Hacia los 130 años de creación de la Universidad del Zulia

"Buscar la verdad y afianzar los valores transcendentales", misión de las universidades en su artículo primero, inspirado en los principios humanísticos. Ley de Universidades 8 de septiembre de 1970.

REVISTA TÉCNICA
DE LA FACULTAD DE INGENIERÍA

Una Revista Internacional Arbitrada
que está indizada en las publicaciones
de referencia y comentarios:

- SCOPUS
- Compendex
- Chemical Abstracts
- Metal Abstracts
- World Aluminium Abstracts
- Mathematical Reviews
- Petroleum Abstracts
- Current Mathematical Publications
- MathSci
- Revencyt
- Materials Information
- Periódica
- Actualidad Iberoamericana

UNIVERSIDAD DEL ZULIA

REVISTA TÉCNICA
DE LA FACULTAD DE INGENIERÍA

VOLUME 43   SEPTEMBER - DECEMBER 2020   NUMBER 3

Catalytic performance of $CuO/ZnO/Al_2O_3$ catalysts under water-gas shift reaction cycles

Angeli Mercedes Barroso Velásquez[1], María Victoria Markovich García[2], Jeannette Josefina Zárraga Colina[1] (iD) *, Alexander José Moronta Cuicas[1] y Victor José Ferrer Villasmil[1,3]** (iD)

[1]Instituto de Superficies y Catálisis, Facultad de Ingeniería, Universidad del Zulia
P.O. Box 15251, Maracaibo 4003A, Venezuela.
[2]Investigación y Desarrollo C.A. (INDESCA), Puertos de Altagracia 4036, Venezuela.
[3]Unidad de Desarrollo Tecnológico, Universidad de Concepción, Concepción 4100000, Chile
*Autor de Contacto: vjfv1975@gmail.com
https://doi.org/10.22209/rt.v43n3a06
Received: 23/01/2020 | Accepted: 25/07/2020 | Available:: 01/09/2020

Abstract

Fresh and spent $CuO/ZnO/Al_2O_3$ industrial catalyst used in a water-gas shift reaction (WGSR) was studied. The samples were characterized by X-ray fluorescence, X-ray diffraction, Temperature programmed reduction and CO chemisorption. The catalytic performance was evaluated under consecutive cycles of WGSR at low temperature (200-250 °C). The spent catalysts exhibited a decrease in surface area, as well as a modification of the crystalline structure, loss of Cu metallic surface and presence of sulfur. WGSR was favored at 250 °C, registering high CO conversions (≈90%) for the fresh sample during successive reaction cycles. The spent catalysts kept a high activity (≈80%), except for the catalyst portion collected at the reactor's top, which could be more affected because of high sulfur content and/or water condensation during the reactor's cooling.

Keywords: reaction cycles; $CuO/ZnO/Al_2O_3$; deactivation; water-gas shift reaction.

Desempeño de catalizadores de $CuO/ZnO/Al_2O_3$ sometidos a varios ciclos de reacción de desplazamiento del gas de agua

Resumen

Se estudió un catalizador industrial de $CuO/ZnO/Al_2O_3$ fresco y usado, empleado en la reacción de desplazamiento del gas de agua (WGSR). Las muestras fueron caracterizadas mediante Fluorescencia de rayos X, Difracción de rayos X, Reducción a Temperatura Programada y quimisorción de CO. El desempeño catalítico del catalizador fresco fue evaluado bajo 3 ciclos consecutivos de la reacción a baja temperatura (200-250 °C). Los catalizadores usados presentaron una disminución del área superficial, así como una modificación de la estructura cristalina, pérdida de superficie metálica del cobre y presencia de azufre. La reacción de WGSR se favoreció a 250 °C, registrando altas conversiones de CO (≈90%) para la muestra fresca durante 3 ciclos sucesivos de reacción. Los catalizadores usados aún mantienen una alta actividad (≈80%), con excepción de la muestra más cercana al tope del reactor, la cual podría estar más afectada como consecuencia de un alto contenido de azufre y/o la condensación de agua durante el enfriamiento.

Palabras clave: ciclos de reacción; $CuO/ZnO/Al_2O_3$; desactivación; reacción de desplazamiento del gas de agua.

Introduction

Water Gas Shift Reaction (WGSR) is a reversible and exothermic reaction (ΔH = -40.6 kJ/mol) [1], in which a catalyst is used to accelerate the reaction between CO and water vapor to generarate CO_2 and H_2. In the industry, this reaction is employed to produce hydrogen and synthesis gas (mixture of CO and H_2), which are widely used in ammonia and methanol plants, for example. Its main role is to decrease the CO content in the gaseous product [2]. The reaction is carried out in two consecutive reactors with different catalytic beds, to maximize the kinetic control in the first one and the thermodynamic control in the second. Thus, iron catalysts operate in a temperature range of 320 to 450 °C to favor the reaction kinetics at higher temperatures; while copper catalysts are operated in a temperature range of 200 to 250 °C, promoting the thermodynamics of the reaction [3].

