Journal of Catalysis 334 (2016) 34-41

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

MWW-type catalysts for gas phase glycerol dehydration to acrolein



JOURNAL OF CATALYSIS

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ARTICLE INFO

Article history: Received 27 May 2015 Revised 10 November 2015 Accepted 18 November 2015

Keywords: Glycerol dehydration Acrolein MCM-22 MCM-36 ITQ-2

$A \hspace{0.1in} B \hspace{0.1in} S \hspace{0.1in} T \hspace{0.1in} R \hspace{0.1in} A \hspace{0.1in} C \hspace{0.1in} T$

The materials derived from MWW layered precursor (MCM-22, MCM-36 and ITQ-2) were synthesized with molar ratio SiO₂/Al₂O₃ = 30, characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), textural analysis by N₂ physisorption, temperature programmed desorption of ammonia (NH₃-TPD) and diffuse reflectance infrared spectroscopy (DRIFTS) of adsorbed pyridine and evaluated in gas phase glycerol dehydration to acrolein. The delaminated material (ITQ-2) has presented better catalytic performance than MCM-22 zeolite or MCM-36 pillared material, in both glycerol conversion and acrolein selectivity. These results were interpreted based on the textural properties and acidity changes. ITQ-2 excellent performance is due to higher accessibility and improved acidity when compared to pillared MCM-36 or parent MCM-22 zeolite. Long-term stability under either nitrogen or air co-feeding was investigated for ITQ-2.

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1. Introduction

Biodiesel is now being used worldwide as an alternative fuel to replace, at least partially, diesel obtained from oil. This renewable fuel is mainly produced from transesterification of vegetable oils using methanol or ethanol, resulting in high amounts of glycerol obtained as a coproduct. However, the economic viability of biodiesel production also depends on the destination of this coproduct. Since its purification for pharmaceutical or cosmetic applications is very expensive, glycerol could be catalytically converted to many interesting chemicals or intermediates [1].

Acrolein is the glycerol-derived product of largest interest because it is used for acrylic acid synthesis, which is an important raw material in the production of polymers used in hygiene products, such as diapers, detergents and wall paints [1,2]. The currently used synthesis of acrolein is based on the selective oxidation of propene over a complex multicomponent BiMoO_x-based

catalyst; therefore, glycerol dehydration to produce acrolein is a promising clean and sustainable technology [3,4].

Glycerol dehydration is an acid-catalyzed reaction where the catalyst acidity is a crucial parameter [5]. Among other active catalyst, such as mixed metal oxides or heteropolyacids, zeolites are promising catalysts due to their appropriate acidity combined to pore structure of designable complexity, usually resulting in high glycerol conversion and acrolein selectivity [6–8]. However, during the reaction the pores of the zeolites can be blocked by coke deposition, occluding the access to the active sites. Thus, fast catalyst deactivation is still the main obstacle for industrial application of glycerol dehydration to acrolein [1], and oxygen co-feeding and new catalyst compositions are the proposed strategies to solve this problem.

A promising alternative would be the use of materials derived from layered zeolites, which can produce new materials through swelling, delamination and pillaring processes, allowing tailoring the structural, textural and acid properties of these materials [9].

MCM-22 (P) was the first lamellar zeolite known, and it combines, in the same structure, pores with different diameters, which allow access to a range of active sites, allowing the study of the effect of its textural and acid properties in the outcome of several reactions. We have recently published results on catalytic dehydration of glycerol to acrolein, proving that H-MCM-22 can be as



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active and as selective as ZSM-5, operating at similar conditions [10].

MCM-22 (P) condenses in a three-dimensional structure by calcination, named MCM-22 zeolite, whose peculiar topology was designed by International Zeolite Association as MWW (from **M**obil t**W**enty-t**W**o). MCM-22 (P) structure consists of layers of 2.5 nm, which contains a two-dimensional sinusoidal channels, whose access windows $(4.0 \times 5.9 \text{ Å})$ are defined by 10 membered rings (MR), and surface semicavities (or cups) of $7.1 \times 7.1 \times 7.0 \text{ Å}$ [11].

