Preparation of carbon-coated alumina by pyrolysis of adsorbed acetylacetone

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A carbon coating has been prepared on the surface of an alumina support by pyrolysis of adsorbed acetylacetone.

Carbon-coated silica and alumina supports are promising for application in catalysis and chromatography.[1–5] Therefore much efforts are being made in order to achieve a desired combination of the physico-chemical properties of both components in novel materials. The main factors affecting the structure of a carbon coating on the support surface are the chemical nature of the carbon precursor and the conditions of its pyrolysis.[1–6]

This work aims at the development of a novel method for coating alumina supports with carbon and the physico-chemical characterization of the designed materials. Carbon-coated alumina was synthesised by adsorption and subsequent pyrolysis of acetylacetone on the support surface. Acetylacetone was selected due to its ability to form surface aluminium acetylacetonate complexes.[7–9] The mechanism of carbon coating deposition and the structure of the prepared samples were monitored by IR, XRD, TG/DTG–DTA, TEM and adsorption measurements.

Precipitated alumina [CK 300, Ketjen, $S_{BET}(N_2) = 259$ m^2 g^{-1}] was used as a support. The as-received support was crushed and sieved to a particle size of 0.25–0.50 mm. A sample was placed in a McBain quartz spring balance and evacuated at 200 °C and 1×10^{-2} Pa for 3 h prior to the adsorption of acetylacetone. After cooling to room temperature, the sample was contacted with saturated vapour of acetylacetone up to reaching the adsorption equilibrium (10–12 h). Afterwards, the sample was evacuated at room temperature to a pressure of 1×10^{-2} Pa to remove an excess of acetylacetone. Then, the sample temperature was increased to 700 °C within 5–6 h under continuous pumping. The sample was kept at this temperature and a pressure of 1×10^{-2} Pa for 1 h in order to complete the pyrolysis of the adsorbed acetylacetone and to remove volatile products.

To prepare samples with an increased carbon content, the adsorption–pyrolysis cycle was repeated up to three times. The above procedure resulted in samples with the carbon content 2.6, 4.6 and 6.3 wt%, denoted hereafter as C(2.6)/Al_2O_3, C(4.6)/Al_2O_3 and C(6.3)/Al_2O_3, respectively.

The carbon content of the samples was determined by gravimetry with a McBain quartz spring balance by calcination at 700 °C for 4 h in air.

Adsorption measurements showed that the contact of the initial alumina with acetylacetone resulted in the strong interaction with the support surface. After evacuation at room temperature, the carbon loading in surface acetylacetonate complexes was found to be 16.6 C at nm^{-2} (Table 1). The carbon loading in the sample after pyrolysis was 5.3 C at nm^{-2}, which corresponds to 31.6% carbon yield.

Sample C(2.6)/Al_2O_3 was brought into contact with acetylacetone vapour again. The adsorption of acetylacetone appeared to be somewhat higher as compared with that on the initial alumina support and corresponded to carbon loading in surface acetylacetonate complexes of 20.9 C at nm^{-2}. Nevertheless, the carbon yield after pyrolysis was lower and approached 19.6%. The carbon loading in sample C(4.6)/Al_2O_3 was found to be 9.4 C at nm^{-2}.

Table 1 demonstrates that the repetition of the adsorption–pyrolysis cycles resulted in an increase in the carbon content of the samples. Although acetylacetone adsorption increased in each consecutive adsorption cycle, the carbon yield after pyrolysis behaved in the reverse order.

Table 1 Preparation of carbon-coated alumina supports.

Sample	Initial carbon content (wt%)	Adsorbed Hacac/ C at nm^{-2}	Pyrolysis of adsorbed Hacac			
			Carbon yield (%)	Increase of carbon content/ C at nm^{-2}	Final carbon content	
					C at nm^{-2}	wt%
Al_2O_3	0	16.6	31.6	5.3	5.3	2.6
C(2.6)/Al_2O_3	2.6	20.9	19.6	4.1	9.4	4.6
C(4.6)/Al_2O_3	4.6	36.2	10.2	3.7	13.1	6.3
C(6.3)/Al_2O_3	6.3	40.2	8.1	3.3	16.4	7.8

IR spectroscopy confirmed a strong interaction of acetylacetone with the initial alumina support (Figure 1, curve *2*). The distinct IR bands at 1550, 1535 and especially 1295 cm^{-1}, which are typical of surface aluminium acetylacetonate complexes,[7–9] are observed. These complexes resulted from the interaction of acetylacetone with the coordinatively unsaturated Al^{3+} sites.[8,9] Moreover, the IR bands at 1595, 1468 and 1405 cm^{-1} derived from the adsorbed acetylacetone[8] are clearly seen. The IR bands at 1727 and 1707 cm^{-1}, characteristic of the keto form of acetylacetone,[10] are not observed. Therefore, we can conclude that a shift of the keto–enol equilibrium occurred upon the adsorption, and acetylacetone was present on the alumina surface preferably in the enol form.

