Contents lists available at SciVerse ScienceDirect



Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Iron-containing defect-rich mixed metal oxides for Friedel-Crafts alkylation

Benjamin Jäger^a, Antje Wermann^a, Peter Scholz^a, Matthias Müller^b, Udo Reislöhner^c, Achim Stolle^a, Bernd Ondruschka^{a,*}

^a Institute for Technical Chemistry and Environmental Chemistry, Friedrich-Schiller University Jena, Lessingstr. 12, D-07743 Jena, Germany

^b Otto-Schott Institute, Friedrich-Schiller University Jena, Fraunhoferstr. 6, D-07743 Jena, Germany

^c Institute for Solid State Physics, Friedrich-Schiller University Jena, Max-Wien-Platz 1, D-07743 Jena, Germany

ARTICLE INFO

Article history: Received 19 April 2012 Received in revised form 10 July 2012 Accepted 19 July 2012 Available online 28 July 2012

Keywords: Combustion synthesis Crystallite size Friedel–Crafts alkylation Liquid-phase catalysis Mechano-chemical synthesis Microstrains Spinels

ABSTRACT

Several stable iron-containing spinel oxides with the composition $CuFe_2O_4$ or $FeCr_2O_4$ were prepared by different methods including thermal nitrate decomposition, combustion synthesis, and mechano-chemical synthesis. Materials were compared to commercially available spinels produced by conventional ceramic route with respect to their structural properties and catalytic activity. Phase compositions and microstructures of the catalysts were studied in detail. The catalysts were tested in the Friedel–Crafts alkylation of various aromatic compounds with different alkyl halides as alkylating agents. Microstructural properties (microstrains) of the synthesized binary oxides have been identified as a reason for the increased reactivity. Even at low reaction temperatures of 50-70 °C catalysts maintained their high activity resulting in TOFs of up to $3000 h^{-1}$ and excellent selectivity with total heterogeneous behavior in catalysis.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The Friedel–Crafts alkylation is a well-known widely-used organic reaction for C–C bond formation between aromatics and alkyl halides, alcohols, or esters. Bulk chemicals like ethylbenzene from ethylene and benzene or pharmaceutical compounds are produced using this methodology. The traditional reaction is carried out in the liquid homogeneous phase using Lewis acids in either (over)stoichiometric (e.g. AlCl₃) or catalytic amounts (e.g. FeCl₃) [1]. Heterogeneously catalyzed Friedel–Crafts alkylations are still an important field of research [2–7]. Among those catalysts iron-containing compounds are favored [2,4,5,8–11]. Besides mesoporous materials [2–4,11,12] and zeolites [13,14] the application of mono- or mixed metal oxides has been described also [5–7,9,15].

For the synthesis of oxidic materials like spinels several methods are known from the literature. Among these the ceramic route as high temperature reaction between solids (>1000 °C) is the classic way. Thermal decompositions of metal precursors, i.e. salts like nitrates, can be realized at lower temperatures but it still several hours are required for the reaction. Furthermore, the combustion synthesis allows the preparation of spinels [16–18] in very short time, whereby high temperatures are generated by a redox reaction from an oxidant and a fuel component. The fast progression and the evolution of large amounts of gases lead high cooling rates resulting in materials with smaller crystallites and increased number of defects [16]. Spinels with similar structural characteristics [19,20] can be obtained following a mechanochemical route with the advantage that low bulk temperatures (\approx 50 °C) are reached due to the milling process [21–23]. The structural factors should have an impact on the existence of Lewis acidic sites and therefore they should influence the catalytic activity in the Friedel–Crafts alkylation. Additionally the Fe-content can influence the acidity shown for materials with the formula CuCr_{2–x}Fe_xO₄. Lewis acidity increased along with a rise of the iron content [9].

This work is focused on the comparison of the activity and structural properties of oxidic materials prepared by different synthetic procedures: namely, ceramic route (CR), thermal nitrate decomposition in a muffle furnace (MF), combustion synthesis (CS1), scaled-up combustion synthesis (CS10), and mechano-chemical synthesis (MS). The Friedel–Crafts alkylation is used as a model reaction proving the formation of defects due to their action as Lewis acidic sites. Especially from combustion synthesis and mechano-chemical synthesis highly defective materials and therefore active catalysts are expected. Furthermore, it is anticipated that the spinel phases can be synthesized in a faster reaction and/or at lower reaction temperatures.

^{*} Corresponding author. Tel.: +49 3641 948400; fax: +49 3641 948402. *E-mail address*: Bernd.Ondruschka@uni-jena.de (B. Ondruschka).

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.apcata.2012.07.025

2. Experimental

Reagents, solvents, and metal precursors were purchased from commercial suppliers (Sigma–Aldrich, Merck) and were employed without further purification. Weights of metal precursors used for catalyst preparation were corrected by means of the purity of the respective metal salts. Commercially available spinels (denoted as CA) were purchased from Ferro GmbH and Sigma–Aldrich. After their synthesis catalysts were ground to free-flowing powders prior to application.

2.1. Catalyst preparation

2.1.1. Thermal decomposition (MF series)

Thermal nitrate decomposition was carried out with the metal nitrates in molar ratio 1:2 for achieving $M\tilde{i}M\tilde{i}_2O_4$ following a modified literature procedure [24]. The respective amounts of metal salts for 1 g oxide material were diluted in distilled water (20 ml). The solution was evaporated to dryness and afterwards heated in a muffle furnace for 6 h at 300 °C and for additional 4 h at 800 °C under static air in each step.

