Preparation and physicochemical characterization of thermally stable nano-sized hopcalite catalysts

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Abstract

Hopcalite catalyst precursors were prepared by coprecipitation under constant pH and temperature. The thermal behavior of catalyst precursor was investigated using TG and DTA. The crystal structure and solid-solid interactions were studied using powder X-ray diffraction (PXRD). The particle sizes of the prepared solids were computed using Scherer equation. The surface area of the prepared catalysts using adsorption of nitrogen at 77 K and the catalytic activity towards CO oxidation by O2 were investigated. The computed values for the crystallite size of Cu1.5Mn1.5O_4 phase ranged between 52 and 80nm for all solid samples. The produced Cu1.5Mn1.5O4 phase remained as a nanocrystalline solid even by heating at 950°C. The kinetics of thermal decomposition of catalyst precursors suggest a mechanism for the solid-solid interaction between these oxides and clarify the formation of nanosized hopcalite spinel. The activation energy data derived from thermal kinetics revealed that the best chemical composition of the hopcalite system which shows a large surface area and higher catalytic activity is that with Cu/Mn =3.

2. Experimental

2.1 Materials

All studied catalyst samples were prepared by a coprecipitation method vigorous stirring using a molar solution of copper and manganese nitrate salts (Cu(NO3)2.3H2O and Mn(NO3)2.4H2O) and sodium carbonate as a precipitating agent at constant temperature (60˚C) and controlled pH(8). The precipitates were aged for 12 h then washed by distilled water until the absence sodium and nitrate ions in the filtrates. After that all the precipitates were dried at 110 ˚C for 12 h then calcined in air for 3 h at different calcination temperatures (350, 450, 550, 750 and 950˚C).The nominal mol ar compositions of the prepared solids are in Cu/Mn (mol/mol), whereas the ratios of Cu/Mn were 1/1, 1/2, 1/3, 2/1and 3/1 for the catalysts formulae, CuMn-I, CuMn-II, CuMn-III, CuMn-IV and CuMn- V, respectively.

3. Results and Discussion

Table 1 Crystalline phases, Crystallite size of $Cu_{1.5}Mn_{1.5}O_4$ phase, S_{BET} and activation energy calculated from thermal kinetic data 1

Catalyst Symbol	Crystalline phase	Crystallite size (nm)	S_{BET} (m^2/g)
CuMn-I-350°C	Amorphous	-	48
CuMn-I-450°C	Amorphous	-	38
CuMn-I-550°C	$Cu_{1.5}Mn_{1.5}O_4$/ Mn_2O_3	62	23
CuMn-I-750°C	$Cu_{1.5}Mn_{1.5}O_4$	73	12
CuMn-I-950°C	$Cu_{1.5}Mn_{1.5}O_4$	68	3
CuMn-II-350°C	Amorphous	-	46
CuMn-II-450°C	Amorphous	-	34
CuMn-II-550°C	$Cu_{1.5}Mn_{1.5}O_4$/ Mn_2O_3	80	20
CuMn-II-750°C	$Cu_{1.5}Mn_{1.5}O_4$/ Mn_2O_3	96	10
CuMn-II-950°C	$Cu_{1.5}Mn_{1.5}O_4$/ Mn_2O_3	82	3
CuMn-III-350°C	Amorphous	-	38
CuMn-III-450°C	Amorphous	-	30
CuMn-III-550°C	Mn_2O_3/ $Cu_{1.5}Mn_{1.5}O_4$	60	15
CuMn-III-750°C	Mn_2O_3/ $Cu_{1.5}Mn_{1.5}O_4$	68	9
CuMn-III-950°C	Mn_2O_3/ $Cu_{1.5}Mn_{1.5}O_4$	61	2
CuMn-IV-350°C	Amorphous	-	79
CuMn-IV-450°C	Amorphous	-	55
CuMn-IV-550°C	$Cu_{1.5}Mn_{1.5}O_4$/ Mn_2O_3 /CuO	48	43
CuMn-IV-750°C	$Cu_{1.5}Mn_{1.5}O_4$/ Mn_2O_3 /CuO	81	15
CuMn-IV-950°C	$Cu_{1.5}Mn_{1.5}O_4$/ Mn_2O_3 /CuO	90	4
CuMn-V-350°C	Amorphous	-	81
CuMn-V-450°C	Amorphous	-	60
CuMn-V-550°C	$Cu_{1.5}Mn_{1.5}O_4$/CuO	52	49
CuMn-V-750°C	$Cu_{1.5}Mn_{1.5}O_4$/CuO/$CuMn_2O_4$	79	18
CuMn-V-950°C	$Cu_{1.5}Mn_{1.5}O_4$/CuO/$CuMn_2O_4$	86	6

