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Catálisis, cinética y reactores

EXPLORING THE REGENERATION OF MORDENITE CATALYST IN DIMETHYL ETHER CARBONYLATION REACTION

EXPLORANDO LA REGENERACIÓN DE LA MORDENITA EN LA REACCIÓN DE CARBONILACIÓN DE DIMETILÉTER

M.Á. Vázquez, P. García-Haro, F. Vidal-Barrero, P. Ollero de Castro*

Bioenergy Group, Chemical and Environmental Engineering Department Escuela Técnica Superior de Ingeniería, Universidad de Sevilla Camino de los Descubrimientos s/n, 41092 Seville, Spain

Abstract

Dimethyl ether (DME) carbonylation to produce methyl acetate (MA) over mordenite catalysts is attracting much attention because of its application in the design of new concepts of thermochemical biorefineries. However, mordenite suffers from a fast deactivation (coking) that has not been properly studied. In the present work, we study the regeneration of the catalyst in several cycles aiming to help the future industrial application of mordenite catalysts in MA production. Both diluted and pure air have been successfully tested for catalyst regeneration. The results show that, in both cases, not only complete restoration of initial activity is achieved, but also a slight activity improvement is observed after reactivation. Additionally, a plausible explanation of the observed results is given in the present work, which is supported by the literature and analyses carried out to mordenite samples.

Keywords: carbonylation, mordenite, regeneration, methyl acetate, bioethanol.

Resumen

La carbonilación de dimetiléter (DME) catalizada con mordenita para producir acetato de metilo (MA) está siendo objeto de un gran interés dada su aplicación en el diseño de nuevos conceptos de biorrefinería termoquímica. Sin embargo, la mordenita sufre de una rápida desactivación por coquización que no ha sido investigada suficientemente. En el presente trabajo, estudiamos la regeneración del catalizador durante varios ciclos con el objetivo de contribuir en la futura aplicación industrial de la mordenita para la producción de MA. Para la regeneración se ha empleado exitosamente tanto aire diluido como puro. Los resultados muestran, para ambos casos, no sólo una completa recuperación de la actividad inicial del catalizador sino, además, una ligera mejora de ésta tras la reactivación. Además, en el presente trabajo se da una explicación plausible de los resultados obtenidos, apoyada en la literatura y en los diferentes análisis practicados a las muestras de mordenita.

Palabras clave: carbonilación, mordenita, regeneración, acetato de metilo, bioetanol.

1 Introduction

Dimethyl ether (DME), which can be commercially obtained from syngas through methanol (MeOH) dehydration process, has been recently studied as a potential renewable platform chemical in thermochemical biorefineries (Haro *et al*., 2012, 2014; Haro, Ollero, *et al*., 2013; Haro, Trippe, *et al*., 2013). Biorefineries are facilities focused on producing high value-added products like fuels, compounds, heat and electricity from biomass through a variety of routes (Sacramento-Rivero *et al*., 2010). A thermochemical biorefinery is a facility which processes biomass by means of pyrolysis and/or gasification to produce fuels (transportation, heat/electricity generation), chemicals (high-value commodities), materials and services (heat, electricity) (Haro *et al*., 2014). One of the chemical routes that has attracted attention is the hydrocarbonylation of DME since it represents an example of platform chemical for the development on new process concepts of thermochemical biorefineries (Haro *et al*., 2014). In this route, ethanol is indirectly produced from DME in two steps, at mild conditions, with a high global selectivity using inexpensive and environmentally friendly catalysts (San *et al*., 2009; Li *et al*., 2010; Zhang *et al*., 2010; Wang *et al*., 2012; Gao *et al*., 2018). In the first step, DME reacts with CO to produce methyl acetate (MA) in the presence of an acidic zeolite. It has been experimentally determined

that H-Mordenite (H-MOR) is the most active zeolite for DME carbonylation (Cheung *et al*., 2006, 2007; Bhan *et al*., 2007). In the second step, the ester is hydrogenated yielding ethanol (and methanol as byproduct) in the presence of a Cu-based catalyst (Liu *et al*., 2013; Ye, Guo and Zhang, 2016). The use of this kind of catalyst in the latter step is not surprising since Cu-based catalysts are commonly employed for synthesis of alcohols from syngas through Fischer-Tropsch processes (Araujo-Ferrer *et al*., 2013). In addition, the methanol co-produced in the second step might be dehydrated to yield more DME (closing the loop), being water the only byproduct in the whole process.