MCM-36 is obtained by swelling MCM-22 (P) with cetyltrimethylammonium bromide (CTABr) and pillaring using tetraethoxysilane (TEOS) as SiO₂ precursor [12]. Mesopores are thus created during the post-synthesis modification process, allowing improved access to protonic sites present in the zeolite structure, turning this an attractive candidate for catalytic and sorption applications [13,14]. The pillared derivative is a peculiar material with double porosity: microporous in crystalline layers and mesoporous in interlayered region, resulting in a structure similar to pillared clays.

Other possibility is to delaminate CTA⁺-swelled MCM-22 (P) producing an interesting material denominated ITQ-2 [15]. ITQ-2 possesses high external surface area, which allows the reaction to occur not only inside the 10 MR channels but also in the semicavities (cups) open to the external surface, with 12 MR windows that confer zeolitic environment to reactants, products and transition states formed during reaction [16,17].

Improved catalytic performances in acid reactions are reported in the literature for MWW-derived materials [18,19]. The pillaring process increases the accessibility to protonic sites, which are mainly located in mesopores created by silica pillars, resulting in high catalytic activity of MCM-36 when compared with MCM-22 [20]. Similarly, the delamination process increases the acid site accessibility, by decreasing diffusion limitations, and thus ITQ-2 provides access of larger molecules to the acid sites, usually causing an increase in activity and selectivity in many acid catalyzed reactions [21].

Aiming to determine the effects of pillaring and delamination processes on glycerol conversion and acrolein selectivity, MCM-36 and ITQ-2 were synthesized, characterized and evaluated in gas phase glycerol dehydration, under co-feeding either by nitrogen or by air. Their catalytic performances were compared to parent MCM-22 zeolite.

2. Experimental

2.1. Catalysts synthesis

MCM-22 (P) (SiO₂/Al₂O₃ = 30) was prepared as described previously [10]. To produce MCM-22, the layered precursor material was calcined by heating under dry nitrogen (1 °C min⁻¹) up to 550 °C and keeping at this temperature for 6 h under dry air (50 mL min⁻¹).

MCM-36 was obtained according to the procedure reported by Maheshwari et al. [22], mixing the MCM-22 (P) slurry with an aqueous solution of 29% CTABr and an aqueous solution of 40% tetrapropylammonium hydroxide (TPAOH). The pH of the resulting mixture was 13.8. The mixture was allowed to stir for 16 h at room temperature, after which, the particles were recovered by repeated cycles of centrifugation and washing. The swollen MCM-22 (P) powder was mixed with TEOS (tetraethoxysilane), stirred for 25 h at 80 °C under nitrogen atmosphere, then filtered and dried at room temperature. The resulting solid was hydrolyzed in water (pH = 8, controlled with NaOH) for 6 h at 40 °C, then filtered, dried at room temperature and calcined using the same method applied to MCM-22 zeolite. ITQ-2 synthesis proceeded according to the methodology proposed by Concepción et al. [23]. The precursor was mixed with an aqueous solution of CTABr 29% and an aqueous solution of tetrapropylammonium hydroxide (TPAOH, 40%). The resulting suspension was refluxed for 16 h at 80 °C. The layers were forced apart by placing the slurry in an ultrasound bath for 1 h. Separation of the solids was done by acidification of the medium with concentrated hydrochloric acid until the pH < 2, followed by centrifugation. The resulting material was calcined in the same way as explained for the other MWW-derived materials.

The MWW derived materials were converted to their acid form by ion exchange with a solution NH_4NO_3 1 mol L^{-1} (Synth), at ambient temperature for 24 h, followed by calcination in a N_2 flow (50 mL min⁻¹) at 550 °C.

