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CHARACTERIZATION OF CINCHONIDINE DOPED MONTMORILLONITE SUPPORTED NOBLE METAL CATALYSTS BY THERMOANALYTICAL METHODS

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Abstract

The characterization of new cinchonidine doped K-10 montmorillonite supported noble metal catalysts is described. Our aim was the mapping of thermal stability of these new catalytic materials by thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermoanalysis (DTA) methods accompanied by X-ray diffraction (XRD) measurements.

The catalysts were prepared by various methods including conventional, microwave and ultrasonic treatments. They were characterized first by X-ray diffraction to verify the stability of montmorillonite crystal structure during preparation. Then, TG and DTG methods were applied to determine their stability under the experimental conditions usually applied. The main changes observed were the loss of water and the decomposition of the organic modifiers in the higher temperature region. The catalyst showed the best performance were prepared and characterized using microwaves and ultrasonic irradiation in order to get more insight to the effect of preparation methods on their stability. As a consequence, the catalysts were found to be stable and regenerable under 450–500 K, however, higher temperatures resulted in the complete destruction of the catalysts.

Keywords: DTA, DTG, immobilized cinchonidine, Pt/K-10 montmorillonite, TG, thermal stability

Introduction

The synthesis of optically pure chiral pharmaceuticals and agrochemicals has gained significant actuality and potential. Heterogeneous catalytic enantioselective hydrogenation being a tool for asymmetric synthesis has a special importance taking into account the industrial requirements [1–2]. Recently, due to environmental considerations and safety concerns there is an accelerating tendency to substitute the hazardous, waste productive homogeneous methods to heterogeneous ones. As a consequence, supported metal catalysts play an important role in industrially important chemical processes. These industrial requirements provide significant impor-

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tance for the growing efforts concerning catalyst preparation [3–5] and the design of new catalysts of crucial importance in enantioselective heterogeneous catalysis.

Clays are useful materials as catalyst support, especially for immobilization of organic modifiers on their surface [6]. One of the most promising candidates for this purpose is the commercially available K-10 montmorillonite [7, 8]. Its properties can be modified by ion-exchange or intercalation [9–11]. Both processes are excellent ways to immobilize chiral modifiers on the surface or in the interlamellar space of clays. As a result, the modification of clays by organic compounds is one of the most popular research areas in clay chemistry, however, only sporadically applied for the preparation of chirally modified clays [12–14].

In the case of each catalytic transformation the stability of catalysts during the reaction is of determining role. As a results, to study the catalysts under different experimental variables, such as temperature, reactant/catalyst ratio, space velocity etc. is a necessary challenge for all catalytic chemists. According to this the clay catalysts are still extensively studied by thermoanalytical methods [15–19].

Extending our recent studies [20, 21] in the enantioselective hydrogenations, in the present paper we disclose the thermal characterization of newly prepared K-10 montmorillonite supported metal catalysts containing anchored cinchonidine (CD), which is a viable alternative in asymmetric hydrogenations.

Experimental

Materials

K-10 montmorillonite (Aldrich) used as support has been characterized by a French group [22]. Its specific surface area was found to be S_{BET}=250 $m^2 g^{-1}$. The preparation of the catalysts by conventional method was described earlier [23], while the preparation by microwave and sonochemical methods will be described elsewhere [24]. The catalysts will be abbreviated as follows: I-first the organic guest was intercalated followed by the introduction of the metal; II-first the metal then the organic guest were added; CD-cinchonidine or CD·HCl–CD hydrochloride was used.

Characterization

X-ray diffraction

The stability of clay structure and the position of cinchonidine were studied by X-ray diffractometry with a Phillips PW 1820 diffractometer (CuK_α λ=0.154 nm, PW 1830 Phillips generator with options of 50 kV and 40 mA). The basal distances were calculated by the Bragg equation using the PW 1877 automated powder diffraction program with an accuracy of ±0.01 nm.

Thermal analysis

The thermal analytical measurements were performed using a MOM Derivatograph-Q (Hungary) apparatus. The finely powdered material was placed on a plati-

num sample holder and investigated under the following conditions: 100 mg of sample, heating rate 10 deg min^{-1}, temperature range 298 to 1300 K. The measurements were carried out under nitrogen and air, respectively.

