

**Supplementary Information:**  
**N-substituted carbamates synthesis using urea as carbonyl source over  
TiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst**

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

## Experimental

### Catalysts characterization

The loadings of Ti, Cr and Ni were determined on an inductively coupled plasma-atomic emission spectrometry (ICP-AES) (ThermoElemental Company in the USA) by dissolving the samples in aqueous nitric acid.

The BET surface areas, pore volumes and average pore diameters of the catalysts were obtained with physisorption of N<sub>2</sub> using a Micromeritics ASAP 2010.

Surface analysis of the catalysts was performed by X-ray photoelectron spectroscopy (XPS) on VG ESCALAB210 using a Mg K $\alpha$  radiation at a pass energy of 20 eV. The energy scale was calibrated and corrected for charging using the C1s (285.0 eV) line as the binding energy reference.

X-ray diffraction (XRD) was measured on a Siemens D/max-RB powder X-ray diffract meter. Diffraction patterns were recorded with Cu K $\alpha$  radiation (40 mA, 40 kV) over a 2 $\theta$  range of 10° to 90° and a position-sensitive detector using a step size of 0.01° and a step time of 0.15 s.

Temperature-programmed desorption (TPD) of CO<sub>2</sub> and NH<sub>3</sub> was carried out on TPD flow system equipped with an MS detector (DM300, AMETEK, USA) to study the acid-base properties of the catalysts. In a typical experiment, the solid sample (100 mg with particle size 160-200  $\mu$ m) was pretreated at 400 °C for 1 h under nitrogen flow (50 mL min<sup>-1</sup>) and then cooled to room temperature. The sample was subsequently exposed to CO<sub>2</sub> (NH<sub>3</sub>) stream (50 mL min<sup>-1</sup>) at room temperature for 1 h and flushed again with nitrogen for 1 h to remove any physico-adsorbed CO<sub>2</sub> (NH<sub>3</sub>). The desorption profile was recorded at a heating rate of 10 °C min<sup>-1</sup> from room temperature to 500 °C and maintained at this temperature until the MS signal of CO<sub>2</sub> (NH<sub>3</sub>) returned to the baseline. The quantitative analysis for CO<sub>2</sub> (NH<sub>3</sub>) desorption is calculated based on the integration of the corresponding TPD traces, preliminarily calibrated by the injection of pure CO<sub>2</sub> (NH<sub>3</sub>) pulses. CO<sub>2</sub> (NH<sub>3</sub>) pulses (0.1727 mL) were injected into the carrier gas intermittently and the whole process was detected by a MS. The acidic-basic amounts were expressed as the number of CO<sub>2</sub> (NH<sub>3</sub>) molecules per gram of catalyst (mmol CO<sub>2</sub> (NH<sub>3</sub>) per g).