2.2. Catalysts characterization

X-ray diffraction (XRD) patterns were collected on Shimadzu XRD-6000 equipment, operating with a CuK α radiation, generated at a voltage of 40 kV, current 30 mA, using a graphite monochromator, in the region of 1.4–50° 2θ at a scan speed of 2° min⁻¹. Fourier transformed infrared spectra (FTIR) were recorded on a Perkin Elmer Spectrum BX spectrometer in the range of $4000-400 \text{ cm}^{-1}$, using 0.1% KBr pellets, by the accumulation of 16 scans with resolution of 4 cm⁻¹. Thermogravimetry (TG) was conducted on a Shimadzu TGA-50 at temperatures ranging from 25 to 1000 °C, with a heating rate $\beta = 10^{\circ} \text{C min}^{-1}$, under nitrogen or air flow (50 mL min⁻¹). Scanning electron microscopy (SEM) images of various magnifications were obtained in a Shimadzu SS-550 microscope, with an acceleration voltage of 7–15 kV. The samples were previously metallized with gold. Elemental analyses were performed by energy dispersive X-ray spectrometry in a Shimadzu EDX-720. Nitrogen physisorption isotherms were collected at -196 °C in Micromeritics ASAP 2020 equipment, using the BET, BJH and *t*-plot methods to assess textural properties. The samples were pretreated at 350 °C for 3 h under vacuum (2 mmHg) to remove physisorbed species on the sample surface. The acid amount of catalysts was measured by temperature programmed desorption of ammonia (NH₃-TPD) in a Micromeritics Chemsorb 2720 equipped with a thermal conductivity detector (TCD) to measure the NH₃ desorption. The samples were pretreated in He flow (25 mL min⁻¹) at 300 °C for 1 h and cooled to room temperature. The NH₃ adsorption was carried out at ambient temperature in 9.9% mol/mol NH₃/He (25 mL min⁻¹) for 1 h. After the chemisorption, the system was purged with helium at 150 °C for 1 h to eliminate physisorbed ammonia. After cooling to room temperature, the NH₃-TPD was performed by heating the sample from 30 °C to 800 °C (10 °C min⁻¹) while monitoring the TCD signal.

Diffuse reflectance infrared spectra (DRIFTS) of adsorbed pyridine were obtained by using a Perkin Elmer Spectrum 400 spectrometer, operating with a reaction chamber from Harrick and a praying mantis accessory. The samples were pretreated at 350 °C for 1 h prior to the pyridine adsorption, in order to remove any adsorbed water, and then a droplet of liquid pyridine was added on the sample surface. The chamber was heated at 150 °C under flowing argon for at least 30 min, or until no changes were detected in the spectrum. Spectra were collected using 50 scans at 4 cm⁻¹ of resolution.

2.3. Catalytic tests

MWW-precursor derived catalysts were evaluated in gas phase glycerol dehydration to acrolein, at atmospheric pressure, in a continuous flow vertical reactor on borosilicate glass at 320 °C. An aqueous 36.6% glycerol solution was added to the reactor packed with 50 mg of the catalyst, with the aid of a peristaltic pump operating at 0.33 mL min⁻¹ and a nitrogen or air flow (30 mL min⁻¹).

During 10 h of reaction, the condensable products were collected hourly in a cold trap containing a 0.1% solution of hydroquinone and analyzed by a Perkin Elmer Clarus 500 gas chromatograph operating with a flame ionization detector (GC-FID) and OV-315 column (30 m \times 0.32 mm id).

The glycerol conversion and selectivity to acrolein were quantified according to the following equations:

Glycerol conversion (%) =
$$100 \times (n_{glycerol,in} - n_{glycerol,out})/n_{glycerol,in}$$
 (1)

. . .

Acrolein selectivity (%) = $100 \times n_{\text{acrolein,formed}}/n_{\text{glycerol,consumed}}$ (2)

where $n_{glycerol,in}$ is the initial amount of matter of glycerol (mol); $n_{glycerol,out}$ is the final amount of matter of glycerol (mol); $n_{acrolein,-formed}$ is the amount of matter of acrolein (mol) in the effluents; and $n_{glycerol,consumed}$ is the consumed amount of matter of glycerol and corresponds to the difference between $n_{glycerol,in}$ and $n_{glycerol,out}$.