Results and discussion

For the enantioselective hydrogenation studies various K-10 montmorillonite-supported Pt, Pd and Rh catalysts were prepared. The metal loading of the catalysts was 5% in each case, while the cinchonidine concentration altered depending on the preparation method applied. The catalysts prepared and the support were subjected to X-ray diffraction (XRD). The X-ray diffraction patterns of the cinchonidine modified catalysts are shown in Fig. 1.

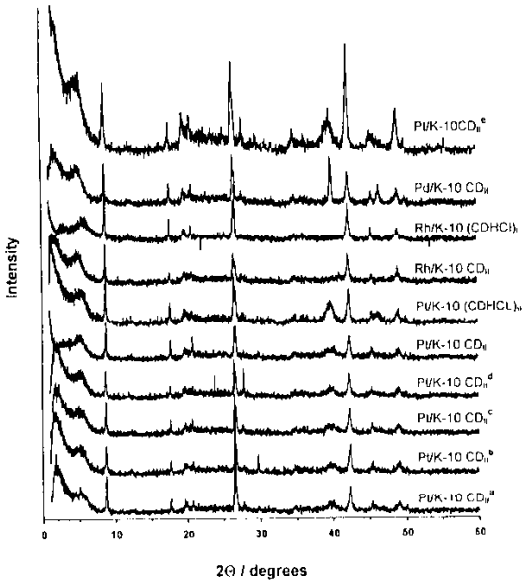

Fig. 1 X-ray diffraction patterns of K-10 montmorillonite supported metal catalysts with anchored cinchonidine prepared by stirring and (a) 10 min 12.5 W ultrasound, probe, (b) 10 min 25 W ultrasound, probe, (c) 10 min 50 W ultrasound, probe, (d) 10 min 30 W ultrasound, bath and (e) 4×15s 400 W microwave heating

Using clay-supported catalysts the question of structural stability always arises. The preparation method of K-10 used in the present study includes a high temperature treatment with mineral acids [22] resulting in both ion-exchange and dealumination. As our solid state ^{29}Si NMR studies demonstrated [25] the main constituent is a quartz-like material as a result of the release of aluminium from the layers in addition to kaolinite and montmorillonite. These constituents are in agreement with the

literature data for K-10 of SüdChemie origin [22], except, that the latter sample contains much less quartz. It seems that the Aldrich sample was treated under more severe conditions which resulted in extensive dealumination and destruction of the structure with the partial loss of crystallinity. The mean basal distance of the montmorillonite sheets was found to be ~10 Å, however, a broad, small peak between the 3–6° 2Θ range indicates the intercalation of cinchonidine into the interlamellar space of the clay. The increase in basal distances of the cinchonidine doped support was found to be ~15 Å. However, the intensity of the peaks clearly shows that using various methods the amount of cinchonidine immobilized strongly altered as it was previously pointed out in the case of phenylethyl amine salts [25]. In the case of microwave and ultrasonic activations the amount of the modifier immobilized is higher then using the conventional method, in agreement with this earlier observation [25].

After the XRD characterization the catalyst samples were studied by thermoanalytical methods such as TG, DTG and DTA. Taking into account the large number of samples studied only the curves for two catalysts as representative examples are displayed (Figs 2 and 3), while the complete set of the thermoanalytical data are summarized in Tables 1 and 2.

As shown, the mass loss steps in TG and DTG curves do not depend on the gaseous environment applied. Under both conditions three main steps can be found below the 1000 K and a fourth close to 1300 K.

The first step is due to the dehydration of the specimens. This involves the removal of adsorbed water. Since the K-10 has relatively high surface area it contains large amount of water on its surface and inside the interlamellar space. The derivatographic patterns also show a mass loss at ~450–500 K which is thought to be characteristics for the thermal decomposition of cinchonidine, which is proven by a separate experiment. The third step at ~700–800 K indicates that the basic sheet-silicate structure is preserved up to this temperature. It should be noted that this temperature

