Synthesis of Copper catalysts by various methods: use on the catalytic wet air oxidation of Ethyl tert-Butyl Ether (ETBE)

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Introduction

Catalytic Wet air oxidation (CWAO) of pollutants has become a promise technique to resolve a great variety of contamination problems in water. Several studies have been achieved in order to develop catalysts suitable to be applied at this technique in the last decades. Noble metals supported catalysts have revealed to be the most important to oxide a great variety of pollutants by CWAO. Nevertheless copper catalysts, normally industrial CuO/Al_2O_3 with 10 % of loading are the most effectives in this process [1]; however the grand problem of copper is the leaching of copper ions into water, for this reason the main purpose of this work is the study of several preparation methods in order to reduce the leaching problem. A series of catalysts were prepared by impregnation, impregnation using urea and sol-gel method. ETBE was selected as a model molecule due to the great problem of the presence of the gasoline oxygenates into rivers, lakes and groundwater [2], for which it is necessary to propose divers techniques of destruction.

Materials and Methods

A series of 9 catalysts were prepared by various methods (see table 1). Loading of Cu $(NO_3)_2$. 1/2 H_2O salt was used in order to obtain catalysts with 5, 10 and 15 wt% in all cases. The catalysts prepared by impregnation method were obtained using Boehmite Catapal B as a support which was impregnated with copper solutions and after calcinated at 400ºC during 4 hours. These catalysts were identified by ICuX, where X represents the copper wt%. The catalysts MCuX were prepared by impregnation method with the difference that a solution of urea was incorporated during the mixing of copper salt solution and Boehmite. The calcinations treatments were carried out at 400ºC during 4 hours too. In the case of sol-gel method used, the catalysts SCuX were obtained mixing butanol and water solution of copper. Immediately aluminum tri-secbutoxide was aggregated with reflux at 70-90ºC and mixed during 24 hours, after this time, the sol obtained was filtered and then dried at 120ºC for a period of 12 hours, thermal treatments were achieved at 400ºC in 4 hours. Characterization was done by BET areas, X ray diffraction, MET, SEM and Hydrogen TPR. Catalytic tests of wet air oxidation of ETBE (1000 ppm in water) were fulfilled using a Parr reactor at 100ºC and 10 bar of oxygen pressure for the period of 1 hour, explained previously. Samples were taken during reactions and analyzed by CPG, TOC measurements and atomic absorption in order to quantify the Cu ions concentration in the solution after reactions.

Table 1. Results of BET analysis, reaction conversion and CO_2 selectivity for the CWAO of ETBE at 100ºC and 10 bar of Oxygen Pressure

Catalyst	Prepa-ration method	Cu wt %	BET area (m^2/g)	Pore diameter (Å)	ETBE Con-version (%)	CO_2 Selecti-vity (%)	Initial rate mol/g_{cat}.s ($x10^{-4}$)	Leaching of Cu (ppm)
SCu5	Sol-gel	5	26	43	82.14	100	7.52	0
SCu10		10	449	101	88.39	100	5.55	0.002
SCu15		15	403	114	80.08	97	5.36	0.069
MCu5	Impregna-tion using urea	5	43	50	70.70	83	4.32	0.032
MCu10		10	384	82	89.35	89	8.94	0.127
MCu15		15	254	68	86.82	94	8.10	0.051
ICu5	Impregnati on	5	30	49	75.60	100	6.15	0.272
ICu10		10	370	68	66.07	100	2.68	0.306
ICu15		15	239	68	72.28	100	5.52	0.020

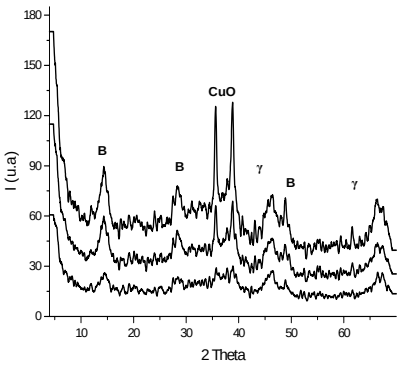

Figure 1. DRX spectrums of a) MCu5 b)MCu10, c)MCu15 catalysts prepared by impregnation method using urea.

Results and Discussion

The biggest BET areas obtained (see table 1) were obtained by sol-gel in the case of SCu10 and SCu15 catalysts. Remarkably it can be seen that the lowest areas were obtained when 5 % of copper was aggregated with values porous diameter comprises between 43-50 Å and between 68-114 Å for the other percentages (10 and 15 wt%). DRX spectrums (see figure 1) show the peaks corresponding to the γ-Al_2O_3, Boehmite and Copper to the catalysts prepared by impregnation using urea. The temperature of calcinations applied did not permit the complete transformation of Boehmite into alumina which is completely transformed at 500ºC. CWAO of ETBE was advantageously achieved in all cases with a good selectivity to CO_2, demonstrating one more time that the copper catalysts are the best to this process. However, only one catalyst did not permit the leaching of copper ions in the reaction

milieu, explained by the fact that ions copper were immovable into aluminum array because of the preparation method. It is important to highlight that in the case of the sol gel catalysts DRX spectrums showed the aluminates copper phase formation which are also active in this case. The greatest initial activities were obtained using SCu5, MCu10 and MCu15 owing to the good particle dispersion improved by the urea presence, observed by TEM and TPR analyses and viewed already with Au catalysts [3] and related with the good activity showed [4]. In conclusion, copper catalysts are one of the best catalysts to be used in the CWAO of pollutants like gasoline oxygenates and represent an alternative method to destroy this compounds noxious waste.

Significance

This work has a fundamental significance by reason of the basic studies are necessaries in order to develop cheap catalysts with high activity and selectivity to CO_2 for the CWAO process, as it is the case of this study.

References

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