Industrially, $CuO/ZnO/Al_2O_3$ catalysts are designed to operate under continuous process conditions in large industrial plants and are very sensitive to water condensation, requiring careful startup and shutdown plant processes [4]. During frequent startup and shutdown processes of the reactor for WGSR, the catalysts are exposed to water condensation when the reactor cools and abrupt vaporization when it is heated. For this reason, catalyst deactivation is more severe under these conditions than continuous operation [5,6].

The behavior of $CuO/ZnO/Al_2O_3$ catalysts under continuous process conditions is well known, however, few researches about the catalyst performance under frequent startup and shutdown conditions have been reported. Considering that the useful life of the catalytic bed at industrial level has a maximum of 4 years under standard operation, there are information gaps regarding how the useful life of catalyst could be modified depending on the cycle operation of the reactor. In the case of a fertilizer plant, the water gas shift reactor is designed to work under continuous conditions, however, during the years 2009 and 2016, it was subjected to reactor shutdowns, exposure to condensate and subsequent startup of the same, until the replacement of the catalytic bed. Consequently, the evaluation of the catalyst that was downloaded from the reactor is of interest, to evaluate if its remaining activity is enough to be used for a longer time, and if not, determine what are the main physicochemical causes of its deactivation.

Experimental

Catalysts

Four samples of $CuO/ZnO/Al_2O_3$ catalysts were used: Three samples corresponding to the catalytic bed of a low temperature water gas shift reactor, being the Cat-B, Cat-M and Cat-T samples, the portion of catalyst removed from the bottom, middle and top of the reactor, respectively (Feed flows from the top to the bottom), while the fourth sample corresponds to the fresh catalyst.

X-ray fluorescence (XRF)

To determine the chemical composition of the samples, a Shimadzu EDX-700HS spectrometer was used, equipped with a Rh radiation source that operated at 50 kV and 30 mA.

Nitrogen adsorption

N_2 adsorption isotherms were determined at -196 °C using a Micromeritics ASAP 2020 sortometer. The isotherm was determined by injecting N_2 gas to the sample at small pressure intervals until reachs the N_2 saturation pressure (P/Po = 1). The specific surface area values were determined using the BET method, while the pore radius was determined using the BJH method.

X-ray diffraction (XRD)

The crystalline phases present in the samples were determined by a Bruker D8 X-ray diffractometer, operating with CuKα radiation at 40 kV and 30 mA, with a step size of 0.025° 2θ, time per step of 1 s and a measurement range of 15-70° 2θ.

CO chemisorption

Metallic dispersion was studied by CO chemisorption in a Micromeritics AutoChem II 2920 equipment, using 300 mg of sample. The sample was initially pretreated with H_2 at 150 °C for 0.5 h and then at 250 °C for 1 h with a heating rate of 10 °C min^{-1} and a flow of 30 ml min^{-1}. At the end of the reduction treatment, the sample was kept at 250 °C and the gas was switched to He (30 ml min^{-1}) for 1 h at 250 °C. Subsequently, the sample was cooled in the same He flow up to 35 °C and then start the adsorption stage where increasing pressures of CO (100-500 mmHg) were introduced into the system. The metallic dispersion (%) and metallic surface area (S_{Cu}(%)) were determined by equations 1 and 2, respectively [7]:

$$Metallic\,dispersion(\%) = 100 * \left(\frac{Vs * SF}{SW * 22414}\right) * GMW \quad (1)$$

$$S_{Cu}(\%) = 100 * \left(\frac{Vs}{SW * 22414}\right) * SF * 6.123 \cdot 10^{23} * S_{BET} \quad (2)$$

Where:

Vs: Volume sorbed (cm^3 at standar conditions of pressure and temperature)
SF: Stoichiometric factor. The value was assumed 1 considering that CO is adsorbed mostly linearly on Cu [8]
SW: Sample weight (g)

GMW: Gram molecular weight (g mol^{-1})
S_{Cu}: Metallic surface of Cu (m^2 g of metal^{-1})
S_{BET}: calculated specific surface area (m^2 g of sample^{-1})

Temperature-programmed reduction (TPR)

TPR measurements were carried out on a Micromeritics AutoChem II 2920 equipment, employing 100 mg of sample. Samples were pretreated at 120 °C in Ar flow (30 ml min^{-1}) for 1 h. Subsequently, a flow of H$_2$(10%)/Ar (30 ml min^{-1}) was passed through the sample and starting to compute H$_2$ consumption from room temperature up to 350 °C, using a heating rate of 10 °C min^{-1}. The experimental H$_2$ consumption was calculated by means of the AutoChem II 2920 software using the TCD calibration with CuO while the theoretical H$_2$ consumption was calculated assuming a complete CuO reduction, considering the XRF analysis of samples.