Many efforts have been devoted to the development of catalyst for the carbonylation of DME, but only mordenite catalysts exhibits moderate catalytic activity compared to similar commercial processes (acetic acid production using homogeneous catalysts) (Sunley and Watson, 2000; San *et al*., 2009; Yang *et al*., 2011). The unique structure of mordenite, composed of a combination of eight and twelve-membered rings (8MR, 12MR), is responsible of its catalytic properties (Bhan *et al*., 2007). However, the catalyst is rapidly deactivated by coke deposition during reaction (Liu *et al*., 2010; Xue, Huang, Ditzel, *et al*., 2013a; He *et al*., 2016). The fast deactivation of the catalyst represents a challenge for a future industrial application of the DME carbonylation route.

The strategies to improve the catalyst activity and/or minimize the deactivation by coke include: promotion of mordenite with metals e.g. Cu (Xue, Huang, Ditzel, *et al*., 2013b; Zhang *et al*., 2013; Reule and Semagina, 2016) or Co (Ma *et al*., 2018); the saturation of 12MR channels with pyridine (Liu *et al*., 2010; Li *et al*., 2018); improvement of mass transfer for reactants and products using crystal size reduction (nano-sized mordenite) (Liu *et al*., 2015; Ma *et al*., 2017; Wang *et al*., 2019); and selective dealumination of 12MR channels (Xue, Huang, Zhan, *et al*., 2013).

A different strategy, poorly investigated for this application, is regeneration of mordenite (whether the catalyst has been promoted with metals or not). The regeneration consists in combustion of the coke formed during reaction (aiming to recover catalytic activity without producing any irreversible damage in catalyst structure). Reule *et al*. (Reule and Semagina, 2016) showed that it is possible to regenerate a mordenite catalyst doped with Cu and Zn using hydrogen at 400 ºC, and recovering around 73% of initial (maximum) activity. Liu *et al*. (Liu *et al*., 2017) investigated optimal conditions for burning off coke

after DME carbonylation. They reported complete restoration of initial DME conversion after catalyst regeneration using 3% O_2 at 320 ºC for 3 hours and then at 550 ºC for 6 hours. The regenerated sample showed a similar behavior compared with the fresh catalyst.

The commercial application of DME carbonylation for MA production requires a reduced loss of activity of the catalyst after several cycles of reaction-regeneration. Additionally, catalyst regeneration with diluted air might be expensive at industrial scale, so use of atmospheric air would be preferred. However, no further studies have analyzed stability of mordenite for more than one regeneration cycle, the exception being two patents (Becker, Ditzel and Kaiser, 2012; Ditzel and Law, 2012). There are no studies analyzing regeneration with pure air.

In this work, we further investigate regeneration capability of mordenite catalysts in carbonylation of DME. Firstly, we analyze catalyst regeneration using diluted air at medium-low temperature, so regeneration is conducted at mild conditions. Up to three reaction-regeneration cycles are analyzed to observe catalyst performance. Secondly, we explored the possibility of burning off the coke formed during DME carbonylation with air under controlled conditions.

The present paper is structured as follows: section 2 describes experimental details, such as the description of lab facilities, operating conditions and methodology for catalytic tests and sample analyses; section 3 presents results of catalytic tests together with a discussion on observed improvement of catalyst activity after regeneration using diluted and pure air. A plausible explanation of such results, based on literature and several sample analyses, is also given. Finally, the conclusions of the work are exposed in section 4.

2 Experimental details

Mordenite was provided in acidic form (H-MOR) as powder by Tosoh Co. (SiO_2/Al_2O_3=18). The as-received powder was pressed at 2 tons in a stainless-steel die. Then, the solid was crushed and sieved between 300-500 microns. Zeolites are highly hygroscopic, so before each test, the catalyst was firstly dried in a muffle furnace for 3 hours in order to remove water and to accurately weight the desired amount of catalyst to be loaded into the

reactor. Permanent gases (Ar, Air Liquide, 99.999% and CO, Air Liquide, 99.97%) and liquid DME (Air Liquide, 99.99%) were used, respectively, by means of two mass flow controllers and a Mini-Coriflow (Bronkhorst Hi-Tech). Ar was used as diluent agent and inert for quantification. Synthetic air (Air Liquide, 20% O_2/80% N_2) was used as oxidizing agent, which was mixed with Ar for regenerating tests with diluted air.

Catalytic tests were performed in a lab-scale facility equipped with a fixed-bed stainless steel reactor (8.75 mm inner diameter and 330 mm length) heated by an electrical oven. H-MOR (0.67 g) was mixed with silicon carbide (SiC, 3.55 g) and loaded into the reactor. Two additional beds of SiC were placed upstream and downstream the catalyst bed in order to provide physical support to the catalyst during reaction. A three-point thermocouple parallel to the reactor axis was inserted to control the bed temperature. Since mordenite tends to get moisture during the reactor loading, before each reaction test, the sample was dried under flowing Ar (50 NmL/min) at 500 °C (4°C/min) for 10 hours to remove water. After this treatment, the reactor was slowly cooled down and pressurized with Ar up to the reaction temperature and pressure (170 °C, 11.1 bar). Then, the bypass mode was enabled and the reactant mixture (29.03% Ar, 64.52% CO, 6.45% DME, total flow 62 NmL/min) was fed.

