

Modification of Surface and Catalytic Properties of Cu nanostructure Catalysts used in Methanol Synthesis and Steam Reforming



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Abstract

A series of CuO/ZnO/Al₂O₃ nanocrystalline solid catalysts were prepared by thermal treatment of catalyst precursors prepared via coprecipitation method at constant temperature. The effect of the change in pH, chemical composition and thermal treatment for all the prepared solids on the physicochemical, surface and catalytic properties was investigated. The crystal structure of the different prepared solids was studied using XRD analysis. The crystallite size calculated from XRD patterns using Scherer equation did not altered effectively by changing the pH of the prepared catalyst precursors. The surface characteristics of various calcined adsorbents were investigated using nitrogen adsorption at 77K and their catalytic activities were determined using water gas shift reaction (WGS) at temperature ranged between 403 and 573 K. Only CuO and ZnO were identified for the solids calcined at 623K. The catalyst with Cu/Zn =1 and prepared at pH=7 showed the smallest crystallite size (20 nm) and biggest surface area (SBET= 98m²/g). During the catalytic test relatively high conversion of CO into CO₂ at a temperature =423K was observed (96%) for the previous catalyst.

2. Experimental

Cu-ZnO-Al₂O₃ solid catalysts were prepared by coprecipitation method at a temperature of 65°C and pH values were varied between 7 and 9. The precipitate was prepared by mixing an appropriate concentrations of aqueous Na₂CO₃ solution and copper, zinc and aluminium nitrates solution under vigorous stirring. The suspension was aged for 12 h then the precipitate was filtered, washed thoroughly with deionized water till free from nitrate and sodium ions, and dried at 80°C for 16 hr. Thermal treatment was carried out in air at 400°C for 3 h. all the chemicals were of analytical grade supplied by BDH. To prepare the catalyst precursors, a unit of catalyst preparation was constructed (see the picture). A Mettler-Toledo pH –meter were used to measure the pH of the precipitate throughout the precipitation and a controlled flow rate of the solutions were achieved in order to keep the pH at constant value. The chemical compositions of the prepared solids were calculated in Cu/Zn molar ratio and Al content was fixed at 10 mol% of the total molar ratio. The nominal molar compositions were Cu/Zn=1, 2 and 3 mol/mol and the pH was 7,8 and 9. The calcined products denoted CAT-I-7, CAT-I-8, CAT-I-9, CAT-II-7, CAT-II-8, CAT-II-9, CAT-III-7, CAT-III-8 and CAT-III-9 according to Cu/Zn molar ratios and pH values.