2.1.2. Combustion synthesis (CS series)

Glycine and metal nitrates were used as fuel and oxidant, respectively. Glycine and nitrate were set to a 1:1 molar ratio. The respective amount of metal salts for 1 g oxide material and glycine were dissolved in distilled water (20 ml). Excess water was removed by heating to 100 °C under atmospheric pressure for 5 h until gel-formation. Afterwards, the mixture was heated to the combustion temperature of 200–250 °C on a heat plate with maximum power (415 W). After the gas evolution stopped (ca. 10 s), metal oxide foams with a low material density were achieved (CS1 series, cf. Supplementary Information video CS 1g).

The procedure was scaled up to 10g oxide material as product (CS10 series). The respective amounts of metal nitrates and glycine were dissolved in distilled water (100 ml) and the excess water was removed by heating to 100 °C under atmospheric pressure for approximately 5-7 h until gel-formation. The ignition also took place at 200–250 °C on a heat plate and the gas evolution was finished after 20–30 s.

2.1.3. Mechano-chemical synthesis (MS series)

The materials were synthesized in a ball mill "Pulverisette 7 classic line" (Fritsch GmbH) by using the respective oxides FeO and Cr_2O_3 or CuO and Fe_2O_3 in stoichiometric amounts to receive $FeCr_2O_4$ or $CuFe_2O_4$, respectively. Magnesia-stabilized zirconium oxide was used as material for the grinding beaker (45 ml) and the grinding balls (8 mm × 10 mm, ball to powder mass ratio of 9:1). The reaction was carried out at 500 min⁻¹ with 13 min milling time followed by 2 min pause and in reverse mode. This program was applied 64 times, resulting in a total reaction time of 16 h.

2.2. Catalyst characterization

Thermogravimetric analyses were carried out using a Shimadzu DTG 60 with platinum crucible under flowing air atmosphere of 30 ml min⁻¹, heating rate 10 K min⁻¹ from room temperature up to 900 °C. X-ray powder diffractograms were obtained on a Siemens D5000 diffractometer using Cu K_{\alpha} radiation. The microstructural properties of the spinel phases were calculated by whole pattern fitting with the software TOPAS (Bruker AXS GmbH) using the Pawley method. The space groups and additional phases were determined by searching the JCPDS database. BET surface was determined by N₂ sorption using Autosorb-1 (Quantachrome GmbH). Mößbauer spectra were obtained at room temperature with a velocity-scanning spectrometer using ⁵⁷Co in a rhodium matrix as source.

Particle size measurements were performed using a Coulter LS 230 laser diffraction particle size analyzer working in the range from 40 nm to 2 mm.

2.3. Catalytic tests

Reactions were carried out in batch mode in a round bottom flask equipped with reflux condenser connected to a washing flask for trapping the evolved HCl gas. $CuFe_2O_4$ was applied with 0.16 mol% (4 mg) referred to benzyl chloride (10.69 mmol) and related to the formal stoichiometry of the spinel $CuFe_2O_4$. The aromatic compound *o*-xylene (106.9 mmol) was used as reagent and solvent in a ratio 10:1 referred to the alkylating agent for suppressing overalkylation. The $CuFe_2O_4$ catalyst was suspended in *o*-xylene followed by application of benzyl chloride. The reaction was carried out for 10 min at 80 °C using oil bath for heating.

The reusability of the catalysts was tested with $FeCr_2O_4$ CS10 in the alkylation of *o*-xylene for both alkylating agents benzyl chloride and cyclohexyl chloride. The extreme small amount of catalyst makes it impossible to carry out a recycling by filtration. Therefore, the reaction system was cooled down, analyzed and reused completely.

2.4. Product analysis

Analysis of the reaction mixtures was carried out using a GC-FID (HP 6890) with *n*-decane as internal standard. Exact measurement conditions are available in the Supplementary Information. Calibrations were made by dilution of a stock solution of the alkylating agent covering the expected range of concentrations with six points. The reaction products were identified by GC–MS Agilent 6890N and in the case of cyclohexyl-dimethyl-benzenes by NMR spectroscopy (selective NOESY, Bruker Avance) additionally for identifying the isomers (cf. Supplementary Information).

3. Results and discussion

The combustion synthesis is much faster than thermal nitrate decomposition. After gel formation the reaction is finished within seconds (as shown in Supplementary Information Video), often with bright glowing and under evolution of large amounts of gases. Comparably, 10 h are required for classical thermal synthesis by decomposition of the nitrate precursors. For the mechano-chemical synthesis the longest reaction time of 16 h was applied, but it can be carried out near room temperature without any need of external heating. A calcination step is avoided thus, preventing the healing of lattice defects [25]. In comparison with other "mechano-chemical" routes the active phases are formed during the comminution of the reagents and not until after additional thermal treatment.

3.1. Catalyst characterization

The TGA/DTA investigations of the catalysts (cf. Supplementary Information Fig. S1) revealed stable oxide phases for all materials without any relevant changes in the sample mass except for CuFe₂O₄ MS. Residual CuO leads to a weight loss due to the formation of Cu₂O during the heating process. In conclusion, the thermal nitrate decomposition as well as the combustion synthesis leads to complete conversion of the precursors and no metal nitrate remained in the final catalysts.