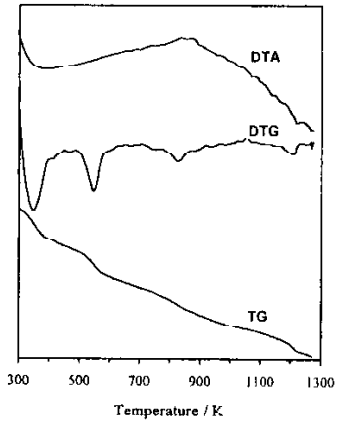

Fig. 2 TG, DTG and DTA patterns of Rh/K-10 $CDHCl_t$ catalysts recorded in inert (N_2) atmosphere

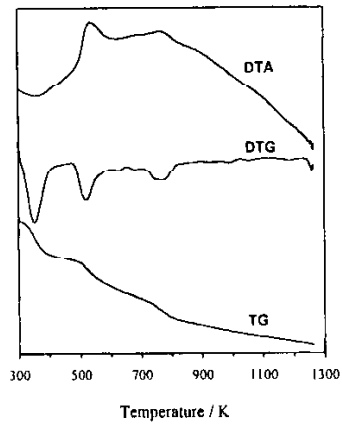

Fig. 3 TG, DTG and DTA patterns of Pt/K-10 $CDHCl_{II}$ catalysts recorded in oxidative (air) atmosphere

region is lower than that characteristic for the usual 'ideal' montmorillonites, and close to those called 'nonideal' ones [9]. It is not surprising taking into account the NMR data mentioned above with respect to the K-10 montmorillonite. As Figs 2 and 3 show smaller steps or peaks can be seen around the main mass loss steps.

Table 1 Characteristic thermoanalytical data of K-10 supported metal catalysts containing immobilized cinchonidine measured under nitrogen

Catalysts	Temperature of mass loss/K			DTA**/K
	T_1	T_2	T_3	T
Pt/K-10 CD_{II}[a]	339	631	*	783
Pt/K-10 CD_{II}[b]	340	625	*	783
Pt/K-10 CD_{II}[c]	338	624	962	807
Pt/K-10 CD_{II}[d]	335	*	*	*
Pt/K-10 CD_{II}[e]	338	625	970	798
Pt/K-10 CD_{II}	329	625	842	773
Pt/K-10 $(CDHCl)_{II}$	335	605	835	770
Pd/K-10 CD_{II}	337	603	835	776
Rh/K-10 CD_{II}	336	610	*	794
Rh/K-10 $(CDHCl)_I$	344	544	825	848

* Cannot be detected

** Temperature of exotermic heat effect; (a) 10 min 12.5 W ultrasound, probe, (b) 10 min 25 W ultrasound, probe, (c) 10 min 50 W ultrasound, probe, (d) 10 min 30 W ultrasound, bath and (e) 4×15 s 400 W microwave heating

Table 2 Characteristic thermoanalytical data of K-10 supported metal catalysts containing immobilized cinchonidine measured under air

Catalysts	Temperature of mass loss/K			DTA*/K	
	T_1	T_2	T_3	T_1	T_2
Pt/K-10 CD_{II}[a]	348	541	779	570	773
Pt/K-10 CD_{II}[b]	348	582	780	596	748
Pt/K-10 CD_{II}[c]	348	544	782	569	763
Pt/K-10 CD_{II}[d]	351	544	782	573	753
Pt/K-10 CD_{II}[e]	347	543	784	577	758
Pt/K-10 CD_{II}	349	552	781	573	753
Pt/K-10 $(CDHCl)_{II}$	349	521	768	536	764
Pd/K-10 CD_{II}	350	613	814	628	835
Rh/K-10 CD_{II}	351	665	777	675	773
Rh/K-10 $(CDHCl)_I$	357	665	797	673	782

* Temperature of exotermic heat effect; (a) 10 min 12.5 W ultrasound, probe, (b) 10 min 25 W ultrasound, probe, (c) 10 min 50 W ultrasound, probe, (d) 10 min 30 W ultrasound, bath and (e) 4×15 s 400 W microwave heating

Similar features can be seen on DTA patterns. There is a difference, however, between patterns recorded in inert and air atmosphere. While the patterns obtained under nitrogen are smooth except for a broad peak found at 700–800 K, the measurements under air resulted in an additional relatively sharp peak at 450–500 K. A comparison with TG, DTG patterns shows that the first peak at 400–500 K is characteristic for the oxidative removal of the immobilized organic modifier, while the second one is thought to be characteristic for the complete dehydroxylation and collapse of the clay structure, in agreement with the data described for 'nonideal' montmorillonites [9].