Catalytic activity

The WGSR was performed at 200 and 250 °C, using a composition feed of 70% H$_2$O and 30% of CO(10%)/He mixture, with a flow of 15 ml min^{-1} of CO(10%)/He mixture and 35 ml min^{-1} of steam through the catalytic bed. CO(10%)/He mixture was dosed by means of a mass flow controller, while the steam was generated by injecting 0.026 ml min^{-1} of liquid water into an evaporator (equivalent to 35 ml min^{-1} of steam determined at 20 °C and 1 atm) using a GILSON 307 HPLC pump, to finally mix both streams and introduce it into the reactor. The tubings and connections were heated to avoid steam condensation. The reaction was carried out in a PID Microactivity Effi equipment with a space velocity of 1626.9 h^{-1} and the outlet gas was analyzed with a ThermoStar Pfeiffer Vacuum spectrometer. For the reaction of fresh and spent samples, 1.2 g of the sample initially dried at 120 °C for 1 h in N$_2$ (35 ml min^{-1}) were used. After drying, the sample was reduced in H$_2$ at 230 °C for 60 min (25 ml min^{-1}). Three consecutive reaction cycles (1 h each one) were performed for the fresh sample at the two temperatures studied. Between each reaction cycle, the sample reached room temperature in a flow of reaction gas and then switched to N$_2$ for 30 min. For comparative purposes, the spent samples were subjected to a single reaction cycle.

Results and discussion

XRF

Table 1 reports the chemical composition of studied samples, indicating that the catalyst contains a high copper percentage. This is characteristic of Cu/ZnO/Al$_2$O$_3$ catalysts used in the industry [9]. Copper is the active phase, while zinc oxide and alumina act as a textural promoter and support, respectively [10]. As will be discussed later, carbon and hydrotalcite (presence of Mg) were detected by XRD, however, these elements were not identified by XRF, therefore only sulfur, copper, zinc oxide and aluminum oxide were considered. The percentage of CuO tends to decrease slightly for the spent samples. It is not ruled out that under the reaction conditions used and given the condensation of water, a portion of the copper may be present in this condensate as a hydrated oxide [11].

Table 1. Chemical composition (wt.%) of samples.

Sample	CuO	ZnO	Al$_2$O$_3$	S
Fresh	56.9	29.5	13.7	-
Cat-B	53.5	31.7	14.4	0.08
Cat-M	54.2	31.8	13.9	0.09
Cat-T	53.7	31.4	14.8	0.12

All spent samples showed presence of sulfur (S) regardless of the position of bed from which they are located. The sulfur content was high in the sample from the upper zone of the catalytic bed (Cat-T). This sulfur could have its origin in the process gas which accumulates in the upper zone as the reaction time progresses [12]. Considering that a large amount of water is necessary to favor the direct reaction of WGSR (H$_2$O/CO > 3), this water can wash the sulfur to lower zones of the catalytic bed and to cause a premature deactivation of the catalyst [12].

Nitrogen adsorption

Nitrogen adsorption measurements showed a type II isotherms [13-15] (Figure not included). The desorption curve obtained for the samples generated an H3-type hysteresis loop, characteristic of solids consisting of aggregates or agglomerates of particles forming slit shaped pores with nonuniform size and/or shape [13]. The surface area of the fresh catalyst was 64.5 m^2 g^{-1} (Table 2), in good agreement with the values reported in the literature (60-80 m^2 g^{-1}) [16,17]. However, the decrease of the surface area (82%) and the pore volume (73%) of spent samples compare to the fresh one is remarkable.

The decrease in the specific surface area (S_{BET}) could be due to a sintering process of copper in the spent samples after being subjected to different reaction cycles, producing a blockage of the alumina pores together with the loss of metallic surface area of Cu available as an active site for WGSR [5,15,18].

Table 2. Physical and textural properties of the samples.