3. Results and discussion

3.1 Thermal analysis

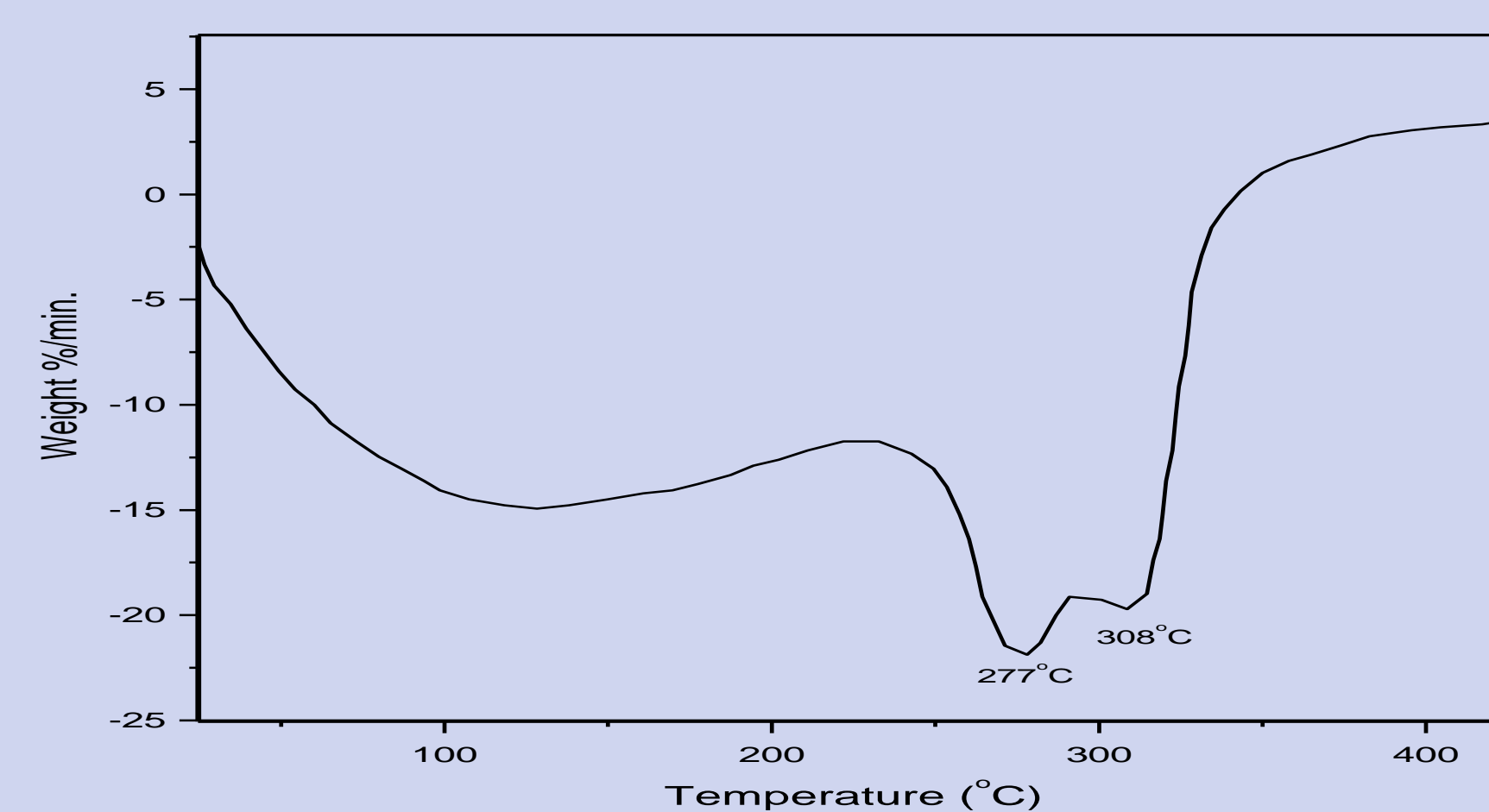


Fig.1 DTA of CAT-7-I precursor

The two simultaneous endothermic peaks are strong and represent the decomposition of the catalysts precursors into their corresponding oxides. So, the optimum calcinations temperature should not exceed 400°C to avoid the grain growth of metal oxides. The obtained results are in good agreement with literature (1,2)