The pyrolysis resulted in degradation of surface aluminium acetylacetonate complexes, which is accompanied by the disappearance of the above bands in the IR spectrum (see Figure 1, curve *3*). The IR bands at 1620, 1570 and 1400 cm^{-1} are seen, of which that at 1570 cm^{-1} can be attributed to carboxyl groups in the carbon coating.[11,12]

The adsorption of acetylacetone on sample C(2.6)/Al_2O_3 (Figure 1, curve *4*) occurs similarly to the case of the initial alumina support. The main difference between the interaction of acetylacetone with the Al_2O_3 support and sample C(2.6)/Al_2O_3 concerns the low-frequency shift of all IR bands in the latter case, which reflects a change in the nature of the adsorption sites due to the shielding of the alumina surface with the deposited carbon.

The adsorption of acetylacetone on sample C(4.6)/Al_2O_3 (Figure 1, curve *5*) is completely different from that on C(2.6)/Al_2O_3. The difference consists in the absence of the IR band at 1285 cm^{-1}, which is typical of surface aluminium acetylacetonate complexes.[7,9] This means that aluminium sites are no longer involved in the interaction with acetylacetone molecules. In other words, in sample C(4.6)/Al_2O_3, the carbon coating completely blocks or shields the coordinatively unsaturated Al^{3+} sites.

Table 2 Textural and surface properties of carbon coated alumina supports.

Sample	Pore volume/ cm^3 g^{-1}	V_{hexane}/V^{a}_{water} ($p/p_0 = 0.05$)	$S_{BET}(N_2)$/m^2 g^{-1}
Al_2O_3	0.64	1.00	259
C(2.6)/Al_2O_3	0.62	1.37	241
C(4.6)/Al_2O_3	0.61	1.40	241
C(6.3)/Al_2O_3	0.59	1.57	241

[a] V_{hexane} and V_{water} correspond to the amounts of adsorbed hexane and water, respectively, converted to liquid volume.

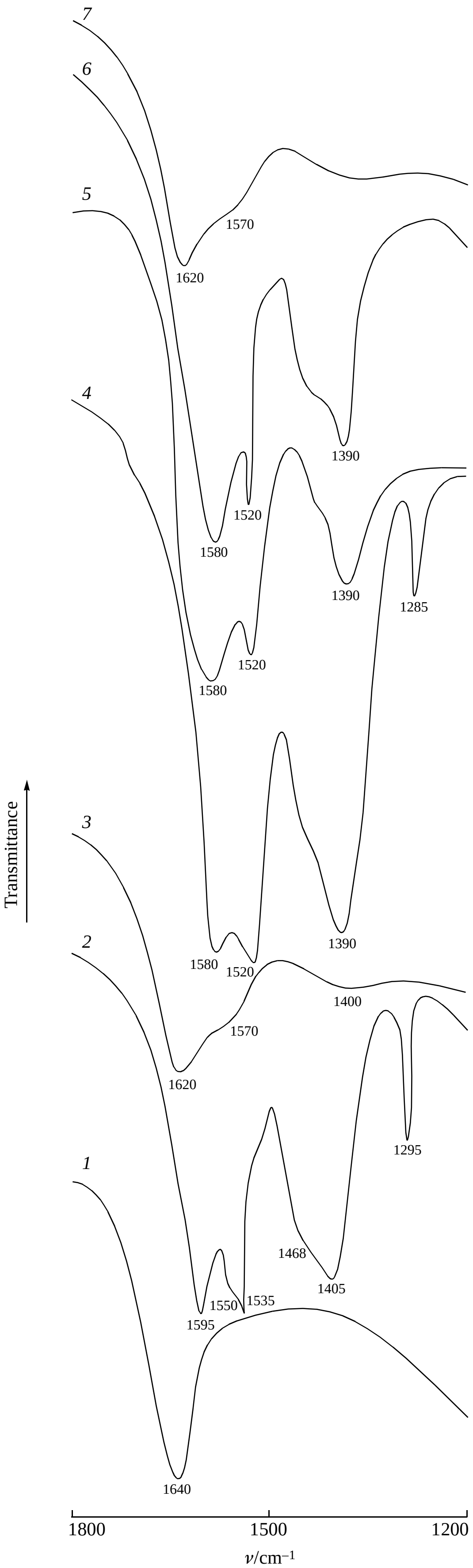

Figure 1 IR spectra of alumina supports at different stages of coating with carbon: (*1*) initial Al_2O_3; (*2*) Al_2O_3 with adsorbed acetylacetone; (*3*) sample C(2.6)/Al_2O_3; (*4*) sample C(2.6)/Al_2O_3 with adsorbed acetylacetone; (*5*) sample C(4.6)/Al_2O_3 with adsorbed acetylacetone; (*6*) sample C(6.3)/Al_2O_3 with adsorbed acetylacetone; (*7*) sample C(6.3)/Al_2O_3 sample with adsorbed acetylacetone subjected to pyrolysis.