X-ray powder diffraction (XRPD) was used for investigation of the phase composition (cf. Supplementary Information Fig. S2 and S3). Furthermore, diffractograms allowed the determination of the crystallite sizes D (integral breadth) and microstrain ε (Table 1). The details of the fitting procedure are described elsewhere [26]. For CuFe₂O₄ metastable cubic spinel phase was detected for samples

Microstructural investigation, detected phases, BET surface and mean particle size of the catalysts.^a

Sample	D(nm)	$\varepsilon \left(4 \times 10^3\right)$	Space group	Detected phases	BET $(m^2 g^{-1})$	d ₅₀ (μm)
CuFe ₂ O ₄ CA	11.87 (45)	0.0(13)	Fd-3m	CuFe ₂ O ₄	29.51	13.7
CuFe ₂ O ₄ MF	134 (67)	129 (21)	I41/amd	$CuFe_2O_4$; Fe_2O_3 ; CuO	0.93	214
CuFe ₂ O ₄ CS1	37.2 (25)	159.7 (91)	Fd-3m	CuFe ₂ O ₄ ; CuO; Fe ₂ O ₃ ; CuFeO ₂	6.42	70.1
CuFe ₂ O ₄ CS10 cubic	99 (27)	97 (21)	Fd-3m	CuFe ₂ O ₄ cub.; CuFe ₂ O ₄ tetr.; CuO; Fe ₂ O ₃	6.32	120
Tetragonal	24.1 (46)	278 (54)	I41/amd			
CuFe ₂ O ₄ MS	11.3 (10)	282 (44)	Fd-3m	$CuFe_2O_4$; Fe_2O_3 ; CuO	6.28	8.48
Fe(Fe,Cr) ₂ O ₄ CA	77.5 (30)	74.5 (37)	R-3c	Cr _{1,3} Fe _{0,7} O ₃ ; Fe ₂ O ₃ ; Cr ₂ O ₃	3.94	0.887
FeCr ₂ O ₄ MF	78.3 (50)	92.5 (55)	R-3c	Cr _{1,3} Fe _{0,7} O ₃ ; Fe ₂ O ₃ ; Cr ₂ O ₃	8.27	0.52
FeCr ₂ O ₄ CS1	7.08 (26)	181 (15)	Fd-3m	FeCr ₂ O ₄	126.90	85.5
FeCr ₂ O ₄ CS10	14.3 (20)	310 (55)	Fd-3m	$FeCr_2O_4$; Cr_2O_3 ; (Fe_2O_3)	59.70	70
FeCr ₂ O ₄ MS	-	_	R-3c	Cr ₂ O ₃ ; Fe ₂ O ₃ ; FeO	5.34	3.68

^a The values in parentheses are referred to the error of the given value. It indicates the error of the last two given decimals. For example 11.87 (45) represents 11.87 ± 0.45. Italicized values indicate results, where the calculated error exceeds the calculated value.

prepared by the CS1 and the MS method indicating a quenching process during preparation [27]. Otherwise, the MF method resulted in the formation of the tetragonal spinel phase. During upscaled combustion synthesis CS10 both the cubic and the tetragonal phase of CuFe₂O₄ were formed. Analysis of mechano-chemically synthesized CuFe₂O₄ MS not indicated the presence of a ZrO₂ phase resulting from abrasion processes of the milling tools. Only CuFe₂O₄ MS led to a spinel phase. Due to the extreme hardness of Cr₂O₃ no spinel phase was formed during the mechano-chemical treatment of FeO and Cr₂O₃ since no particle refinement took place, which would form reactive species. The only observed reaction was oxidation of FeO to Fe₂O₃. Diffractograms show that in most samples additional phases are present and that formation of such phases takes place in nearly all used synthetic procedures. Catalyst FeCr₂O₄ CS1 contains of a phase-pure cubic spinel (Fd-3m), while the MF method as well as the CA led to a product exhibiting the trigonal space group R-3c.

In Table 1 the results of microstructural investigation, measured BET surfaces, and the mean particle sizes d_{50} are listed (example histogram for the particle size distribution cf. Supplementary Information Fig. S4). The crystallite size *D* and the amount of microstrain ε were calculated by whole pattern fitting of the diffractograms.

Fe-containing FeCr₂O₄ prepared by the thermal decomposition (MF) and by combustion synthesis (CS) as well as the commercially available material (CA) were subjected to Mößbauer spectroscopy (Fig. 1) in order to determine the structure around the Fe centers. This would allow affirmation to the structural determination from XRPD studies and location of Fe in the spinel crystal structure.

The material FeCr₂O₄ CS10 (Fig. 1c) exhibits an isomer shift of 0.17 mm s^{-1} relative to the standard 57 Fe/Rh and a quadruple splitting of 0.89 mm s⁻¹ (Table 2). Due to the cubic structure of FeCr₂O₄ CS10 (Table 1) and the fact that it is a normal spinel iron should be located on tetrahedral sites with a cubic symmetry. Therefore, one single line is expected [28] and confirmed for FeCr₂O₄ in some studies [29,30]. Regarding FeCr₂O₄ CS10 a quadruple splitting is observed leading to the consequence of a distorted structure due to local defects around the iron centers. Similar quadruple splitting was found in an oxidized FeCr₂O₄ spinel containing Fe³⁺ leading to a cation deficient structure [31] and underlining the results obtained by XRPD (high ε , cf. Table 1). The Mößbauer spectra of FeCr₂O₄ CA and MF (Fig. 1a and b) show a different structure. Both materials exhibit a magnetic splitting nearly similar to the spectrum of Fe₂O₃ [32,33]. Regarding the XRPD results this confirms the finding of a trigonal space group belonging to Cr_{1.3}Fe_{0.7}O₃ which can be considered as Cr-substituted iron oxide. Last mentioned spectra consist of two individual sextets confirming the presence of Cr_{1.3}Fe_{0.7}O₃ and residual Fe₂O₃ as additional phase. The central peak pair near 0 mm s⁻¹ for the less intensive sextet cannot be resolved and is fitted as one broader peak due to its low intensity.



Fig. 1. Mößbauer spectra of $FeCr_2O_4 CA(a)$, MF(b) and CS10(c) at room temperature fitted by Lorentzian profiles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

Results of the Mößbauer spectra fitting for $FeCr_2O_4$ CA, MF and CS10.

Sample	Signal	Isomer shift Δ (mm s ⁻¹)	Magnetic splitting ^a δ (mm s ⁻¹)	Line width Γ (mm s ⁻¹)
CA	1st sextet	0.310	16.648	0.28
	2nd sextet	0.135	15.721	0.75
MF	1st sextet	0.358	14.867	0.44
	2nd sextet	0.141	13.557	1.31
CS10	Doublet	0.169	0.879 ^b	0.63

^a Magnetic splitting is referred to the distance of the outer lines.