3.1. Kinetics of thermal decomposition of catalyst precursors

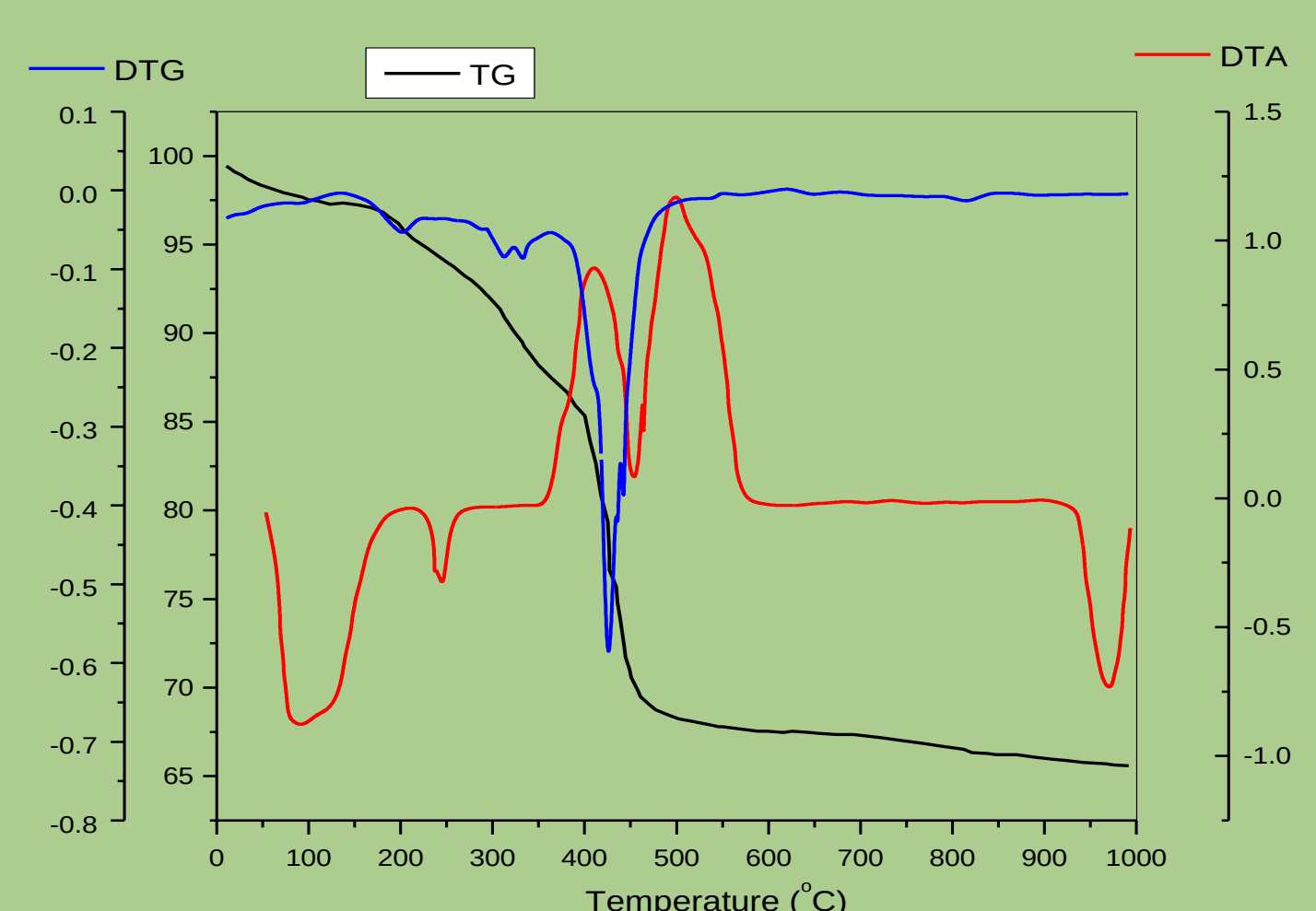

Fig. 1 TG, dTG and DTA of CuMn-III solid precursor

The thermal behavior of the prepared solids revealed that all the catalyst precursors decompose, thermally, completely in the temperature range 400-500 °C producing the corresponding metal oxides.The two peaks at 53-96 and 225-336 °C correspond to departure of water of crystallization and the decomposition of catalyst precursor into their metal oxides, respectively [1]. The activation energy E_a of different solid samples increase progressively with an increase in the copper content (33, 56 and 73 kJ $mol^{-1}$for CuMn-I, CuMn-II and CuMn-III, respectively)..The agreement between both composite and Coats-Redfern methods [2] in calculating E_a values confirm the best selection of these two methods in following up the kinetics of thermal analysis of decomposition for these systems.

