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Use of Ni/Al-MCM-41 catalysts for the exhaustive hydrodechlorination of 1,2,4-trichlorobenzene

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Several Ni/Al-MCM-41 catalysts were tested in the gas phase hydrodechlorination of 1,2,4-trichlorobenzene at atmospheric pressure. They showed high activity and selectivity towards benzene at reaction temperatures between 473 and 523 K with values of 100% conversion and 100% benzene selectivity at 523 K for all of them.

KEY WORDS: hydrodechlorination; 1,2,4-trichlorobenzene; Ni/Al-MCM-41.

1. Introduction

Chlorinated organic compounds are undesirable byproducts of petroleum refining, are highly toxic to the environment, and demand efficient hydrodechlorination processes. Catalytic hydrodechlorination seems to be more suitable, efficient and ecologically attractive than incineration for treating organochlorinated compounds for which only severe incineration conditions can prevent the formation of polychlorinated dibenzodioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs) at high temperatures. However, they cannot prevent the recombination to dioxins and furans again once the temperature of the fumes emitted is lowered [1,2].

Catalytic hydrodechlorination has been widely studied with bulk, supported and bimetallic noble-metal catalysts [3–13] and more recently with Ni catalysts [14–19]. There are many data concerning catalytic hydrodechlorination for the reaction of hydrogen with chlorobenzene [3–7,14,15], but information for the more complex polychlorinated aromatic compounds is less abundant.

In previous studies, we performed the hydrodechlorination of 1,2,4-trichlorobenzene on Ni/Al_2O_3 [18] and $Ni/NiAl_2O_4$ [19] catalysts. The ability of the spinel-supported nickel catalysts to hydrodechlorinate this polychlorinated compound to benzene was higher than the alumina-supported nickel catalysts at the same nickel content and at the same reaction conditions. From the characterization and catalytic behaviour of these supported nickel catalysts, we concluded that the hydrodechlorination of 1,2,4-trichlorobenzene could be a sensitive-structure reaction since the activity and selectivity to benzene can be related to the specific active centres of the catalysts which showed weak hydrogen interaction. This has been also associated with the presence of nickel particles with octahedral morphology [18,19].

The application of mesoporous materials MCM-41, as adsorbents, catalysts and catalytic supports, has been investigated because of their high surface area, uniformity in the pore size (between 2 and 10 nm), thermal stability and acid–base properties [20–22]. This family of materials has large channels in a hexagonal array, long-range order and surface areas above 700 m^2/g.

Our goal consists of obtaining new nickel systems, more resistant to the HCl toxicity, with the ability to catalyse the exhaustive hydrodechlorination of polychlorinated aromatic compounds. Owing to the higher surface area of these mesoporous materials than the usually used supports, the nickel nitrate precursor could be better dispersed, and after thermal decomposition could lead to small nickel particles with defined morphology and with a homogeneous distribution over the support. In this way, several Al-MCM-41 samples were prepared and studied as supports of nickel catalysts for the hydrodechlorination of 1,2,4-trichlorobenzene in the gas phase. The samples were characterized by different techniques in order to correlate the activity with the structural characteristics of the catalysts.

2. Experimental

Three Al-MCM-41 supports were synthesized by adding $C_{14}H_{29}(CH_3)_3NOH$ as a surfactant to the appropriate amounts of TMA (tetramethylammonium silicate solution), HiSil-233 and PHF alumina (whose preparation

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was patented by Cramer *et al.* [23]) in order to obtain the samples S_1 (Si/Al = 24) and S_2 (Si/Al = 75) and changing the silica source (HiSil-233 by Ludox) in the preparation of sample S_3 (Si/Al = 24). Then, the mixtures were heated in an autoclave at 383 K for 2 days. The surfactant was eliminated following the method described elsewhere [24].