3.2 XRD

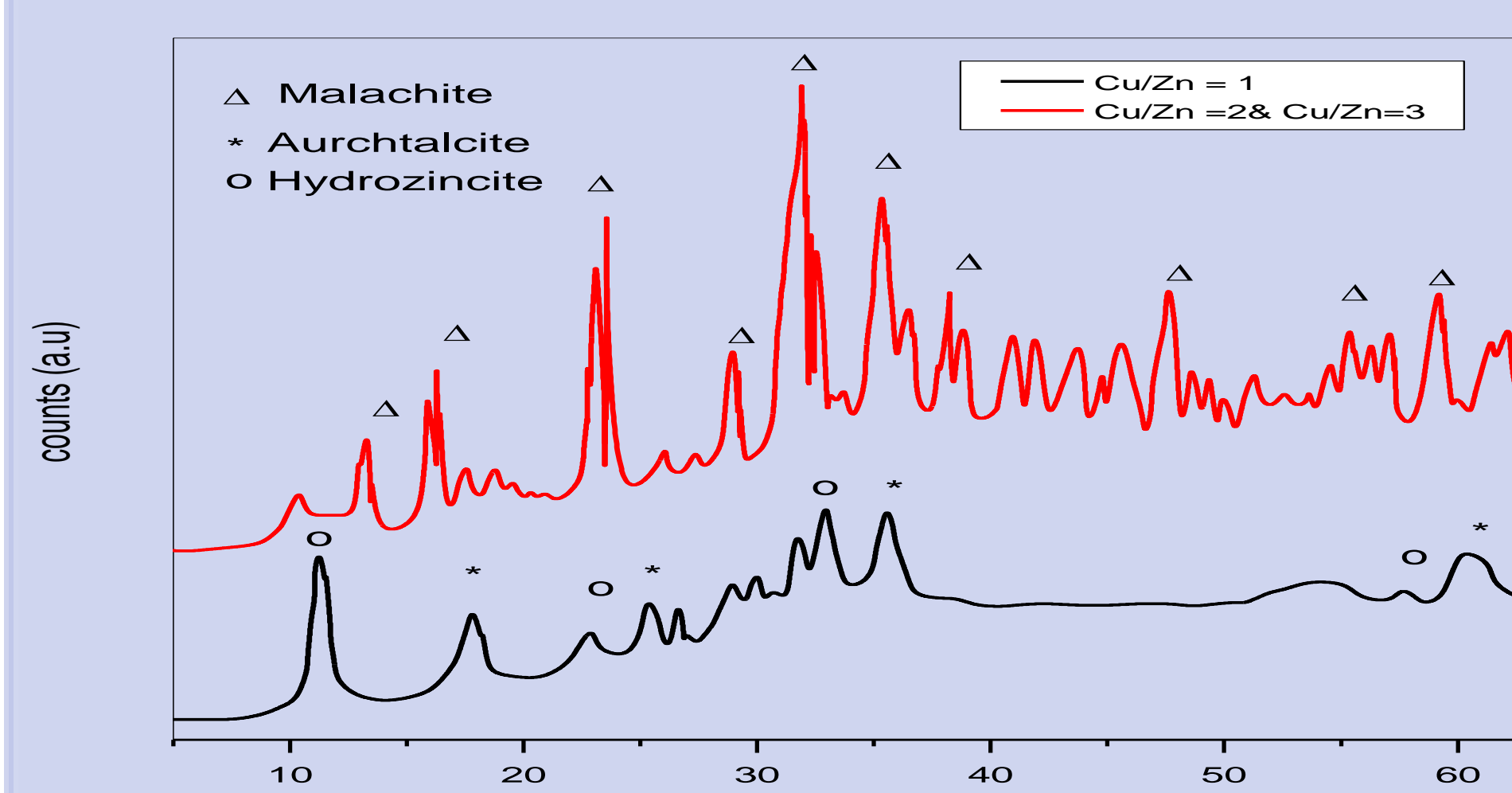


Fig. 2 X-ray diffractograms of uncalcined catalyst precursors.