3.2. X-ray investigations of various prepared solids

X-ray diffractograms of different solids calcined at 550,750 and 950°C were determined. The obtained results are illustrated in Table 1 columns 2 and 3 . It is obvious from this Table that, the solid samples calcined in air at 550°C consisted of a well crystalline $Cu_{1.5}Mn_{1.5}O_4$ phase (d spacing = 4.78, 2.92, 2.5, 2.34, 2.39, 1.69, 1.60, 1.46 Å.) and Mn_2O_3 phase (d spacing = 3.82, 2.72, 1.41 Å) [3]. CuO phase is present in CuMn-IV and CuMn-V samples, which is mainly, due to the excess molar ratio of Cu/Mn. Moreover, the formation of $Cu_{1.5}Mn_{1.5}O_4$ phase at relatively low temperature (550°C) is mainly related to the method of preparation of catalyst precursors [3]. Increase in the calcination temperature from 550 to 750°C led to the formation of $Cu_{1.5}Mn_{1.5}O_4$ phase which remained stable even by heating at 950°C. This finding may reflect the thermal stability of the spinel formed at this elevated temperature. The computed values for the crystallite size of $Cu_{1.5}Mn_{1.5}O_4$ are tabulated in Table 1. It is worth to mention that the produced Cu1.5Mn1.5O4 phase remained as a nanocrystalline solid even by heating at 950°C.