These supports were impregnated with aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and calcined under air at 623 K for 20 min (catalytic precursors PS_1, PS_2, PS_3) to obtain (after reduction at 673 K for 6 h in pure hydrogen flow) a final composition of 0.21 g Ni/g support (catalysts CS_1, CS_2 and CS_3). We chose this Ni content in order to compare the catalytic activity results of the Ni/Al-MCM-41 catalysts with those obtained (for the same content of Ni) with Ni/Al_2O_3 [18] and $Ni/NiAl_2O_4$ [19] catalysts. One catalyst was also prepared with a final composition of 0.42 g Ni/g support S_3 (catalyst CS_3B) in order to see the effect of the Ni content on the structure and the activity for the hydrodechlorination reaction.

The catalysts were always handled under air-free conditions after the reduction step. They were transferred in degassed isooctane and under hydrogen atmosphere at room temperature. The isooctane surface-impregnated samples were further isolated from the air either with gold film for the SEM study or with sticky tape for XRD monitoring. A glove box was used for mounting. The catalytic activity was measured *in situ* in the reactor itself after reduction. Gas purges, positive gas pressures and Schlenk techniques were used when necessary.

Powder X-ray diffraction (XRD) patterns of the samples were obtained with a Siemens D5000 diffractometer using a nickel-filtered Cu K_α radiation. The crystalline phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS). The 2θ angles (with the relative intensities in parentheses), taken from the JCPDS files, are the following: 37.29(91), 43.30(100) and 62.91(57) for the NiO phase and 44.51(100), 51.85(42) and 76.36(21) for the Ni phase.

Adsorption–desorption isotherms have been measured at 77 K with a static volumetric instrument (Micromeritics ASAP 2000) and BET surface areas were obtained assuming a value of 0.164 nm^2 for the cross-section of the nitrogen molecule.

Temperature-programmed reduction studies (TPR) were performed in a Perkin-Elmer TGA 7 microbalance equipped with a 273–1273 K programmable temperature furnace. Each sample (30 mg) was heated in a 5 vol% H_2/Ar flow (80 cm^3/min) from 293 K to 1123 K at 5 K/min.

Scanning electron micrographs were obtained with a JEOL JSM-35C scanning microscope operating at an accelerating voltage of 35 kV, a work distance (wd) of 16 mm and a magnification value of 4500×.

Temperature-programmed desorption (TPD) was obtained with a Fisons QTMD 150 gas desorption unit equipped with a 273–1273 K programmable temperature furnace and a mass spectrometer detector. Catalyst precursors were reduced in the same conditions as those in which the catalysts were prepared. The samples were then cooled at room temperature, evacuated at low pressures (<1 Pa) and the H_2 TPD of the fresh catalysts were obtained by heating at a rate of 10 K/min up to 800 K under vacuum.

Hydrogen chemisorption was measured with a Micromeritics ASAP 2010C instrument equipped with a turbomolecular pump. Samples had been reduced previously under the same conditions as those in which the catalysts had been prepared. After reduction, the chemisorbed hydrogen was removed in a stream of 30 ml/min of He for 30 min at 683 K. The sample was subsequently cooled to 303 K in the same He stream. The chemisorbed hydrogen was analysed at 303 K. The nickel surface area was calculated assuming a stoichiometry of one hydrogen molecule per two surface nickel atoms and an atomic cross-sectional area of 6.49×10^{-20} m^2/Ni atom.

The hydrodechlorination of 1,2,4-trichlorobenzene was studied in a fixed-bed flow tubular reactor (1.1 cm internal diameter and 20 cm length) and heated in an oven equipped with a temperature control system.

The catalytic reaction was tested in the gas phase at 1 bar pressure, pure hydrogen flow of 1 ml/s, catalyst volume of 0.06 cm^3, an H_2/reactant ratio of 1500 (high H_2 flow rates were used to favour 1,2,4-trichlorobenzene transport at room temperature) and reaction temperatures between 523 and 423 K.

The catalysts did not show external diffusion limitations. The reaction products were analysed by means of an on-line gas-chromatograph HP-5890 equipped with a packed column and a flame ionization detector.