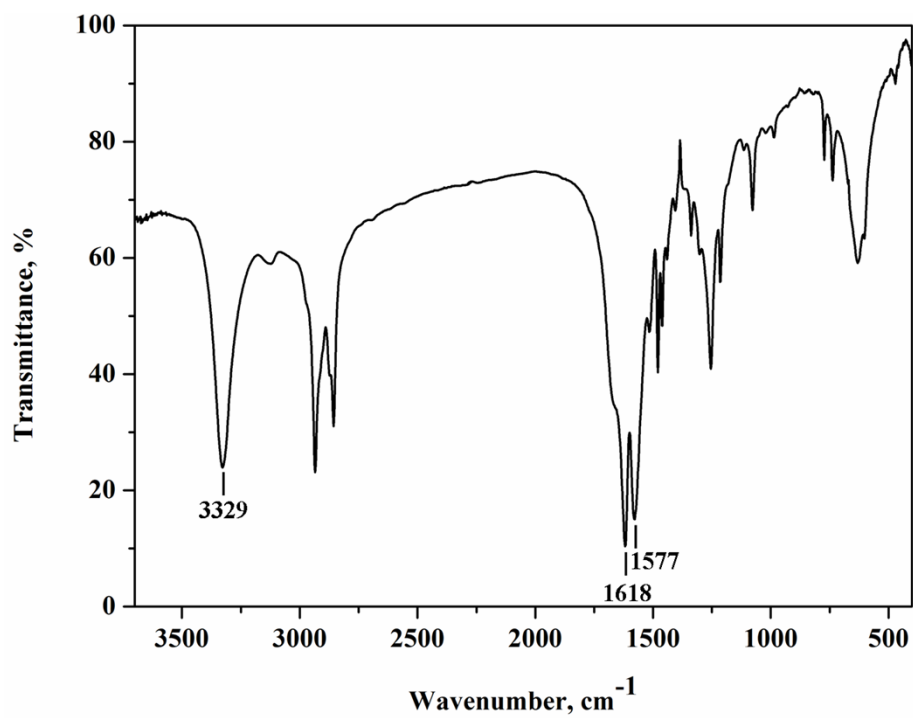


Fig. S1. FT-IR of the solid by-products

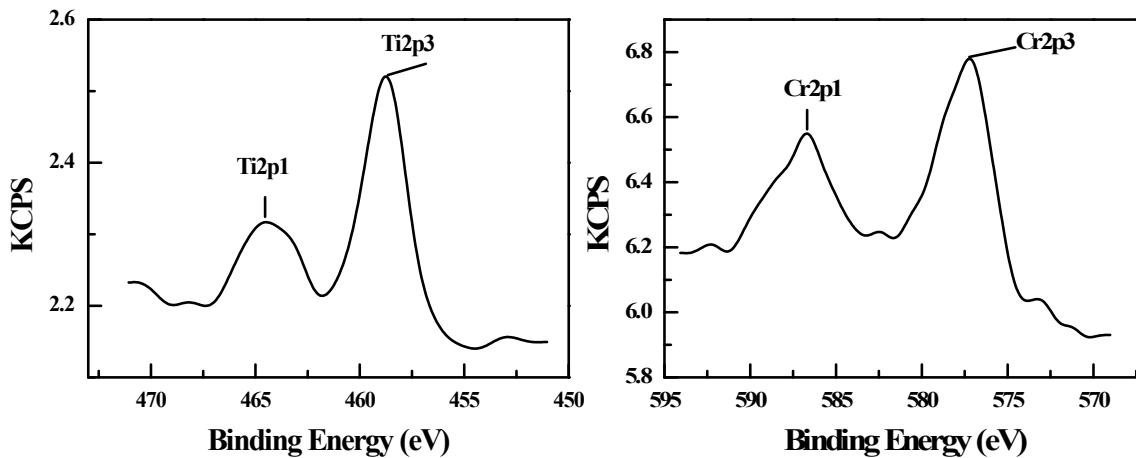


Fig. S2. XPS spectra of 1.4wt% TiO<sub>2</sub>-6.1 wt% Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>

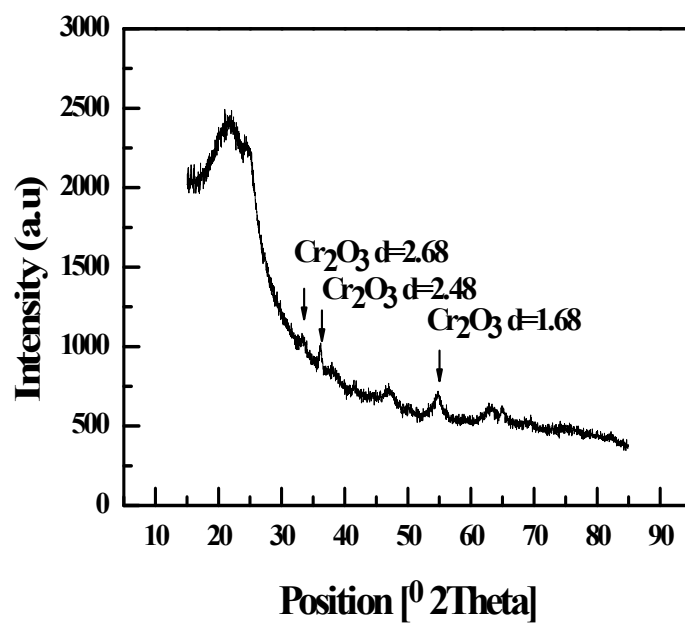


Fig. S3. XRD patterns of 1.4wt% TiO<sub>2</sub>-6.1 wt% Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>

Table. S1. Typical physicochemical properties of 1.4wt% TiO<sub>2</sub>-6.1 wt% Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>

Catalyst	Ti & Cr loadings	Ti(Cr)/Si atom% Bulk	Ti(Cr)/Si atm% Surface	Surface area/m <sup>2</sup> /g	Pore volume /cm <sup>3</sup> /g
SiO <sub>2</sub>				601.1	0.74
1.4wt% TiO <sub>2</sub> - 6.1 wt% Cr <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	Ti 1.4wt% Cr 6.1 wt%	Ti/Si 2.0 Cr/Si 7.9	Ti/Si 2.4 Cr/Si 8.6	434.3	0.49