The IR spectrum of sample C(6.3)/Al_2O_3 (Figure 1, curve *6*) is similar to that of C(4.6)/Al_2O_3 (Figure 1, curve *5*) and confirms the proposed mechanism of the adsorption of acetylacetone on a carbon-coated alumina support.

Characterization of the samples using XRD did not reveal any peaks which should be attributed to ordered carbon structures.[13] Therefore, the presence of either an amorphous carbon coating or a thin graphite layer can be assumed.

Regardless of the carbon content, the thermoanalytical characterization of the samples in air exhibits the intense weight loss in DTG patterns around 500 °C, which coincides with the exothermic peak in DTA curves. The oxidation proceeds in one step in a narrow temperature range. This suggests that degradation of a single carbon phase occurs. Moreover, no separate carbon phase is observed in the TEM images of the samples. Therefore, we may suppose that carbon uniformly coats the alumina surface.

The shape of the nitrogen adsorption–desorption isotherms and the hysteresis loops were found to be similar for all samples. The pore volume and the apparent surface area of all carbon-coated samples appeared to be somewhat less than those of the initial alumina support (Table 2). This means that the porous structure of the initial alumina support was not changed upon carbon deposition. Moreover, a pore mouth plugging did not occur, and carbon appeared to be uniformly distributed over the surface of the alumina support.

The adsorption isotherms of hexane and water were measured in order to evaluate the influence of the carbon coating on the hydrophilicity of the initial alumina support. The difference between the hexane and water adsorption is most pronounced at low p/p_0. At p/p_0 of 0.05, the hexane-to-water adsorption ratio increases from 1 for the initial alumina to 1.57 for sample C(6.3)/Al_2O_3 (Table 2). This means a progressive decrease in the hydrophilicity of carbon-coated samples and hence an increase in the alumina coverage with carbon upon increasing carbon content.

In summary, a carbon coating on alumina supports can be prepared by pyrolysis of adsorbed acetylacetone. The carbon content can be increased by the repetition of acetylacetone adsorption–pyrolysis cycles. The carbon coating does not influence the pore structure of the initial alumina support but decreases its hydrophilicity. Carbon appears to be uniformly distributed on the support surface whose coverage increases with an increase in the carbon loading. This results in almost complete shielding of the alumina surface at a carbon loading of 13.1 C at nm^{-2}.

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References

1 K. Kamegawa and H. Yoshida, *J. Colloid Interface Sci.*, 1993, **159**, 324.
2 P. R. Vissers, F. P. M. Mercx, S. M. A. M. Bouwens, V. H. J. de Beer, and R. Prins, *J. Catal.*, 1988, **114**, 291.
3 T. Zhang, P. D. Jacobs and H. W. Haynes, Jr., *Catal. Today*, 1994, **19**, 353.
4 R. Leboda, *Chromatographia*, 1981, **14**, 524.
5 K. Bebris, A. V. Kiselev, Yu. S. Nikitin, I. I. Frolov, L. V. Tarasova and Ya. I. Yashin, *Chromatographia*, 1978, **11**, 206.
6 Th. Vergunst, F. Kapteijn and J. A. Moulijn, in *Preparation of Catalysts VII*, eds. B. Delmon, P. A. Jacobs, R. Maggi, J. A. Martens, P. Grange and G. Poncelet, Elsevier, Amsterdam, 1998, vol. 118, p. 175.
7 J. A. R. van Veen, G. Jonkers and W. H. Hesselink, *J. Chem. Soc., Faraday Trans.*, 1989, **85**, 389.
8 M. Alexander, D. M. Bibby, R. F. Howe and R. H. Meinhold, *Zeolites*, 1993, **13**, 441.
9 A. Kytokivi, A. Rautiainen and A. Root, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 4079.
10 R. Mecke and E. Z. Funck, *Electrochemie*, 1956, **60**, 1124.
11 J. A. R. van Veen, P. C. de Jong-Versloot, G. M. M. van Kessel and F. J. Fels, *Thermochim. Acta*, 1989, **152**, 359.
12 T. J. Bandosz, J. Jagiello and J. A. Schwarz, *Langmuir*, 1996, **12**, 6480.
13 J. V. Sanders, J. A. Spink and S. S. Pollack, *Appl. Catal.*, 1983, **5**, 65.

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