Conversions and selectivities were defined by the following equations: Conversion (%) = (mol of 1,2,4-trichlorobenzene consumed) × 100/(mol of 1,2,4-trichlorobenzene charged); Selectivity (%) = (mol of one product of reaction) × 100/(mol of 1,2,4-trichlorobenzene consumed). The conversion and selectivity values given in section 3 were measured when the “plateau” of the stationary regime was reached, after about 2 h for all catalysts. The carbon mass balance of the process was always held.

3. Results and discussion

3.1. Characterization of supports

The small angle X-ray powder diffraction pattern of the three “as synthesized” Al-MCM-41 samples showed the four peaks characteristic of these MCM-41 materials. After calcining (figure 1), sample S_3 shows a highly ordered hexagonal structure whereas samples S_1 and S_2 show a broader and less intense main peak

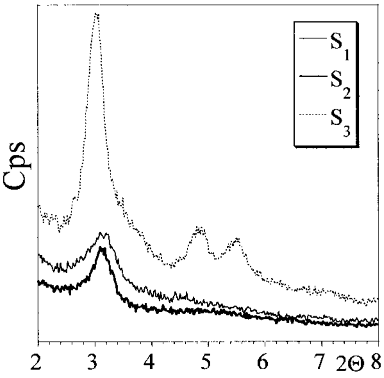

Figure 1. X-ray diffraction patterns of the "as-calcined" samples S_1, S_2 and S_3.

which represents poor crystallinity and indicates a distortion of the long-range ordering of the structure.

The three supports have very large surface areas, 1200 ± 25 m^2/g, mesopores in the range 2.8–3.1 nm and pore volumes around 0.88 ± 0.01 cm^3/g.

3.2. Characterization of the catalyst precursors

After impregnating/calcining the supports, a new NiO phase was detected by XRD. The reducibility of these catalyst precursors was estimated by TPR in order to study the level of interaction NiO–support. Figure 2 shows the TPR profile of the catalytic precursor PS_1 which is representative of the reducibility behaviour of these NiO/Al-MCM-41 samples. Leaving aside the initial drift due to losses of water, a relevant weight loss can be observed from 300 to 400 °C (with a maximum at 330 °C) which almost corresponds to the theoretical weight loss (~4.5%) and a smaller weight loss from 470 °C to 650 °C which could be due to the reduction of a small amount of NiO which is stronger interacting with the support but mainly due to the condensation of hydroxyl groups of the support.

The observation of the catalytic precursors by SEM do not reveal the presence of octahedral forms of NiO (which we observed, in previous studies [18,19], for the same content of Ni in the catalytic precursors NiO/α-Al_2O_3 and NiO/$NiAl_2O_4$) because of the high area of these supports that provide enough surface for the NiO to be more dispersed. However, we cannot reject the possibility that the octahedral particles were very small and, therefore, they cannot be observed by SEM.

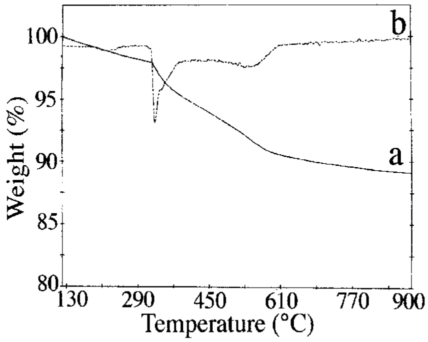

Figure 2. (a) TPR plot of the catalytic precursor PS_1; (b) derivative of plot (a).

3.3. Characterization of the catalysts

Table 1 shows several results of characterization of the catalysts. After impregnation of the supports, calcination and reduction, there is a partial collapse of the structure for all catalysts. This fact can be perfectly observed in figure 3 for catalysts CS_3 and CS_3B when comparing with the support S_3. There is a dramatic decrease of the pore volume and BET area (see table 1) values. This is mainly due to the partial pore blocking by the deposited Ni. We still find essentially uniform mesopores with a pore average diameter in the range 24–29 Å.