The reactant mixture passed through a pre-heater to ensure complete vaporization of DME under reaction conditions. The effluent from the reactor (or from the by-pass line) was diverted to the analytical devices through heated lines to avoid condensations. Such analytical devices were a quadrupole mass spectrometer (MS) (Hiden Analytical, QGA) connected in parallel to a gas chromatograph (GC) (Agilent, 6890N) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID).

The MS was used to quantify the concentrations at the outlet of the reactor with high sampling frequency. The GC was used to identify those desorbed compounds that were not scanned by the MS during the treatment. Ar (m/z=40), CO (m/z=12), DME (m/z=46), MA (m/z=74), MeOH (m/z=32) and water (m/z=17) were scanned by the MS with conveniently selected m/z so as to minimize quantification errors associated to overlapping of identical m/z values corresponding to different species as a consequence of their fragmentation patterns.

The facility was also equipped with a by-pass line in order to detect when the reactant mixture concentration was stable and to enable the calibration of the MS before each test.

Once the concentration of the gaseous mixture detected by the MS became stable, the device was calibrated and gas flow was directed through the reactor to start the catalytic test. The carbonylation tests were allowed to continue until the MA productivity declined 50% with respect to maximum MA activity peak. Then, the regeneration procedure started.

Firstly, after cutting off the reactant feeding through the bed, the catalyst sample was flushed with Ar (50 NmL/min) at 170 °C, whereas the pressure was slowly dropped to ambient pressure to facilitate desorption of remaining reaction compounds. This step lasted until only pure Ar was detected by MS and corroborated by GC. Then, reactor temperature increased up to 350 °C (4 °C/min), keeping this temperature until all the remaining adsorbed compounds from the zeolite surface (mainly DME, MA, MeOH, water and light hydrocarbons) were fully removed, which were additionally confirmed by both MS and GC.

After the thermal treatment, Ar flow was partially substituted by synthetic air at 350 °C so 5% v/v O_2 (total flow 64 NmL/min) was present in the gaseous mixture. When pure air instead of diluted air was used for regenerating the sample, no Ar was mixed with the flow of synthetic air, so just 64 NmL/min of synthetic air was fed to the reactor.

By the procedure described above, coke oxidation started under mild conditions to avoid any damage to mordenite structure. When combustion products, which were monitorized by MS, were not further detected, reactor temperature increased up to 500 °C (4 °C/min) to burn off the heavier fraction of the coke formed during reaction.

Once the regeneration process finished (i.e. no further combustion products were detected), the sample was dried at 500 °C under flowing Ar, which also served to inert the reactor. Then, conditions for DME carbonylation reaction were resumed as previously described.

When all the experiments finished, mordenite samples were unloaded from the reactor and stored for conductometric titration to determine their acid density.

The spent catalyst samples were collected and sieved to separate SiC from the catalyst particles. Then, they were dried in a muffle furnace at 110 °C for 3 hours to remove humidity. Each dried sample

was weighted and dissolved in 100 mL deionized water under continuous stirring. The same procedure was followed for a fresh H-MOR sample previously calcined at 500 ºC, which was used as a reference to determine the acidity loss of the spent samples.

Conductometric titrations were performed using a previously calibrated portable conductivity meter (Crison 524), being readings normalized to 20 ºC. A NaOH solution (GlobalChem, 0.1N±0.0002/20ºC) was used to neutralize the samples by successive additions of 0.2 mL from a burette at 1-minute intervals (enough time to stabilize the readings from the conductivity meter) under continuous stirring of the suspension. The addition of the base continued far beyond the end point to minimize quantification errors. To correct the conductance readings associated to the increase of the suspension volume, they were multiplied by the factor (V+v)/V; where V is the initial volume of the suspension and v is the actual volume of the suspension after the addition of the NaOH aliquot, according to what specialized literature recommends (Vogel, 1989).

Then the corrected conductance readings were plotted against the volume of NaOH added, obtaining a typical titration curve for each sample (see Figure S11 in Appendix). The end point was determined analytically by linear regression of six points situated before and after it (being the exact point the intersection).

[H^+] was obtained by applying the following formula:

$$[H^+] = \frac{V_{ep} \cdot N}{m} \tag{1}$$

Where V_{ep} is the volume of NaOH added corresponding to the end point, N is NaOH normality and m is the mass of the sample.