The formaldehyde, acetaldehyde, propionaldehyde and acetone selectivities were confirmed by high performance liquid chromatography (HPLC) after derivatization with 2,4-dinitrophenylhydrazine. The HPLC analyses were performed on an Agilent Series 1100 equipped with a Bruker C18 column (250 mm \times 2.1 mm) using as mobile phase a gradient mixture of water: acetonitrile.

3. Results and discussion

3.1. Catalysts preparation and characterization

The XRD of the materials derived from MWW precursor is presented in Fig. 1.

MCM-22 (P), containing hexamethyleneimine (HMI) in the structure, shows the typical pattern found in the literature [10] for this material, with a low angle diffraction at $2\theta = 3.22^{\circ}$ (d = 2.74 nm) which is an indicative of its layered nature. The calcination produces deep changes in the XRD patterns due to the condensation of the lamellae into the 3D structure of MCM-22 zeolite. By swelling MCM-22 (P) with CTA⁺ cations, the low angle peak is shifted to lower values ($2\theta = 1.74^{\circ}$), indicating the increase of basal spacing from 2.74 to 5.08 nm. Pillaring with TEOS followed by calcination makes small modifications into the XRD pattern, a peak at nearly the same position ($2\theta = 1.56^{\circ}$) of the swollen precursor is observed, indicating that the formation



Fig. 1. XRD profiles of the materials derived from MWW precursor obtained with $SiO_2/Al_2O_3 = 30$.

of the SiO₂ pillars maintained the basal distance in essentially the same value as the swollen material, and this is consistent with the production of MCM-36 pillared material [13,14]. Finally, sonication of the swollen material causes partial amorphization, due to disordered sheet-like structure expected for ITQ-2 [15,16]. No peaks were observed at low angle region for ITQ-2 sample, suggesting an efficient exfoliation during the synthesis procedure.

FTIR spectra (Fig. 2) show that the MWW bands are preserved upon pillaring and delamination processes. In CTA⁺-MCM-22 sample bands between 3000 and 2800 cm⁻¹ are observed and were assigned to C-H stretching vibrations in -CH₃ and -CH₂ groups, corresponding to the presence of CTABr, which was used in the swelling step. Wider bands were observed in MCM-36 material due to the presence of SiO₂ pillars. A band at ~960 cm⁻¹ in the spectrum of ITQ-2 indicates the presence of Si(OH) terminal groups, that increase upon delamination [24].

TG experiments were performed in the calcined samples of MCM-22, ITQ-2 and MCM-36 and observed a flat line in this temperature range, ruling out any possibility of residues due to precursors used in the preparation.

Elemental analyses by EDX (Table 1) are in good agreement with nominal values, indicating that no significant changes in the SiO₂/Al₂O₃ molar ratio occurred during the preparation of ITQ-2 from MCM-22. However, for MCM-36, the experimental SiO₂/Al₂O₃ molar ratio (51) is larger than the nominal value (30), due to the addition of SiO₂ during the pillaring step to form the pillars.

The morphologic analyses by SEM of materials derived from MWW-type precursors are shown in Fig. 3.

MCM-22 is formed by platelet crystallites aggregated in toroidal particles [10]. MCM-36 and ITQ-2 are composed of platelet agglomerates, resulting from the disaggregation of the toroidal particles of MCM-22, which suggest that the material also delaminate during the pillaring process [25,26].

The isotherms of the materials derived from layered precursor are presented in Fig. 4.

MCM-22 isotherm is of type Ib [27], characteristic of microporous materials, but is also observed the presence of secondary mesopores created by crystallite pilling. MCM-36 preserves this isotherm profile, except for the shape of the hysteresis loop that changes dramatically. ITQ-2 isotherm is of type IV, characteristic of mesoporous materials, due to the presence of secondary mesopores created by the exfoliation step. The hysteresis loop, which is associated with the pores shape and structure, shows that



Fig. 2. Infrared profiles of the MWW precursor derived materials obtained with $SiO_2/Al_2O_3 = 30$.