However, there are several facts such as the small differences observed in the values of pore volume and BET area for CS_3 and CS_3B (with the double nickel content), the higher pore volume and BET area observed for catalyst CS_2 (whose support is the most siliceous of the three), and the decrease in the reflections at lower 2θ (XRD) for the catalysts, which permit us to suggest that the modification of the support structure is mainly produced by a partial collapse of the porous texture after introducing the nickel by the impregnation to

Table 1
Characterization of catalysts

Catalysts	CS_1	CS_2	CS_3	CS_3B
Crystallographic phases (XRD)	Ni, MCM-41	Ni, MCM-41	Ni, MCM-41	Ni, MCM-41
BET areas (m^2/g)	240	835	420	404
Metallic area (m^2/gNi)	92	66	58	62
Pore volume (cm^3/g)	0.16	0.50	0.29	0.25
Pore size average (Å)	27.9	29.3	27.7	24.8
H_2 T_D (K) (TPD)[a]	466 (s)	446 (m) 548 (s)	439 (vw) 565 (s)	514 (s) 598 (s)

[a] T_D: Maxima of hydrogen desorption temperature peaks. s = strong; m = medium; vw = very weak.

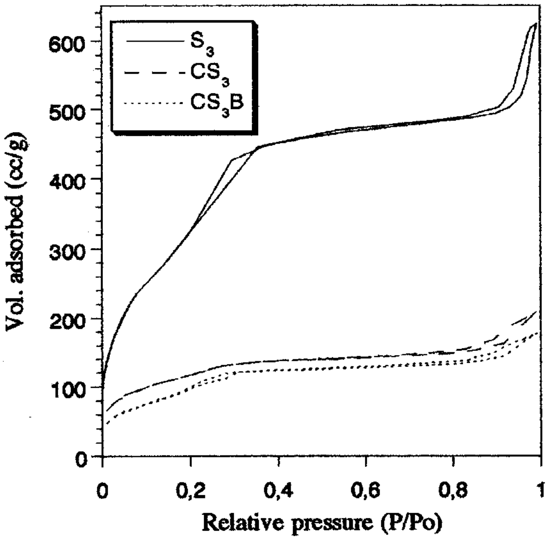

Figure 3. Adsorption–desorption nitrogen isotherms for the support S_3 and the catalysts CS_3 and CS_3B.

incipient wetness method together with a certain destruction of the support walls (more important for the less siliceous supports). This is in agreement with Liu *et al.* [25] who recently reported a similar behaviour for several Pd(Mg(Al)O)/HMS catalysts, which they also attributed to pore blocking and partial destruction of the HMS (hexagonal mesoporous silica) walls. We also think that the acid pH of the nitrate solutions used in the impregnation of the supports and later evaporation of water during calcination could contribute to the partial destruction of the pores.

The four catalysts are completely reduced under the reduction conditions used. No NiO phase was detected in any case (table 1). This is in agreement with the low level of NiO–support interaction observed by TPR. The catalysts have metallic areas between 58 and 92 m^2/g Ni (table 1), calculated from hydrogen chemisorption.

The mechanisms of adsorption–desorption of hydrogen can become extremely complex [26–31], especially over supported catalysts, because phenomena related to the interaction between the active phase and the support can interfere. The number and approximate population of the various adsorbed species depend on many factors: how the catalyst was prepared, the kind of support used and the experimental conditions of the measurement such as the weight of the sample examined, the flow rate of the carrier gas, the use of ultra-high vacuum (UHV) or the shape of the reactor system which affect conditions for removal of desorbed hydrogen.

The H_2 TPDs of the Ni/Al-MCM-41 catalysts show different desorption profiles but all of them have a large amount of hydrogen desorbed in the range 400–560 K (see table 1). Therefore, an important amount of activated hydrogen is available at the reaction temperatures used (523–423 K) for all catalysts.