3 Results and discussion

Figure 1 shows that MA productivity reached a maximum of 0.36 mmol/g·h during DME carbonylation using a fresh sample. The catalytic test was interrupted when MA productivity was just 50% from the maximum value, which happened after approximately 30 hours on stream. After regenerating the mordenite with 5% O_2, activity was not only completely recovered, but slightly enhanced. In fact, after first regeneration cycle, MA productivity reached a maximum of 0.39 mmol/g·h (+8% compared to fresh sample).

After the sample was in reaction for a second time and, therefore, deactivated (defined again as a 50% activity loss), it was regenerated using the same procedure (second cycle). This two-times regenerated sample showed same behavior than upon the first regeneration cycle. Moreover, deactivation rate (defined here as the average slope of MA productivity tail after the maximum) was similar after two cycles (see Figure S2 in Appendix). These results suggest that no accumulation of coke happened between regenerations, i.e. a complete removal of coke was achieved.
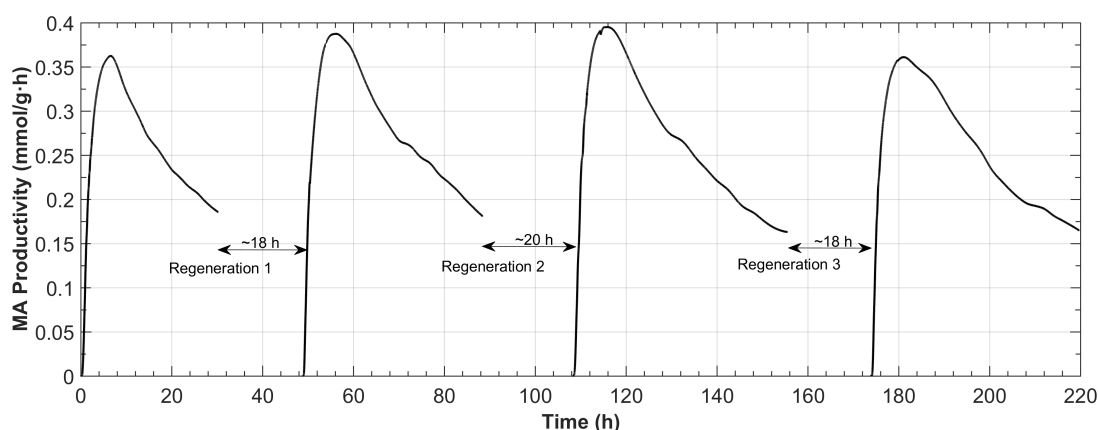

Fig. 1. MA productivity during DME carbonylation for fresh and regenerated (with 5% O_2) samples. Operating conditions: 0.67 g H-MOR, 170 ºC, 11.1 bar, 29.03% Ar/64.52% CO/6.45% DME, total flow=62 NmL/min.
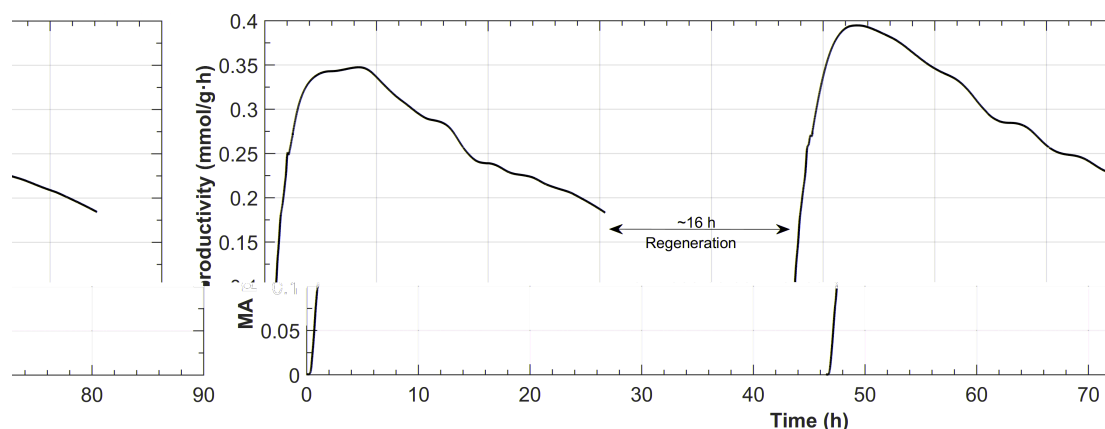
Fig. 2. MA productivity during DME carbonylation for fresh and regenerated (with air) samples. Operating conditions: 0.67 g H-MOR, 170 ºC, 11.1 bar, 29.03% Ar/64.52% CO/6.45% DME, total flow=62 NmL/min.