 Table 1

 Elemental and textural analysis of the MWW precursor derived materials.

Sample	SiO_2/Al_2O_3	$S_{\rm BET} (m^2 { m g}^{-1})$	$S_{\rm micro} \left({\rm m}^2 {\rm g}^{-1} ight)^{\rm a}$	$S_{\text{external}} (\text{m}^2 \text{g}^{-1})^{\text{a}}$	$V_{\rm micro}~({\rm cm}^3~{\rm g}^{-1})^{\rm a}$	$V_{\rm meso}~({\rm cm}^3~{\rm g}^{-1})^{\rm b}$	$d_{\rm meso} ({\rm nm})^{\rm b}$
MCM-22	28.4	565	435	130	0.191	0.327	10.2
MCM-36	51.1	603	175	428	0.074	0.319	10.4
ITQ-2	37.2	852	169	684	0.072	0.564	19.8

^a Determined by BET and *t*-plot methods.

^b Determined by BJH method.





(b)



(C)

Fig. 3. SEM images of the MWW precursor derived materials: (a) MCM-22; (b) MCM-36 and (c) ITQ-2.



Fig. 4. Adsorption isotherms of the MWW precursor derived materials. Filled and hollow symbols indicate adsorption and desorption branches, respectively.

MCM-22 and ITQ-2 have plate-shaped particles aggregated (hysteresis loop of H3 type), and MCM-36 presents slit-shaped pores (hysteresis loop of H4 type) [28].

The textural properties calculated from the isotherms (Table 1) show a decrease in the micropore volume and the creation of a relatively significant mesoporosity, as indicated by the increase in the mesopore volume observed for the pillared and delaminated samples. The remarkable decrease in micropore volume was caused by the disappearance of MWW supercage during the layers expansion. The increase in external surface area observed for MCM-36 and ITQ-2 is coherent with the mesopores formation and delamination observed for each material. Based on Table 1 results and the analysis of literature data which study MWW type zeolites in catalytic reactions [29–32], it can be concluded that textural properties depend on the quality of pillaring and delamination steps.

Results from textural analyses show that materials derived from MWW-type precursor present improved access to the active sites, allowing studying the influence of pores shape, size and structure in the glycerol dehydration reaction.

The acid sites densities were investigated by NH_3 -TPD (Fig. 5) and quantification is presented in Table 2.

MCM-22 profile shows moderate and strong acid sites, desorbing at 253 and 421 °C, respectively. The pillaring process causes a significant decrease in total density of acid sites for MCM-36 [25], probably due to the silica pillars, which increase the total mass of non-acidic material [33]. Desorption peaks are shifted to lower temperatures (243 and 416 °C), indicating lower acid site strength than MCM-22. The delaminated material (ITQ-2) presents a similar profile to the MCM-22, also shifted to lower temperatures (207 and 378 °C), with a higher total density of acid sites, probably due to the exposition of the sites located in the surface cups, but with lower acid site strength than MCM-22. The acid site strength



Fig. 5. NH₃-TPD profiles of the MWW precursor derived materials.

decrease may be attributed to a partial dealumination during the swelling or pillaring processes [32]. Based on the analysis of NH₃-TPD results and literature data with materials derived from MWW-type precursors [29–32], it can be concluded that acid properties are deeply dependent on the efficiency of pillaring and delamination processes, since these steps influence in the distribution/exposition of the active sites.

The nature of acid sites was investigated by DRIFTS of adsorbed pyridine and spectra are shown in Fig. 6. It was possible to detect the bands associated with Brönsted acid sites at 1540 cm^{-1} and Lewis acid sites in the region of $1450-1440 \text{ cm}^{-1}$. In addition, a band at nearly 1490 cm^{-1} was observed in the spectra of Fig. 6, which can be attributed to pyridine adsorbed on both Brönsted and Lewis acid sites, as well as H-bonded pyridine. Since the bands at 1540 and $1440-1450 \text{ cm}^{-1}$ have approximately equal extinction coefficients [34], the ratio of their integral intensities can be used as a direct ratio of Brönsted and Lewis acid site densities (B/L).