Sample	S_{BET} $(m^2 g^{-1})$	S_{Cu} $(m^2 g^{-1})$	V_p $(ml g^{-1})$	Porous size (nm)	Metallic dispersion (%)	H_2 experimental consumption (µmol g_{cat}^{-1})
Fresh	64.5	13.4	0.20	11.4	2.08	10833 (9822)
Cat-B	12.6	1.6	0.08	21.9	0.25	10322 (9352)
Cat-M	12.2	1.4	0.07	21.3	0.22	10421 (9378)
Cat-T	11.6	0.7	0.06	19.6	0.11	10533 (9361)

Values in parenthesis correspond to the theoretical hydrogen consumption of the samples

XRD

XRD patterns of samples are illustrated in Figure 1. The fresh sample (Figure 1a) showed an amorphous structure. However, for the three spent samples, a similar and well-defined diffraction signals were observed, indicating a change in crystallinity of samples after 7 years of use. Our interpretation is based on the results and assignments made by other authors in catalysts or similar phases [9,19-21], using the same wavelength (Cu Kα) to obtain their diffractograms. The diffraction peaks at 36°, 39° and 62° 2-θ in the fresh sample can be assigned to CuO presence [9,19]. Besides, the weak signals observed at 22° and 47° 2-θ corresponds to hydrotalcite [19], however the presence of Mg by XRF was not detected. Regarding the spent samples, the signals corresponding to CuO located at the same 2-θ angle values observed in the fresh sample. The signals corresponding to hydrotalcite disappear and the typical ZnO signals (32°, 37°, 43°, 46°, 56°, 63° and 67° 2-θ) were observed, with the highest intensity registered at 37° 2-θ, corresponding to the (100) crystalline plane of ZnO [19]. Despite of the low intensity, signals at 49° and 66° 2-θ can be observed, which are characteristic of γ-alumina [4,20]. The reduction treatment together with the reaction's conditions cause that some of copper oxide present in the fresh sample can be reduced to copper during operations. For this reason, the presence of signals that can be assigned to metallic copper (44 ° and 51 ° 2-θ) are reported in the spent samples [18].
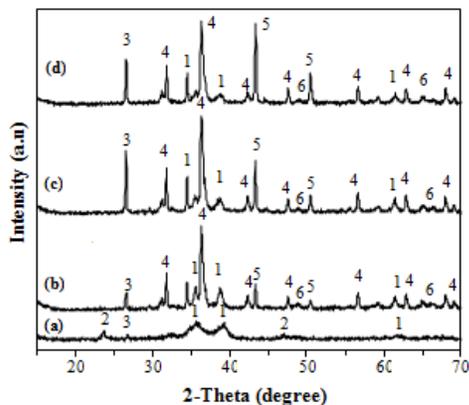

Figure 1. X-ray diffraction patterns of samples. (a) Fresh sample; (b) Cat-B; (c) Cat-M; (d) Cat-T. Diffraction signals corresponding to: (1) CuO; (2) Hidrotalcite; (3) Carbon (Graphite); (4) ZnO; (5) Cu metallic; (6) γ-Alumina.

The signals corresponding to metallic copper improve their definition and intensity as the position in the catalytic bed is higher (closer to the reactor's top), as can be seen in Figure 1 (b) to (d). In this sense, although metallic Cu has been reported the active site for WGSR, it is possible that the low activity is related to sulfur poisoning [21,22]. This aspect will be discussed in the catalytic activity section. It is noteworthy the presence of a signal at 26° 2-θ corresponding to the (002) plane of graphite-like carbon [23], weakly present in the fresh sample and changing in intensity, indicating that the reaction conditions together with the location of the catalytic bed promote the formation of crystals of this phase. XPS tests performed by Agarwal et al. [24] in $Cu/ZnO/Al_2O_3$ catalysts indicated that an increase in the temperature of steam methanol reforming reaction, causes that the signal corresponding to carbon be higher and acute due to the increase in the amount of carbonaceous deposits on the catalyst surface. This result would be indicating that the Cat-M and Cat-T samples are exposed to higher reaction temperatures than Cat-B sample.

CO chemisorption

Table 2 also reports the percentage of metallic dispersion of samples. It is observed that the metallic dispersion in the fresh sample is 2.08% and drastically decreased in the spent samples to values below 0.3%. As for the dispersion, the Cu metal surface values (S_{Cu}) maintained the same decreasing trend (Table 2). In this regard, the participation of sulfur as "poison" of Cu is not ruled out, reducing the availability of surface Cu. The evident decrease in dispersion of the spent samples could be the consequence of a sintering process of Cu particles and/or the decrease of the adsorptive capacity of active Cu sites by carbon, which would cause the loss of a large part of the samples' surface area after the catalytic reaction [15,18,25,26].

