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Evaluation of the relative acid strength of copper supported in γ-alumina by TG and DSC

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Abstract

The relative acid strength of copper was evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC) methods, using *n*-butylamine as a molecular probe. The total acidity was calculated from TG curves whereas the relative acid strength was determined from DSC curves, using the Borchardt–Daniels kinetic model. Acidity and active sites were measured by IR spectroscopy. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Alumina may act as a catalyst or as support. It has low cost, good mechanical stability, and a porous structure with high surface area and temperature stability. For many years, catalysts supported on alumina had been of considerable interest due to several technological applications.

In 1971 Knozinger [1] represented alumina surface in a thermal dehydroxylation/hydroxylation process where Lewis acid sites are unsaturated Al and the Brønsted sites the "negative" oxygens.

The acid–base properties of the metal oxide supports (like γ-alumina) can have a significant effect on the product selectivity exhibited by a heterogeneous catalyst. There has been much work carried out in order to understand the structure of the alumina surface and the nature of the acid–base sites [2].

In the present work we have investigated the relative acid strength of copper supported on γ-alumina, with the aim of understanding the nature of surface active species.

Evaluation of the relative acid strength was performed by TG and DSC methods using *n*-butylamine as a molecular probe.

2. Experimental

The copper catalyst supported on γ-alumina (Union Carbide) was prepared by impregnation method with

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the precursor salt solution (nitrate) and was submitted to thermal treatment. Calcination took place at 723 K, for 5 h in a N_2 flow, followed by reduction under H_2 flow (100 ml min^{-1}), for 3 h at 523 K.

Structural analysis was carried out by infrared spectroscopy (4000–400 cm^{-1}), using an FT-IR MIDAC with KBr pellets.

The chemical composition of the copper catalyst (34.66%) was determined by atomic absorption spectroscopy (AAS), with a Varian (model AA-175) instrument.

The acidity of the compounds were evaluated with samples (10–50 mg) previously saturated with *n*-butylamine, using a thermobalance (Shimadzu TA-50H) to heat the sample from 303 to 1273 K under N_2 flow (50 ml min^{-1}). The total acidity was calculated from the absolute mass of *n*-butylamine desorbed from the acid sites of the catalysts, expressed in acid sites per gram.

The estimation of the relative acid strength by DSC (2010 TA Instrument) using the Borchardt–Daniels kinetic model was made by monitoring the thermal decomposition of the saturated samples at the temperature range 303–873 K, with a heating rate 10 K min^{-1}, under a N_2 flow (50 ml min^{-1}). These decompositions are exothermic and were used for the calculation of the kinetic parameters involved in the process, activation energy, reaction order and heat of reaction [3].

Table 1
FT-IR data

Cu/γ-Al_2O_3	Assignments [4]
1638	NH bending (LAS)
1497	$\delta_{ass}CH_3CH_2$ (BAS+LAS)
1600	$\delta_{ass}CH_3CH_2$ (BAS)
1385	δCH_2
1261	$\delta_{ass}CN$

Wave number (cm^{-1}).

3. Results and discussion

The description of the acid properties of a solid with a relatively high surface area involves the determination of the acid density, strength and nature of the sites.

The adsorption of *n*-butylamine is widely used as a molecular probe in the characterization of acid character of solid surface [4,5].

Table 1 presents FT-IR data of the Cu/γ-alumina catalyst with *n*-butylamine. The measurements showed that Cu/γ-alumina presented Lewis active sites (LASs) less pronounced than Brønsted active sites (BASs). Fig. 1 and Table 1 show the assignments and intensities of the frequencies of the Cu/γ-alumina catalyst bands. IR also presents a

