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DSC CHARACTERIZATION OF ZSM-5/MgO/Al_2O_3 CATALYSTS

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The physico-chemical characterization of magnesium-modified ZSM–5 zeolite catalysts has been performed by differential scanning calorimetry. Evidence has been found of the formation of magnesium oxide and the magnesium spinel phase in alumina-bonded ZSM–5 catalysts. DSC proved a suitable technique for characterization of these systems.

In previous work [1], catalysts based on modified ZSM–5 zeolite were studied for the selective production of *p*-xylene by toluene alkylation with methanol. These materials contained magnesium oxide as a component improving the zeolite selectivity for *p*-xylene, and alumina as a binder. It was further found that the same modification resulted in a lowered deactivation rate in the conversion of methanol to olefins. It was shown that alumina was not an inert component, and the catalytic properties were influenced by the extent of chemical interaction between MgO and Al_2O_3, as revealed by the X-ray diffraction spectra. As such an interaction is presumably dependent on the method of preparation, different catalysts were prepared by the addition of MgO and Al_2O_3 to ZSM–5 zeolite by different procedures, and were analyzed by X-ray diffraction and differential scanning calorimetry to assess whether the latter is a suitable technique for characterization of the composition of these systems.

Experimental

Catalysts

The methods of preparation of the catalysts are reported in Table 1. Binding was effected by mixing the zeolite with boehmite (AlOOH) in acid solution, extruding the mixture and even drying at 383 K. The impregnation was performed by adding magnesium acetate solution to the previously degassed zeolite any drying at 383 K.

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Table 1 Methods of preparation and composition of the catalysts

Catalyst	Method of preparation	Al_2O_3, wt%	MgO, wt%
1. HZ	Furnished 1 by Assoreni (Si/Al = 17)	—	—
2. HZAl	Binding 1 with boehmite	46.0	—
3. MgZ	Impregnating 1 with magnesium acetate	—	22.0
4. MgZAl1	Impregnating 2 with magnesium acetate	40.0	13.2
5. MgZAl2	Impregnating 2 with magnesium acetate after calcination at 500°	40.0	13.2
6. MgZAl3	Binding 3 with boehmite	40.0	13.2
7. MgAl	Impregnating boehmite with magnesium acetate	75.2	24.8

All the catalysts were calcined at 800 K in flowing air overnight. Chemical compositions were checked by chemical analysis by the atomic absorption method: they are reported in Table 1 as Al_2O_3 and MgO weight percentage contents.

Reference materials

The sample of magnesium oxide was prepared by thermal decomposition of magnesium acetate at 800 K in flowing air; the sample MgAl was prepared by impregnating boehmite with magnesium acetate solution the MgO/Al_2O_3 ration was the same as in the catalyst ZSM–5/MgO/Al_2O_3 and calcining at 800 K in flowing air.

Thermal analysis was performed with a Mettler TA 3000 system operated with the following parameters: temperature range 273–773 K, heating rate 10 deg/min, sample weight 10^{-2} g. X-ray diffraction analysis was performed with a Philips diffractometer.

Results and discussion

The X-ray diffraction analysis indicated [2] that in all the catalysts investigated the crystalline structure of the zeolite was preserved after chemical modification through the introduction of magnesium. The broad signals typical of microcrystalline Al_2O_3 appeared in the bonded catalysts. Magnesium was detected as crystalline MgO in MgZ (no binder), while it appeared mainly as magnesium-aluminium mixed oxide and in smaller amount as magnesium oxide in the samples containing alumina (MgZAl1, MgZAl2 and MgZAl3), the lowest amount of MgO being detected in MgZAl2. However, this method allowed only a rough estimation of the amounts of MgO and Mg-Al mixed oxide. This was especially true for the mixed oxide, which has the same spinel structure as Al_2O_3 and exhibits signals very close to those of Al_2O_3; therefore, it has to be detected from the shifts of the broad signals of alumina (from $2\theta = 45.9°$ to $44.9°$ and from $67°$ to $65.3°$ for the strongest signals).

The DSC spectra of the catalysts displayed endothermic peaks due to the desorption of physically adsorbed water and decomposition of surface hydroxyls [3, 4]. The curves for the catalysts are shown in Fig. 2. The signals at 425 and 493 K allow distinction of the formation of magnesium oxide and of magnesium spinel, respectively.