The abovementioned sample was regenerated for a third time. In this case, maximum of MA productivity was also the same than that obtained with the fresh sample. Nevertheless, integrated MA productivity was still higher respect to the fresh sample. We can conclude that after the first regeneration, mordenite increased its activity from 7.78 mmol/g to 8.96 mmol/g (see Figure S1 in Appendix), which represents an increment of over 15%. Practically, same activity was obtained after second regeneration of the sample (9.08 mmol/g). For the third regeneration (third cycle), a decline in the integrated MA production (8.69 mmol/g) was observed, but the sample still exhibited over 11% more activity than in the first test.

It has been previously reported that an enhancement of the catalyst stability is possible by dealumination (i.e., selectively removing the Al species located in the 12MR channels). Additionally, dealuminated mordenite exhibited a slightly higher MA productivity peak together with lower deactivation rate, resulting in higher integrated productivity of MA (Xue, Huang, Zhan, *et al*., 2013). In our experiments, we observed an attenuated but similar effect after first regeneration (see Figure S2). Therefore, a plausible explanation of the slight enhancement of catalyst activity could be a limited migration of Al from the 12MR channels to extra-framework positions (where Al has no catalytic activity for the reaction or deactivation by coking).

In Figures S3-S8, evolution of combustion products (CO_2, CO and H_2O) formed during the three regeneration treatments is shown. In all the cases, a major peak of water accompanied by minor peaks of CO_2 and CO were detected, just after putting the sample in contact with the oxidizing agent at 350 ºC. During the increase of bed temperature from 350 ºC to 500 ºC, further combustion was observed, being CO_2 the main product followed by CO and H_2O. The small amount of water formed at higher temperatures in the second step of the regeneration (from 350 to 500 ºC) led to a very low water partial pressure, which limited possible damages to catalyst framework, according to Guisnet *et al*. (Guisnet and Ribeiro, 2011).

Despite being aware that regeneration with pure air applied to industrial conditions might involve problems associated to high temperatures in the bed causing catalyst sintering and/or structural damages, we consider interesting to study this option under controlled conditions. With such aim, a new fresh sample was loaded into the reactor. After a first catalytic test, with a MA peak activity of 0.35 mmol/g·h, the sample was regenerated following same procedure as described above. After regeneration, the next reaction test showed a MA peak activity of 0.39 mmol/g·h of MA, again the same value obtained when regenerating with 5% O_2, as shown in Figure 2.

Figure 3 shows DME concentration from the reactor effluent during first 15 minutes for fresh and air-regenerated samples. During this period, reactant mixture displaces inert gas initially confined in the reactor. Then, DME is adsorbed (both physically and chemically) on mordenite surface and reacts with active centers to form intermediate methyl groups, with DME outlet concentration dropping to zero as long as there are active centers available for adsorption. Once mordenite is saturated, DME starts to rise up, tending to reach its initial concentration (forming a U-shape curve).
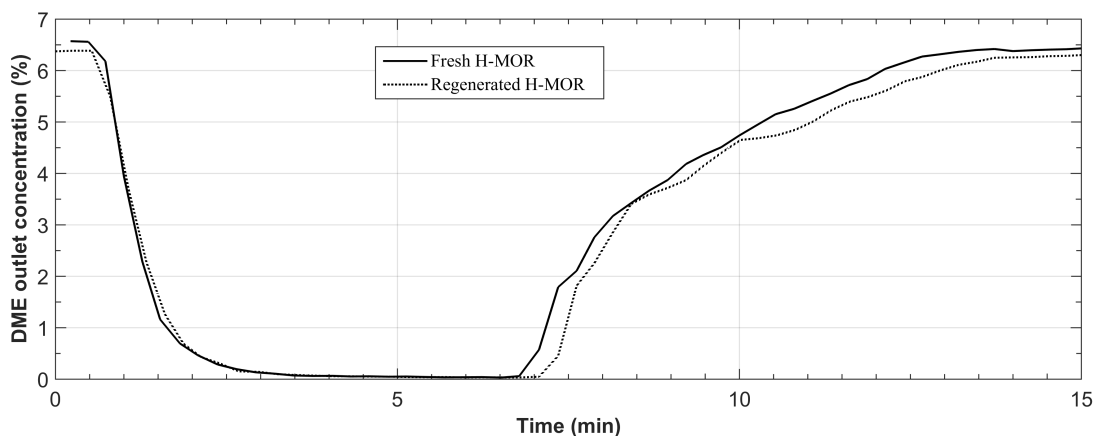
Fig. 3. Saturation of fresh and air-regenerated H-MOR samples with DME during initiation phase.