Conclusions

The XRD and thermal analytical characterization (TG, DTG, DTA) of new K-10 montmorillonite-supported metal catalysts containing immobilized chiral modifier were described. Each catalyst contains more or less cinchonidine inside the interlamellar space, which is the weakest point with respect to their thermal stability. The thermoanalytical features of the catalysts did not depend on the microwave or ultrasonic irradiation applied during preparation. Each catalyst were found to be stable and recyclable below 500 K. First, close to 383 K the adsorbed water content removed. Then the thermal decomposition of cinchonidine immobilized started at 450–500 K in inert gas, while it was oxidatively removed at the same temperature in air. In conclusion the catalyst samples were found to be stable in the usual range of organic reactions, consequently their thermal stability is a supporting factor in their application.

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References

1 J. A. Rabo, in (I. Guczi, F. Solymosi, P. Tétényi, Eds.) Proc. 10th Int. Congr. Catal., Akadémiai Kiadó, Budapest 1993, p. 1.
2 G. Jannes and V. Dubois (Eds.), Chiral Reactions in Heterogeneous Catalysis, Plenum Press, New York, London 1995.
3 H. Heinemann, Stud. Surf. Sci. Catal., 101/A (1996) 69.
4 B. Delmon and J. T. Yates (Eds.), Preparation of Catalysts I-VI, Stud. Surf. Sci. Catal., Vol. 1, 3, 16, 31, 63, 91 (1975–94).
5 Y. Iwasawa (Ed.), Tailored Metal Catalysts, D. Riedel, Dordrecht 1986.
6 E. Nemecz, Clay Minerals, Akadémiai Kiadó, Budapest 1981.
7 M. Balogh and P. László, Organic Chemistry Using Clays, Springer-Verlag, Berlin, Heidelberg 1993.
8 T. Cseri, S. Békássy, F. Figueras, E. Cseke, L. C Menoyral and R. Dutatre, Appl. Catal. A, 132 (1995) 141.
9 B. K. G. Theng, The Chemistry of Clay-Organic Reactions, Halsted Press (a Wiley division), New York 1974.
10 T. J. Pinnavaia, Science, 220 (1983) 365.
11 P. László, Science, 235 (1987) 1473.
12 T. J. Pinnavaia, ACS Symp. Ser., 192 (1982) 241.
13 M. Mazzei, W. Marconi and M. Riocci, J. Mol. Catal., 9 (1980) 381.
14 S. Shimazu, K. Ro, T. Sento, N. Ichikuni and T. Uematsu, J. Mol. Catal., 107 (1996) 297.
15 R. Carleer, G. Reggers, M. Ruysen and J. Mullens, Thermochim. Acta, 323 (1998) 169.
16 M. R. S. Kou, S. Mendioroz and M. I. Guijarro, Thermochim. Acta, 323 (1998) 145.
17 L. Pöppl, E. Tóth, M. Tóth, I. Paszli, V. Izvekov and M. Gábor, J. Therm. Anal. Cal., 53 (1998) 585.
18 V. Balek, Z. Malek and E. Klosova, J. Therm. Anal. Cal., 53 (1998) 625.
19 I. C. Chisem, S. D. Cosgrove and W. Jones, J. Thermal Anal., 50 (1997) 757.
20 B. Török, K. Felföldi, G. Szakonyi and M. Bartók, Ultrasonics Sonochem., 4 (1997) 301.
21 B. Török, K. Felföldi, G. Szakonyi, K. Balázsik and M. Bartók, Catal. Lett., 52 (1998) 81.
22 C. Cativiela, F. Figueras, J. M. Fraile, J. I. Garcia, J. A. Mayoral, L. C. Ménorval and E. Pires, Appl. Catal. A, 101 (1993) 253.
23 K. Balázsik, B. Török, G. Szakonyi and M. Bartók, Appl. Catal. A, (in press).
24 K. Balázsik, B. Török, G. Szakonyi and M. Bartók, J. Mater. Sci. Lett, (in preparation).
25 B. Török, Gy. Szöllösi, M. Rózsa-Tarjáni and M. Bartók, Mol. Cryst. Liquid Cryst., 311 (1998) 289.