Some studies correlate the binding strength of the chemisorbed hydrogen and the activity for a specific reaction [18,19,29,32]. For example, there is a quantitative correlation between the weakly bound hydrogen and the specific activity of supported-nickel catalysts for benzene hydrogenation at 323 K [32]. Another study [29] shows that toluene hydrogenation activity on nickel/alumina catalysts at 393–483 K is directly related to the amount of hydrogen desorbed at low temperatures (<450 K). In this case, the reaction rate shows a maximum at approximately 443 K and the decrease in the reaction rate above this temperature is caused by the decay of this kind of hydrogen.

In previous work [18,19], we established that the activity for the hydrodechlorination of 1,2,4-trichlorobenzene on several Ni/Al_2O_3 and $Ni/NiAl_2O_4$ catalysts is related to the amount of hydrogen available below 600 K whereas the selectivity towards benzene is mainly due to the simultaneous adsorption of the aromatic compounds and the hydrogen which takes place at lower temperatures (350–500 K). It seems clear that the different states of hydrogen could be correlated to the activity and selectivity of Ni/Al-MCM-41 catalysts.

3.4. Catalytic activity

Table 2 shows the conversions and product distributions at the "plateau" of the Ni/Al-MCM-41 catalysts in the hydrodechlorination of 1,2,4-trichlorobenzene in the gas phase. Table 2 also shows the TOF (turnover frequencies) corresponding to the conversion values <100% for all catalysts. The TOF for the catalysts were calculated from H_2 chemisorption data as the number of converted molecules of 1,2,4-trichlorobenzene per second divided by the total number of surface nickel atoms.

These catalysts show high conversions and high selectivities towards benzene in the hydrodechlorination of 1,2,4-trichlorobenzene, especially in the range 523–473 K. Regarding conversion values, the most active catalyst is CS_3B at all the reaction temperatures tested. This catalyst also shows the highest TOF values (table 2) when they can be compared at the same reaction conditions. This can be explained by the presence, for this catalyst, of two intense hydrogen desorption peaks with maxima at 514 and 598 K (table 1) which are related to its higher nickel content and to its active centres structure. These facts allow the availability of more hydrogen during the reaction.

The main reaction product was benzene at higher reaction temperatures (523–498 K) for all catalysts. Other reaction products were obtained at lower reaction temperatures: chlorobenzene (in small amounts), 1,2-dichlorobenzene and 1,4-dichlorobenzene. It is also important to point out that no other reaction products, like cyclohexane, chlorocyclohexane or metadichlorobenzene, were detected as with Rh, Ru, Pt and Pd catalysts [4,8,10].

Table 2
Catalytic behaviour of catalysts for the hydrodechlorination of 1,2,4-trichlorobenzene

Catalyst	T (K)[a]	Conversion (%)	TOF ($\times 10^{-4}$) (s^{-1})	Selectivity			
				Bz	ClBz	o-Cl_2Bz	p-Cl_2Bz
CS_1	523	100	–	100	0	0	0
	498	100	–	100	0	0	0
	473	100	–	70	0	20	10
	448	36	2.5	12	1	59	28
	423	17	1.2	1	64	30	
CS_2	523	100	–	100	0	0	0
	498	100	–	100	0	0	0
	473	61	6.2	82	0	15	3
	448	21	2.4	21	1	65	13
	423	12	1.2	11	1	76	12
CS_3	523	100	–	100	0	0	0
	498	71	8.0	91	0	0	9
	473	46	5.1	52	1	40	7
	448	17	1.9	8	1	79	12
	423	14	1.5	7	1	80	12
CS_3B	523	100	–	100	0	0	0
	498	100	–	90	2	8	0
	473	100	–	64	11	18	7
	448	78	4.1	27	22	34	17
	423	39	2.1	4	16	52	28

[a] T: reaction temperature; Bz: benzene; ClBz: chlorobenzene; o-Cl_2Bz: 1,2-dichlorobenzene; p-Cl_2Bz: 1,4-dichlorobenzene.