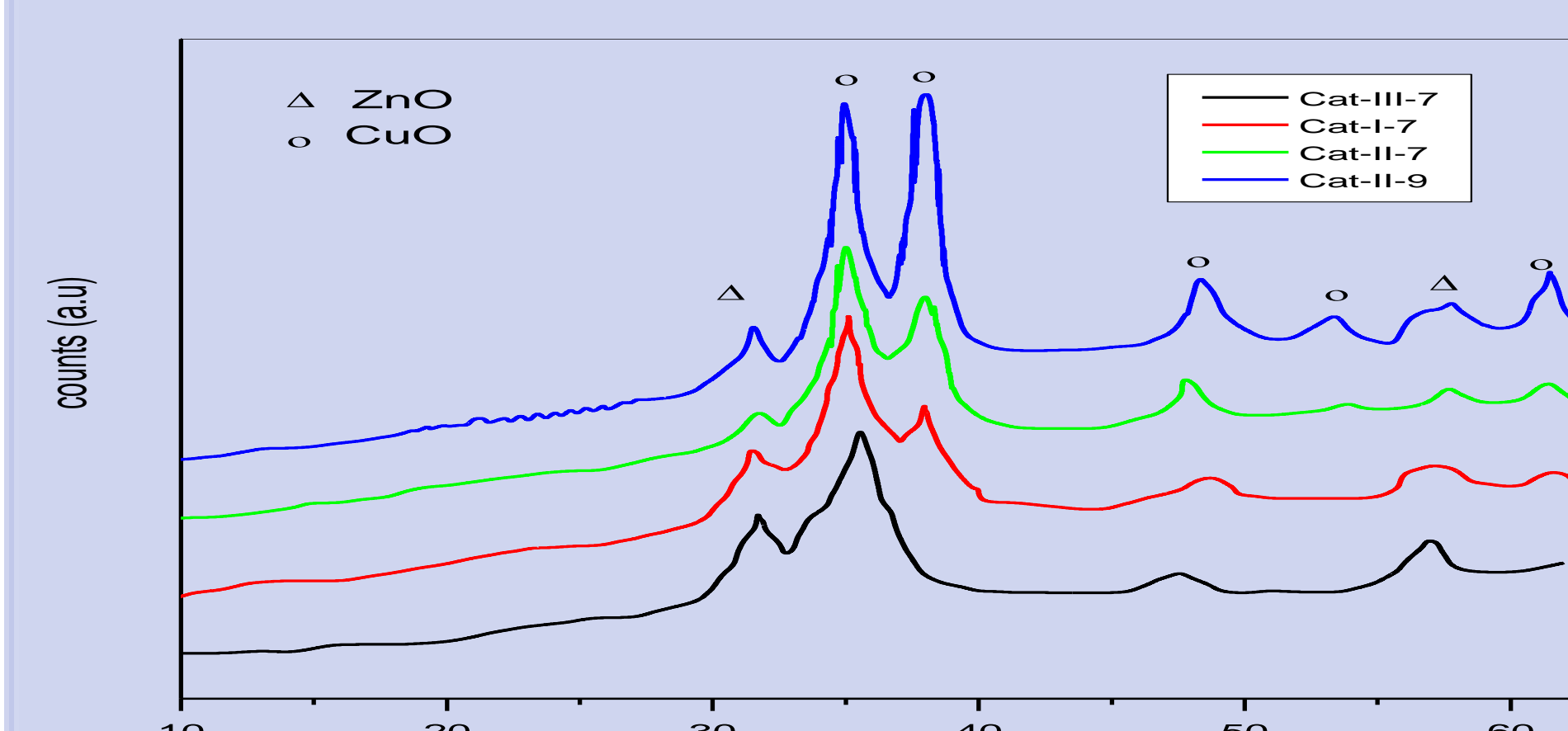


Fig. 3 X-ray diffractograms of different investigated solid catalysts

It is seen in figure 2 that, the catalysts with lower Cu/Zn ratio consisted, mainly, of a mixture of aurichtalcite and hydrozincite phases, while those with higher Cu/Zn ratio consist of malachite phase. (3,4). XRD patterns for different calcined samples are represented in Fig. 3. It is shown from this figure that, only CuO and ZnO phases were obtained. However the percentage abundance and the degree of crystallinity of CuO phase increases with the increase in Cu/Zn ratio. The crystallite size calculated using Scherer equation and the obtained results are given in Table 1 column 2. It is shown from this table that the crystallite size of various solids did not altered effectively by changing the pH of the prepared catalyst precursors. The crystallite size of CuO increases monotonically with the increase in Cu/Zn ratio and solid sample with Cu/Zn =1 has a small crystallite size value (20 nm).

Table 1 Crystallite size and texture properties of different catalysts

Catalyst formula	CuO crystallite size (nm)	S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	r (Å)
CAT-I-7	24	95	0.194	41
CAT-I-8	25	93	0.152	35
CAT-I-9	27	90	0.133	28
CAT-II-7	34	80	0.154	25
CAT-II-8	33	82	0.160	26
CAT-II-9	36	78	0.148	24
CAT-III-7	20	98	0.213	45
CAT-III-8	22	90	0.133	28
CAT-III-9	26	84	0.159	26