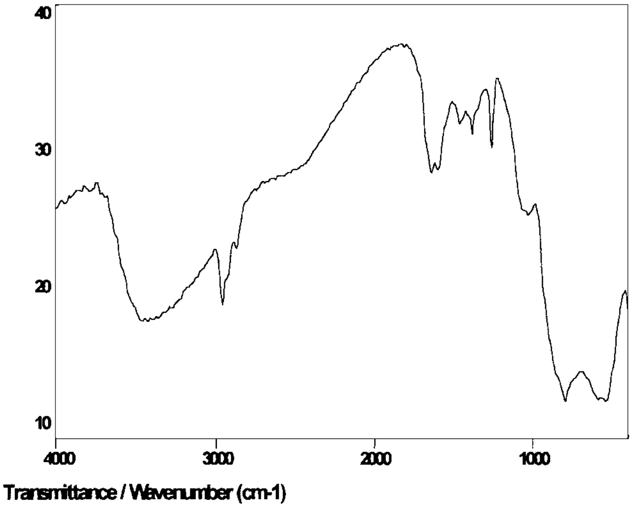

Fig. 1. IR spectra (4000–400 cm^{-1} region) in KBr pellets of the Cu/γ-Al_2O_3 catalyst.

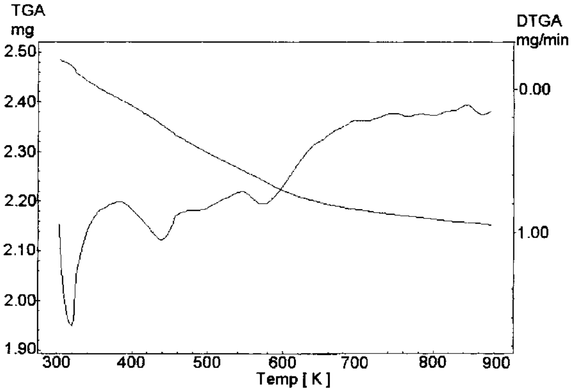

Fig. 2. TG curve of the Cu/γ-Al_2O_3 catalyst.

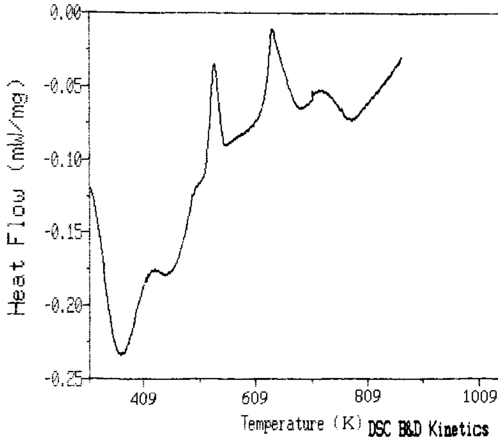

Fig. 3. DSC curve of the Cu/γ-Al_2O_3 catalyst.

characteristic water band. This water is admitted together with the amine as a result of a less perfect drying procedure.

The TG and DTG curves of the Cu/γ-alumina are shown in Fig. 2. It is possible to see clearly four peaks in the DTG curves of the catalysts corresponding to weight loss steps in the TG curve. Peak 1 represents the desorption of the water; peak 2, desorption of the *n*-butylamine from weak acid sites; peak 3, dissociation of *n*-butylamine to ammonia and butene from medium acid sites; peak 4, degradation of diamines from strong acid sites [5–7].

The acid strength kinetic parameters (Table 2) are determined by the Borchardt–Daniels kinetic model [3].

The DSC curve of catalysts showing the exotherms relative to acid site distribution is illustrated in Fig. 3. This corresponds to the desorption and thermal decomposition of *n*-butylamine in weak, medium and strong acid sites, respectively. The enthalpies are directly proportional to the acid strength in each specific temperature range.

From the application of the Borchardt–Daniels kinetic model programs, curves were plotted showing

Table 2
Total acidity and strength kinetic parameters of the Cu/γ-Al_2O_3 catalyst

	Desorption water	Acid Sites		
		Weak	Medium	Strong
TG/DTG				
Total acidity (acid sites per gram)$\times 10^{20}$	–	2.9	4.4	0.9
Temperature range (K)	303–386	386–480	480–554	554–877
DSC/Borchardt–Daniels kinetic model				
Temperature range (K)		472–550	550–689	689–778
Reaction order		6.3	3.0	6.3
Activation energy (kJ mol^{-1})		642.1	500.6	1060.2
Log Z (min^{-1})		62.7	40.6	77.2
Heat of reaction (J g^{-1})		8.7	11.3	3.7
TG/DSC				
Acid strength/(J per acid site)$\times 10^{-20}$		3.2	2.6	4.1