From the ratio B/L and total density of acid sites, it was possible to calculate the density of Brönsted acid sites (BAS) and Lewis acid sites (LAS) shown in Table 2. The pillaring process resulted in a decrease mainly in the Lewis acid sites for MCM-36, while Brönsted acid sites are not affected. On the other hand, exfoliation promoted only a slight decrease in the Brönsted acid sites density, but increased the Lewis acid sites density. This could be a consequence of extra-framework aluminum (EFAL) formation inside ITQ-2 pores during its preparation, contributing for improved acidity [35]. The precipitation of extra-framework material during



Fig. 6. FTIR spectra of adsorbed pyridine collected at 150 $^\circ\mathrm{C}$ for MWW precursor derived materials.

pH adjustment after exfoliation was already reported in the literature [36,37].

3.2. Catalytic test

The glycerol conversion using materials derived from MWWtype precursor is shown in Fig. 7. Catalytic results show that all materials are highly active in gas phase glycerol dehydration. In the first hours of reaction, MCM-22 has presented higher conversion than ITQ-2 or MCM-36, but deactivates by coke formation and after 3 h, glycerol conversion is inferior to that observed for MCM-36 catalyst. Based on the results in Fig. 7 and Table 3, MCM-36 presents the best glycerol conversion, remaining with conversions over 80% during 6 h of reaction. On the other hand, ITQ-2 showed a gradual decrease since the first hours, which is related to the high available acidity of this material.

Catalytic performance seems to be a combination of improved porosity and acid site amount and distribution for each type of catalyst. Although ITQ-2 has a higher mesoporosity than MCM-36 (see Table 1), it is important to understand that the structure of these materials is quite different. ITQ-2 is constituted by exfoliated layers and its area is primarily external area, while MCM-36 is a pillared material, in which MWW layers are separated by SiO₂ pillars. These differences should be accounted in considering coke formation in these catalysts. However, it would be expected that if the accessibility is restricted, deactivation will be faster.

Recently, Park et al. [38] studied the coke formation mechanism for H-ZSM-5, showing that the condensation of coke precursors is promoted within its narrow pore structure, which results in the rapid deactivation of the catalyst. For aluminosilicophosphate nanosphere, on the other hand, condensed carbonaceous compounds are observed and the deactivation is delayed due to the relatively uninterrupted diffusion of materials (reactants, products, or potential coke precursors).

Table 2			
Acid properties of the MWW	precursor derived materials by	/ NH ₃ -TPD and	DRIFTS-pyridine.

Sample	NH ₃ -TPD	NH ₃ -TPD			DRIFTS-pyridine		
	$T_{\mathrm{m},1}$ (°C)	$T_{m,2}$ (°C)	Density of acid sites (mmol g^{-1})	BAS (mmol g^{-1})	LAS (mmol g^{-1})	B/L	
MCM-22	253	421	1.19	0.35	0.84	0.42	
MCM-36	243	416	0.78	0.37	0.41	0.90	
ITQ-2	207	378	1.27	0.31	0.96	0.32	



Fig. 7. Glycerol conversion and acrolein selectivity over MWW catalysts. Feed composition: T = 320 °C; 36.6% glycerol; glycerol flow = 0.33 mL min⁻¹, catalyst weight = 0.10 g, N₂ flow = 30 mL min⁻¹.