Hence, the valleys of adsorption of DME are formed by three contributions: inert gas displacement, physisorption and chemisorption, being the first two contributions identical under same reaction conditions. Moreover, duration of saturation period for mordenite directly depends on number of acid sites, being DME adsorption mostly dominated by those located within the 8MR channels (Rasmussen *et al.*, 2017). Therefore, any significant alteration in adsorption valleys is exclusively attributable to an alteration in the amount of Brönsted acid sites (BAS) within the zeolite framework (and more specifically in selective 8MR channels). As can be seen in Figure 3, DME valleys formed by saturation of fresh and regenerated sample are almost identical, suggesting that the catalyst did not experiment any detrimental structural change within the 8MR channels after regenerating with air. This result is compatible with the hypothesis of a slight migration of Al atoms located in the 12MR channels to extra-framework positions upon regeneration.

Table 1 resumes total areas of valleys during DME adsorption for all tests performed. It should be remarked that these values are not representative for the total amount of chemisorbed DME during mordenite saturation (and, hence, the amount of BAS) as the aforementioned contributions of inert gas displacement and DME physisorption (which are identical for all the tests) have not been discounted from the total. As it can be seen, these values range from 2.09 to 2.29 mmol/g, which confirm that DME adsorption capacity of the catalyst remained almost intact.

Table 1. Total areas of the valleys during mordenite saturation with DME.

Run	Total Area (mmol/g)
Fresh H-MOR (I)	2.14
After 1st regeneration	2.09
After 2nd regenerationa	2.19
After 3rd regenerationa	2.29
Fresh H-MOR (II)	2.12
After regenerationb	2.17

It has been reported that conductometric titration is a reliable method for determination of BAS concentration in acidic zeolites like ZSM5 and mordenite (Crocker *et al.*, 1993). Furthermore, it was confirmed that the strong base utilized in this analysis does not neutralize extra-framework Al species in mordenite (Mohammadi and Zanjanchi, 2001), so a straightforward quantification of total BAS (i.e. both in the 8MR and in the 12MR channels within the mordenite framework) can be obtained using this method.

Table 2 shows the results obtained for the spent samples (labeled as H-MOR-A and HMOR-B) and a fresh sample. The fresh sample was calcined (for comparison) since it was reported that high temperatures might alter acid sites concentration due to thermal migration of Al (Mohammadi and Zanjanchi, 2001). It is shown that, despite being regenerated a different number of times and by two different oxidizing agents, both spent samples exhibited practically the same acid sites concentration (about 25% lower with respect to the fresh sample).

Table 2. Brönsted acid sites concentration for fresh and regenerated samples determined by conductometric titration.

Sample	[H$^+$] (mmol/g)
Fresh H-MORa	1.19
H-MOR-Ab	0.89
H-MOR-Bc	0.87

[a]Fresh sample calcined at 500 ℃ with Ar during 10 hours. [b]Deactivated sample after three reaction-regeneration cycles with 5% O$_2$. [c]Deactivated sample after one regeneration with air.

These findings together with the fact that the acid centers located in the 8MR remained almost intact in all the cases (excluding the possibility of Al migrating from the 8MR channels) confirm the hypothesis that migration of Al mainly occurred in the 12MR channels (responsible for coking).

Conclusions

The results obtained in the present work allows us to conclude that (1) there is no negative effect after several regeneration cycles and 2) there is a slight improvement of catalyst productivity after the first regeneration cycle. Both results have been validated for regeneration with diluted and pure air. A plausible explanation to these results is that catalyst structure is not negatively affected during regeneration while there is an initial migration of Al from the mordenite structure (12MR) to extra-framework positions without affecting those located in 8MR channels, which are the highly selective active sites for DME carbonylation. This hypothesis is based on evidences from our conductometric titration analyses of spent samples and from analyses of DME adsorption valleys during saturation phase of H-MOR, which show that there is around 25% less BAS concentration in spent samples with respect to a fresh one, while DME adsorption capacity of all samples (whose main actors are BAS located within the 8MR channels) remained almost intact.

The possibility of regeneration (whether with diluted or pure air) without damaging the catalyst structure contributes to development of the DME carbonylation for industrial applications like ethanol synthesis.