^b In this case only a quadruple splitting is observed.



Scheme 1. Catalytic Friedel-Crafts alkylations used as model reactions.

3.2. Catalytic activity

The Friedel–Crafts alkylation of *o*-xylene (Scheme 1) as an activated aromatic compound and benzene as non-activated aromatic compound as well as other arenes were used for investigation of the effect of catalyst preparation on the catalytic properties. Additionally, the reactivity in a reaction using cyclohexyl chloride, which leads to a less stabilized cation/complex than benzyl chloride, was tested.

A blank test with the most reactive system *o*-xylene and benzyl chloride for 6 h at 140 °C resulted in a conversion of benzyl chloride <1%. Results obtained for the Friedel–Crafts alkylation of *o*-xylene with benzyl chloride are summarized in Table 3. The selectivity *S* refers to the main product 1,2-dimethyl-4-(phenylmethyl)benzene. Alkylation in the *ortho*-position to 1,2-dimethyl-3-(phenylmethyl)benzene took place to a negligible extent only. Furthermore, consecutive alkylation products are detected.

The reactions proceeded very fast and with the more active catalysts they are completed within 10 min. The required reaction temperature correlates with the reactivity of the catalysts allowing working at lower temperatures for more active catalysts. Differences in the reactivity are visible, even if the same material is used resulting from different synthetic routes. Regarding $CuFe_2O_4$ the differences are less pronounced than for $FeCr_2O_4$. Using $CuFe_2O_4$ the reaction takes place in the range from 50–80 °C, whereas with prepared FeCr₂O₄ and the commercial product on-set temperatures of 60 and 110 °C are required to see any conversion, respectively. Comparison of the reached TOFs depending on the necessary reaction temperature (Fig. 2) shows the differences in the activity of the materials obtained by the different synthetic routes (TOFs were calculated by dividing the amount of main product by the amount of catalyst and the reaction time [34]). Obviously CAseries catalysts need the highest temperature of 110 °C for reaching comparable TOFs. With the MF or CS1 catalysts high TOFs can be achieved working at lower temperatures of 70-80°C. When using CS10 catalysts TOFs of 500–1000 h⁻¹ are reached at 60 °C. Highest activity is detected for catalysts from the MS series (e.g. 2000 h⁻¹ at 50°C).

The alkylation of *o*-xylene with cyclohexyl chloride yields two isomers in relevant amounts. Due to lower stability of the cyclohexyl cation it is more reactive and attacks both available positions in *o*-xylene. In Table 4 the results of the alkylation with cyclohexyl



Fig. 2. Comparison of turn-over frequencies (TOFs) in dependency of the required reaction temperature for the alkylation of *o*-xylene with benzyl chloride using the catalysts of the different synthetic routes (reaction conditions: 106.9 mmol *o*-xylene, 10.69 mmol benzyl chloride, 0.16 mol% catalyst, 10 min).

chloride are summarized. The further difference in selectivity to the main product corresponds to a consecutive alkylation of cyclohexyldimethylbenzene to dialkylated products.

In the alkylating reaction with cyclohexyl chloride only FeCr₂O₄ CS catalysts show activity in which CS10 (78% conversion at 140 °C after 60 min) is more active than CS1 (50% conversion). Similar to the other reaction the FeCr₂O₄ MS catalyst is less reactive than CS1 or CS10 leading to 49% conversion at 140 $^\circ\text{C}$ and 120 min. With CuFe₂O₄ catalysts no alkylation reaction can be observed at increased reaction temperatures and times. Just a small amount of cyclohexyl chloride is converted. Instead a side reaction leading to oxidation of one methyl group of o-xylene in <1% takes place (identified with GC-MS). The resulting cation is less stabilized and therefore more reactive than the cation formed by reaction of benzyl chloride. This leads to the formation of a higher amount of the ortho-product compared to reaction of benzyl chloride. The amount of alkylation in the ortho-position is nearly independent from the achieved conversion or the used reaction temperature and seems to be characteristic for the alkylating agent cyclohexyl chloride in combination with the catalysts tested.

The lower reactivity of cyclohexyl chloride can be checked by using benzyl chloride and cyclohexyl chloride as alkylating agents in a parallel reaction. The results are summarized in Fig. 3. At the used reaction conditions benzyl chloride reaches total conversion whereas the conversion of cyclohexyl chloride is incomplete (Fig. 3a). The product distributions (Fig. 3b) confirm that benzyl chloride is the more active compound

90

Catalytic activity at the specified reaction conditions for the Friedel–Crafts alkylation of o-xylene with benzyl chloride.^a

Catalyst	<i>T</i> (°C)	X (%)	S (%)	$TOF(h^{-1})$	p/o^{b}
CuFe ₂ O ₄ CA	80	>99	88	3300	>99:1
CuFe ₂ O ₄ CA	70	0	_	-	-
CuFe ₂ O ₄ MF	70	>99	88	3300	>99:1
CuFe ₂ O ₄ MF	60	0	_	-	-
CuFe ₂ O ₄ CS1	80	>99	88	3300	>99:1
CuFe ₂ O ₄ CS1	70	0	_	-	-
CuFe ₂ O ₄ CS10	80	>99	87	3263	>99:1
CuFe ₂ O ₄ CS10	70	11	94	388	>99:1
CuFe ₂ O ₄ MS	60	>99	88	3300	>99:1
CuFe ₂ O ₄ MS	50	58	92	2001	>99:1
Fe(Fe,Cr) ₂ O ₄ CA	110	>99	87	3263	>99:1
Fe(Fe,Cr) ₂ O ₄ CA	100	15	>99	563	>99:1
FeCr ₂ O ₄ MF	90	0	-	-	-
FeCr ₂ O ₄ CS1	70	5	>99	188	>99:1
FeCr ₂ O ₄ CS10 ^c	70	>99	87	1631	>99:1
FeCr ₂ O ₄ CS10 ^{c,d}	70	53	92	1829	>99:1
FeCr ₂ O ₄ CS10 ^c	60	57	92	983	>99:1
FeCr ₂ O ₄ CS10 ^{c,d}	60	18	97	655	>99:1
FeCr ₂ O ₄ CS10	70	97	88	3201	>99:1
FeCr ₂ O ₄ CS10 ^d	70	26	96	1872	>99:1
FeCr ₂ O ₄ CS10	60	25	96	900	>99:1
FeCr ₂ O ₄ CS10 ^d	60	8	>99	600	>99:1
FeCr ₂ O ₄ MS	60	1	>99	38	>99:1

