\Delta C_a = C_{aw} - C_a$, in %, difference of acetone concentration in the case of water presence (C_{aw}) and absence (C_a) in the inlet stream. $\Delta S_a = S_{aw} - S_a$, in %, difference of acetone selectivity in the case of water presence (S_{aw}) and absence (S_a) in the inlet stream.

or decreased, depending on the reaction temperature and (ii) acetone concentration in the products mixture and its selectivity was profoundly enhanced in the whole range of reaction temperature. Below 300 °C of reaction, the 2-propanol conversion significantly increased in the case of water present the inlet mixture, and the increment reached a maximum 40.9% at 300 °C. Above 300 up to 400 °C, water presence in the inlet stream led to 2-propanol conversion decreasing. This result clearly shows that water addition may directly involve in the reaction, strongly affecting the catalytic activity: it may promote the catalytic activity below 300 °C but inhibits the catalytic activity at higher temperature. For explanation water promotion/inhibition effect, it is assumed that, below 300 °C, water molecule is associated with the catalyst surface on which new species like hydroxyls are formed by water dissociation, these hydroxyl groups may serve as new active sites responsible for enhancement of isopropanol conversion through a modified reaction pathway by which the new hydroxyls groups directly involve in the reaction. Above 300 °C, however, adsorption competition on the surface active sites between the reactant (isopropanol) and water molecule occurs, water molecules might strongly adsorb on the active sites but they are not dissociated into hydroxyl species, which probably poisons some of the active sites. Because these sites could not easily be refreshed due to water strong adsorption, adsorption of isopropanol on these sites was accordingly inhibited, thus lowering the total conversion of isopropanol.

It is worthy to notice that the acetone selectivity is independent of isopropanol conversion when water was present in the reaction mixture: relative to that obtained in the water absence, it always increases either isopropanol conversion increasing at a reaction temperature below 300 °C or decreasing at a temperature above 300 °C. It is easy to understand that below 300 °C, some of new hydroxyls were formed on the catalyst surface, which promotes acetone formation; thus, the acetone selectivity is enhanced. Above 300 °C, on the one hand, when water is added, the reaction of isopropanol dehydration to water must be inhibited from the view point of chemical reaction equilibrium; on the other hand, it can be also understood that, the added water may strongly adsorb on the active sites responsible for isopropanol dehydration, this suppresses dehydration reaction,



Scheme 1. Acetone formation through a hydroxyls-assisted mechanism on the surface of Mg-Al-O solid in the case of water presence in the inlet stream. This reaction pathway is a modified dehydrogenation route accompanying water formation by dehydration.

and thus lowered the propene selectivity. As a consequence, although the total conversion of isopropanol decomposition is reduced, the selectivity of dehydrogenation reaction was relatively enhanced. Therefore, in the whole reaction temperature range between 50 and 400 °C, selectivity to acetone is enhanced relative to that obtained in the case of water absence.

Above results and discussion show that acetone can be formed through more than one pathway: (i) a normal dehydrogenation route and (ii) a hydroxyl-assisted dehydrogenation route. Because the lattice oxygen ions in oxide are electron-donors, and hence they show basic character, these ions would be the basic sites responsible for acetone formation. In the case of water absence from the inlet stream, due to the strong interaction between the lattice oxygen and the H atom in the –OH group linked with –CH(CH₃)₂, the H–O bond is broken, producing a H⁺ which is trapped by lattice oxygen ion and an alkoxide carbonion species ((CH₃)₂HCO[−]) which linked with a neighbor cationic site (Lewis acid sites). Simultaneously, the active α-H in the alkoxide carbonion species reacts with the H⁺ trapped by lattice oxygen, forming a hydrogen molecule; while, the alkoxide carbonion species transformed to acetone, thus a normal dehydrogenation pathway is finished [15]. However, in the case of water presence, in the reaction procedure, H₂O may be dissociated to form OH[−] that is associated with cationic sites along with H⁺ trapped by lattice oxygen; therefore, many hydroxyls and H⁺ ions coexist on the surface of the catalyst. Hydrogen atom in the OH group of isopropanol might react with hydroxyl group linked on the catalyst surface to produce water and an alkoxide carbonion species, (CH₃)₂HCO[−], followed by the reaction between the active α-H in alkoxide carbonion species and the H⁺ bounded on the surface oxygen lattice, to yield molecular hydrogen and

acetone. Therefore, the hydroxyl-assisted mechanism is a modified dehydrogenation pathway accompanying by dehydration, this postulated reaction pathway is illustrated in Scheme 1.

4. Conclusion

Catalytic evaluation of isopropanol decomposition over a sol–gel magnesia-alumina oxide catalyst shows that dehydrogenation and dehydration, together with bimolecular reaction, take place to produce acetone and propene along with less than 8% of isopropylether. The reaction parameters such as reaction temperature and feed composition remarkably affect on the catalytic activity and selectivity. Increasing the reaction temperature leads to isopropanol conversion increasing but acetone selectivity decreasing. Water addition in the inlet stream not only enhances acetone selectivity through a hydroxyl-assisted reaction pathway, but also promotes or inhibits the total conversion of isopropanol that depends upon the reaction temperature.

Acknowledgements

This work is financially supported by an international collaboration funding granted by CONACyT (Mexico)-NSF (China) (no. J200.489/2004) and China 973 Program granted by China Ministry of Science and Technology (no. 2004CB720603). The authors appreciate Dr. J. Navarrete and Dr. Gomez for their technical assistance.

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