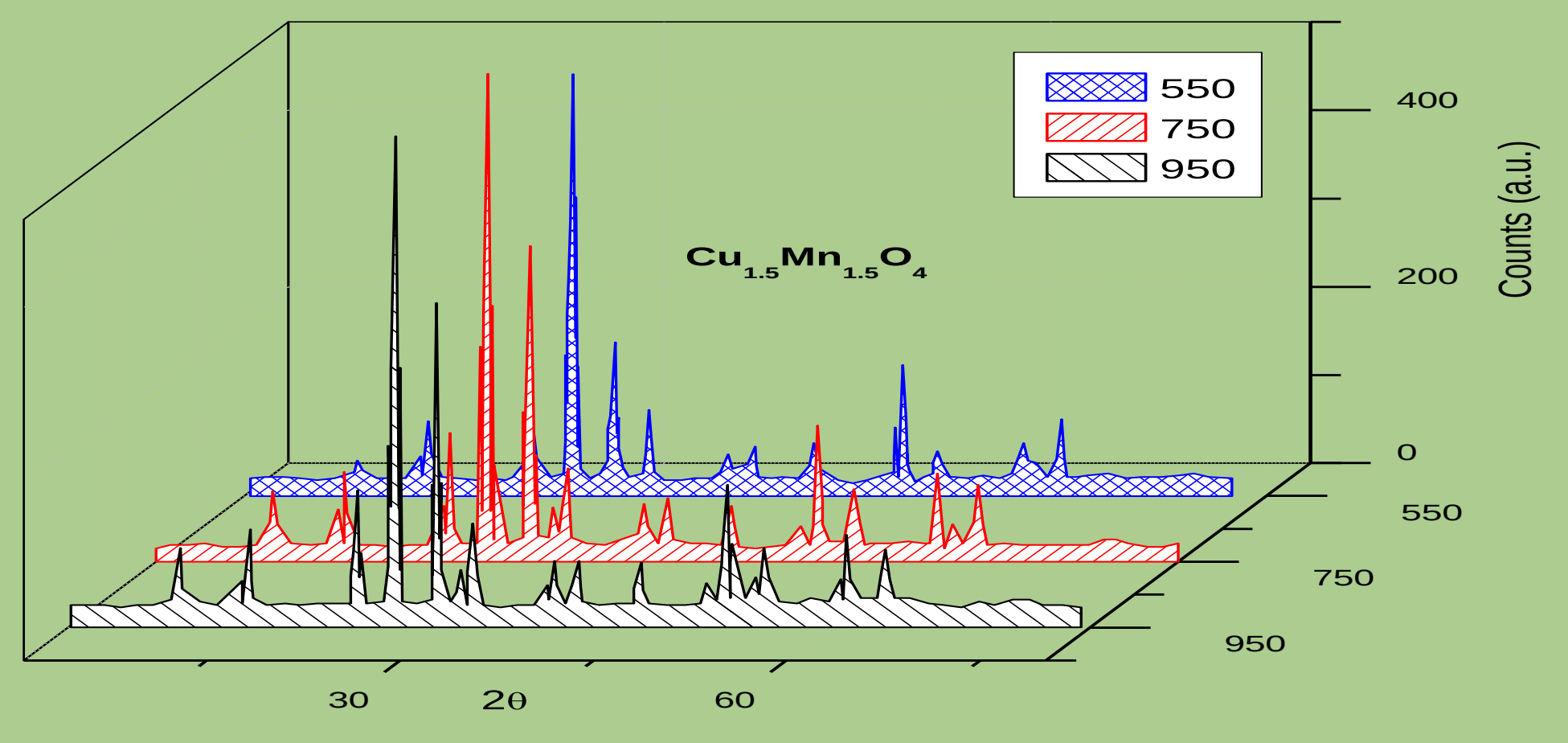

Fig. 2 XRD diffractograms of CuMn-III

3.3. Surface area measurements

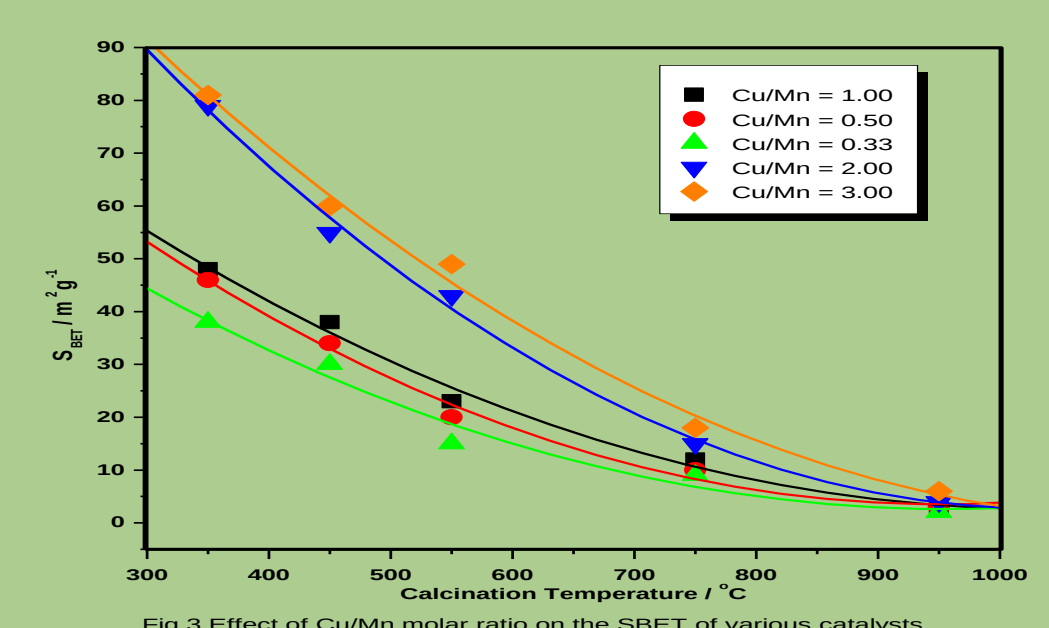

Fig.3 Effect of Cu/Mn molar ratio on the SBET of various catalysts calcined at different calcinations temperature.