^a Reaction conditions: 106.9 mmol o-xylene, 10.69 mmol benzyl chloride, 0.16 mol% catalyst, 10 min.

^b Ratio of 1,2-dimethyl-4-(phenylmethyl)benzene to 1,2-dimethyl-3-(phenylmethyl)benzene.

 $^{\rm c}$ $m_{\rm cat}$ was increased to 0.32 mol%.

^d Reaction time was decreased to 5 min.

Table 4

Catalytic activity at the specified reaction conditions for the Friedel-Crafts alkylation of o-xylene with cyclohexyl chloride.^a

Catalyst	<i>T</i> (°C)	t (min)	X (%)	S (%)	$TOF(h^{-1})$	p/o ^b
CuFe ₂ O ₄ CS1	140	120	1	-	-	-
CuFe ₂ O ₄ CS10	140	120	3	-	-	-
CuFe ₂ O ₄ MS	140	120	1	-	-	-
FeCr ₂ O ₄ CS1	140	60	50	95 ^b	297	79:21
FeCr ₂ O ₄ CS10	140	120	95	91	270	80:20
FeCr ₂ O ₄ CS10	140	90	86	85	305	78:22
FeCr ₂ O ₄ CS10	140	60	78	90 ^c	439	79:21
FeCr ₂ O ₄ CS10	140	10	31	>99	1163	78:22
FeCr ₂ O ₄ CS10	120	60	32	98 ^c	196	79:21
FeCr ₂ O ₄ CS10	120	30	15	91 ^d	171	78:22
FeCr ₂ O ₄ CS10	120	10	0	-	-	-
FeCr ₂ O ₄ CS10	110	60	0	-	-	-
FeCr ₂ O ₄ MS	140	120	49	86 ^d	132	78:22

^a Reaction conditions: 106.9 mmol o-xylene, 10.69 mmol cyclohexyl chloride and 0.16 mol% catalyst.

^b Ratio of 4-cyclohexyl-1,2-dimethylbenzene to 3-cyclohexyl-1,2-dimethylbenzene.

^c Side product cyclohexene from elimination reaction of cyclohexyl chloride detected (< 2%).

^d Cyclohexene is the only detectable side product.

and therefore at first 1,2-dimethyl-4-(phenylmethyl)benzene is formed followed by the alkylation of further o-xylene with cyclohexyl chloride forming 4-cyclohexyl-1,2-dimethylbenzene and 3-cyclohexyl-1,2-dimethylbenzene. The overall selectivity for monoalkylated products and the ratio of isomers formed by alkylation with cyclohexyl chloride is comparable to the experiments with just one alkylating agent. Therefore the two reaction systems do not seem to interact with each other.

In Table 5 the alkylation results of other aromatic compounds (Scheme 2) with benzyl chloride are summarized. Due to the fact that benzene is a non-activated aromatic compound, higher temperatures and longer reaction times are needed compared to the alkylation of *o*-xylene and other arenes. Additionally, the alkylation of toluene was carried out at higher temperatures but medium reaction time of 30 min is possible. Activated arenes like *o*-xylene, *p*-xylene, and mesitylene can be alkylated at lower temperatures and short reaction times of 10 min. The substrate durene needs higher temperatures for melting allowing a homogeneous reaction solution. The selectivities in Table 5 referred to



Scheme 2. Other aromatic compounds used in the Friedel–Crafts alkylation with benzyl chloride.

the respective monoalkylated products. Difference to 100% selectivity is attributed to consecutive alkylations affording dialkylated products and in small amounts intramolecular alkylation of benzyl chloride.

For all substrates the alkylation with benzyl chloride can be carried out successfully. The selectivity to monoalkylated products is in the same range as observed for the reaction with *o*-xylene. Only if benzene is converted the selectivity is significantly lower due



Fig. 3. Catalytic activity at specified reaction conditions for the Friedel–Crafts alkylation of *o*-xylene with benzyl chloride and cyclohexyl chloride. Conversion of the alkylating agents (a), selectivity to the specified products (b) (reaction conditions: 106.9 mmol *o*-xylene, 10.69 mmol benzyl chloride and cyclohexyl chloride, 0.16 mol% FeCr₂O₄ CS10, 140 °C).