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Appendix

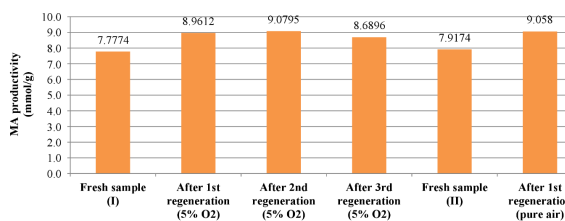*Integrated MA productivity for fresh and regenerated H-MOR sample*

Fig. S1. Integrated MA productivity for fresh and regenerated H-MOR samples after 30 hours on stream

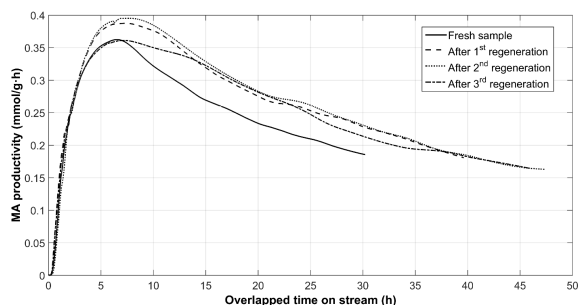*MA productivity vs overlapped time on stream*

Fig. S2. MA productivity vs overlapped time on stream for fresh and regenerated sample with 5% O_2

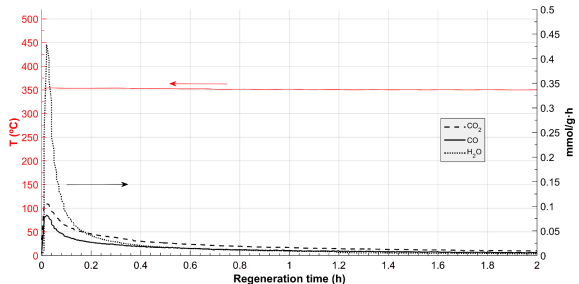*Combustion products during regeneration of H-MOR*

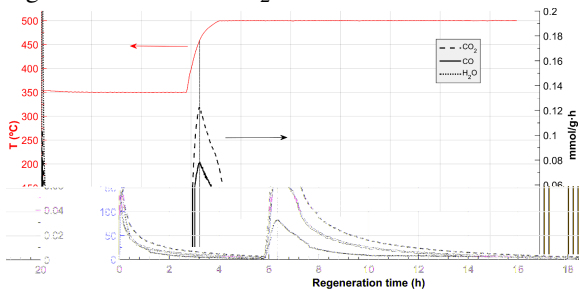Fig. S3. Combustion products detected during first regeneration with 5% O_2 at 350 ºC

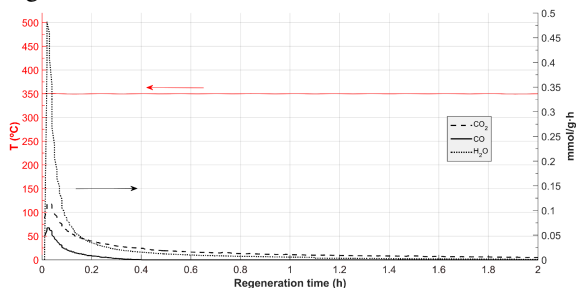Fig. S4. Combustion products detected during first regeneration with 5% O_2 from 350 to 500 ºC

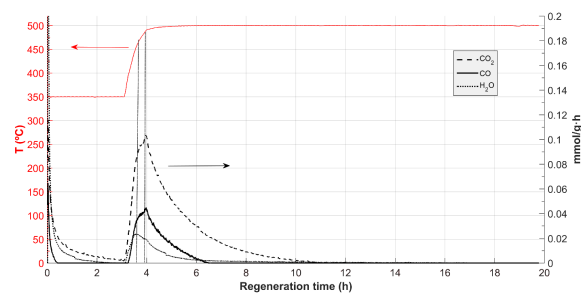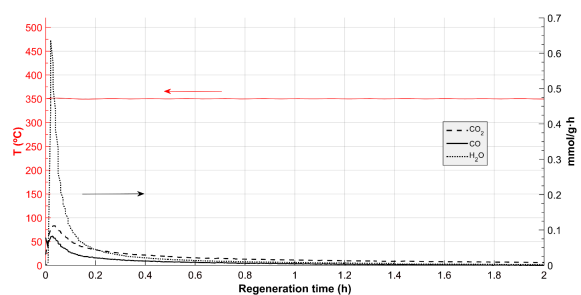Fig. S5. Combustion products detected during second regeneration with 5% O_2 at 350 ºC

Fig. S6. Combustion products detected during second regeneration with 5% O_2 from 350 to 500 ºC