3.3 Catalytic activity of various solids towards water- gas shift reaction (WGS)

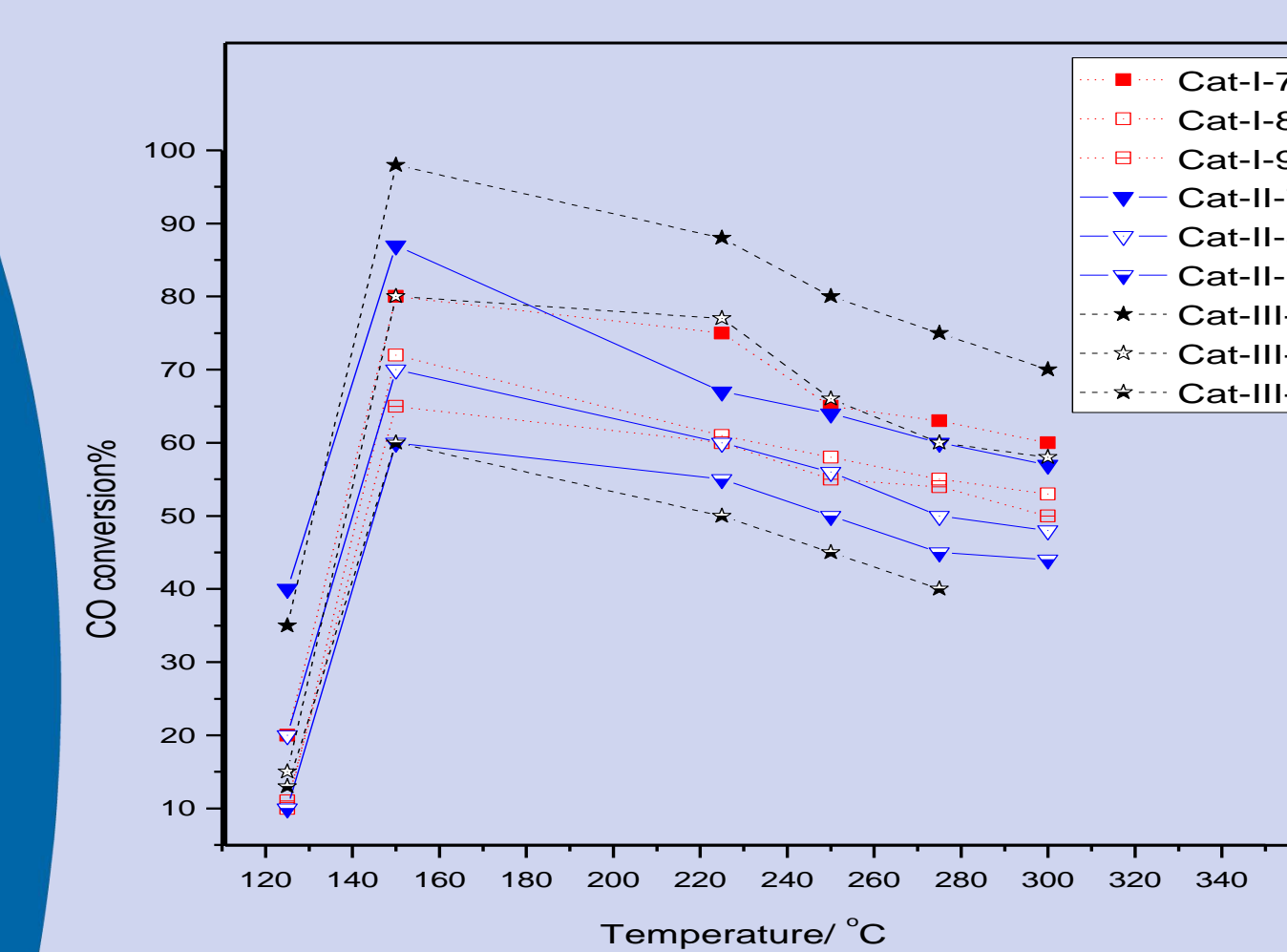


Fig. 4 Temperature dependence on the catalytic activity of various investigated catalysts

Fig.5 represents the durability (life time) of the most active catalyst. It is observed that the catalyst under investigation deactivates exponentially with time in the first hours until it reached a constant rate after 16 hours.

Reduction of catalyst solids was carried out with 3% H₂ in He temperature ramped from 140 to 240°C at 20°C/h, after which the diluted hydrogen stream was replaced by pure H₂. After cooling to 60°C in pure He, the flow was switched to the reaction mixture. The standard composition of the reaction gas was 37.5% H₂, 1.25 % CO, 25% H₂O, 12.5 % CO₂ and He (balance).