Fable 5 Catalytic activity at the specified reaction conditions for the Friedel–Crafts alkylation of other aromatic compounds with benzyl chloride. ^a							
Catalyst	$m_{\rm cat}$ (mol%)	Educt	<i>T</i> (°C)	t (min)	X (%)	S (%)	$TOF(h^{-1})$
FeCr ₂ O ₄ CS10	2.50	Benzene	80	120	>99	75	15
FeCr ₂ O ₄ CS10	1.25	Benzene	80	120	78	77	24
FeCr ₂ O ₄ MS	1.25	Benzene	80	120	>99	74	30
FeCr ₂ O ₄ MS	0.63	Benzene	80	120	90	75	54
CuFe ₂ O ₄ MS	0.63	Benzene	80	120	>99	74	59
CuFe ₂ O ₄ MS	0.01	Benzene	80	120	>99	73	3673
FeCr ₂ O ₄ CS10	0.16	Toluene	90	30	99	90	1106
FeCr ₂ O ₄ CS10	0.16	o-Xylene	70	10	97	88	3201
FeCr ₂ O ₄ CS10	0.16	o-Xylene	60	10	25	96	900
FeCr ₂ O ₄ CS10	0.16	<i>n</i> -Xylene	70	10	97	87	3174

60

70

60

100

10

10

10

10

^a Reaction conditions: 106.9 mmol arene, 10.69 mmol benzyl chloride.

0.16

016

0.16

0.16

to the effect that Friedel–Crafts alkylation yields a product with higher activity toward additional alkylation compared with benzene. Lower activity is manifested in the calculated TOFs also. Just with $CuFe_2O_4$ MS a TOF of >3600 h⁻¹ could be realized with the unsubstituted arene.

p-Xylene

Mesitylene

Mesitylene

Durene

4. Discussion

FeCr₂O₄ CS10

FeCr₂O₄ CS10

FeCr₂O₄ CS10

FeCr₂O₄ CS10

Besides the pure activity of the catalysts, the heterogeneity of the reaction is a very important factor. Therefore, heterogeneity tests were carried out with the model reaction system *o*-xylene and benzyl chloride by stopping the reaction after 10 min and separation of the catalyst by hot filtration. Afterwards the reaction mixture was allowed to react for further 20 min. As shown in Fig. 4, no further reaction takes place in case of FeCr₂O₄ CS10. Therefore, the reaction can be considered as completely heterogeneous without any metal traces present in solution after removal of the catalyst. If Fe₂O₃ was used, the reaction rate is not affected by the hot-filtration step, which indicates a rather homogeneous catalytic reaction. With CuO and Cr_2O_3 nearly no reaction takes place. This fact allows the assumption that Fe in the spinel is the active element and neither Cu nor Cr contributes to catalysis under the reaction conditions investigated. But this arrangement allows the formation of stable heterogeneous catalysts in contrast to Fe₂O₃.

34

96

11

>99

97

95

>99

92

1239

3437

416

3461

In Fig. 5 the conversion-selectivity plot for the alkylation of *o*-xylene with benzyl chloride is presented. It can be seen that the selectivity depends on the conversion and is nearly independent from the used catalyst. In contrast the conversion reveals a dependency on the used catalyst in combination with the applied reaction temperature. At low conversion the selectivity reaches maximal values of >99%. But also at full conversion the selectivity does not drop below 87% (e.g. catalysts FeCr₂O₄ CS1, CuFe₂O₄ MS, CuFe₂O₄ CS10).

For investigation of important parameters on the conversion of benzyl chloride, reaction time, reaction temperature, and catalyst amount were varied using 2³ factorial plan. The response data used for statistical evaluation are summarized in Table 6. Results

Tat	le	6		
			~	

Used data for statistical analysis.^a

Catalyst	$m_{\rm cat}$ (mol%)	<i>T</i> (°C)	<i>t</i> (min)	X (%)	S (%)
FeCr ₂ O ₄ CS10	0.16	60	5	8	>99
FeCr ₂ O ₄ CS10	0.16	60	10	34	96
FeCr ₂ O ₄ CS10	0.16	70	5	26	>99
FeCr ₂ O ₄ CS10	0.16	70	10	97	88
FeCr ₂ O ₄ CS10	0.32	60	5	18	>99
FeCr ₂ O ₄ CS10	0.32	60	10	57	92
FeCr ₂ O ₄ CS10	0.32	70	5	53	92
FeCr ₂ O ₄ CS10	0.32	70	10	>99	87

^a Reaction conditions: 106.9 mmol o-xylene, 10.69 mmol benzyl chloride.



Fig. 4. Heterogeneity tests for FeCr₂O₄ CS10, Fe₂O₃, CuO, and Cr₂O₃. Negative reaction times indicate reaction in presence of catalysts, which have been removed at t = 0 min (reaction conditions: 106.9 mmol *o*-xylene, 10.69 mmol benzyl chloride, 0.16 mol% catalyst, 60 °C).



Fig. 5. Conversion-selectivity plots for the alkylation of *o*-xylene with benzyl chloride for different catalysts (cf. Table 3) (reaction conditions: 106.9 mmol *o*-xylene, 10.69 mmol benzyl chloride, 0.16 mol% catalyst, reaction time 5 or 10 min).



Fig. 6. Conversion-selectivity plots for the alkylation of *o*-xylene with cyclohexyl chloride for two $FeCr_2O_4$ catalysts (cf. Table 4) (reaction conditions: 106.9 mmol *o*-xylene, 10.69 mmol cyclohexyl chloride, 0.16 mol% catalyst).

indicated that the reaction time has the major influence on the reaction (52%) followed by the reaction temperature (37%). Interestingly, variation of the catalyst amount contributes only to an extent of 8% as already demonstrated by using of very small catalyst amounts for a successful reaction. Statistical analysis revealed that parameter interactions are not significant.

Fig. 6 shows the conversion-selectivity plot for the alkylation of *o*-xylene with cyclohexyl chloride. Also in this case the selectivity is quite stable (85–99%) over the complete range of conversion. But the selectivity does not reach its maximum at low conversions due to a side reaction of the alkylating agent, namely the elimination of HCl leading to cyclohexene.