Temperature-programmed reduction (TPR)

Figure 2 illustrates the TPR profiles of the samples studied. The fresh sample showed a broad reduction profile, with a maximum at 179 °C and a shoulder at 225 °C. Cat-B and Cat-M spent samples presented a single reduction signal with a maximum located at 261 and 244 °C, respectively. For Cat-T sample, a reduction

profile with a broad reduction signal was registered, and whose deconvolution showed two maxima located at 244 and 284 °C. The reduction of pure CuO is characterized by a broad signal whose maximum is located at 342 °C, while ZnO is not reducible in the range of 25 to 600 °C [27-30]. For TPR profiles of the samples studied, especially that corresponding to the fresh sample, it is possible that the presence of ZnO promotes the reduction of copper oxide at lower temperatures than those reported for pure CuO [27]. The first reduction signal can be assigned to the simultaneous reduction of Cu^{2+} and Cu^{1+} species, while the higher temperature signal would be related to the reduction of copper species strongly interacting with alumina and ZnO [25,29]. In this sense, Turco et al. [28] studied the reducibility of $Cu/ZnO/Al_2O_3$ catalyst, registering a broad reduction signal composed by two low resolution maxima, located at the same temperature range assigned to the reduction of pure CuO. This signal can be attributed to the reduction of different Cu^{2+} structures incorporated in octahedral sites of alumina. In the case of Cat-B and Cat-M samples, a single broad reduction signal was recorded, where the phenomena before cited would be occurring. XRF results showed that the copper oxide content of these samples is around 53% and justifies the formation of a broad profile in the spent samples, which is associated with the reduction of large copper oxide particles [29].

For all samples, an experimental H_2 consumption (Table 2) is slightly higher than the theoretical (between 10-12%). Two hypothesis can be raised in this regard: 1) In addition to the complete reduction of the CuO present, the reduction of some promoter that is believed to be present in the initial composition of the catalyst (XRD results and the presence of hydrotalcite) could occur, 2) Errors in the calibration of the equipment, considering that this error (10-12%) remains constant for all the samples. The difference in the reduction profile of the Cat-T sample compared to Cat-B and Cat-M samples indicate changes in the interaction of Cu species promoted by agents such as water condensation and sulfur, conditions that are favored because of the proximity of the catalytic bed and the reactor's feed.
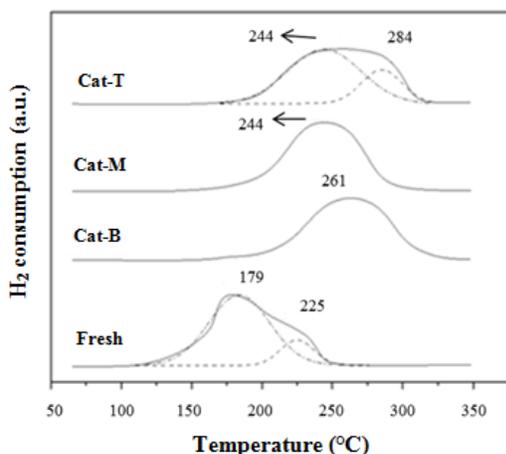

Figure 2. TPR profiles of samples. Dotted line corresponds to the signal deconvolution.

Catalytic activity

The CO conversion vs. reaction time for the fresh sample at 200 and 250 °C are reported in Figure 3. At 200 °C, this sample reached CO conversions around 80%, which increased close to 90% when the test was performed at 250 °C. On the one hand and from the thermodynamic point of view, lower temperatures favor the progress of the reaction, given the exothermic nature of the reaction, but on the other hand, an increase in temperature promotes the reaction rate and in this sense it moves towards kinetic control and allows the catalyst to do its function. This is the reason why, when the reaction was carried out at 200 °C, the conversion decreased slightly after 3 consecutive reaction cycles.

The effectiveness of $Cu/ZnO/Al_2O_3$ catalysts towards WGSR depend on the availability of surface Cu [25], and they also show good catalytic performance in a temperature range between 150-250 °C. However, after 3 reaction cycles at 250 °C, the CO conversion reaches 73%, decreasing up to 61% after 8 reaction cycles [5]. In the case of the fresh sample used in this investigation, after 3 reaction cycles the CO conversion at 250 °C was 90%, this value being higher than that reported by Guo et al. [5], indicative of the high stability of the sample. Nonetheless, the number of cycles employed may not be enough to cause a significant drop in the catalytic activity.
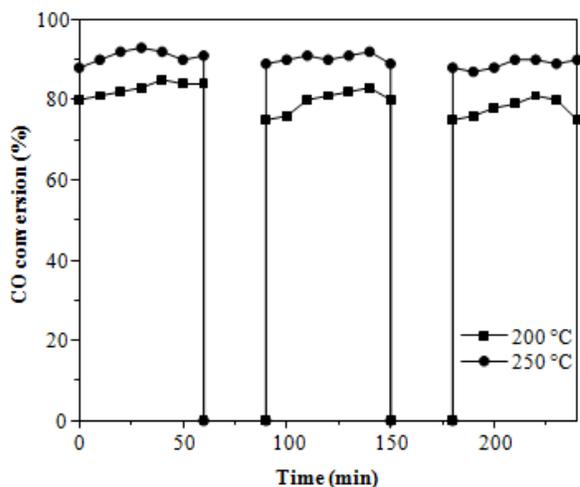

Figure 3. Catalytic activity of fresh sample evaluated during 3 consecutive reactions cycles. (■) 200 °C, (●) 250 °C.