Table 3
Product selectivity during gas phase glycerol dehydration after 2 and 10 h of time or
stream

Catalyst	MCM-22	MCM-36	ITQ-2
Conversion (%) Acrolein yield (%)	99.8 (20.2) 49.9 (4.3)	89.0 (10,5) 6.7 (0.1)	58.1 (17.6) 44.4 (7.2)
Molar selectivity (%) Acrolein Acetol Formaldehyde Acetaldehyde Acetone Allylic alcohol Propionic acid Propionaldehyde	50.1 (21.3) 2.0 (0) 4.6 (13.6) 5.5 (15.3) 0.2 (0.4) 0.3 (0) 4.2 (0) 0.1 (0.7)	$\begin{array}{c} 7.5 \ (1.3) \\ 1.6 \ (0.2) \\ 0.7 \ (5.6) \\ 0.8 \ (5.6) \\ 0.1 \ (0.1) \\ 0 \ (0) \\ 1.1 \ (0.2) \\ 0.1 \ (0.4) \end{array}$	76.5 (40.1) 7.3 (1.4) 4.0 (17.3) 4.8 (20.7) 0.3 (1.2) 0.4 (0.2) 5.3 (0.3) 0.3 (2.8)
Others Coke (%) ^a	33.0 (48.7) 24.6	88.1 (86.5) 20.4	1.2 (16.1) 37 0
eone (/o)	2 110	2011	5710

^a Coke content after 10 h of run determined by TG under air flowing.

It is important to mention that MCM-36 has a lower total acid site density (Table 2), but stronger acid sites than ITQ-2. Probably, the stronger acid sites present in the MCM-36 are responsible for the better stability. The surface coverage by carbonaceous deposits would be a consequence of a delicate balance between the oligomerization that occurs preferentially on weak acid sites and leads to coke formation, and cracking of the coke precursors on strong acid sites, leading to different products, including light compounds. This explanation has been previously used in the study of alkylation of isobutane, comparing catalysts of different acid strength and its impact on coke formation [39].

The almost parallel conversion profiles observed in Fig. 7a for MCM-22 and ITQ-2 suggest that the pore system where the reaction takes place is very similar in these two solids, that is, in these cases, the zeolitic acid sites (in surface cups and/or inside the interlayer channel) control the behavior of the conversion along time, while the values of conversion are related to the concentration of available sites in each material.

Unlikely, MCM-36 is the least selective solid, because its acid and structural properties probably favor the formation of noncondensable by-products, such as CO, CO_2 and CH_4 , that were not monitored in this work. The less complete molar balance observed for this catalyst is an indication that there is an increase in the formation of gases [40]. It is necessary to consider that, at least in part, SiO₂ pillars contain silanol groups that can catalyze parallel reactions. On the other hand, the initial conversion remains approximately constant due to the fact that the mesoporosity keeps the large spaces available for reaction until coke build up attains a certain point – around ca. 6 h of reaction – where it irreversibly blocks the active sites and one sees a sudden drop in conversion values.

Some other products were observed in the condensate (Table 3), such as acetol (1-hydroxy-acetone), acetaldehyde, formaldehyde, acetone, and propionaldehyde. The by-products production is in accordance with the reaction mechanism proposed by Martinuzzi et al. [41].

Since ITQ-2 and MCM-22 acid sites densities are similar, the results of coke formation have been correlated with the mesopore volume. The difference is that the mesopore volume is almost double in ITQ-2 than in MCM-22. After 10 h of catalytic run, the pores are filled with coke, as recently suggested by Decolatti et al. [42]. Because of this, the amount of coke on ITQ-2 is almost double than in the MCM-22.

According to the literature [43,44], the ratio B/L influences the product distribution. The greater the ratio of Brönsted to Lewis acid sites, the higher the selectivity to acrolein. On the other hand, the greater is the ratio of Lewis to Brönsted acid sites, the higher the selectivity to hydroxyacetone (acetol). However, in the herein reported results, it was not possible to see a clear relationship between product distribution and the ratio B/L.

3.3. Characterization of spent catalysts

The spent catalysts were characterized by TG under air after 10 h of time on stream. From TG data in Fig. 8, three events were detected in the region of 300–800 °C: (i) around 450 °C, corresponding to the burning of thermally unstable coke, probably formed on the external surface of crystallites; (ii) around 560 °C, referring to the burning of coke deposited on the MWW supercages or surface cups and (iii) around 670 °C, carbonaceous deposits in the 10 MR channel [10].