3.4. CO-Oxidation at low temperature

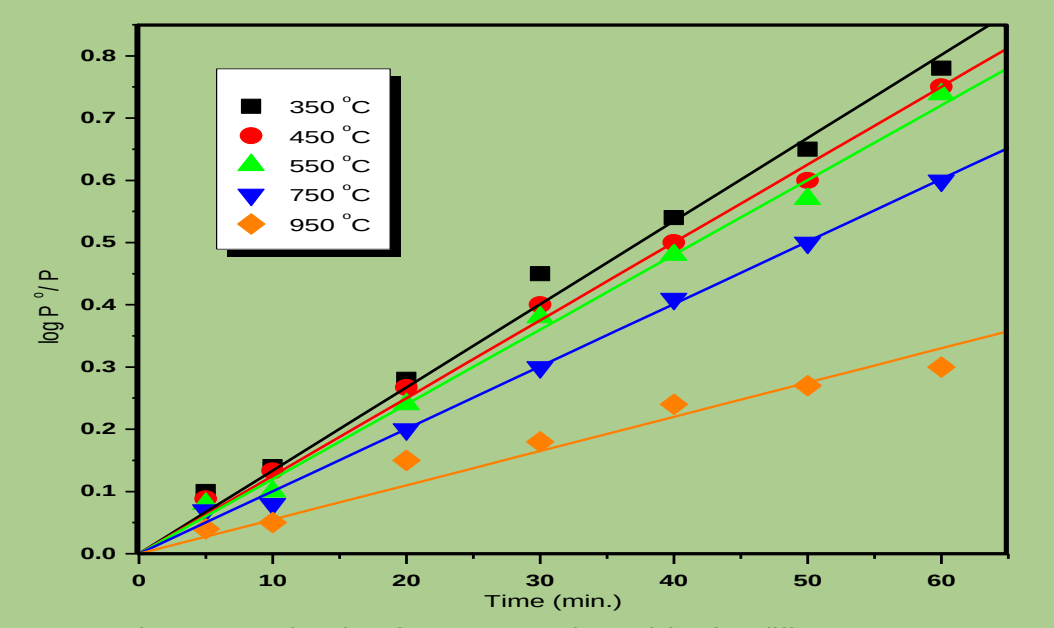

Fig. 4 1st oreder plot of CuMn-III catalyst calcined at different temperature

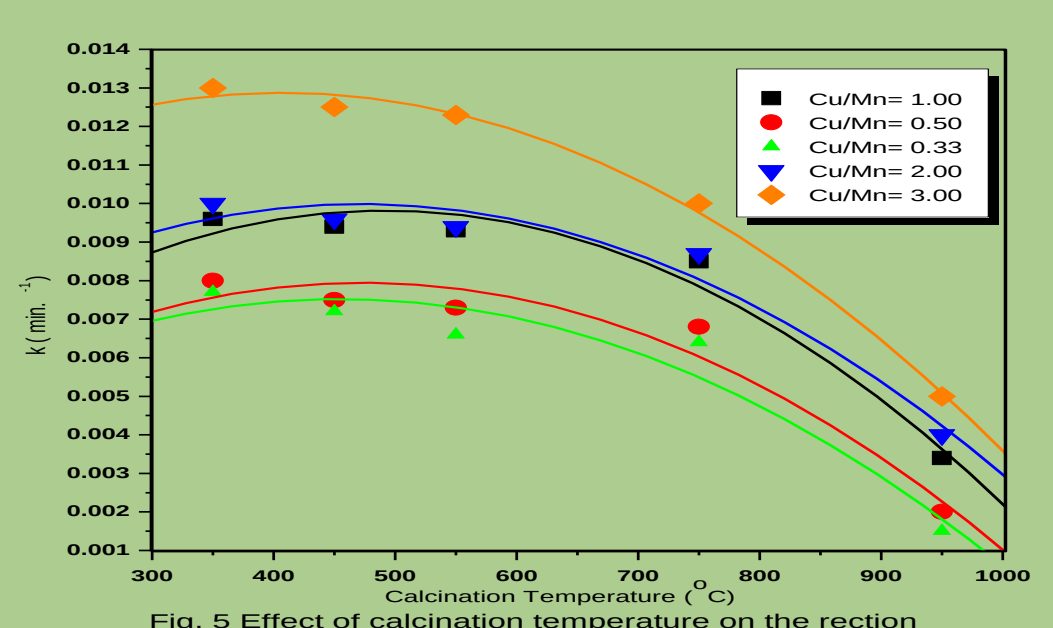

Fig. 5 Effect of calcination temperature on the rection rate constant (k).

4. Conclusions

From the kinetic studies the best methods for the determination of activation parameters are composite and coats-Redfern methods. According to these two matched methods we conclude that Cu/Mn with molar ratio ca 3/1 has the highest value of activation energy, which reflect the thermal stability of the investigated solid catalyst up to 950°C. The change in calcinations temperature from 350 up to 550°C did not much affect the catalytic activity as shown from the reaction rate constant values (k). The increase in the calcinations temperature from 750 to 950°C led to a sharp decrease in the catalytic activity and this is mainly due to the increase in the particle size of Cu1.5Mn1.5O4 crystallites. The catalyst that shows the maximum catalytic conversion of CO into CO_2 is that has Cu/Mn = 3.

5. References

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