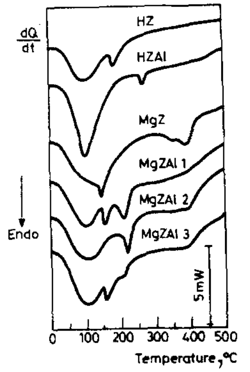

Fig. 1 DSC curves of the catalysts. (For the symbols refer to the text)

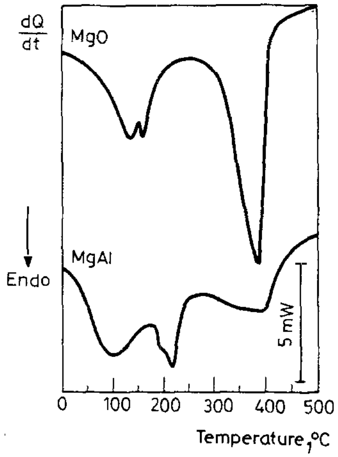

Fig. 2 DSC curves of reference materials. (For the symbols refer to the text)

A broad peak at around 373 K was present for all samples, due to the loss of physisorbed water. The maximum of the peak for magnesium-modified zeolite ranged from 360 to 403 K as it accounted for different water losses relating to different phases present in the catalyst. The same peak temperature was exhibited by the pure zeolite sample HZ and by the MgO sample.

In the curve for ZSM–5, a peak was observed at 495 K, due to the removal of hydroxyls from the surface of the zeolite. In the bonded ZSM–5 sample (HZAl), this peak did not appear, but a new one was detected at 536 K. This was attributed to the removal of surface OH^- from the alumina, in which the zeolite is embedded. In fact, the same peak was detected in the curve of boehmite calcined at 800 K, as at this temperature boehmite is transformed to γ-Al_2O_3.

Zeolite impregnated with magnesium acetate MgZ showed two endothermic effects, at 425 K and 573–673 K, which are characteristic of MgO (Fig. 2). These effects are related to water loss by surface dehydroxylation. The lower-temperature signal can be attributed to reversible water loss by dehydroxylation from adjacent surface OH^- [3]. From the area of these peaks, the MgO content can be evaluated as about 15%. This value is in good agreement with the content estimated by measuring the pore volume loss in the MgZ sample with respect to pure zeolite (HZ), which resulted in about 17% MgO [2]. The balance of magnesium contained in the catalyst should be present inside the zeolite cavities, as magnesium oxide formed on the external surface of the ZSM–5. The curve for MgZAl1 displayed signals typical of MgO (425 K) and MgAl (493 K). The broad band between 570 and 670 K resulted from overlapping signals of the two compounds. The MgO peak at 425 K was not observed for MgZAl2, indicating that MgO had completely reacted with Al_2O_3 in this sample, producing a magnesium spinel surface phase. In contrast, in MgZAl3 the reaction between MgO and Al_2O_3 was less than complete, as can be observed from the small peak of mixed oxide at 495 K.

These results showed that the phase composition of the catalysts depends on the method of preparation. When ZSM–5 bonded with boehmite is calcined and then impregnated with magnesium acetate solution (MgZAl2), magnesium is completely incorporated into the spinel. In fact, by calcination boehmite was transformed into γ-Al_2O_3, which has a spinel lattice as magnesium spinel; when Al_2O_3 is impregnated with magnesium acetate solution, Mg^{2+} ions occupy the vacant cationic sites of the Al_2O_3 without lattice modification, forming a magnesium spinel surface phase. When boehmite-bonded zeolite (not calcined) is impregnated with magnesium acetate solution, this reaction is not complete because boehmite has a different structure (MgZAl1). Formation of magnesium spinel is more hindered kinetically when MgZ (that contains ZSM–5 and MgO) is bonded with boehmite, since Mg^{2+} ions are strongly held in the stable oxide (MgZAl3). The results of the DSC investigation confirm the data obtained with the X-ray technique concerning the presence of magnesium oxide and magnesium spinel phase in the catalyst. However, magnesium spinel formation is more easily detected with DSC than with the X-ray technique.

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References

1 G. Bagnasco, R. Bianchi, P. Ciambelli and G. Russo, Proceed. XVII Congr. Inorg. Chem. (1984) 357.

2 G. Bagnasco, P. Ciambelli, P. Corbo and P. Porta, to be published.

3 F. Freund, Angew. Chem. Internat. Edit., 4 (1965) 445.

4 K. J. D. Mackenzie, Thermochim. Acta, 25 (1978) 277.

Zusammenfassung — Mg-modifizierte ZSM-5-Zeolithkatalysatoren wurden durch DSC charakterisiert. Es wurden Beweise für die Bildung von Magnesiumoxid und Magnesiumspinell in ZSM-5/Aluminiumoxid-Katalysatoren gefunden. DSC hat sich zur Characterisierung dieser Systeme als geeignet erwiesen.

Резюме — С помощью дифференциальной сканирующей калориметрии проведено измерение физико-химических характеристик цеолитных катализаторов ЗСМ-5, модифицированных магнием. В глинозем-связанных цеолитных катализаторах доказано образование окиси магния и магний-шпинельной фазы. Метод ДСК является приемлемым для характеристики таких систем.