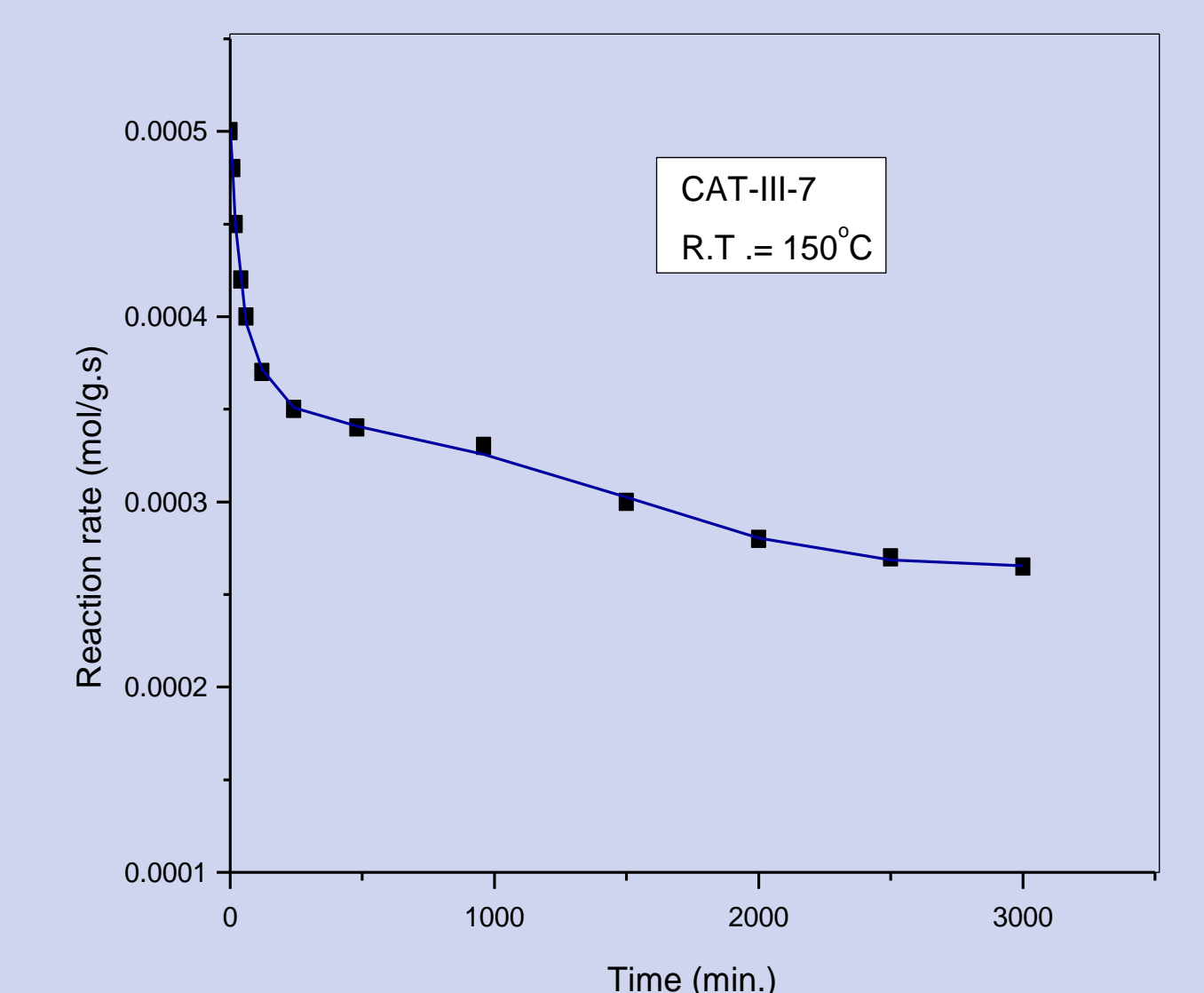


Fig. 5 The time dependence of the reaction rates of the CAT-III-7

4. Conclusions

Nanocrystalline CuO/ZnO/Al₂O₃ catalysts were obtained after calcinations of their hydroxyl carbonate precursors at 400°C. The catalyst with lower Cu/Zn molar ratio and prepared at pH =7 has the smallest crystallite size (20nm). The decrease in the crystallite size was accompanied by an effective increase in the texture properties of the solid catalyst. The results obtained from performing WGS, shows that CAT-III-7 that involves a small crystallite size as well as large surface area and biggest v_p and r- values displays a considerably higher activity. This confirms that the presence of the Cu crystallites in a well dispersed form due to its lower content but concentrated more at the surface of the catalyst precursor.

5. References

- Saito, M. and Murata, V. (2004) 'Development of high performance Cu/ZnO-based catalysts for methanol synthesis and the water-gas shift reaction', *Catalysis Surveys from Asia*, Vol. 8, No. 4, p 285.
- Shishido, T., Yamamoto, Y., Moriok, H., Takaki, K., Takehira, K. (2004) 'Active Cu/ZnO and Cu/ZnO/Al₂O₃ catalysts prepared by homogeneous precipitation method in steam reforming of methanol', *Applied Catalysis A: General*, Vol. 263, No. 2, p 249.
- Yang, R, Fu, Y, Zhang, Yi, Tsubaki, N. (2004) 'In situ DRIFT study of low-temperature methanol synthesis mechanism on Cu/ZnO catalysts from CO₂-containing syngas using ethanol promoter', *Journal of Catalysis*, Vol. 228, No.1, p 23.
- Nowicki, L. (2005) 'kinetics of CO hydrogenation on modified Cu/ZnO catalyst in a slurry reactor', *Chemical Engineering and Processing*, Vol. 44, No. 3, p 383.