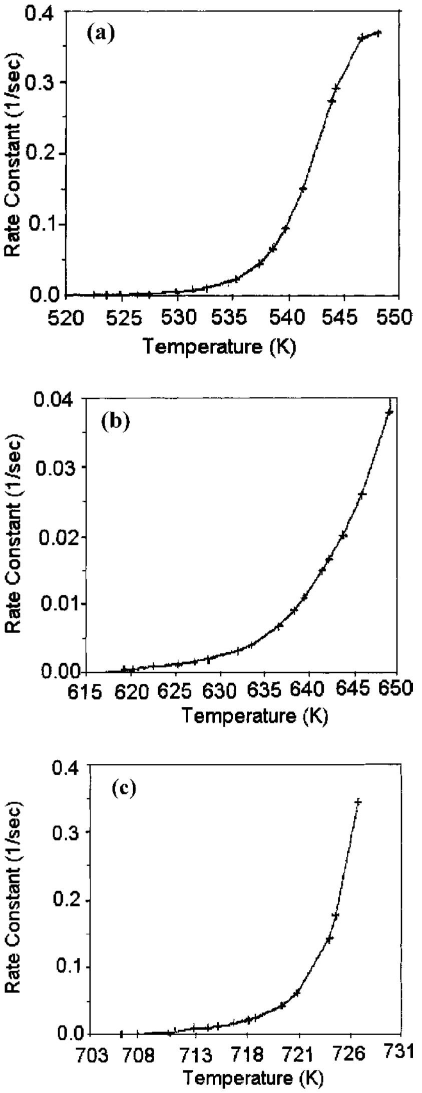

Fig. 4. Rate constant (1/s) versus temperature (1/K) for the deamination process from (a) weak, (b) medium and (c) strong acid sites in the Cu/γ-Al_2O_3 catalyst.

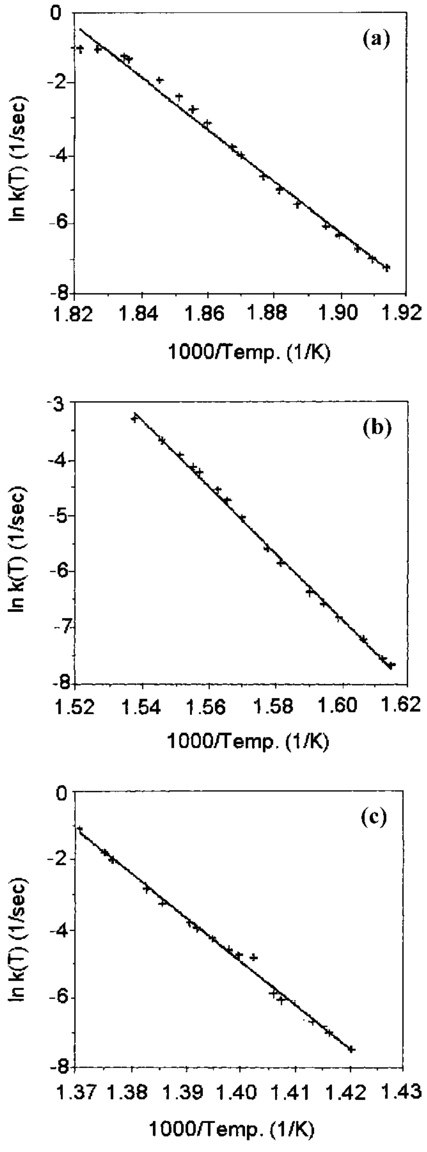

Fig. 5. Arrhenius plots used to obtain the activation energy relative to the deamination process from (a) weak, (b) medium and (c) strong acid sites in the Cu/γ-Al_2O_3 catalyst.

ln $k(T)$ as a function of the inverse of the temperature (1/K), and rate constant (1/s) as a function of the temperature (K) as seen in Figs. 4 and 5. The activation energies of the deamination processes referring to the three exothermic peaks can be obtained from the slope of the straight lines demonstrating that the Borchardt–Daniels kinetic model can be applied satisfactorily to the evaluation of the relative acid site strengths in solid acids [8].

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