In order to compare the catalytic performance of the spent samples, the CO conversion at 200 °C (Figure 4a) and 250 °C (Figure 4b) was evaluated. Cat-B and Cat-M samples presented a similar catalytic behavior under the two reaction temperatures studied, reaching CO conversions between 70-80%. This result, although slightly lower than that obtained for the fresh sample, is indicative

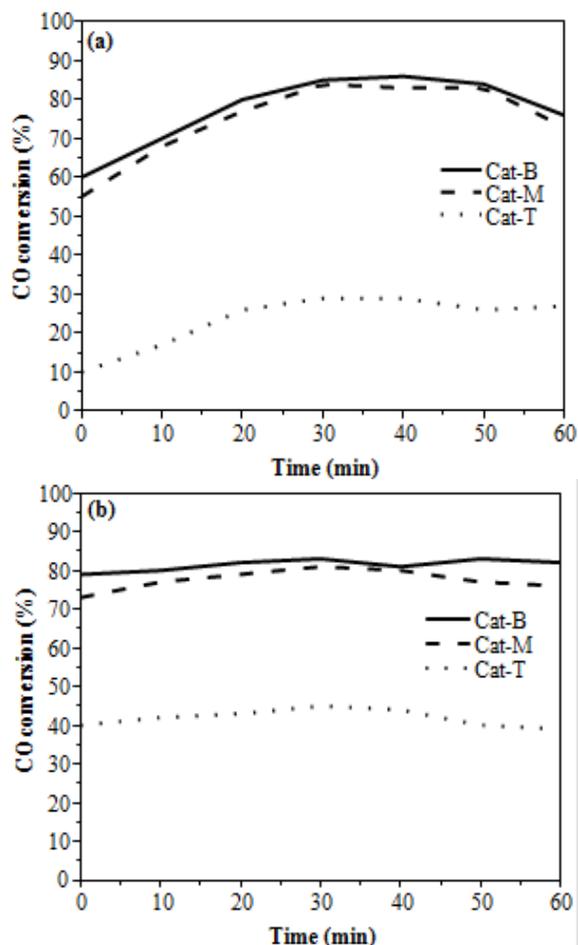that they keep a good activity even after 7 years of use.

Figure 4. Catalytic activity of spent samples. (a) 200 °C; (b) 250 °C.

In the case of Cat-T sample, it had the lowest catalytic performance (between 30-40% of CO conversion). The physicochemical characterization of the spent samples indicates that the Cat-T sample shows a higher structural difference in relation to the fresh one considering its location in the catalytic bed, which makes it more susceptible to sulfur accumulation and water condensation (observed at the industrial operation), affecting its catalytic performance compared to the other two samples [4]. In this regard, $CuO/ZnO/Al_2O_3$ catalysts have been reported to be highly sensitive to chlorine and sulfur poisoning and sintering [31]. Therefore, it is possible to establish two hypotheses to explain the decrease in activity observed for the Cat-T sample: 1) Existence of a sintering process of copper particles caused by frequent shutdowns that lead to changes in process conditions, both in the operating and startup cycles, 2) Sulfur poisoning of the catalyst [21, 22]. Regarding hypothesis 2), Cu-Zn catalysts have been reported to be highly susceptible to sulfur poisoning, indicating that if the active site for WGSR is the Cu metal surface, sulfur poisoning probably occurs by physical blockage of the surface. Considering the XRF results, it is highly likely that the decrease in activity is more related to catalyst deactivation by sulfur poisoning of the active sites rather than sintering phenomenon.

In relation to the catalytic behavior of Cat-B and Cat-M samples, and since these samples have been less affected by the aforementioned process conditions, their relative high activity could be due to the fact that the WGSR has been reported as an insensitive structure reaction [32], where its catalytic activity is independent of dispersion. In this sense, Ginés et al. [32] carried out the WGSR on Cu-Zn-Al mixed oxide catalysts and reported constant reaction frequencies (0.2-0.3 s^{-1}) when the metallic dispersion varied between 0.5-5%. However, these authors observed a decline in its activity by approximately 12% with respect to the fresh sample that may be related to the presence of sulfur.