These results suggested that the coke formed is similar in all three materials and that it could be removed by thermal treatment under oxidative atmosphere.

For evaluating the efficiency of a thermal treatment at 500 °C for 1 h, under air flow (30 mL min⁻¹), to remove coke, an ITQ-2



Fig. 8. (a) Thermogravimetry and (b) derivative thermogravimetry of MWW derived materials after 10 h of catalytic test.



Fig. 9. Evaluation of coke removal by burning at 500 °C, for 1 h, under air flow $(30\,mL\,min^{-1})$ by thermogravimetry.

coked sample was submitted to thermogravimetry experiments and results are shown in Fig. 9.

From room temperature up to 500 °C, one could observe a mass loss of 13.3%, due to thermally unstable coke. After 1 h at 500 °C,



Fig. 10. Glycerol conversion (a) and acrolein selectivity (b) during glycerol dehydration over ITQ-2 catalyst during 3 cycles of 10 h each. Feed composition: T = 320 °C; 36.6% glycerol; glycerol flow = 0.33 mL min⁻¹, catalyst weight = 0.10 g, gas flow = 30 mL min⁻¹.

the mass loss was 10.3%, corresponding to 80% of the total carbon deposits. Above 500 °C, only highly stable coke is still present in the catalyst, corresponding to 5.8% of mass loss and only 19.8% of total carbon deposited in the ITQ-2 catalyst.

3.4. Longtime stability and oxygen co-feeding

Catalytic results obtained during three cycles of 10 h, intercalated by a thermal treatment at 500 °C for 1 h, are shown in Fig. 10, for both nitrogen or air under 30 mL min⁻¹ flow.

In terms of glycerol conversion, ITQ-2 performance was fully re-established after 3 reaction cycles in nitrogen flow. The small differences in the glycerol values can be accounted for by experimental errors. On the other hand, the initial acrolein selectivity is not the same between the first and the second cycle, confirming that the thermal treatment under air flowing did not remove completely the coke deposits. From the TG/DTG data (Figs. 8 and 9), it is possible to see that only thermally unstable coke was removed (*ca.* 80%), leaving more stable species unchanged (ca. 20%). Still comparing the acrolein selectivity under nitrogen flow, one could observe that the selectivity losses with time on stream are less pronounced in the third than in the second reaction cycle.

It is possible to see in Fig. 10a that initial deactivation occurs for both nitrogen and air, but in a lesser extension in the last case. ITQ-2 reaches higher values of glycerol conversion under oxidative conditions. Acrolein is still the major product, with high selectivity (Fig. 10b), but trace amounts of acetic, acrylic and propionic acids were detected in the condensate. Acrolein selectivity increased by using air instead of nitrogen as carrier gas during catalytic tests, mainly because oxygen favors a continuous removal of coke precursors that regenerates acid sites at reaction temperature. The decrease of acrolein selectivity in each reaction cycle is a consequence of coke formation that changes accessibility and acidity of the catalysts. Even though acrolein selectivity decreases during a 10 h run, it has been almost fully regenerated in the following cycles.

4. Conclusions

Catalysts derived from MWW-type precursors are active and selective in gas phase dehydration of glycerol to acrolein. The delaminated material ITQ-2 showed higher selectivity to acrolein because of the improved textural properties when compared to MCM-22. The pillared material MCM-36 presented higher glycerol conversion, but lower selectivity to acrolein, as a combined result of acid sites density decreases and obstruction of sites by SiO₂ pillars. The main deactivation mechanism is coke formation, but the ITQ-2 catalyst can be regenerated by burning under oxidative conditions. The ITQ-2 is the best candidate for a stable catalyst for the dehydration of glycerol to acrolein under oxidative conditions among the MWW-derived materials here studied.

Acknowledgment

The authors acknowledge the financial support from the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq – Process n°. 476657/2010-5).

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