The selectivity of the reaction is directly related to the conversion for each catalyst. When the conversion increases, the selectivity towards benzene increases. The selectivities of the four catalysts towards benzene are high (table 2) at the higher reaction temperatures tested. Catalysts CS_1 and CS_2 have 100% conversion and 100% selectivity towards benzene between 498 and 523 K. At low reaction temperatures (448–423 K), the main product was 1,2-dichlorobenzene for all catalysts and the most selective catalyst towards benzene was CS_2 (11% at 423 K for 12% of conversion). Interestingly, catalysts CS_1 and CS_2, which desorb hydrogen at temperatures a lower than CS_3 or CS_3B (table 1), are more selective to benzene. Also, the most active catalyst (CS_3B) is not the most selective to benzene since its surface is covered by comparatively more strongly adsorbed hydrogen than catalysts CS_1 and CS_2 and, therefore, the chlorinated compounds have less competition with the hydrogen for the adsorption. This is in agreement with the behaviour observed for other supported nickel catalysts [18,19]. The result of this is that larger amounts of intermediate chlorinated compounds are obtained for catalyst CS_3B (see table 2). On the other hand, the catalysts with more hydrogen desorbed at lower temperatures (350–500 K) are more selective towards benzene. Chlorinated molecules can be adsorbed, which makes possible the easier subsequent dechlorination of the same molecule and leads to larger amounts of benzene.

The appearance of specific chlorinated intermediates during the hydrodechlorination process for all the catalysts could be related to the stepped reaction mechanism, which is the same as the scheme discussed for Ni/Al_2O_3 and $Ni/NiAl_2O_4$ catalysts [18,19]. First, 1,2,4-trichlorobenzene loses one chlorine to give 1,2-dichlorobenzene and 1,4-dichlorobenzene. If the dechlorination goes on, these dichlorobenzenes lose one more chlorine to give chlorobenzene which is transformed to benzene very quickly, before desorbing. The fact that metadichlorobenzene was not observed and more orthodichlorobenzene was formed than paradichlorobenzene for our Ni/Al-MCM-41 catalysts might be attributed to the inductive and steric effects which form the $PhCl_n$ bonds, as proposed by Coq *et al.* [10] derived from the rate equations used for Pd catalysts [4].

The conversion and selectivity values of these Ni/Al-MCM-41 catalysts are better than those achieved by using Ni/Al_2O_3 (16% of conversion and benzene selectivity of 73% at 523 K) and $Ni/NiAl_2O_4$ (82% of conversion and benzene selectivity of 87% at 523 K) under the same conditions of reaction at the "plateau" [18–19].

These Ni/Al-MCM-41 catalysts did not show deactivation in the 24 h time-run. This leads us to assume that these catalysts exhibit good resistance to the HCl action, although it should be confirmed with longer time experiments.

The catalytic behaviour of these catalysts can be explained (by XRD) in terms of their total reduction

Table 3
Metallic areas and H_2 TPD data for several supported nickel catalysts

Catalyst	Metallic area (m^2/g Ni)	H_2 T_D (K) (TPD) [a]
Ni/Al-MCM-41 (CS_2)	66.0	446 (m), 548 (s)
Ni/α-Al_2O_3	1.5	420 (s), 700 (w)
Ni/$NiAl_2O_4$	4.2	430 (s), 570 (s), 770(s)

[a] T_D: Maxima of hydrogen desorption temperature peaks. s = strong; m = medium; w = weak.

degree and the surface structure of each catalyst (BET area, metallic area, H_2 TPD). These Ni/Al-MCM-41 catalysts show higher metallic areas and more hydrogen available at the reaction temperatures tested (523–423 K) than Ni/Al_2O_3 and Ni/$NiAl_2O_4$ catalysts (see table 3). Then the importance of the characteristics of the nickel particles on the conversion and selectivity values seem clear. The high activity of the Ni/Al-MCM-41 catalysts can be related to the ordered structure of the support Al-MCM-41, which can involve a better distribution of the nickel particles. The selectivity to benzene is consequently high. However, some differences are observed in our Ni/Al-MCM-41 catalysts as a consequence of the support influence on the characteristics of metallic particles for each sample. Catalyst CS_2, which shows the highest selectivity to benzene, has the support with the highest Si/Al ratio.

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