Conclusions

Fresh and spent $CuO/ZnO/Al_2O_3$ samples were characterized and evaluated in the WGSR. The surface area, pore volume, metallic surface area and metallic dispersion of the spent samples decreased comparing to the fresh sample and the location of the sample in the catalytic bed, possibly due to a combined effect of sintering process of copper particles and/or decresase in the adsorptive capacity of copper active sites by sulfur and carbon. The presence of sulfur was registered in all spent samples, which would be affecting their catalytic performance. XRD results of spent samples reported a better-defined crystal structure than the fresh one, indicative of a change in its crystallinity when they are subjected to the reaction process. The intense carbon signal observed in XRD tests for Cat-M and Cat-T samples compared to Cat-B could be because in the first 2 catalytic beds the reaction temperature remains higher than in the last bed. TPR profiles suggested that an agglomeration of the copper oxide particles could occur because of the high copper content of the samples and the consecutive cycles of activity, promoting the displacement of the reduction signal of these oxides at higher temperatures. WGSR was favored at 250 °C for the fresh sample, registering high CO conversions (≈90%) during three successive reaction cycles. Although the spent samples showed a lower catalytic performance compare to the fresh sample submitted to three activity cycles, it was observed that they still keep a high activity (≈80%), with the exception of Cat-T sample, which was the most affected by the condensation of water during the reactor's shutdown and subsequent heating of the catalytic bed, as well as the high sulfur content, which could have caused the loss of active sites due to poisoning rather than sintering.

Acknowledgements

References

[1] Chianese S., Loipersbock J., Malits M., Rauch R., Hofbauer H., Molino A. and Musmurra D.: "Hydrogen from the high temperature water gas shift reaction with an industrial Fe/Cr catalyst using biomass gasification tar rich synthesis gas". Fuel Process. Technol., Vol. 132, (2015) 39-48.

[2] Newsome D.: "The water-gas shift reaction". Catal. Rev. Sci. Eng., Vol. 21, N° 2 (1980) 275-318.

[3] Rangel J., Marchetti G. and Rangel M.C.: "A thorium-doped catalyst for the high temperature shift reaction". Catal. Today, Vol. **77**, N° 3 (2002) 205-213.

[4] Ilinich O., Ruettinger W., Liu X. and Farrauto R.: "$Cu-Al_2O_3-Cu-Al_2O_4$ water-gas shift catalyst for hydrogen production in fuel cell applications: Mechanism of deactivation under start-stop operating conditions". J. Catal., Vol. 247, N° 1 (2007) 112-118.

[5] Guo P., Chen L., Yu G., Zhu Y., Qiao M., Xu H. and Fan K.: "Cu/ZnO-based water-gas shift catalysts in shut-down/start-up operation". Catal. Commun., Vol. 10, N° 8 (2009) 1252-1256.

[6] Shishido T., Nishimura S., Yoshinaga Y., Ebitani K., Teramura K. and Tanaka T.: "High sustainability of $Cu-Al-O_x$ catalysts against daily start-up and shut-down (DSS)-like operation in the water-gas shift reaction". Catal. Commun., Vol. 10, N° 7 (2009) 1057-1061.

[7] Micromeritics Instrument Corporation. (2009). Automated catalyst characterization system. Operator's Manual AutoChem II 2920 V4.00.

[8] Zeradine S., Bourane A. and Bianchi D.: "Comparison of the coverage of the linear CO species on Cu/Al_2O_3 measured under adsorption equilibrium conditions by using FTIR and mass spectroscopy". J. Phys. Chem. B, Vol. 105, N° 30 (2001) 7254-7257.

[9] Kowalik P., Konkol M., Antoniak K., Prochniak W. and Wiercioch P.: "The effect of the precursor ageing on properties of the $Cu/ZnO/Al_2O_3$ catalyst for low temperature water-gas shift". J. Mol. Catal. A: Chem., Vol. 392 (2014) 127-133.

[10] Forzatti P. and Lietti L.: "Catalyst Deactivation" Catal. Today, Vol. 52, N° 2-3 (1999) 165-181.

[12] Boomer E., Morris H and Argue G.: "Apparent formation of copper carbonyl". Nature, Vol. 129 (1932) 438.

[12] Brenna G.: "New catalyst for the H_2 production by water-gas shift reaction processes", Tesis doctoral, Facultad de Química Industrial de la Universidad de Bologna, 2010.

[13] Leofanti G., Padovan M., Tozzola G. and Venturelli B.: "Surface area and pore texture of catalysts". Catal. Today, Vol. 41, N° 1-3 (1998) 207-219.

[14] Kam R., Selomulya C., Amal R. and Scott J.: "The influence of La-doping on the activity and stability of Cu/ZnO catalyst for the low-temperature water–gas shift reaction". J. Catal., Vol. 273, N° 1 (2010) 73-81.

[15] Deraz N.: "Surface and catalytic properties of Cu/Zn mixed oxide catalysts". Colloid Surface A, Vol. 190, N° 3 (2001) 251-260.