In Table 7 a comparison of the used catalysts with data available in the literature is done. Also with benzene as educt, the TOF for FeCr₂O₄ CS10 is higher than the material used by Ghorpade et al. [9]. In the alkylation of *o*-xylene the TOFs are much higher than the values found in the literature. The TOF for FeCr₂O₄ CS10 reaches $3200 h^{-1}$ at $70 \circ C$ or $983 h^{-1}$ at a lower reaction temperature of $60 \circ C$. The particle sizes, crystallite sizes, or BET surfaces are not able to explain the high activity of the CS or MS catalysts only. Therefore, the amount of microstrains seems to be the determinant. The most active catalyst FeCr₂O₄ CS10 contains the highest amount of microstrains. Within the studied catalysts of the CuFe₂O₄ type the presence of the tetragonal phase leads to more active catalysts compared to cubic single phase CuFe₂O₄ resulting in the best performance when using the pure tetragonal phase catalyst CuFe₂O₄ MF. Regarding the cubic phase CuFe₂O₄ catalysts this



Fig. 7. Recycling tests for FeCr₂O₄ CS10 used in the alkylation of *o*-xylene with benzyl chloride (a) and cyclohexyl chloride (b) (reaction conditions: 106.9 mmol *o*-xylene, 10.69 mmol alkylating agent, 0.16 mol% catalyst at 70 °C and 10 min (a) and at 120 °C and 60 min (b)). For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

Comparison of calculated TOFs for some heterogeneously catalyzed Friedel–Crafts alkylations with benzyl chloride (cf. Tables 3–5).

Catalyst	Educt	$TOF(h^{-1})$	Reference
CuFeCrO ₄	Benzene	6 (80 °C)	[9]
FeCr ₂ O ₄ CS10	Benzene	24 (80 °C)	This work
FeCr ₂ O ₄ MS	Benzene	54 (80 °C)	This work
CuFe ₂ O ₄ MS	Benzene	3673 (80°C)	This work
Fe-JLU-15 (70)	Benzene	492 (70 °C)	[4]
ZnFe ₂ O ₄	Toluene	289 (70 °C)	[15]
FeCr ₂ O ₄ CS10	Toluene	1106 (90 °C)	This work
ZnTiO ₃	p-Xylene	<1 (70 °C)	[7]
FAPO ₄	p-Xylene	3 (80 °C)	[10]
FeCr ₂ O ₄ CS10	p-Xylene	1239 (60 °C)	This work
FeCr ₂ O ₄ CS10	p-Xylene	3174 (70°C)	This work
Fe/Al-MCM-41	o-Xylene	10 (140 °C)	[11]
FeCr ₂ O ₄ CS10	o-Xylene	983 (60 °C)	This work
FeCr ₂ O ₄ CS10	o-Xylene	3201 (70°C)	This work
CuFe ₂ O ₄ MF	o-Xylene	3300 (70°C)	This work
CuFe ₂ O ₄ MS	o-Xylene	3300 (60 °C)	This work
CuFe ₂ O ₄ MS	o-Xylene	2001 (50°C)	This work
FeCr ₂ O ₄ CS10	Mesitylene	416 (60 °C)	This work
FeCr ₂ O ₄ CS10	Mesitylene	3467 (70°C)	This work
FeCr ₂ O ₄ CS10	Durene	3461 (100°C)	This work

result is exceeded by the application of $CuFe_2O_4$ MS containing only the cubic spinel phase but with the highest amount of microstrains in the whole row of the respective materials. Also at a reaction temperature of 50 °C the TOF still reaches 2001 h⁻¹.

The reusability of the catalysts was tested with $FeCr_2O_4$ CS10 in the alkylation of o-xylene for both alkylating agents benzyl chloride and cyclohexyl chloride (Fig. 7). While the TON (turnover number, calculated as mole converted alkylating agent per mole catalyst) for benzyl chloride (Fig. 7a) keeps quite stable (TON = 625–619) the TON for cyclohexyl chloride (Fig. 7b) decreases, especially between the third and fourth reaction cycle. This indicates a significant deactivation of the catalyst when using cyclohexyl chloride as alkylating agent. The selectivities to the monoalkylated products in both cases drop due to enrichment of the alkylated products which are more prone to consecutive alkylation.

5. Conclusion

Several very active iron containing binary oxides for the Friedel-Crafts alkylation have been synthesized by different synthetic routes. Differences in the catalytic activity of the materials obtained from the respective synthetic procedures were found. The amount of microstrains as a measure of the defect concentration is identified as the major characteristic parameter of the catalyst. Neither the crystallite or particle size nor the BET surfaces are responsible for the observed differences in the catalytic activity. Therefore, both the CS (combustion synthesis) and MS (mechano-chemical synthesis) methods are able to produce structures with significant increased numbers of defects than other synthetic routes. Thus, those procedures yield more active catalysts for the Friedel-Crafts alkylation. The combustion synthesized materials exhibited higher activity than the commercially available oxides, wherein the CS10 catalysts obtained from the scaled-up combustion synthesis revealed higher activity than the CS1-type. With respect to the achieved TOFs two rows of activity were found depending on the reaction temperature. For CuFe₂O₄ the activity behaves like CA ~CS1 < CS10 < MF < MS and for FeCr₂O₄ CA \approx MF < CS1 \leq MS < CS10. The mechano-chemical synthesis, without heating the materials to the usually needed high temperatures for calcination or phase formation, resulted in active catalysts also. Therefore, the mechano-chemical activation in the synthesis of CuFe₂O₄ MS leads to the phase formation of a spinel just by grinding the individual oxides. The TOFs for the Friedel-Crafts alkylation of o-xylene are much higher than the values found in literature even at lower temperature (50–70 °C). Also less reactive aromatic compounds or sterical hindered arenes can be alkylated successfully with comparably high TOFs at mild reaction conditions and less reactive alkylating agents like cyclohexyl chloride. Employing cyclohexyl chloride a higher tendency for the formation of both possible isomers is observed. Also with this reaction system TOFs > $1000 h^{-1}$ can be achieved. Overall, the material CuFe₂O₄ MS is the best catalyst for achieving high TOFs in the alkylation with benzyl chloride at low temperatures. FeCr₂O₄ CS10 shows the best performance with a broad range of educts and is also able to convert cyclohexyl chloride whereby the CuFe₂O₄ catalysts show hardly any conversion.