Fig. S7. Combustion products detected during third regeneration with 5% O_2 at 350 ºC
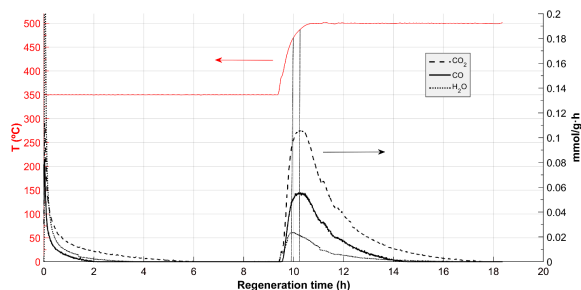

Fig. S8. Combustion products detected during third regeneration with 5% O_2 from 350 to 500 ºC
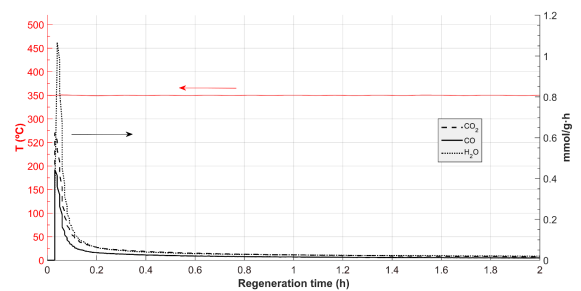

Fig. S9. Combustion products detected during regeneration with pure air at 350 ºC.
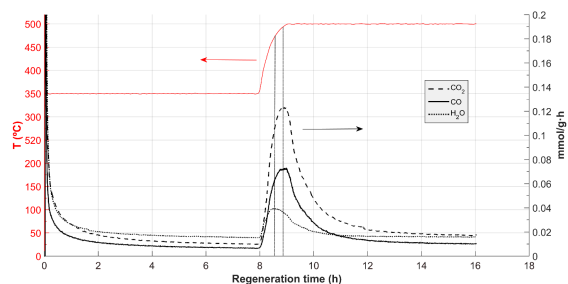
Fig. S10. Combustion products detected during regeneration with pure air from 350 to 500 ºC.

Conductometric titration curves

Table S1 summarizes the results from the titration of the fresh and spent H-MOR samples.

Table S1. Titration results for fresh and spent H-MOR samples

Sample	Mass (g)	End point (mL)	[H$^+$] (mmol/g)
Fresh H-MORa	0.4387	5.2	1.19
H-MOR-Ab	0.475	4.21	0.89
H-MOR-Bc	0.2513	2.18	0.87

[a]Fresh sample calcined at 500 ºC with Ar during 10 hours.
[b]Deactivated sample after three reaction-regeneration cycles with 5% O_2.
[c]Deactivated sample after one regeneration with air.

Figure S11 shows the corrected conductances plotted against the volume of NaOH added during titrations.
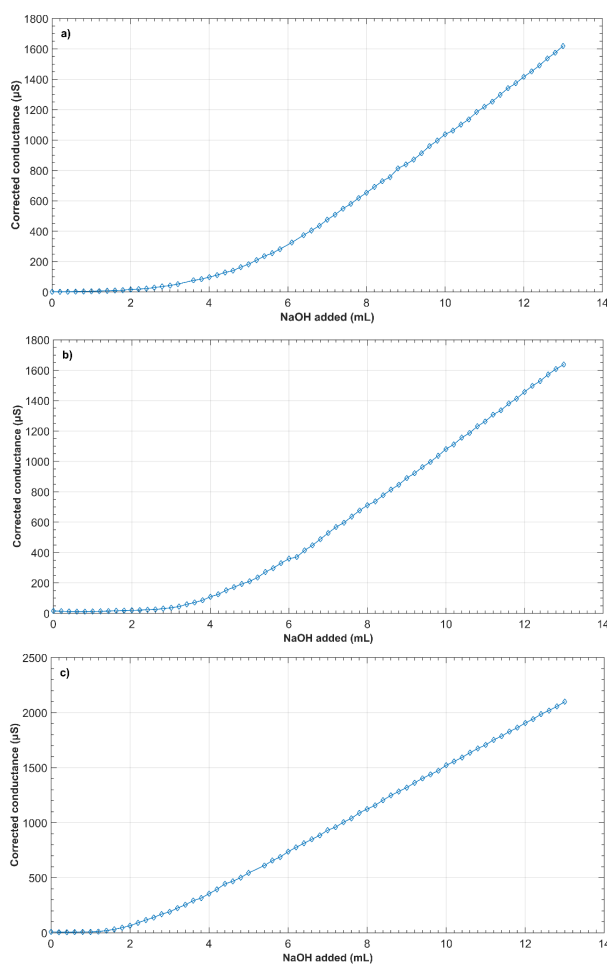

Fig. S11. Titration curves: a) precalcined fresh sample, b) spent sample after three regenerations with 5% O_2, c) spent sample after one regeneration with air.