[16] Nishida K., Atake L., Li D., Shishido T., Oumi Y., Sano T. and Takehira K.: "Effect of noble metal-dopping on $Cu/ZnO/Al_2O_3$ catalysts for water-gas shift reaction: Catalyst preparation by adopting "memory effect" of hydrotalcite". Appl. Catal. A: Gen., Vol. 337, N° 1 (2008) 48-57.

[17] Chen W. and Jheng J.: "Characterization of water gas shift reaction in association with carbon dioxide sequestration". J. Power Sources, Vol. 172, N° 1 (2007) 368-375.

[18] Liu X., Guo P., Xie S., Pei Y., Qiao M. and Fan K.: "Effect of Cu loading on Cu/ZnO water gas shift catalysts for shut-down/start-up operation". Int. J. Hydrogen Energ., Vol. 37, N° 8 (2012) 6381-6388.

[19] Melián-Cabrera I., López Granados M. and Fierro J.: "Reverse topotactic transformation of a Cu-Zn-Al catalyst during wet Pd impregnation: Relevance for the performance in methanol synthesis from CO_2/H_2 mixtures". J. Catal., Vol. 210, N° 2 (2002) 273-284.

[20] Nishimura S., Shishido T., Ebitani K., Teramura K. and Tanaka T.: "Novel catalytic behavior of Cu/Al_2O_3 catalyst against daily start-up and shut-down (DSS)- like operation in the water gas shift reaction". Appl. Catal. A: Gen., Vol. 387, N° 1-2 (2010) 185-194.

[21] Moulijn J., van Diepen A. and Kapteijn F.: "Catalyst deactivation: is it predictable? What to do?". Appl. Catal. A: Gen. Vol 212, N° 1-2 (2001) 3-16.

[22] Kung H.: "Deactivation of methanol synthesis catalysts - A review". Catal. Today, Vol. 11, N° 4 (1992) 443-453.

[23] Arrebola C., Caballero A., Hernán L. and Morales J.: "Graphitized carbons of variable morphology and

crystallinity: A comparative study of their performance in lithium cells". J. Electrochem Soc., Vol. 156, N° 12 (2009) A986-A992.

[24] Agarwal V., Patel S. and Pant K.: "H_2 production by steam reforming of methanol over $Cu/ZnO/Al_2O_3$ catalysts: Transient deactivation kinetics modeling". Appl. Catal. A: Gen., Vol. 279, N° 1-2 (2005) 155-164.

[25] Figueiredo R., Dantas A., Carvalho de Andrade H. and Fierro J.: "Effect of low steam/carbon ratio on water-gas shift reaction". Catal. Today, Vol. 107-108, (2005) 671-675.

[26] Marécot P., Akhachane A., Micheaud C., and Barbier J.: "Deactivation by coking of supported palladium catalysts. Effect of time and temperature". Appl. Catal. A: Gen., Vol. 169, N° 1 (1998) 189-196.

[27] Fierro G., Lo Jacono M., Inversi M., Porta P., Ciocii F. and Lavecchia R.: "Study of the reducibility of copper in CuO-ZnO catalysts by temperature-programmed reduction". Appl. Catal. A: Gen., Vol. 137, N° 2 (1996) 327-348.

[28] Turco M., Bagnasco G., Costantino U., Marmottini F., Montanari T., Ramis G. and Busca G.: "Production of hydrogen from oxidative steam reforming of methanol I. Preparation and characterization of Cu/ZnO/ Al_2O_3 catalysts from a hydrotalcite-like LDH precursor". J. Catal., Vol. 228, N° 1 (2004) 43-55.

[29] Millar G., Holm I., Uwins P. and Drennan J.: "Characterization of precursors to methanol synthesis catalysts Cu/ZnO system". J. Chem. Soc. Faraday Trans., Vol. 94, N° 4 (1998) 593-600.

[30] Semprún L., Solano R., Sánchez J., Carruyo G., Ramos M., Enao J., Atencio R., Bandosz T., Seredych M. and Moronta A.: "Remoción de H_2S utilizando una arcilla natural modificada con un surfactante e incorporando Cu, Fe y Zn en la estructura". Rev. Téc. Ing. Univ. Zulia, Vol. 34, N° 1 (2011) 66-76.

[31] Ayastuy J., Gutiérrez-Ortiz M., González-Marcos J., Aranzabal A and González-Velasco J.: "Kinetics of the low-temperature WGS reaction over a $CuO/ZnO/Al_2O_3$ catalyst". Ind. Eng. Chem. Res. Vol. 44, N° 1 (2005) 41-50.

[32] Ginés M., Amadeo N., Laborde M. and Apesteguía C.: "Activity and structure-sensitivity of the water-gas shift reaction over Cu-Zn-Al mixed oxide catalysts". Appl. Catal. A: Gen., Vol. 131, N° 2 (1995) 283-296.