Acknowledgments

For carrying out the BET measurements and NMR spectroscopy the support of the Institute for Physical Chemistry (A. Schmidt) and the Institute for Inorganic and Analytical Chemistry (Dr. M. Friedrich), respectively of the Friedrich-Schiller University Jena are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2012.07.025.

References

- I. Iovel, K. Mertins, J. Kischel, A. Zapf, M. Beller, Angew. Chem. Int. Ed. 44 (2005) 3913–3917.
- [2] C. Anand, P. Srinivasu, S. Alam, V.V. Balasubramanian, D.P. Sawant, M. Palanichamy, V. Murugesan, A. Vinu, Microporous Mesoporous Mater. 111 (2008) 72–79.
- [3] C. Anand, B. Sathyaseelan, L. Samie, A. Beitollahi, R.P. Kumar, M. Palanichamy, V. Murugesan, E.R. Kenawy, S.S. Al-Deyab, A. Vinu, Microporous Mesoporous Mater. 134 (2010) 87–92.
- [4] Y. Du, S. Liu, Y. Ji, Y. Zhang, F. Liu, Q. Gao, F.S. Xiao, Catal. Today 131 (2008) 70–75.
- [5] V. Rajpara, S. Banerjee, G. Sereda, Synthesis (2010) 2835-2840.

- [6] C. Tagusagawa, A. Takagaki, A. Iguchi, K. Takanabe, J.N. Kondo, K. Ebitani, T. Tatsumi, K. Domen, Catal. Today 164 (2011) 358–363.
- [7] N. Pal, M. Paul, A. Bhaumik, Appl. Catal. A 393 (2011) 153-160.
- [8] F. Adam, A.E. Ahmed, Chem. Eng. J. 145 (2008) 328-334.
- [9] S.P. Ghorpade, V.S. Darshane, S.G. Dixit, Appl. Catal. A 166 (1998) 135-142.
- [10] H. Hentit, K. Bachari, M.S. Ouali, M. Womes, B. Benaichouba, J.C. Jumas, J. Mol. Catal. A: Chem. 275 (2007) 158–166.
- [11] M.E. Preethi, S. Revathi, T. Sivakumar, E-J. Chem. 5 (2008) 467-472.
- [12] K. Bachari, O. Cherifi, J. Mol. Catal. A: Chem. 253 (2006) 187–191.
- [13] D. Mravec, M. Michvocík, M. Hronec, P. Moreau, A. Finiels, P. Geneste, Catal. Lett. 38 (1996) 267–270.
- [14] P.G. Smirniotis, E. Ruckenstein, Ind. Eng. Chem. Res. 34 (1995) 1517-1528.
- [15] M.M. Shinde, M.R. Sawant, J. Chin. Chem. Soc. 50 (2003) 1221-1226.
- [16] U. Zavyalova, B. Nigrovski, K. Pollok, F. Langenhorst, B. Müller, P. Scholz, B. Ondruschka, Appl. Catal. B 83 (2008) 221–228.
- [17] L.H. Ai, J. Jiang, Powder Technol. 195 (2009) 11-14.
- [18] N.M. Deraz, J. Anal. Appl. Pyrol. 88 (2010) 103-109.
- [19] T. Verdier, V. Nivoix, M. Jean, B. Hannoyer, J. Mater. Sci. 39 (2004) 5151-5154.
 [20] E. Manova, D. Paneva, B. Kunev, C. Estournès, E. Rivière, K. Tenchev, A. Léaustic,
- I. Mitov, J. Alloys Compd. 485 (2009) 356–361. [21] G. García-Pacheco, J.G. Cabañas-Moreno, H. Yee-Madeira, F. Cruz-Gandarilla,
- Nanotechnology 17 (2006) 2528. [22] S. Bid, S.K. Pradhan, Mater. Chem. Phys. 82 (2003) 27–37.
- [22] V.G. Harris, D.J. Fatemi, J.O. Cross, E.E. Carpenter, V.M. Browning, J.P. Kirkland, A. Mohan, G.J. Long, J. Appl. Phys. 94 (2003) 496–501.
- [24] W.M. Shaheen, A.A. Ali, Mater. Res. Bull. 36 (2001) 1703-1716.
- [25] M. Casas-Cabanas, G. Binotto, D. Larcher, A. Lecup, V. Giordani, J.M. Tarascon, Chem. Mater. 21 (2009) 1939–1947.
- [26] B. Jäger, A. Stolle, P. Scholz, M. Müller, B. Ondruschka, Appl. Catal. A 403 (2011) 152–160.
- [27] J.E. Tasca, C.E. Quincoces, A. Lavat, A.M. Alvarez, M.G. González, Ceram. Int. 37 (2011) 803–812.
- [28] N.N. Greenwood, Angew. Chem. 83 (1971) 746-755.
- [29] H.B. Mathur, A.P.B. Sinha, C.M. Yagnik, Solid State Commun. 3 (1965) 401-403.
- [30] M.J. Rossiter, J. Phys. Chem. Solids 26 (1965) 775–779.
- [31] E. Schmidbauer, Phys. Chem. Miner. 14 (1987) 533-541.
- [32] Y.R. Uhm, W.W. Kim, S.J. Kim, C.S. Kim, C.K. Rhee, J. Appl. Phys. 93 (2003) 7196–7198.
- [33] M. Ristic, S. Music, M. Godec, J. Alloys Compd. 417 (2006) 292-299.
- [34] T. Choudhury, N.M. Misra, Bull. Mater. Sci. 34 (2011) 1273–1279.